SUBMARINE HYDROTHERMAL WEATHERING, GLOBAL EUSTASY, 
AND CARBONATE POLYMORPHISM IN PHANEROZOIC MARINE OOLITES

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ABSTRACT: The age and fabric of 347 Phanerozoic marine oolites have been compiled in order to evaluate secular variations in the original mineralogy of these physicochemically precipitated sedimentary carbonates. Variation in the abundance of oolite correlates with positions of global sea level; ooids were common during transgressions and regressions but were rare during lowstands and highstands. The rarity of oolite during continental emergence (early Cambrian, Permo-Triassic, late Tertiary-Quaternary) probably relates to a diminished areal extent of shallow-carbonate environments. Causes for a similar paucity during continental submergence (Silurian-Devonian, late Cretaceous) are more problematic; higher atmospheric CO₂ and lower hydrospheric CO₃⁻ concentrations during highstands may have inhibited abiotic carbonate precipitation.

Ooids coeval with highstands display a preponderance of fabrics evincing a primary calcite mineralogy; ooids formed during lowstands are more diverse but record dominance of aragonite. Variations in cortical mineralogy relate more closely to flooded continental areas than to sea-level elevations, supporting the suggestion of MacKenzie and Pigott (1981) that variations in hydrospheric carbonate concentrations were more important in determining Phanerozoic ooid mineralogy than were magnesium-calcium concentrations. These data on oolite abundance and mineralogy demonstrate that abiotic Phanerozoic marine carbonates have been responsive to secular changes in atmospheric-hydrospheric chemistry and global eustasy, and suggest that these changes are directly related to past rates of submarine weathering and sea-floor hydrothermal activity.

INTRODUCTION

Since the pioneering study by Sorby (1879), it has been recognized that coatings of oolitic allochems exhibit a variety of fabrics and compositions in modern and ancient marine and nonmarine units. Modern marine cortices are almost exclusively aragonite with constituent acicular crystallites oriented parallel to grain exteriors. In ancient marine limestones, low-magnesium calcite cortices exhibit one of two general fabrics; dominantly, they are acicular crystallites oriented normal to grain exteriors, but equant interlocking crystals also occur (e.g., James and Klappa 1984). Although Sorby (1879) recognized that these two fabrics, radial and sparry, related to different diagenetic histories, this distinction was ignored by subsequent workers; because modern cortices are predominantly metastable aragonite whereas ancient cortices are predominantly radial low-magnesium calcite, many individuals concluded that ancient radial ooids arose through some sort of diagenetic recrystallization of tangential aragonite precursors.

This misconception persisted for over a century until Sandberg (1975) demonstrated that calcified aragonite consists of interlocking crystals of equant, anhedral spar. Ancient radial ooids, therefore, must exhibit fabrics in calcitic cortices. In light of the fact that calcite ooids were virtually unknown from modern shallow-marine settings, Sandberg (1975) further concluded that atmospheric-hydrospheric chemistry must be different today than it was when radial calcite ooids perdominated in shallow-marine settings. Subsequent studies have led to a general acceptance of this notion of nonuniformity of primary cortical compositions through Phanerozoic time. In addition, Holocene radial high-magnesium calcite ooids are now known from a few settings and serve as modern analogues for ancient radial calcite grains. It is also now apparent that the relative abundance of aragonite and calcite ooids has varied cyclically throughout the Phanerozoic with aragonite dominant during times of general continental emergence (such as we are experiencing today) and calcite dominant during times of general continental submergence. This relationship was first proposed by MacKenzie and Pigott (1981) and is generally supported by fabric data (MacKenzie and Pigott 1981; Sandberg 1983) and trace element data (Kahle 1965; Brand and Veizer 1983) on ooid cortices.

Those chemical processes which link the abundance and mineralogy of such abiotic carbonate components to gross positions of global sea level are poorly understood; such variation, however, must relate to one or more of the parameters that affect oceanic carbonate equilibria such as, but not restricted to, hydrospheric Mg/Ca activities (Sandberg 1975; Wilkinson 1979) or atmospheric pCO₂ (MacKenzie and Pigott 1981; Sandberg 1983). Here we examine the hypothesis that physical and chemical changes which occur in association with seafloor hydrothermal activity are a primary causal mechanism behind the observed relationships between carbonate mineralogy and global eustasy. In the following we 1) document the abundance of calcareous ooids in the Phanerozoic marine rock record, 2) document the range of fabrics exhibited by these grains, 3) evaluate cortical fabrics with respect to their original mineralogies, 4) quantify relationships between primary cortical mineralogies and positions of sea level throughout the Phanerozoic, and 5) discuss these relationships insofar as they relate to long-term variations in atmospheric-hydrospheric chemistry resulting from hydrothermal activity.

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Data on oolite occurrences and fabrics were tabulated from a variety of sources. Thin-section collections at the University of Michigan at Ann Arbor and at the University of Texas at Austin were supplemented with samples loaned or donated by many colleagues in academia and industry. Major geological journals which commonly contain papers on sedimentary geology were perused. In addition, GEOREF data files yielded 1,060 references of publications in which OOI, OOL, or OOM were the first three letters in a title word or abstracted key word. These comprise all indexed North American publications since 1960 and publications exclusive of North America since 1966.

From these sources, 347 oolites were tabulated with respect to their age (by epoch), locality, and stratigraphic occurrence (by formation); siliceous, ferruginous, and dolomitic oolites were excluded from this tabulation. In order to combine redundant reports of oolitic strata which have been the focus of particular attention owing to their economic importance (e.g., the petroliferous Jurassic Smackover Formation of the Gulf Coast), to their scientific importance (e.g., the Pleistocene Miami Oolite of Florida), or to their proximity to academic institutions with strong programs in carbonate geology (e.g., the Mississippiian Ste. Genevieve Limestone of the Midwest), these 347 oolites were lumped by formation or state (or province) into 215 “occurrences.” Although somewhat arbitrary, this grouping places all data into stratigraphic-geographic units of roughly comparable size. Finally, among the 215 occurrences, fabric data were available for 179; these serve as the data base for evaluating original mineralogies.

Ooid Abundances

With respect to abundance, Phanerozoic oolites exhibit a striking quadramodal distribution, with peak abundances during the late Cambrian, late Mississippian, late Jurassic, and Holocene (Fig. 1). Peaks occur at these times regardless of the abundant criteria considered, whether total reports and samples (as in Fig. 1), total occurrences, or total occurrences per unit time. Similar peak occurrences are also apparent in data from MacKenzie and Pigott (1981) and Sandberg (1983). Abundances range from no known upper Ordovician oolites to 6.5 occurrences per million years in Holocene units. This Holocene value is undoubtedly disproportionately high due to emphasis on modern carbonate environments. Cambrian, Mississippian, and Jurassic peaks, however, correspond to 1.4, 1.2, and 0.9 occurrences per million years, respectively, suggesting that age is not directly related to oolite abundance.

Oolite abundances do, however, appear to relate to absolute positions of global sea level. Periods of general continental emergence, such as during the earliest Paleozoic and the Permo-Triassic, correspond to low abundances (Fig. 1). Somewhat surprisingly, similar low abundances also correspond to times of maximum continental submergence; ooids are rare in middle Ordovician to lower Mississippian, and in upper Cretaceous to middle Tertiary sequences (Fig. 1). Although it might be argued that such variation simply records the present relative volumes of shallow marine carbonate, available data on the lithology, thickness, and aerial extent of Phanerozoic units suggest that such an explanation is inadequate. Of the 347 data summarized in Figure 1, 254 (73%) represent North American units. Variations in their abundance are not obviously different than that for the global data set (Fig. 1). Comparison of the North American data with data on the volume and lithology of North America Phanerozoic sediments summarized in Cook and Bally (1977) indicates that low abundances during emergent modes do, in fact, reflect a significantly smaller volume of shallow-marine carbonates laid down during these time periods.

Sequences deposited during submergent modes, on the other hand, comprise relatively large volumes of epicontinental marine carbonate. Upper Ordovician, Silurian, Devonian, and upper Cretaceous sequences are notable in this regard in that they contain many thick, areally extensive, shallow-marine units that largely lack oolitic facies. It appears that during times of maximum continental submergence, some combination of physical and/or chemical factors gave rise to conditions which largely precluded the accretion of carbonate cortices.

Ooid Fabric and Mineralogy

The original mineralogy of calcium carbonate components in marine settings is almost exclusively either calcite or aragonite. Because aragonite is unstable with respect to low-magnesium calcite, aragonite components transform to calcite via dissolution-precipitation processes early in the diagenetic history of most sequences.
In general, these transformations result in a characteristic fabric of interlocking anhedral calcite crystals, either as neomorphic spar, which may preserve gross features of the aragonite precursor as solid and/or liquid inclusions, or as pore-filling spar, which precipitates following complete aragonite dissolution (e.g., Folk and Assereto 1976; Bathurst 1975).

Originally calcitic components retain virtually all fabric elements during diagenesis. Because low-magnesium calcite is a relatively stable phase in most diagenetic environments, low-magnesium calcite components retain original fabrics as well as trace element and isotopic signatures (e.g., Al-Assam and Veizer 1982). High-magnesium calcite, on the other hand, is a metastable phase which rapidly transforms to low-magnesium calcite via dissolution-precipitation reactions. Unlike aragonite calcitization, however, this transition commonly occurs while retaining the finest details of original fabric; extensive compositional changes are accompanied by minimal changes in the shape and orientation of constituent crystals (Towe and Hemleben 1976; Schlager and James 1978).

Since originally calcitic components, either as low- or as high-magnesium calcite, retain fine details of primary fabric whereas originally aragonite components are replaced by sparry calcite, cortical fabrics provide powerful criteria by which to evaluate original mineralogy. Within this broad framework, however, Phanerozoic marine ooids exhibit a variety of fabrics and forms. Many of these have been described elsewhere (e.g., Richter 1983) and therefore are only briefly summarized here.

**ARAGONITE FABRICS**

*Neomorphic Sparry Ooids (NS).*—Coatings which now consist of equant interlocking crystals of calcite are herein referred to as sparry ooids (Fig. 2). Component crystallites range in size from about 20 to 100 microns; original concentric banding is commonly preserved through the alignment of solid and/or liquid inclusions, and by virtue of the fact that spar crystal boundaries commonly coincide with primary laminations. Such fabrics have been reported in former aragonite marine cement (e.g., Mazullo 1980), in former aragonite fossils (e.g., James 1974), in calcitized ooids (e.g., Sandberg 1975), and are now generally accepted as the typical fabric developed during aragonite to calcite transformation.

*Neomorphic Sparry Deformed Ooids (NSD).*—Two variants on sparry ooids occur commonly in Phanerozoic carbonates. The first have been referred to as *elephantine* (connected trunk-to-tail) or *spastolithic* (deformed) grains which exhibit variable degrees of postdepositional deformation. These forms arise when ooids are lithified by calcite (commonly marine) cement before aragonite to calcite transformation. During aragonite dissolution, rigid calcite cement matrices collapse, giving rise to deformed and interconnected ooid shapes (e.g., Conley 1977). Such shapes record the former presence of aragonite cortical laminae as well as early lithification by calcitic cements.

*Neomorphic Sparry Ooids with Dropped Nuclei (NSN).*—Lowered, displaced, or dropped nuclei are a second variant of sparry ooids that occurs commonly in the rock record. Like deformed grains, dropped nuclei record the physical settling of less soluble (in this case nuclear) phases during aragonite dissolution. In such cases, nuclei consist either of terrigenous or calcitic components. Like deformed ooids, dropped nuclei record the former presence of cortical aragonite.
FIo. 4.—Fabrics exhibited by originally calcitic cortices. A) Primary radial ooid from the Jurassic Twin Creek Formation, Wyoming. Such fabrics are the most common of all ooid fabrics. B) Sparry ooids from the Cambrian Bonneterre Formation of Missouri. Such grains are intermediate between sparry ooids and radial ooids in that constituent crystals are coarse but oriented normal to grain exteriors.

SECULAR VARIATION IN ARAGONITE FABRICS

The abundance of ooids exhibiting aragonite fabrics has varied greatly throughout the Phanerozoic (Fig. 3), with abundances corresponding closely to variations in the abundance of all calcareous oolites (Fig. 1). The relative proportion of sparry ooids, deformed sparry ooids, and sparry ooids with displaced nuclei has remained relatively constant with sparry grains the most abundant, deformed grains the next most abundant, and grains with dropped nuclei the least abundant (Fig. 3). On the average, sparry, deformed, and displaced nuclear grains comprise 58%, 28%, and 14%, respectively, of grains exhibiting fabrics recording the former presence of cortical aragonite.

CALCITE FABRICS

Primary Radial Ooids (PR).—Cortices of acicular calcite crystallites normal to grain exteriors are the dominant coating in Phanerozoic ooids. In thin section, these grains exhibit radial variations in color reflecting variable densities of included noncarbonate material and variations in the size and density of constituent crystallites (Fig. 4A); individual crystallites range from 2 to 5 μm in width and 5 to 25 μm in length. Frequently, radial laminae may occur with micritic laminae of equant, anhedral nanograins. These are particularly common in those portions of radial ooids where banding densities are highest (Medwedeff and Wilkinson 1983).

As mentioned earlier, modern marine radial calcite ooids, although rare, exhibit fabrics nearly identical to those seen in ancient counterparts. Modern high-magnesium calcite radial grains are reported from Baffin Bay, Texas (Land et al. 1979), from the Amazon shelf (Milliman and Barretto 1975), and from deeper waters off the Great Barrier Reef (Marshall and Davies 1975). On the basis of this fabric similarity, and because other originally calcitic components in ancient limestones retain fine fabric detail, there is little reason to doubt the interpretations of Sandberg (1975) and Heller et al. (1980) that radial fabrics in ancient ooids record originally calcitic cortices.

Primary Radial Spalled Ooids (PS).—A variant of primary radial ooids occurs when outer layers are separated from inner cortical carbonate. Such grains, reported from a wide variety of oolitic units, have commonly been referred to as spalled because younger laminae have been physically detached from ooid interiors. Most workers have concluded that spalling occurs during burial and compaction when ooids are subjected to lithostatic stress at point contacts between individual grains. Wilkinson et al. (1984), on the other hand, suggest that spalled radial ooids may record the formation of bimineralic aragonite-calcite cortices in which aragonite laminae underwent selective dissolution and in which (the then separated) calcite laminae underwent collapse. In most cases, the former presence of aragonite layers is impossible to demonstrate conclusively. Owing to the fact that bimineralic compositions can be documented only in a few occurrences, and that preserved laminae are exclusively radial, we have tabulated all occurrences of spalled radial ooids as examples of originally calcitic cortices.

Primary Sparry Radial Ooids (PSR).—Thirteen early Paleozoic oolites exhibit a fabric which is intermediate between radial and sparry, consisting of coarse, radiating crystals which widen from their origin at the nucleus to their termination at grain exteriors (Fig. 4B); wedge-shaped crystals commonly attain widths of 100–200 μm. Such grains are commonly “cerebroid” (e.g., Carozzi 1962) in that radial crystals, extending a few microns to a few tens of microns beyond the grain exterior, give rise to scalloped margins in section. Poorly defined pseudouniaxial crosses are common (Fig. 4B). When planes of sections pass either above or below grain centers, the very coarse size of component crystals gives rise to fabrics similar to those in sparry ooids. In such transects, coarse, radial crystals ap-
pear as interlocking mosaics of equant, anhedral spar. Thus, it is often possible to observe a spectrum of fabrics ranging from what appears to be radial (nuclei transected) to sparry (nuclei above or below planes of section) in one thin section.

The original mineralogy of sparry radial ooids is not known with any degree of certainty. Three possibilities are reasonable. The first is that they exhibit primary fabrics similar to those in nonmarine low-magnesium calcite grains from a variety of spelean and artificial (boilers, water-treatment plants), low-salinity settings. Although the reasons for crystal-size variations are unknown, it is at least plausible that sparry radial fabrics are primary attributes of originally calcitic grains. A second possibility is that sparry radial ooids formed as normal radial ooids with fine crystallites, and that these radial crystallites “coalesced” through the diagenetic filling of intercrystalline spaces by later calcite. Coalescence has been documented in radial calcite marine cements by Lohmann (in press), a process that gives rise to coarse radial fabrics with characteristic undulatory extinctions. If crystals in sparry radial ooids were originally finer grained, coalescence could well have produced coarser crystal sizes. A third possibility is that sparry radial ooids were precipitated as coarse aragonite crystals that transformed to calcite while retaining gross characteristics of primary fabric. Coarse radial aragonite ooids, although unknown in modern marine settings, have been reported from several hypersaline lacustrine systems, most notably the Great Salt Lake in Utah (e.g., Halley 1977). Crystals in these grains are truly spectacular, attaining dimensions of several hundreds of microns. Because aragonite to calcite transformations may preserve original fabric elements when aragonite crystals are large, it is at least plausible that, like Great Salt Lake grains, sparry radial ooids were precipitated as aragonite.

Other attempts to evaluate the primary mineralogy of sparry radial grains include those by Freeman (1980), who suggested that sparry radial grains from the Cambrian Bonneterre Formation of Missouri were originally aragonite, and by Sandberg (1983), who suggested that sparry radial fabrics in the Cambrian Mural Limestone of British Columbia were calcitic. Due to these uncertainties, choosing among the three possibilities outlined above is the least secure of the fabric evaluations of original ooid composition. However, given that sparry radial coatings do retain at least some manifestation of original fabric, an attribute common to other originally calcitic components, and that preliminary trace elemental analyses do not indicate significantly elevated strontium concentrations, we have tabulated occurrences of sparry radial ooids, albeit tentatively, as originally calcitic cortices.

**SEcular Variation in Calcitic Fabrics**

The abundance of ooids exhibiting calcitic fabrics has been highly variable throughout Phanerozoic time (Fig. 5), corresponding closely to variations in the abundance of all calcareous ooid grains (Fig. 1). The proportions of these as radial, spalled, and sparry radial grains have varied as well, sparry radial ooids are found only in middle and upper Cambrian and lower Ordovician sequences. While it might be argued that the reason for the lack of correspondence between sparry radial ooid abundances and other calcitic ooid abundances is that they were in fact aragonite, comparison of sparry radial ooid abundances with aragonite ooid abundances (Fig. 3) yields an equally poor correlation. Radial sparry ooids are enigmatic, both with respect to their original mineralogy and their clumped distribution in early Paleozoic rocks.

**Ambiguous Fabrics**

Two additional fabrics which occur commonly in Phanerozoic ooids were not tabulated as recording either aragonite or calcite.

*Micritic Ooids.*—Micritic ooid cortices are composed of equant nannograins, up to 10 μm in diameter, and lack either radial or sparry fabrics in thin sections (Fig. 6A) or SEM images. Such fabrics can arise in one of two ways. In radial ooids, the length of calcite crystallites (oriented normal to grain exteriors) is commonly the same as the thickness of concentric layers that define the banding typical of all such coated grains. Heller et al. (1980) have pointed out that in most ooids, banding density increases (lamina thickness decreases) as grains increase in size. Such increases record the greater importance of grain abrasion over grain growth as grain mass becomes larger. Not infrequently, lamina thicknesses soon approach values of the widths of radial calcite crystals and, as a result,
growth proceeds through the accretion of equant nanograins. Medwedeff and Wilkinson (1983) have further shown that lamina thickness (and the accretion of radial versus equant crystallites) depends both on rates of carbonate precipitation (which is controlled by ambient water chemistry) and rates of cortex abrasion (which is determined by grain mass and levels of physical energy in formational environments). These factors may be nearly equal during the growth of an entire cortex and, as a consequence, resultant fabrics are micritic.

Micritic fabrics, however, also can arise through the activity of microendolithic organisms, primarily cyanophytic algae (e.g., Margolis and Rex 1971). These organisms excavate tubular borings into nearly all carbonate substrates, including ooid cortices during growth; borings are subsubsequently filled with micron-size calcite cement crystals. When borings are dense, complete micritization of grain exteriors results (e.g., Kobluk and Risk 1977). Because micritic fabrics can arise either through the addition of equant nanograins in calcitic ooids or through the activity of microendoliths in calcite or aragonite ooids, and because both processes give rise to nearly identical fabrics, it is not possible to infer the original mineralogy of micritized grains.

**Moldic Ooids.**—The second fabric not equated with an original mineralogy is molds developed during the selective dissolution of ooids (Fig. 6B). The origin of oomoldic porosity is indeed problematic. Since aragonite grains transform to calcite through aragonite dissolution and calcite precipitation, moldic porosity might simply record the former presence of aragonite grains. Sandberg (1983) has pointed out, however, that such interpretations may be incorrect. It is well established that calcite with approximately 13 mole% MgCO₃ has a solubility equivalent to that of aragonite and, therefore, high-magnesium calcites should dissolve as readily as aragonite. Magnesium loss from grains that have undergone high- to low-magnesium calcite transformations also demonstrates that both aragonite and high-magnesium calcite stabilize by precursor-phase-dissolution–calcite-precipitation reactions. Selective dissolution of high-magnesium calcite components, resulting in moldic porosity, however, is a process virtually undocumented in natural carbonate sequences. Although individuals such as Schroeder (1979) and Budd (1983) report limited porosity developed during high-magnesium calcite dissolution in subaerially exposed Cenozoic sequences, these are rare instances. Virtually all magnesian calcite components in carbonate sequences, as stated earlier, transform to low-magnesium calcite while retaining the finest details of original fabric, processes far removed from the wholesale dissolution required for the development of moldic porosity.

The difficulty in evaluating the original mineralogy of moldic ooids is that the basis for correlation between ooid fabric and original mineralogy is empirical, being based on numerous observations of components of known composition in Cenozoic carbonate sequences, and lacks any theoretical chemical underpinning in support of these interpretations. While the bulk of natural observations strongly suggests that oomoldic porosity records the former presence of aragonite, equivalence of magnesian calcite and aragonite solubilities in conjunction with rare reports of molds developed during high-magnesium calcite dissolution precludes a secure correlation between oomolds and aragonite grains. As a result, moldic porosity in oolite units has not been tabulated as recording the former presence of either aragonite or calcite cortices.

**SECULAR VARIATION IN MICRITIC AND MOLDIC FABRICS**

The abundances of micritic and moldic fabrics in Phanerozoic sequences are dissimilar. Micritic ooids, although uncommon, occur with roughly equal frequency in Paleozoic, Mesozoic, and Cenozoic sequences (Fig. 7). Moldic porosity, on the other hand, shows a clumped distribution; it is particularly common in Permo-Triassic
sequences (Fig. 7), a distribution that is similar to that
seen in the abundance of aragonite fabrics (Fig. 3). This
similarity suggests, but only suggests, that most oomolds
were originally aragonite grains.

SECULAR TRENDS IN OOID MINERALOGY

The relative abundance of cortical aragonite and calcite
in Phanerozoic marine carbonates has not remained con-
stant, but, as suggested by MacKenzie and Pigott (1981)
and Sandberg (1983), bears a crude relationship to gross
positions of global sea level (Fig. 8). Quantification of
such a relationship, however, is a less than straightforward
erercise owing to 1) a lack of definitive data on the
absolute positions of global sea level over the past 570
million years, 2) a paucity of quality data on oolite fabrics
in Phanerozoic marine sequences, 3) the necessity of sam-
pling fairly small time intervals in order to establish sig-
nificant correlations between global eustasy and cortex
mineralogy, and 4) the great variation in oolite abun-
dances throughout Phanerozoic time.

Calculation of 95% confidence limits on mean cortical
compositions demonstrates that of the 26 time slices for
which ooid fabric data is available in Figure 8 (no fabric
data for lower Devonian and upper Ordovician units), 11
intervals are represented by a sufficiently small number
of occurrences that mean compositions are not known
with any degree of certainty (95% confidence limits exceed
±50%). Only 15 of the 28 time intervals are represented
by sufficient samples so that average cortical compositions
are meaningful. Comparisons of mean compositions
for these intervals with positions of global sea levels from
Vail and others (1977) indicate a general relationship be-
tween cortical mineralogy and global eustasy. Increased
continental flooding corresponds to increased amounts of

Fig. 8.—Distribution of occurrences of originally calcite and aragonite
oolid cortices. Data tabulated from the 179 Phanerozoic occurrences for
which diagnostic fabric data were available. Note a general correspond-
dence between abundant aragonite cortices and periods of continental
emergence.

Fig. 9.—Relationship between mean aragonite content of ooid cor-
tices and positions of relative global sea level from Vail et al. (1977).
Bars encompass 95% confidence limits around mean compositions. Note
a general trend relating increasing amounts of cortical aragonite to in-
creasing continental emergence.

Fig. 10.—Relationship between mean aragonite in cortical carbonate
and calculated areas of exposed (or flooded) continental crust. Bars
encompass 95% confidence limits as in Figure 9. This correlation is
significant at the 10% level, slightly better than that for Figure 9. Con-
tinental areas calculated from sea-level positions of Vail et al. (1977).
better correlation is obtained between mean cortical mineralogies and calculated areas of continent exposed or flooded. Freeboard data from Hallam (1977). This represents the best correlation (significant at the 5% level) obtained between various data sets on global eustasy and ooid mineralogy.

cortical calcite; increased emergence corresponds to increased amounts of cortical aragonite (Fig. 9). A slightly better correlation is obtained between mean cortical mineralogies and calculated areas of continent exposed or flooded (Fig. 10), with a statistical significance better than the 10% level (i.e., the probability that this degree of correlation is random is less than 10%).

In addition to eustatic data from Vail et al. (1977), mean cortical mineralogies were also compared to epoch-interval freeboard data (as % of continent flooded) from Strakhov (1948), Termier (1952), Schuchert (1955), Vinogradov (1967–69), and Cook and Bally (1977), as summarized by Wise (1974) and Hallam (1977). Among these data sets, variations in the degree of inundation of the U.S.S.R. in Hallam (1977) yields the best correlation with mean cortical mineralogies. The series of paleogeographic and facies maps of the Soviet Union (Vinogradov 1967–69) on which these freeboard data are based (Hallam 1977) are as yet unmatched for any other continental region and allow for the most detailed analysis possible of changes in the aerial extent of seas through the Phanerozoic. The significance of the correlation between ooid mineralogies and these data is better than the 5% level (Fig. 11).

**Significance of Ooid Abundances**

Data on Phanerozoic marine ooids demonstrate that their abundance and composition have varied greatly over the past 570 million years, with differences corresponding to variations in the position of global sea level in that there is a general relationship between high oolite abundances during periods of transgression and regression, and low abundances during periods of continental emergence and submergence (Fig. 1). While a paucity of oolite during emergent modes is readily related to restricted areas of shallow marine deposition and lesser volumes of shallow marine facies, as mentioned earlier, a similar lack of oolite during submergent modes is more problematic in that large volumes of relatively shallow marine carbonate occur in the rock record. Two scenarios for a paucity of highstand oolites seem plausible. The first is that during times of maximum transgression, epicratonic carbonate-producing environments, although extensive, may have been too deeply flooded to allow for development of the wave-agitated settings necessary for ooid formation. Alternatively, highstand marine environments may have been ideal for ooid generation from a physical standpoint, but some aspect of atmospheric-hydrospheric chemistry may have precluded the widespread abiotic precipitation of calcium carbonate.

Ideally, quantitative data on the volume and lithology of various Phanerozoic shallow-marine carbonate facies would allow for the proper choice between these two models. Unfortunately, to our knowledge, such a data set does not exist and any interpretation must rely on more indirect lines of evidence. Several of these, however, suggest that highstand chemical parameters rather than physical parameters precluded the formation of ooids in highstand seas. First, rates of carbonate production determined for a variety of shallow Holocene settings are on the order of 1 m/1,000 yrs. Even if average Phanerozoic carbonate production rates were several orders of magnitude lower, as is suggested by data from Wilson (1975) and Sadler (1981), based on estimates of absolute sea-level positions as Vail and others (1977), they should have been high enough to bring carbonate depositional surfaces well above wave base rather rapidly during periods of maximum flooding. In other words, it is difficult, given estimated rates of marine transgression and regression such as those in Figure 1, and reasonable estimates of rates of carbonate deposition, to envisage situations where epicratonic carbonate environments would remain deeply flooded for any significant length of time, particularly during the long middle Paleozoic and upper Mesozoic-lower Tertiary highstand time intervals during which oolites are rare (Fig. 1).

Second, although carbonate oolites are uncommon in highstand sequences, data from Van Houten and Bhattacharya (1982) demonstrate that just the opposite is the case for chamosite-hematite ironstone oolites (Fig. 12). With the exception of lower and middle Jurassic examples, Phanerozoic ferruginous coated grains are largely restricted to highstand marine sequences. Their abundance in such units requires that highstand marine settings were sufficiently shallow that grains were agitated on the sea floor. This dominance of ironstone oolites and the rarity of calcareous oolites in highstand units strongly suggests that ambient water chemistry rather than ambient wave energy precluded calcite or aragonite ooid growth in highstand seas. Such chemical variations also relate to the mineralogy of cortical carbonates.

**Significance of Ooid Mineralogies**

Three aspects of secular variations in oolite mineralogy are worthy of comment: 1) How significant is the correlation between average cortical composition and global
Just how good is the relationship between cortical mineralogy and global eustasy? We have determined that the best statistical correlation is that between mean ooid mineralogy and continental area flooded or exposed (Figs. 10 and 11). Do these correlations in fact manifest an underlying genetic relationship between these parameters? Each reader ultimately will have to decide both on the basis of the data herein as well as his own cynicism concerning such statistical relationships. It should be noted, however, that these correlations are remarkably high in light of two aspects of the data. The first deals with the accuracy of estimates of global sea levels. Freeboard curves for a variety of continents, particularly North America and Asia, and attempts to quantify such estimates (e.g., Schuchert 1955; Wise 1974; Vail et al. 1977; Hallam 1977) yield highly disparate results. Imprecision in such quantifications may be a significant source of “noise” in such correlations. The second of these aspects is probably even more important and is less easy to evaluate, let alone quantify. This is the degree to which local variations in chemical and physical processes, rather than global secular variations, have determined the original mineralogy of abiotic carbonate precipitates. Considering the Holocene as our best-studied time period, marine calcite and aragonite are known to coexist as both cement and cortical phases. With respect to cement, aragonite is dominant in some localities; (e.g., James and Ginsburg 1979); calcite is dominant in others (e.g., Land and Moore 1980). Even in marine calcite cement, magnesium contents range from less than 4 mole% MgCO₃ (e.g., Schlater and James 1978) to over 18 mole% MgCO₃ (e.g., Longman 1980). In ooids, dominant mineralogies have been shown to vary from dominantly aragonite to increasingly calcitic along a mere 10 km of shore zone in Baffin Bay (Land et al. 1979). Thus, we observe that ooid mineralogies are highly variable and dependent on local conditions within a narrow spatial and temporal framework, yet are also significantly correlated with certain eustatic indexes on a global scale throughout the Phanerozoic. Such a relationship clearly supports the argument that local conditions which determine the relative proportions of cortical calcite and aragonite are themselves ultimately influenced by secular chemical variations on a global scale.

GLOBAL EUSTASY AND ATMOSPHERIC-HYDROSPHERIC CHEMISTRY

If it is accepted that some process or processes have linked dominant cortical mineralogies to positions of global sea level, what then are these processes? Obviously, some parameter (or parameters) which influence marine carbonate equilibria must be centrally involved. The two of these that have received the widest attention involve changes in either ambient Mg/Ca ratios of seawater (Sandberg 1975) or atmospheric-hydrospheric CO₂s (Pigott and MacKenzie 1979). Two aspects of each of these variables merit note: 1) What is their influence on the mineralogy of abiotically precipitated carbonate phases? 2) How do potential changes in these variables relate to processes which control positions of global sea level?

Mg/Ca, pCO₂, and Carbonate Polymorphs.—It has long been recognized that ambient Mg/Ca activities are directly (although possibly not causally) related to the precipitated calcium carbonate polymorph. Owing to the fact that low-magnesium calcite, then high-magnesium calcite and aragonite, then aragonite, is the sequence of phases commonly precipitated from fluids with increasing Mg/Ca ratios, Müller and others (1972), Folk (1974), and many others have suggested that the relative concentration of Mg⁺ ions versus Ca⁺ ions may determine the mineralogy of precipitated phases. Because Mg/Ca ratios of modern seas are about 5, and because data from Müller and others (1972) suggest that low-magnesium calcite to high-magnesium calcite plus aragonite Mg/Ca threshold ratios are about 5, Sandberg (1975) and Milliken and Pigott (1977) have invoked variations in marine Mg/Ca ratios to explain inferred differences in cortical mineralogies in Phanerozoic seas.

Pigott and MacKenzie (1979), on the other hand, recognized that the composition of carbonates precipitated at saturation from seawater can be determined by atmospheric pCO₂s at an essentially constant Mg/Ca ratio. They concluded that changes in cortical mineralogy were probably due to changes in atmospheric-hydrospheric CO₂ levels and not to major perturbations in the Mg/Ca ratio of seawater. Low CO₂ levels favor aragonite precipitation;
PRODUCE CARBONATE & PYRITE
INPUT DIAGENETIC & METAMORPHIC CO₂
ERODE SULFATE & ORGANIC CARBON
RESTRICT TERRESTRIAL BIOTAS
INCREASE RESPIRATION & OXIDATION

PCO₂

EMERGE TERRESTRIAL MATERIALS
OXIDIZE SULFIDES
ERODE CARBONATES
ERODE METAL SILICATES
INCREASE PHOTOSYNTHESIS
PRECIPITATE EVAPORITES

SUBMARINE WEATHERING IMPORTANT

Mg/Ca

1. PYROXENE + PLAGIOCLASE + Mg⁺ → CHLORITE + EPIDOTE + Mg²⁺
   DIOPSIDE + ENSTATITE + PLAGIOCLASE + Mg²⁺ → CHLORITE + EPIDOTE + QUARTZ + Ca²⁺
2. H⁺ + HCO₃⁻ → H₂O + CO₂+
   Ca²⁺ + 2HCO₃⁻ → CaCO₃ + H₂O + CO₂↑

SUBMERGENT MODE

CALCITE SEAS

FIG. 13.—Diagrammatic model of highstand geochemical processes. Top = Diagenetic and metamorphic reactions at subduction zones, sulfate reduction and carbonate deposition reactions in epicontinental seas, and decreased photosynthesis serve to elevate atmospheric CO₂ levels (from MacKenzie and Pigott 1981). Bottom = 1) Idealized greenschist metamorphic reactions at hydrothermal ridges convert plagioclase and mafic minerals to chlorite and epidote while removing magnesium (and adding calcium and hydrogen) ions from convecting sea water. 2) Both H⁺ and Ca⁺ ions liberated during basalt alteration drive additional CO₂ into the atmosphere. Mg/Ca ratios of sea water are depressed.

high CO₂ levels favor calcite (and possibly dolomite) formation.

Mg/Ca, pCO₂, and Global Eustasy.—What processes link positions of global sea level to Mg/Ca ratios and to CO₂ levels in marine systems? With respect to CO₂, MacKenzie and Pigott (1981) suggested that submergence gives rise to 1) low rates of erosion and deposition of terrigenous clastic sediments, 2) widespread deposition of carbonates, and 3) increased rates of production of CO₂ from diagenetic and metamorphic reactions at subduction zones, all of which result in relatively high atmospheric CO₂ levels, and the dominance of calcite in Phanerozoic seas (Fig. 13). They further suggested that emergence promotes 1) weathering in terrestrial environments, 2) erosion of carbonates, 3) erosion of metal silicates, and 4) increased photosynthesis, all of which result in low atmospheric CO₂ levels and the increased dominance of aragonite in Phanerozoic seas (Fig. 14).

With respect to Mg/Ca ratios, it was originally proposed by Sandberg (1975) that the explosive diversification of planktonic protists in the Mesozoic and the subsequent deposition of large volumes of calcium carbonate in deep ocean basins served to elevate Mg/Ca ratios (primarily through calcium removal) and cause aragonite production in post-Jurassic seas. As subsequently pointed out by Sandberg (1983), however, such a mechanism for changing Mg/Ca ratios is not in accord with the abundance of lower Paleozoic or upper Paleozoic-lower Mesozoic cortical aragonite, nor the dominance of cortical calcite in upper Mesozoic-lower Tertiary seas (Fig. 8).

It is now recognized that the principal control on oceanic Mg/Ca ratios relates not to the abundance of planktonic protists, but to the hydrothermal alteration of basalts at midoceanic ridges. Numerous studies (e.g., Bischoff and Dickson 1975; Hajash 1975; Wolery and Sleep 1976; Bloch and Hofmann 1978; Edmond et al. 1979; Bender 1983) have demonstrated that rates of greenschist metamorphism at spreading hydrothermal ridge systems may have an overwhelming influence on Mg²⁺ and Ca²⁺ concentrations in ocean water. During such submarine weathering, the Mg/Ca ratio of circulating seawater is drastically lowered, primarily through magnesium removal (e.g.,

EMERGENT MODE

ARAGONITE SEAS

FIG. 14.—Diagrammatic model of lowstand geochemical processes. Top = Subaerial oxidation of sulfides, erosion of carbonates and metal silicates, and increased photosynthesis serve to depress atmospheric CO₂ levels (from MacKenzie and Pigott 1981). Bottom = Decreased magnesium removal at cooler ridges and addition of magnesium ions from the weathering of silicates serve to elevate ambient Mg/Ca ratios.
Bloch and Hofmann (1978), but to some degree because of calcium addition (e.g., Bender 1983). Because changes in the gross position of global sea level directly relate to global rates of seafloor spreading (e.g., Pittman 1978) and because rates of ridge spreading directly relate to rates of convective heat loss during seawater-basalt exchange reactions (e.g., Bender 1983), it is apparent that Mg/Ca ratios should decrease during periods of submergence and rapid spreading (Fig. 13), achieving minimum values during highstands, and should increase during periods of sealevel lowstands and decreased rates of spreading (Fig. 14), achieving maximum values during lowstands. Hence, low Mg/Ca ratios (highstands) should facilitate calcite precipitation; high Mg/Ca ratios (lowstands) should facilitate aragonite precipitation.

In fact, changes in pCO2 and ambient Mg/Ca as related to rates of spreading and global eustasy (Figs. 13 and 14) both should change in a simultaneous and complementary fashion to influence cortical mineralologies. During submergent modes, pCO2 elevating reactions as outlined by MacKenzie and Pigott (1981) and Mg/Ca ratio suppressing reactions at submarine ridges as outlined by DeVore (1983) should both facilitate calcite precipitation (Fig. 13). In addition, Ca2+ and H+ ions, liberated during magnesium-exchange reactions between seawater and hot basalt (Fig. 13), should shift marine carbonate equilibria such that additional CO2 is liberated to the atmosphere. Conversely, during emergent modes, CO2 depressing reactions as outlined by MacKenzie and Pigott (1981) decreased rates of magnesium removal at hydrothermal ridges and increased delivery of magnesium (from subaerial weathering reactions) to oceans by rivers, all favoring cortical aragonite precipitation (Fig. 14).

Recently, Berner and others (1983) have developed a mathematical model which was used to hindcast atmospheric CO2 levels from the late Cretaceous (100 m.y.) to the present based on various seafloor-spreading curves. A significant conclusion of this modeling effort was that, regardless of which specific spreading-rate curve was considered, all evidence suggests a marked decline in CO2 levels during this period. Based on the arguments made above, this trend should be manifested by a transition from predominantly calcite (late Cretaceous) to predominantly aragonite (present-day) cortical mineralologies. This is indeed what we have observed (Fig. 8). In general, both subaerial and submarine chemical processes favor emergent-mode calcite and submergent-mode aragonite precipitation.

**SUMMARY**

Given that expected variations in both Mg/Ca ratios and pCO2s with changes in global sea level are in accord with observed variations in the cortical mineralogy of Phanerozoic marine oolites, can an estimation of the relative importance of these two variables be made? Since the two variables are themselves related, a quantitative answer to this question would require a comparison of the partial time derivation of each parameter during periods of emergence and submergence with the critical threshold values that control cortical mineralogy. Unfortunately, inadequate data now exist to make these calculations. However, two qualitative aspects of the data on ooid abundances and cortical mineralogy suggest that MacKenzie and Pigott (1981) and Sandberg (1983) are correct in their suggestion that ooid composition is primarily (although indirectly) controlled by CO2 levels. The first of these is that carbonate oolites are strikingly rare in highstand sequences, while both ferric oxide and chamosite-coated grains are common. If Mg/Ca ratios alone were suppressed during these time periods, there is little reason to expect that such changes would inhibit abiotic carbonate formation. On the contrary, abundant experimental data suggest that elevated Mg/Ca ratios suppress rates of carbonate precipitation while lower Mg/Ca ratios enhance precipitation. Atmospheric CO2 levels, on the other hand, may have reached sufficiently high levels during periods of maximum submergence that physicochemical carbonate precipitation was inhibited. This is not to imply that carbonate sediments were not forming; they surely were and in vast volumes. It does imply, however, that the degree of carbonate saturation may have been lower, that spontaneous nucleation and growth of abiotic carbonate crystals on ooids was inhibited, and that widespread and diverse communities of calcareous metazoans were, even more than today, responsible for carbonate production in shallow, highstand seas.

The second aspect of the ooid data that implies a predominant role for variations in atmospheric CO2 levels is that there is a better correlation between mean cortical mineralogy and areas of continents flooded or exposed than there is between mineralogy and positions of global sea level. While less compelling than ooid abundance data, this relationship suggests that ooid mineralologies were more closely tied to areas of continents flooded than to simple rates of spreading as reflected in vertical changes in sea level. MacKenzie and Pigott (1981) suggest that rates of weathering, oxidation, and reduction of various earth-surface carbonates, sulfates, silicates, and oxides, may have had a significant influence on atmospheric CO2 levels (Figs. 13 and 14). Because the importance of these processes relates to areas of continent exposed or flooded, by implication it was CO2 levels as determined by the rates of these processes that controlled the mineralogy of abiotic carbonate phases throughout the Phanerozoic.

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REFERENCES


