

# LOW-MAGNESIAN CALCITE MARINE CEMENT IN MIDDLE ORDOVICIAN HARDGROUNDS FROM KIRKFIELD, ONTARIO<sup>1</sup>

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**ABSTRACT:** Middle Ordovician (Trentonian) biosparites from the Bobcaygeon and Verulam formations near Lake Simcoe, Ontario, exhibit numerous features demonstrating lithification near the sediment/water interface. These include planar erosion surfaces which truncate shells and intraclasts, undercut hummocks on upper surfaces, vertical borings which cross-cut fossil debris and early cement, and a diverse fauna of encrusting organisms which grew attached to lithified surfaces. A marine origin for early cement is indicated by the development of hardgrounds within a transgressive regionally overlapping sequence, the occurrence of dozens of such units within normal marine sediments, and a lack of features recording early oxidation and/or partial dissolution during exposure to meteoric water.

Marine cement from four of these units, examined in thin section, by SEM, and by cathodoluminescence, consists of clear zoned syntaxial overgrowths on echinoderm debris and equant spar on trilobite, bryozoan, and brachiopod fragments. As such, this cement: 1) is morphologically identical to meteoric phreatic low-magnesian calcite cement from calcitized Pleistocene sequences, 2) is interpreted as having been precipitated as low-magnesian calcite, 3) is anomalous in habit and inferred composition in comparison with Holocene marine cement, and 4) demonstrates that generalizations which relate cement morphology and composition to environmental water chemistry in modern diagenetic systems may not be valid when applied to more ancient carbonate sequences.

## INTRODUCTION

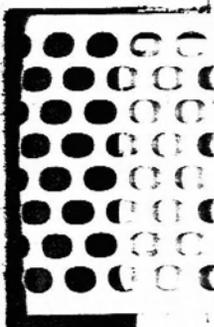
Recent studies in carbonate diagenesis have focused on two particular aspects of carbonate cements. First, studies have documented, primarily through study of Holocene and calcitized Pleistocene carbonate sequences, the relationship between pore-water chemistry and the cement phase which is precipitated. Second, studies have related cement mineralogy and composition to characteristic crystal habits.

In modern environments, relationships between water chemistry and cement mineralogy and composition are relatively straightforward: low-magnesian calcite is typically precipitated from supersaturated meteoric water, whereas high-magnesian calcite and aragonite develop in marine and hypersaline water (see, e.g.,

Müller et al., 1972). The relative activity of magnesium and calcium ions within the solution is believed to be the principal parameter of pore-water chemistry which predicates such cement compositions. Meteoric water typically has a Mg/Ca ratio less than unity, whereas the Mg/Ca ratio in sea water is close to 5 and is even higher in many hypersaline brines (Folk and Land, 1975). Almost without exception, the mineralogy and composition of Holocene carbonate cement can be directly related to the general chemistry of the water in which it precipitates (Folk, 1974).

The relationships between cement crystal habit, composition, and mineralogy are less clear-cut, however, owing to similar morphologies exhibited by several phases. Acicular habits, for example, develop in some low-magnesian calcites (see, e.g., Binkley et al., 1980), may develop in high-magnesian calcite (see, e.g., James et al., 1976), and characterize all abiotic marine aragonite (see, e.g.,

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Ginsburg and James, 1976). Although similar habits characterize cements of different mineralogies and compositions, it has generally been concluded that, for crystals more than about ten microns in size, low-magnesian calcite is typically equant to slightly elongate in form with crystal size increasing from substrates (see e.g., Land, 1971) and that high-magnesian calcite occurs as acicular crystals in isopachous crusts (Longman, 1980); aragonite is also fibrous, occurring as isopachous crusts or as radiating botryoidal masses, commonly exhibiting square termination (see, e.g., Assereto and Folk, 1980).

Employing generalizations which relate pore-water chemistry to cement composition and mineralogy, and those which relate cement composition and mineralogy to crystal habit, numerous attempts have been made to infer environments of cementation for ancient carbonate sequences from the morphology of cement crystals now composed entirely of low-magnesian calcite. Inherent in such an approach, however, are two basic assumptions: 1) that the physical conditions within cementation micro-environments of Quaternary carbonates are analogous to those in ancient sequences, and 2) that the chemistry of meteoric and marine water has remained relatively constant over geologic time.



In contrast to a strict application of this uniformitarian model to ancient carbonates, several workers have suggested that some, as yet undocumented, feature of world ocean chemistry has changed during the Phanerozoic, such that some Paleozoic carbonates, which were primarily calcitic in composition, have been largely replaced by aragonite components in Cenozoic seas. These changes from calcite to aragonite have been suggested for marine carbonate mud (Folk, 1974; Sandberg, 1975), marine fossils (Pigott and MacKenzie, 1979; Wilkinson, 1979), marine ooids (Kahle, 1974; Sandberg, 1975; Wilkinson and Landing, 1978; Heller et al., 1980), and marine syndimentary cement (Folk, 1974). Although far-reaching in implication, many aspects of this concept remain unresolved, not the least of which is the nature of such oceanic chemical evolution which may involve changes in Mg/Ca activities (Folk, 1974; Sandberg, 1975), atmospheric  $PCO_2$  (Pigott and MacKenzie, 1979; Pigott et al., 1980), or some other variable which influences calcium carbonate equilibria in marine water. In addition, the timing of

these mineralogic successions remains to be evaluated. Sandberg (1975) suggested that, in response to the explosive evolution of marine planktonic organisms during the Jurassic and Cretaceous, aragonite became the dominant marine carbonate phase at the end of the Mesozoic. Pigott and MacKenzie (1979) and Pigott et al. (1980), however, suggested that, in response to declining  $PCO_2$  in the earth's atmosphere, calcite (and possibly dolomite) ceased to be the dominant primary marine carbonate phase during the Carboniferous. It is also entirely plausible that, as suggested by Sandberg and Popp (1981), such changes have been non-linear through time. MacKenzie and Pigott (1981) and Pigott (1981) postulated that high atmospheric  $CO_2$  levels and calcite precipitation corresponded to periods of high global sea levels, whereas low sea levels and low  $PCO_2$ 's correlate with an abundance of aragonite. Such long-term cyclicity may have resulted in the dominance of aragonite in Cambrian, Pennsylvanian, Permian, Triassic, Late Tertiary, and Quaternary seas, whereas calcite was the dominant phase in Ordovician, Silurian, Devonian, Mississippian, Jurassic, Cretaceous, and Early Tertiary seas. While equally tenable arguments could be based on other criteria, the timing and nature of such mineralogic successions can not now be unequivocally resolved owing to a lack of data on the primary composition of various Phanerozoic marine carbonate components.

Clearly, determining the applicability of Quaternary diagenetic models to ancient carbonate sequences is basic to carbonate geology. Do the morphologies of syndimentary marine high-magnesian calcite and aragonite cements from Holocene settings serve as adequate criteria to identify all marine cement in the rock record (e.g. Longman, 1980) or, in fact, have past oceans precipitated low-magnesian calcite as shallow marine cement owing to differing chemistries (see, e.g., Folk, 1974)? In order to evaluate this question, we have examined the habit, mineralogy, and composition of early cement within the Middle Ordovician Bobcaygeon and Verulam formations exposed near Lake Simcoe, Ontario.

#### ORDOVICIAN HARDGROUNDS

##### *General Setting*

In its type area near Lake Simcoe, Ontario, the Simcoe group consists of interbedded lime-

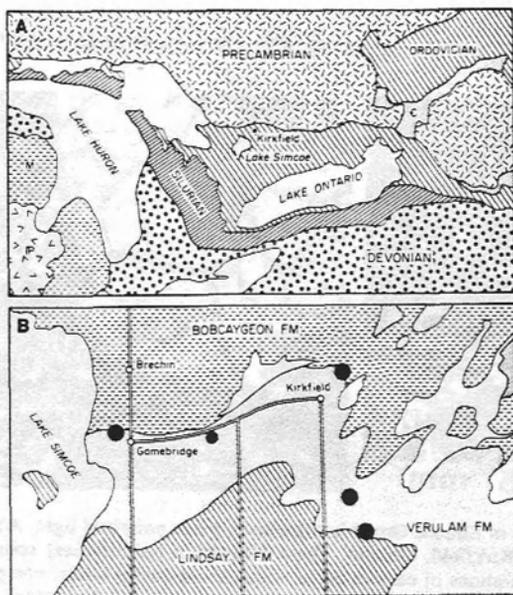


FIG. 1.—Location maps of the Simcoe Group and hardgrounds. A) Generalized geologic map of the central Great Lakes region showing the aerial distribution of Paleozoic rocks. Note that in the Kirkfield area, Ordovician sediments lie directly on Precambrian crystalline rocks. B) Geologic map of the Kirkfield area showing the distribution of the Bobcaygeon, Verulam, and Lindsay formations east of Lake Simcoe. Black dots locate exposures of Ordovician hardgrounds; larger dots locate outcrops of hardgrounds examined during this study.

stones and silty shales which were deposited unconformably on the eroded surface of the Canadian Shield during a Middle Ordovician transgression (Brett and Liddell, 1978; Liberty, 1969; Winder, 1960). Limestones within the Bobcaygeon and Verulam formations exposed near Kirkfield, Ontario (Fig. 1), are biomicrites and biosparites that commonly exhibit abundant burrows, cross-lamination, ripple marks, small channels, intraclasts, and highly abraded fossil debris (Brett and Liddell, 1978). On the basis of these features, Liberty (1969) suggested that these units record deposition in subtidal normal marine settings. The regional onlap of Middle Ordovician units onto Precambrian granites and gneisses of the Canadian Shield in this area supports such an interpretation (Brett and Liddell, 1978).

#### Hardground Surfaces

Numerous limestone units within this sequence exhibit features indicative of syndimentary lithification. These include dark stain-

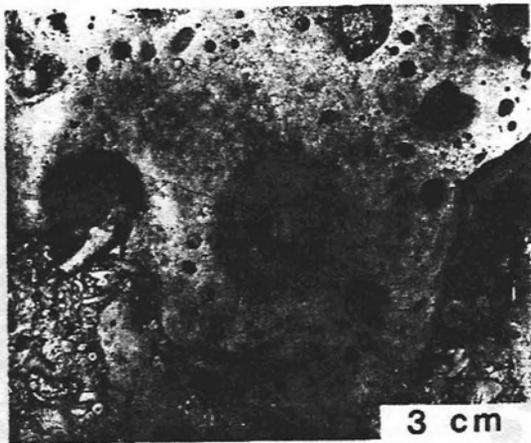


FIG. 2.—Upper surface of an irregular hardground hummock which was partially buried by skeletal debris, primarily crinoidal. Note the numerous vertical *Trypanites* borings.

ing on irregular surfaces, undercut knobs, borings, and encrusting fossils (Brett and Liddell, 1978).

The most conspicuous aspect of these surfaces is abundant borings of the ichnogenus *Trypanites*, which are circular in horizontal section, 0.1 to 2.0 mm in diameter, and exhibit straight-sided walls that taper to a roundly pointed terminus (Fig. 2).

These vertical borings may penetrate downward to depths of 3 centimeters. Depressions on upper surfaces are commonly filled with skeletal debris consisting primarily of crinoid ossicles and brachiopod and bryozoan fragments. Rarely, limestone pebbles, derived from surrounding lithified sediment, occur in the depressions. Cross sections of hardground hummocks exhibit irregular profiles, with a relief of 5 to 10 cm, that grade laterally into planar surfaces which truncate shells and intraclasts. Certain hardgrounds in the Kirkfield area also served as substrates for a diverse fauna of encrusting organisms, including encrusting bryozoans and stalked echinoderms that grew attached to lithified surfaces (Brett and Liddell, 1978). Many hardgrounds also exhibit a dark staining in their upper few millimeters recording the concentration of iron and/or manganese oxides at the hardground surface. Similar Fe-Mn staining is reported from modern marine hardgrounds (see, e.g., Land and Moore, 1980; Schlager and James, 1978).

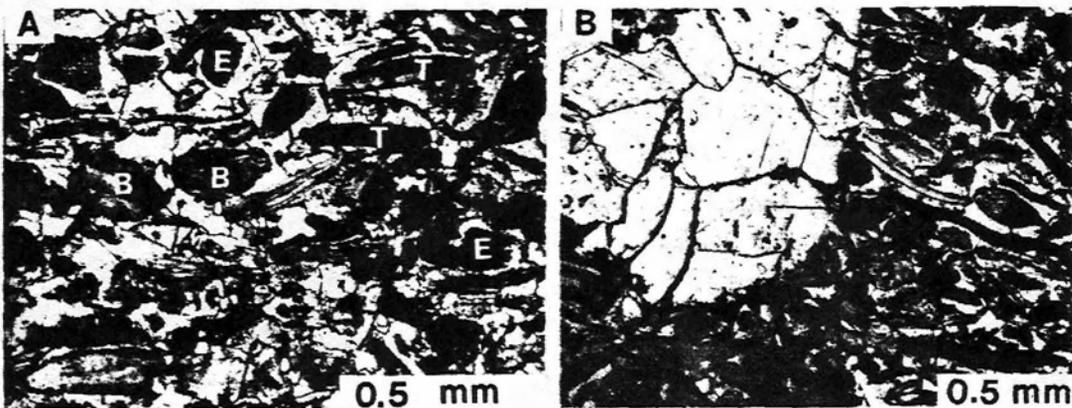


FIG. 3.—Thin section photomicrographs of Simcoe Group hardgrounds, plane polarized light. A) Lithology typical of Ordovician hardgrounds exposed near Kirkfield, Ontario. These biosparites (grainstones) consist of well-sorted shell debris in clear calcite spar. Two generations of cement occur within these coarse sands, one precipitated during initial lithification near the sediment/water interface, and one precipitated sometime after burial by younger units. Although the two generations of cement cannot be differentiated in this photomicrograph, cathodoluminescence demonstrates that each occupies approximately equal volumes of intergranular pore space near the hardground surface. Note abundant echinoderm ossicles (E) and common brachiopod (B) and trilobite (T) debris. B) Boring of the ichnofossil *Trypanites* which occurs densely on upper hardground surfaces. Immediately below the boring micrite has surrounded early cement and filled the remaining intergranular pore space. Lateral to the boring the residual pores were filled by a second generation of calcite spar which also filled the boring. Note truncated fossil debris and early cement along the boring margin.

#### Hardground Cements

Early cement in Simcoe Group hardgrounds can be differentiated from later porefilling cement employing two unequivocal criteria: 1) Crystals which are crosscut by *Trypanites* borings must be early because they predate bioerosion (Figs. 3B and 4A), and 2) pores lined by crystals are filled with later micrite. These crystal linings must be early cements because micrite emplacement into intergranular pores only occurred in immediate association with *Trypanites* borings, and hence, mi-

crite must surround cement crystals that were precipitated prior to boring excavation (Figs. 3B and 4B).

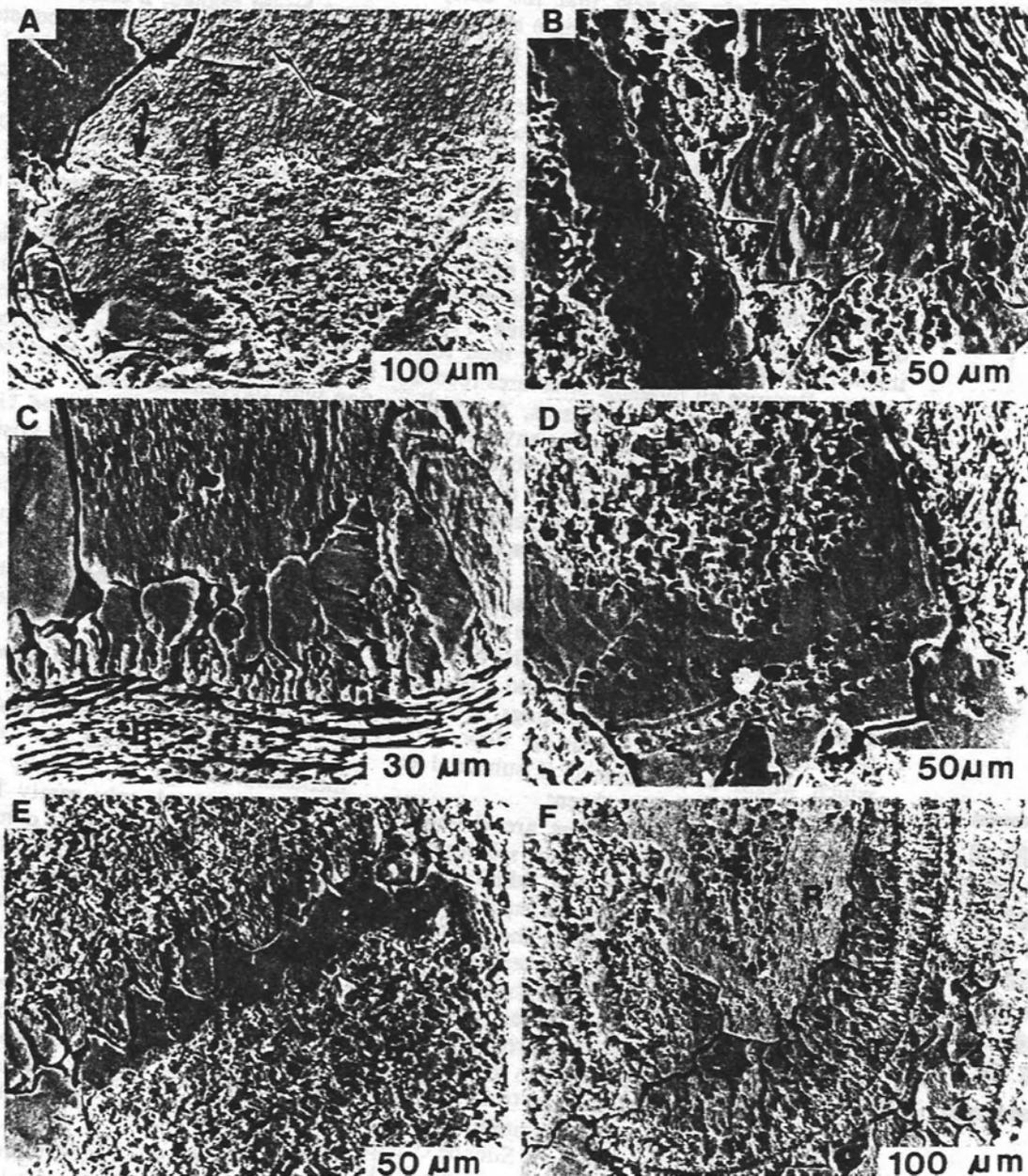
It was also found that early cements could be differentiated on the basis of their luminescence. In contrast to later calcite spar, which is generally non-luminescent, early cements typically luminesce a bright orange. This difference allowed us to estimate that early cements occupied approximately 50 percent of the intergranular pore space immediately below hardground surfaces prior to their penetration by *Trypanites* borings (Fig. 3A

FIG. 4.—Scanning electron photomicrographs of Simcoe Group hardground cements. Samples were polished and etched for 60 seconds in 50 percent glacial acetic acid. A) Contact between calcite-filled *Trypanites* boring (upper portion) and lithified biosparite (lower portion). Note that the boring margin (arrows) crosscuts both an echinoderm fragment (E) and an early syntaxial rim (R) which cemented the echinoderm fragment to other grains. Relationships such as these allow for the differentiation between early cements and later calcite spar. The late calcite spar (S) which fills this portion of the boring is in crystallographic registry with both the echinoderm fragment and the rim cement. B) Micrite (M), such as that seen below the *Trypanites* boring in Figure 3B, filling the pore space remaining after early cementation. In this field of view cements consist of euhedral calcite spar (S) on a brachiopod fragment (B) and syntaxial rims (R) on an echinoderm ossicle (E). Small patches of micrite within biosparites occur only in immediate contact with borings. Such relationships also allow for the recognition of early cements. C) Equant calcite spar (S), typical of early cement, on brachiopod, bryozoan, and trilobite debris in Simcoe Group hardgrounds. In this field of view note a brachiopod fragment (B) which serves as the cement substrate, and a coarsening of cement crystal size toward the pore interior (top of photograph). D) Echinoderm ossicle (E) surrounded by an early syntaxial calcite rim (R). Note the growth banding and inclusion-rich zones within this overgrowth which record the successive positions of crystal faces during cementation. E) Early equant spar (S) on a trilobite fragment (T) in contact with an early syntaxial rim (R) on an echinoderm fragment (E). F) Fabrics typical of Simcoe Group syndimentary hardground cements. Note equant calcite spar (S) on trilobite debris (T) and syntaxial rims (R) on echinoderm ossicles (E).

and B). The remaining pore space was then filled either with micrite in areas immediately surrounding borings or subsequently by calcite spar (Figs. 3B and 4B).

Early cements exhibit two typical habits which are always directly related to the nature of their respective substrates. Equant calcite spar occurs exclusively on common trilobite and brachiopod debris and on rare bryozoan fragments (Fig. 4B, C, E, and F). The equant

spar on these polycrystalline substrates typically exhibits a coarsening of crystal size away from grain substrates toward pore interiors (Fig. 4C). Conversely, unit crystal echinoderm ossicles serve as substrates for syntaxial overgrowths as rim cement (Fig. 4D, E, and F). These rims commonly exhibit euhedral growth bands through micro-relief developed during etching in acetic acid or through inclusion-rich zones within the overgrowth (Fig. 4D). With



the exception of these narrow zones, however, both syntaxial rims and equant spar are clear inclusion-free calcite.

#### INTERPRETATION

The fabric and composition of these cements, and the lithology, fauna, and stratigraphic setting of limestones within the Simcoe group strongly suggest that the early cements are syndepositional in origin and that cementation took place in a marine phreatic environment. Numerous macroscopic features of the hardground surfaces demonstrate that cementation repeatedly gave rise to well-lithified substrates which were modified by both physical and biological processes. Both pre-lithification and postlithification biogenic structures (burrows and borings respectively) are intimately associated in many of the hardgrounds, the walls of which exhibit varying degrees of sharpness, recording a range in sediment firmness (lithification) during their formation. Because all biogenic structures record the activity of marine organisms, the sediments must have been in a marine environment during cementation. Similarly, Brett and Liddell (1978) suggest, on the basis of taphonomic evidence, that a definite sequence of marine faunas grew on these surfaces during progressive lithification from soft, to firm, to well-indurated sediment. Such a sequence of faunas requires continuous marine conditions during cementation. In addition, the lithology and fauna of these limestones and shales indicate deposition in subtidal settings. Evidence for intertidal and/or supratidal deposition, which would be anticipated if subaerial exposure had occurred, is absent.

These hardground surfaces are devoid of features suggesting oxidation or selective dissolution which would record lithification by meteoric water during subaerial exposure. Also, hardground units are typically about 10 cm in thickness and are commonly overlain by even thinner shales. The thinness of these units precludes the possibility that pores were filled with meteoric water derived through recharge on land which lay kilometers to the northeast. Literally dozens of these units (the lower 3 m at Kirkfield, for example, contain at least 5 such horizons) occur within the Simcoe Group, a regionally onlapping sequence in the Kirkfield area, and similar hardgrounds have been

recognized in other Ordovician units throughout the midcontinent region of North America. The ubiquity of hardground units within these normal marine limestones, and the total lack of features which would have developed during subaerial exposure demonstrate that syndepositional cementation repeatedly lithified marine substrates during the deposition of this Ordovician carbonate sequence.

Simcoe Group hardground cements luminesce a bright orange, a characteristic typical of relatively manganese-rich carbonates. Meyers (1978) concludes that such  $Mn^{+2}$  enrichment in calcite cement is due to carbonate precipitation in reducing pore waters and is relatively unaffected by (values of) pH or temperature in intergranular voids. We conclude that although cementation repeatedly took place at the sediment/water interface in a normal marine setting, cement precipitation within Ordovician hardgrounds took place in reducing microenvironments from pore waters that were somewhat isolated, as the presence of  $Mn^{+2}$  in such cements precludes open communication with oxygenated water.

Clearly, the habit of Simcoe Group hardground cements precludes the possibility that they were precipitated as aragonite since they bear little resemblance to known calcitized aragonite from other ancient sequences (see e.g., Mazzullo, 1980; Sandberg, 1975). Were Simcoe Group hardground cements, then, precipitated as low-magnesian calcite or as high-magnesian calcite?

The subdivision of calcite cement into low-magnesian calcite (0–5 mole %  $MgCO_3$ ) and high-magnesian calcite (10–18 mole %  $MgCO_3$ ) is somewhat artificial in that Quaternary cementation settings are typically either marine or meteoric, and only rarely have cements from waters of intermediate composition been evaluated. As a result, recent cements are characteristically either magnesium-deficient or magnesium-enriched, depending on whether they were formed in meteoric or marine water respectively. In the context of Ordovician seas, however, there is no compelling reason why these calcites could not have had an intermediate composition between low-magnesian calcite and high-magnesian calcite, possibly in the range of 5–10 mole percent  $MgCO_3$ .

Simcoe Group hardground cement lacks microdolomite inclusions, which would indi-

cate a magnesian calcite precursor (Lohmann and Meyers, 1977). Echinoderm debris within Simcoe Group limestones, which surely were high-magnesian calcite, however, also lack microdolomite, suggesting that magnesium loss from former magnesian calcites took place without significant fabric modification.

The most significant aspect of the hardground cements is that they are identical to modern meteoric cement composed of low-magnesian calcite. Although acicular habits may be found as low-magnesian calcite, as high-magnesian calcite, and as aragonite, almost without exception non-micritic equant cement crystals in Quaternary carbonates are low-magnesian calcite. Equant calcite spar around polycrystalline brachiopod, bryozoan, and trilobite debris in Kirkfield hardgrounds is morphologically identical to meteoric low-magnesian calcite cement in calcitized Pleistocene sequences (see, e.g., Bathurst, 1975). Although syntaxial rim cement around echinoderm ossicles may be precipitated as either low-magnesian calcite (see, e.g., Longman, 1980) or as high-magnesian calcite (see, e.g., Myers and Lohmann, 1978), rim cement in Kirkfield hardgrounds is similar to meteoric low-magnesian calcite overgrowths reported from many Quaternary carbonate sequences. Even though the habit of rim cement does not lead to an unequivocal interpretation of calcite composition, the lack of acicular habits typical of known high-magnesian calcite, the similarity of equant calcite spar on non-echinoderm debris to known low-magnesian calcite, the abundance of rim cement on echinoderm debris from modern meteoric settings, and the formation of both cement types repeatedly at the same time within these Ordovician hardground units leads us to conclude that the composition of both cements was more nearly like that of modern meteoric cement than like modern marine cement. That is, they were precipitated as low-magnesian calcites.

#### DISCUSSION

Synsedimentary shallow marine cements that lithified Simcoe Group hardgrounds are mineralogically and morphologically identical to Holocene meteoric cements and are seemingly anomalous for cements precipitated in shallow marine settings. As pointed out by many workers, the relationships between car-

bonate cement mineralogy, composition, crystal habit, and physical and chemical environmental variables are complex. To date they have only been approximated by observation in natural and experimental systems. Several points, however, are relevant to an evaluation of the Ordovician marine cement.

Are Holocene marine cements exclusively aragonite and/or magnesian calcite, or is the inferred low-magnesian calcite composition of the hardground cement truly anomalous when compared to Holocene counterparts? Reported occurrences of Holocene marine cement indicate that they are almost exclusively precipitated as aragonite and/or high-magnesian calcite. Several notable exceptions do exist, however, as cement in synsedimentary marine hardgrounds forming at considerable depths in cold waters below the oceanic thermocline or stratified layer. Within such settings slow sedimentation, in conjunction with the stabilization of aragonite and high-magnesian calcite, results in the lithification of carbonate sediment through the precipitation of rhombic polyhedral crystals of low-magnesian calcite (Schlager and James, 1978). Such Quaternary cements are known from only a few deep-marine settings, environments surely dissimilar to those in which the Ordovician biosparites were deposited. However, they serve to show that in some modern marine settings, the magnesium concentration in calcite cement, as well as carbonate saturation in seawater, decreases with depth and that the path of seafloor diagenesis in such carbonates converges with that of meteoric systems (Schlager and James, 1978).

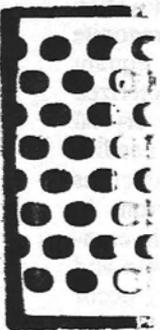
If all Holocene shallow marine cements are either aragonite or high-magnesian calcite, do these two metastable phases always exhibit characteristic crystal habits? Could Ordovician hardgrounds have been cemented by aragonite and/or high-magnesian calcite with equant crystal morphologies? All well-characterized aragonite cements exhibit an elongate crystal form that may range in size from small needles a few microns in width and about ten microns in length, to large laths tens of microns in width and hundreds of microns in length, commonly with square terminations (Assereto and Folk, 1976). Longer crystals frequently occur as radiating botryoidal masses (Ginsburg and James, 1976) or as uniform isopachous crusts (see, e.g., Longman, 1980). A possible ex-



ception to the generalization that all aragonite is acicular is coarse prismatic or blocky aragonite from fringing reefs along the north coast of Jamaica (Land and Moore, 1980). It is not clear, however, whether these are secondary recrystallization fabrics or merely large acicular aragonite crystals cut normal to their C-axis, or if, in fact, they are a primary equant aragonite spar. With this possible exception, all Holocene aragonite cements exhibit highly acicular crystal morphologies.

High-magnesian calcite is more variable in habit and typically occurs as micritic or steep-sided rhombic crystals (see, e.g., James et al., 1976) distributed either as isopachous layers (see, e.g., Longman, 1980), as pseudopellets (see, e.g., Macintyre, 1977), or as small spherulitic micro-ooids (see, e.g., Land and Moore, 1980). Where such crystals have grown to ten or more microns, however, they typically occur as rims of fibrous isopachous cement (see, e.g., Davies, 1977). With respect to coarse (non-micritic) cements, then, both high-magnesian calcite and aragonite are almost invariable acicular in shallow lithified Holocene marine substrates.

Thus, Holocene shallow marine cements are almost exclusively aragonite and/or high-magnesian calcite, and these two phases typically exhibit acicular crystal habits as coarse marine cement. Because Ordovician hardground units exhibit numerous features demonstrating repeated submarine lithification near the sediment/water interface, and because the cement which gave rise to this lithification is identical to meteoric low-magnesian calcite, such Ordovician cementation is truly anomalous when compared to reported Holocene counterparts.



If unknown from Holocene marine settings, how does the Ordovician low-magnesian calcite cement compare with marine cement reported from other ancient sequences? Two points are relevant to any discussion of cementation in older Phanerozoic systems. First, fibrous symsedimentary marine cement is known from rocks as old as Early Cambrian (James and Kobluk, 1978) and has been reported from numerous carbonate sequences throughout the Phanerozoic. More specifically, several of these have been identified as either former high-magnesian calcite (see, e.g., Lohmann and Meyers, 1977) or as former aragonite (see e.g., Mazzullo, 1980), based on included mi-

crodolomites (or elevated magnesium concentrations) or on elevated strontium concentrations, respectively. There is little doubt that fibrous isopachous cement, probably as high-magnesian calcite, and botryoidal fans, probably as aragonite, have formed repeatedly over (at least) the past 600 million years. Discounting diagenetic modification of fabrics and compositions, these symsedimentary cements exhibit a striking similarity to their Holocene counterparts.

Second, most ancient symsedimentary cements record lithification in reefal settings (e.g., Cambrian: James and Kobluk, 1978; Devonian: Walls et al., 1979; Permian: Mazzullo, 1980; and many other Mesozoic and Cenozoic units). Despite the abundance of hardground surfaces in ancient non-reefal sequences, few reports document the nature of the early cement which lithified the surfaces. These few, however, lend qualified support to our interpretation of Kirkfield cement. Although lower Ordovician hardgrounds in Sweden contain some pendant botryoids, similar to pendant ex-aragonite described by Assereto and Folk (1980), much of the early cement is interpreted as having been precipitated as low-magnesian calcite (Lindström, 1979, 1980). Hardground cement in the Mountain Lake Member of the Ordovician Bromide Formation in Oklahoma is identical to that in Kirkfield hardgrounds in that it consists of syntaxial rims on echinoderm fragments and sparry calcite mosaics on other fossil debris. As with limestones in the Simcoe Group, Bromide Formation hardgrounds occur within a transgressive subtidal sequence, contain borings, and exhibit attached echinoderm holdfasts on lithified upper surfaces (Longman, 1976). Similarly, abundant bored and cracked hardground horizons occur within the Ordovician Galena Group of the Upper Mississippi Valley. Individual hardground units within this sequence were repeatedly cemented by sparry low-magnesian calcite on the Ordovician sea floor (Delgado, 1979).

Cements within some younger hardgrounds exhibit morphologies more similar to those from non-reefal Holocene settings. Borings in Jurassic hardgrounds of northern France, for example, cross-cut syntaxial cement on echinoderm grains similar to that in Kirkfield hardgrounds, but other early cement is fibrous, suggesting an original composition of aragon-



ite or high-magnesian calcite (Purser, 1969). Similarly, Marshall and Ashton (1980) interpret early fibrous cement in oolitic hardgrounds from the Jurassic of eastern England as having been precipitated as high-magnesian calcite, analogous to aragonite-cemented Holocene ooids from the Bahamas (Dravis, 1979; Harris, 1978).

Several generalizations can be drawn from reported occurrences of marine cement in different settings through time. Isopachous fibrous cements have formed in reefal accumulations since the Early Cambrian and were probably precipitated as magnesian calcite. Botryoidal fans, probably aragonite, also occur in reefs as old as Cambrian (James, 1981). The few documented non-reefal marine cements in some Late Paleozoic, Mesozoic, and Cenozoic sequences exhibit habits, and probably had compositions, similar to Holocene non-reefal cements which are aragonite and/or magnesian calcite. Conversely, cements reported from some Early Paleozoic non-reefal units suggest that, as in Simcoe Group hardgrounds, dominant cement morphologies were equant spar on polycrystalline substrates and syntaxial rims on monocrystalline substrates. Both were probably precipitated as low-magnesian calcite.



Ultimately, the significance of low-magnesian calcite cement in early Paleozoic hardgrounds, or for that matter the relevance of the composition and mineralogy of any cement, is related to those physical and chemical parameters which control carbonate precipitation. From an environmental standpoint, the difference between shelf hardground cement and reefal cement constrains any speculation as to the significance of the various precipitated phases. The difference between these two settings most probably is related to the degree of communication pores enjoy with the overlying seawater. Considerably larger vugs in reefal masses, and the stronger currents generated by tides and waves in such shelf-margin settings, result in the movement of large volumes of marine water through pores during cement precipitation. Cementation within such systems, then, is frequently rapid, and cement composition and mineralogy directly reflect the chemistry of the normal marine water in which cement forms.

Conversely, in non-reefal shelf sand, current velocities may be greatly reduced at the sedi-

ment/water interface by bottom drag, pore volumes are relatively small in comparison to those in reefs, and communication with surrounding marine water may be so restricted that exchange occurs largely by diffusion through water. Such restricted communication is documented by luminescent Kirkfield hardgrounds. Even though cementation took place within a few millimeters of the sediment/water interface, pore waters during cement precipitation were probably anoxic. Pore waters were somewhat removed from direct and rapid communication with overlying marine water, and cementation may have taken place much more slowly than in coeval reefal settings.

Nevertheless, the precipitation of low-magnesian calcite as non-reefal cement in early Paleozoic hardgrounds cannot be dismissed as simply reflecting a localized intergranular water chemistry, completely removed from, and unrelated to, that of the overlying sea water. Low-magnesian calcite marine cement, in either reefal or non-reefal systems, is unreported from any shallow Holocene settings, and its precipitation in early Paleozoic units must, to some degree, record a difference in the composition of world ocean water.

The mineralogy and fabric of Kirkfield hardground cement have been unmodified since its precipitation near the Middle Ordovician sea floor. The similarity of these crystals to meteoric cement in Quaternary sequences substantiates the suggestion of Folk (1974) that some Paleozoic marine cement was, in contrast to modern marine counterparts, composed of low-magnesian calcite. Variation in the primary composition of Phanerozoic carbonate components is also recorded in the fabrics of ooids, metazoan body fossils, and, possibly, carbonate muds.

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