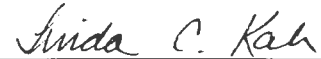


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I am submitting herewith a thesis written by Mark D. Pollock entitled "Morphology of Molar-tooth Structure in Precambrian Carbonates: Influence of Substrate Rheology and Implications for Genesis." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

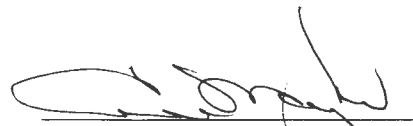


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**MORPHOLOGY OF MOLAR-TOOTH STRUCTURE IN
PRECAMBRIAN CARBONATES:
INFLUENCE OF SUBSTRATE RHEOLOGY
AND
IMPLICATIONS FOR GENESIS**

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee, Knoxville

Mark D. Pollock

May 2003

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ABSTRACT

Molar-tooth structure (MT) is an unusual Precambrian carbonate fabric characterized by variously shaped voids filled with uniform, equant microspar. A worldwide distribution of MT in Meso- and early Neoproterozoic rocks may be related to secular changes in substrate rheology and ocean chemistry through the Proterozoic. Unfortunately, the use of MT as a tool for understanding environmental evolution is limited because its genesis is still poorly understood. Recently, however, Furniss et al. (1998) showed experimentally that gas generated by decaying organic matter within unconsolidated mud can reproduce MT crack morphologies. A gas expansion hypothesis allows MT morphologies to be modeled as an interaction between the expansive force of the gas and the cohesion of the surrounding substrate. Three scenarios arise: 1) if the expansive force is significantly less than substrate cohesion, a blob morphology should result; 2) if the expansive force exceeds substrate cohesion, a ribbon morphology should result; and 3) if expansive force is significantly greater than the substrate cohesion, gas should diffuse randomly through the sediment pore space leaving no distinct void.

Evidence for each scenario is observed in MT from the 1.4 Ga Helena Formation, Belt Supergroup, Montana. Within similar, fine-grained carbonate substrates, an array of MT morphologies are behaviorally consistent with increasing gas production. However, the greatest variation in MT morphology occurs when cracks interact with sediments of differing grain size and, presumably, initial cohesion. MT cracks are observed to track or diffuse within coarse-grained layers, consistent with their greater permeability. In rare cases, coarse-grained material is observed to have collapsed into underlying cracks prior to precipitation of void-filling MT cement. Other MT structures become horizontal underneath and between microbial lamina, suggesting greater cohesiveness of these layers. These petrographic relationships are significant in that they support MT genesis by gas expansion, are inconsistent with other models of MT genesis, and suggest a strong rheologic control on MT morphologies.

Cathodoluminescence reveals MT microspar to have dull-luminescent cores with more brightly luminescent polygonal overgrowths. Experimentally produced vaterite, precipitated in the presence of dissolved organic molecules, are similar in size and morphology to the cores of MT microspar, suggesting that precipitation of MT microspar may have been aided by the presence of dissolved organics, perhaps linked with gas production by decay of organic material within the host substrate. In this scenario, migration of dissolved organic molecules from the surrounding substrate came in contact with supersaturated Mesoproterozoic seawater within MT voids, resulting in the precipitation of MT microspar. The presence of MT microspar as a first-generation cement within oolitic grainstones suggests that migration of dissolved organics from the underlying substrate could induce precipitation, even at the sediment-water interface.

Restriction of MT structures to the Meso- and early Neoproterozoic was likely related to a secular decrease of carbonate saturation through the Proterozoic. Whereas higher saturation and more rapid lithification of older substrates inhibited void formation, lower saturation in the Neoproterozoic likely prevented the rapid cementation necessary to preserve gas-produced voids. A critical level of carbonate saturation during the Mesoproterozoic and early Neoproterozoic, however, limited immediate substrate lithification, allowing void production, but remained high enough to allow environmental catalysts to initiate precipitation of MT microspar within voids and pore space.

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INTRODUCTION

Molar-tooth (MT) structures are an unusual Precambrian carbonate fabric in which ptymatically folded or broken sheets of uniform, finely crystalline calcite spar occur within a laminated carbonate matrix (Furniss et al. 1998). MT structures are both abundant and widespread (Fig. 1) within Mesoproterozoic (1600 – 1000 Ma) to early Neoproterozoic (1000 – 545 Ma) subtidal to intertidal environments (James et al. 1998), yet only rarely are found in older or younger successions (e.g., Bishop and Sumner 2002). The restricted occurrence of MT structures may therefore provide clues to particular environmental conditions present during Mesoproterozoic to early Neoproterozoic time. The morphology of MT structures is quite variable, ranging from: 1) straight, folded, and faulted sheet cracks with ribbon shapes; to 2) spheroidal blobs, which commonly show radial extension of sheet cracks; to 3) interconnecting frameworks of variously oriented ribbons or blobs. Observations of sedimentary laminae compacted around vertical ribbons and clasts of MT cement reworked as intraclasts (Smith 1968; O'Connor 1972) suggest that MT structures formed near the sediment-water interface by rapid cementation of voids or cracks in relatively unconsolidated fine grain matrix. Microsparitic carbonate that fills MT voids, however, does not display typical cement or neomorphic textures, such as crystal growth perpendicular to void walls or gradations into micrite, suggesting unusual conditions of crack cementation.

Although MT structures have been described repeatedly over the last century, the origin of these structures has remained enigmatic. Most studies have focused on determining the origin of MT voids as resulting from tectonic fracturing (Daly 1912), replacement of algal (O'Connor 1972; Moussine-Pouchkine and Bertrand-Sarfati 1997) and evaporitic (Eby 1977) structures; mudcrack deformation (Demicco and Hardie 1994), syneresis (Horodyski 1976; Young and Long 1977), diastasis (Cowan and James 1992) earthquake-induced dewatering (Fairchild et al. 1997;

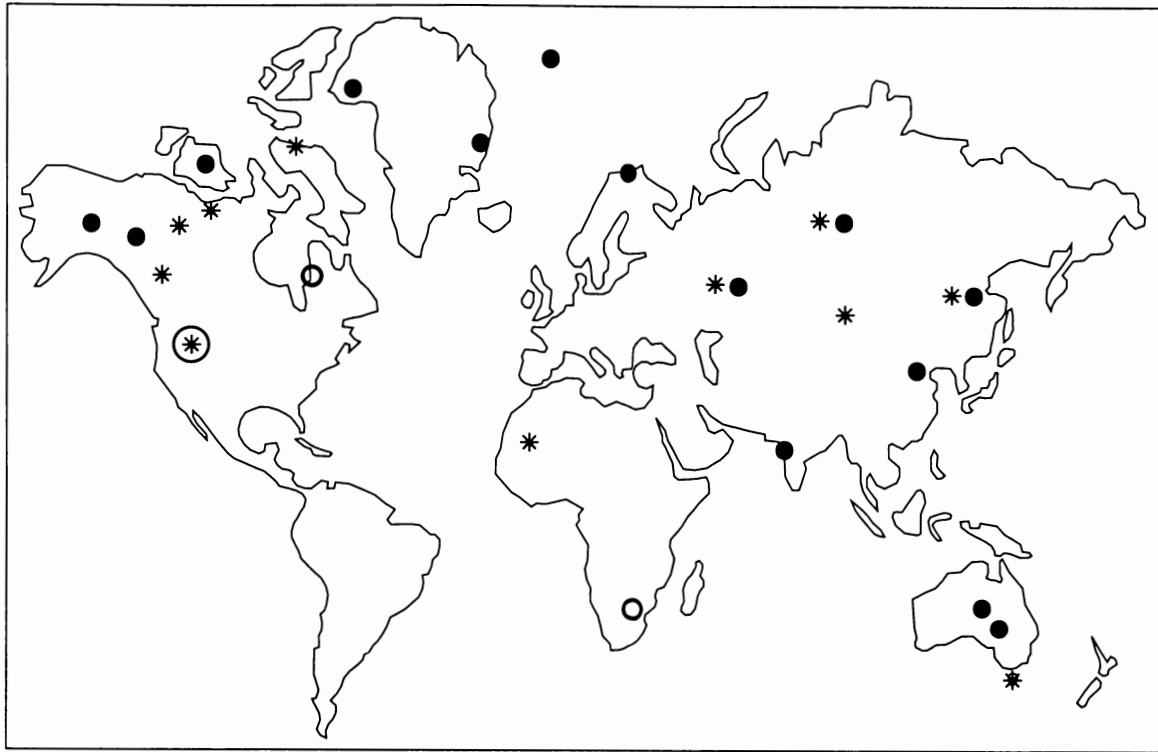


Figure 1. Documented occurrences of MT structures worldwide. See James et al. (1998) and Shields (2001) for locality references. Solid circles indicate Neoproterozoic occurrences; asterisks indicate Mesoproterozoic (1600-1000Ma) occurrences ; open circles indicate Paleoproterozoic and Archean (>1600 Ma) occurrences. Circled asterisk shows location of MT structures from the ~1400 Ma Helena Formation, Belt Supergroup.

Pratt 1998a), or gas expansion (Furniss et al. 1998). Fewer studies have focused on the origin of MT microspar fill (Eby 1977; Gellatly 1998; Frank and Lyons 1998), although this void-filling cement appears critical to the preservation of early-formed MT voids within uncompacted substrates.

Observations of thick, sea floor-encrusting CaCO_3 cements in the Archean and Paleoproterozoic, which grade to more micritic and slowly lithified substrates of the Neoproterozoic, suggest an overall decrease in marine calcium carbonate saturation through the Precambrian (Grotzinger 1989; Knoll and Swett 1990; Kah and Knoll 1996; Bartley et al. 2000). Because MT structures dominate in the transitional period between these differing regimes of carbonate precipitation (James et al. 1998), their abundance in the Meso- to early Neoproterozoic, as well as the unusual character of MT microspar, may be related to secular changes in the carbonate saturation state of marine systems.

A better understanding of MT genesis may result from constraining the parameters that control the morphology of MT structures. A syndepositional to early diagenetic origin for MT suggests that the complex morphologies of these structures result from a relationship between the mechanism of void formation, substrate rheology, and the timing and degree of subsequent cementation and compaction. Thus, morphological features of MT should provide insight into the mechanism of crack formation and void cementation. The purpose of this project is therefore to document field and petrographic relationships between molar-tooth morphology, depositional environment, and substrate composition in order to constrain rheologic controls on molar-tooth forms. Inferred rheologic constraints can then be used to test the compatibility of preexisting models of MT crack formation. Ultimately, if the origin of MT structures can be deciphered, MT structures might prove to be a valuable tool for understanding evolution of marine carbonate systems during the Meso- to early Neoproterozoic.

I. MOLAR-TOOTH STRUCTURES

Morphology

The term “molar-tooth” was first used by Bauerman (1885) to describe vertical to horizontal, crenulate sheets of calcite within rocks of the Belt Supergroup, Montana, which he likened to surface markings on the molar teeth of elephants. In outcrop, MT structures are visible on weathered surfaces where they appear as sharply bounded, light to dark gray, recessive features surrounded by buff-colored dolomitic lime mudstone. They occur predominantly within fine-grained carbonate rocks and are generally absent or rare within siltstone and sandstone. MT morphologies may be classified into two basic shapes: ribbons and blobs (O'Connor 1972). MT ribbons are vertical to horizontal cracks that may be straight to crenulated, or ptygmatically folded to broken (Fig. 2A and 2B); in three dimensions, ribbons have a sheet like geometry. MT ribbons typically measure a few mm in width and a few cm to tens of cm in length; horizontal ribbons are generally longer and less deformed than vertical structures. MT blobs appear as ovoid to circular voids (Fig. 2C and 2D), which measure a few mm to 1cm in diameter and commonly have protrusions of MT ribbons; in three dimensions blobs have spheroidal morphologies. Both blob and ribbon morphologies may occur together, forming interconnecting frameworks.

Calcitic Pods

Daly (1912) included an additional morphology within the definition of MT, which O'Connor (1972) termed horizontal structure. These calcitic, pod-shaped nodules typically parallel bedding and measure from one to several cm in thickness and several to tens of cm in length (Figs. 3A-D). Pods are composed dominantly of microspar but of a less uniform

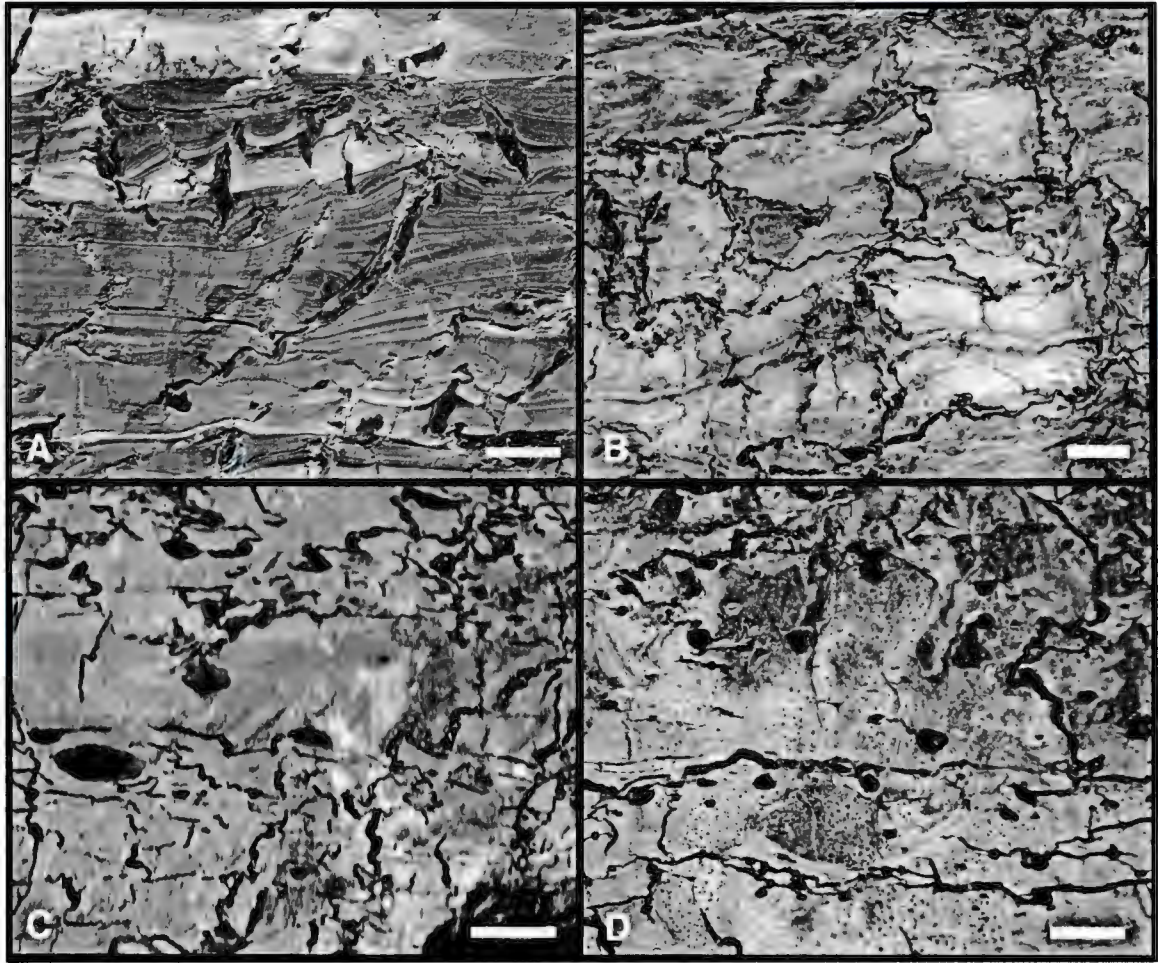


Figure 2. Morphologies of MT structures in the Mesoproterozoic Belt Supergroup include variously oriented, crenulated and broken sheet cracks termed ribbons (A, B), and spheroidal bodies that show protruding ribbons termed blobs (C, D). A) Compaction of sediment laminae around thick, straight, vertical ribbons demonstrates early lithification of MT voids. B) Vertical and horizontal ribbons can form complex interconnecting networks. C) MT blobs commonly show initial protrusions of ribbon morphologies. D) Ribbon protrusions can link blobs into networks. Scale bar is 1cm in all photos.

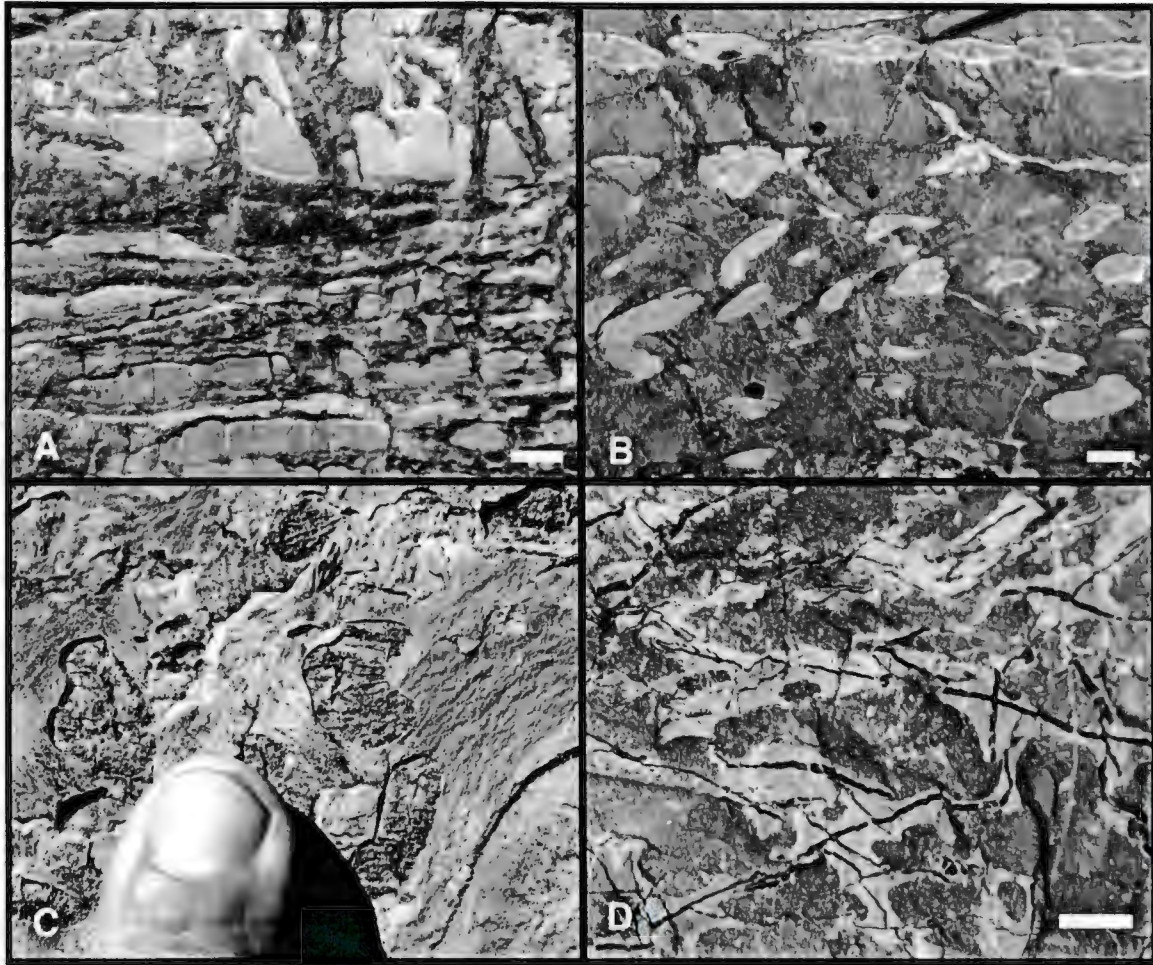


Figure 3. Various morphologies of calcitic pods that may or may not be genetically related to MT formation. A) Discontinuous horizontal pods grade into segmented and irregular shaped horizontal pods. B) Horizontally oriented, elipsoidal to subspheroidal pods, and vertically oriented folded/wavy pods, which display morphologies similar to some MT structures. C) Silty lamination across subspherical pods, suggesting that pods are early cemented nodules rather than void fills. D) Horizontal and vertical MT ribbons with pod-like halos, suggesting that early cementation of pods may be related to cementation of MT structures. Scale bar is 1cm in all photos.

nature than that which fills MT voids. Many workers have rejected the inclusion of pods or nodules into the definition of MT because they appear unrelated to those forms originally described by Bauerman (Smith 1968; Eby 1977; Winston and Lyons 1997; Furniss et al. 1998). Unlike blob and ribbon morphologies, some pods contain detrital material that may be randomly distributed, or form horizontal laminations (Fig. 3C) that pass into the surrounding matrix (O'Connor 1972; Eby 1977). These observations suggest that pods, unlike typical MT structures, probably do not fill open void space, suggesting pods reflect early lithification of sediments, rather than MT formation.

However, at least some pod-shaped nodules show a close relationship to ribbon and blob forms (Fig. 3D). Meter-scale cycles may show vertical transitions in from 1) horizontal pods (Fig. 3A) to 2) vertically oriented pods with wavy, ribbon-like morphologies (Fig. 3B) to 3) ribbons with pod halos (Fig. 3D) some with upward protruding ribbons, and finally to 4) vertical ribbons (O'Connor 1972; Eby 1977). This association suggests a connection between the void filling cement of MT and the pore filling cement of pods, making it difficult to exclude pods as MT. For the purpose of this paper, however, the term MT will be used according to the original description of Bauerman (1885) to refer to ribbon and blob structures. The terms pod and halo will be used to refer to microspar nodules and microspar layers around MT structures respectively, however, recognizing that pods may be polygenetic.

Molar-Tooth Microspar

MT voids are typically filled with an unusual carbonate microspar characterized by uniform, equant crystals ranging from 5-15 μm in diameter (Figs. 4A and 4B). Microspar commonly continues, without break, through interconnected voids, thereby suggesting a common origin for both ribbon and blob morphologies. Although MT microspar does not display typical

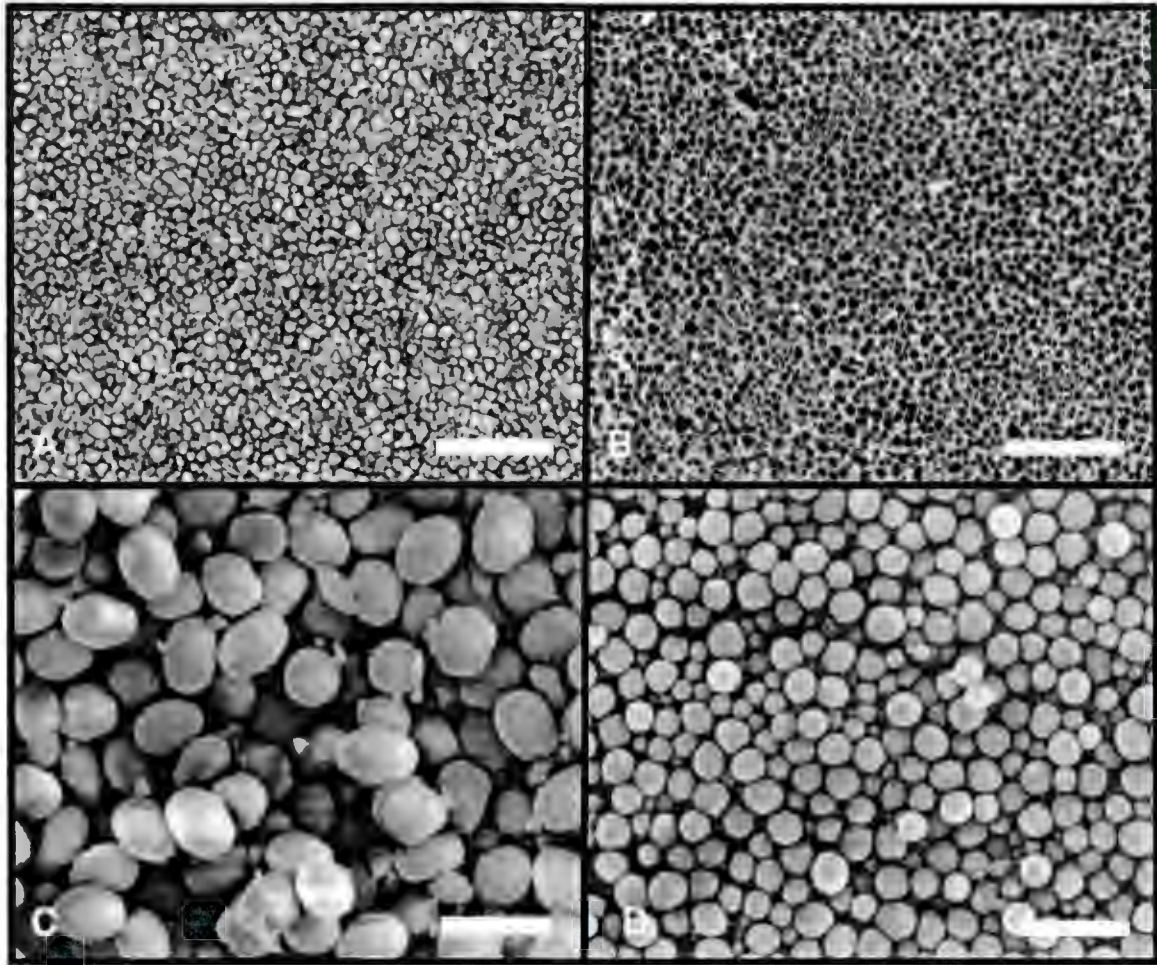


Figure 4. MT microspar cement. A) MT microspar is composed of uniform, equant crystals ranging 5 to 15 μm in diameter and average 7 to 11 μm . B) Cathodoluminescence of MT microspar reveals crystals composed of dullly luminescent, subrounded cores and more brightly luminescent, polygonal overgrowths. Recent calcium carbonate precipitation experiments have produced similar shaped spheroidal vaterite crystals in the presence of dissolved organic molecules (C and D from Naka et al. 2002). Precipitated crystals are similar in size and morphology to rounded dullly luminescent cores of MT structures, suggesting perhaps a similar origin. Scale bar is 100 μm in A and B and 10 μm in C and D.

cement or neomorphic fabrics (i.e., crystal orientation perpendicular to substrate wall, competitive growth boundaries, inward increasing grain size, inclusion-rich crystals, and irregular gradations of crystal size), several observations suggest that MT microspar is, in fact, cement. First, MT structures show sharp contacts with, and are distinct from, the surrounding host sediments, thus suggesting the presence of an original void. Voids typically lack detrital infill or geopetal features that would suggest a detrital precursor to MT microspar. Uniform crystal size distribution and distinct crystal boundaries suggest primary formation as homogeneously nucleated cement. In addition, MT microspar fill is known to contain well preserved acritarchs, cyanobacterial filaments, and spherical microfossils (Furniss et al. 1998), which would probably not have survived replacement (cf. Bartley 1996).

Under cathodoluminescence MT microspar crystals show uniform, rounded 3-5 μm non-luminescent to dull-luminescent cores surrounded by more brightly luminescent, polygonal rims (Fig. 4B) (see also Eby 1977; p. 230). Luminescence characteristics suggest that MT microspar crystals originated as initially micrite-sized, spheroidal particles, which provided nucleation points for later polygonal overgrowths. Interestingly, recent calcium carbonate precipitation experiments have produced rounded to spherical crystals of vaterite ($\mu - \text{CaCO}_3$) in the presence of dissolved organic molecules, specifically poly(amidoamine) dendrimer (Naka and Chujo 2001; Naka et al. 1999). In these experiments Na_2CO_3 and CaCl_2 were injected into a vessel containing poly(amidoamine) dendrimer and distilled water. Crystal formation began immediately after reactant addition. After four days the precipitated crystals were removed and analyzed with XRD and SEM. Whereas rhombohedral crystals of calcite precipitated in the absence of dendrimer, addition of dendrimer to the experiments resulted in both a larger yield of carbonate precipitates and precipitation of subspherical vaterite morphologies. Vaterite crystals precipitated in these experiments (Fig. 4C and 4D) were uniform in size, subspherical, and approximately 1.5 to 3 μm in diameter – identical in size and morphology to the cores of MT cement observed under

cathodoluminescence. By analogy, precipitation of MT microspar may have occurred in the presence of organic molecules, producing spheroidal vaterite crystals. These crystals would have provided the nuclei for later CaCO_3 overgrowth, which ultimately gives MT microspar its characteristic micro-polygonal morphology.

Interestingly, such a scenario presents the possibility that precursor particles may have acted in a detrital or plastic manner before complete cementation occurred, and may therefore record affects of fluid movement within the void space and/or compaction of surrounding sediment. This may explain rare occurrences of grain-size segregation in MT fills that result in flow banding or compaction of MT fill. More frequent incidences of coarser microspar at void cores (Young and Long 1977; Fairchild et al. 1997; Pratt 1998a) and multi-laminated void fills (Moussine-Pouchkine and Bertrand-Sarfati 1997; Bishop 2002) show distinct changes in grain size, and may represent incomplete void-filling or distinct void-filling events. The overall uniform texture of both core and overgrowth suggests, however, that precipitation must have been fairly continuous and rapid.

Morphologically identical microspar is also observed outside MT voids, within pore space of grainstones and intraclasts (O'Connor 1972; Fairchild et al. 1997; Pratt 1998a; Bishop and Sumner 2002; *this study*). These occurrences are typically associated with MT structure-bearing units, suggesting a relationship between the occurrence of pore-filling MT microspar and more typical void-filling microspar. Morphologically similar microspar has also been noted to fill cavities within organic-walled fossils (*Tawuia* and *Chuarina*; Hofmann 1985) that are normally preserved as carbonaceous compressions. Taphonomic experiments on modern cyanobacteria show significant alteration of organic structures within a matter of days to weeks (Bartley 1996), which would suggest that MT microspar must have originally precipitated almost immediately after void formation. That voids are lithified prior to compaction of surrounding sediment (Smith 1968; O'Connor 1972) further indicates rapid precipitation of secondary cement rims.

Gellatly (1998) also suggested that MT microspar was initially vaterite, pointing out that this polymorph of calcium carbonate meets the crystal size and timing constraints of MT microspar genesis. Vaterite is the most thermodynamically unstable polymorph relative to aragonite and calcite, inverting to calcite after precipitation within just a few days at room temperature (Gellatly 1998). However, kinetically it is the most favored of the three polymorphs during rapid crystallization, thus preferring conditions of high CaCO_3 saturation and high rates of crystal nucleation (e.g., Dickenson et al. 2002; Kitamura 2002). Rapid cementation requires high CaCO_3 saturation and is consistent with observations of changing carbonate fabrics throughout the Precambrian, which suggest an overall greater degree of CaCO_3 saturation relative to the Phanerozoic (Grotzinger 1989).

II. PREVIOUS HYPOTHESES OF MOLAR-TOOTH GENESIS

Although observations clearly indicate that MT structures are early diagenetic features formed as voids within uncompacted sediments (Smith 1968; O'Connor 1972; Furniss et al. 1998; Frank and Lyons 1998), the exact mechanism of MT formation has remained enigmatic since these structures were first described over a century ago. Previous studies have primarily focused on mechanisms of MT crack formation, attributing void genesis to a variety of biological, physical, and chemical processes.

Daly (1912), keeping the name “molar-tooth” as described by Bauerman (1884), initially interpreted MT structures as tectonic veins. In this hypothesis, MT structures resulted from calcite precipitation from fluids moving along joint and cleavage surfaces in the host rock. Later workers in the Belt Supergroup also supported this interpretation (Fenton and Fenton 1936; 1937; Rezak 1957). However, because MT structures formed before compaction and lithification of the host substrate, a tectonic fracture mechanism is unlikely.

Vertical and lateral gradations between MT structures and stromatolites (Smith 1968; O'Connor 1972), and the occasional appearance of bilaterally symmetric lamination within some MT microspar fills (Moussine-Pouchkine and Bertrand-Sarfati 1997), have led some workers to propose a biologic or organo-sedimentary origin for MT. However, MT structures commonly cut across sedimentary and stromatolitic lamina, lack organic material that can be locally abundant in matrix sediments, and do not resemble any known organic structures (Horodyski 1976; Eby 1977; Hofmann 1985). Alternatively, MT ribbons that parallel/merge into stromatolites may represent microspar-filled cracks that formed along microbial lamina or within void space produced during desiccation or decomposition of organic structures. In this scenario, the apparent bilateral symmetry of some MT microspar fills may simply reflect the presence of multiple generations of cement fill.

Eby (1975,1977) noted evidence for hypersalinity within the Belt Supergroup, including syndepositionally broken ooids, halite hoppers, haloturbation, and solution-collapse features, and proposed that MT structures were evaporitic in origin. Vertical ribbons were interpreted as shrinkage cracks, horizontal ribbons as thin surface crusts, blobs as trapped gas bubbles, pods as nodular anhydrite, and MT microspar as replacement after evaporitic minerals. However, ribbons are generally too tabular to have been evaporite crystals (Fairchild et al. 1997), and MT fill typically lacks elevated Sr, chalcedony, anhydrite inclusions or other relict fabrics that might suggest a calcium sulfate precursor (Pratt 1998a).

Demicco and Hardie (1994, p.86) suggested that MT structures might represent severely compacted mudcracks. However, lack of detrital infill, upward-opening V-shaped cross sections, horizontal cracks with curled up edges, and MT occurrence in subtidal to lower intertidal environments (James et al. 1998) suggest that MT structures are not subaerial desiccation features. Furthermore, Horodyski (1976) noted an inverse correlation between occurrence of desiccation cracks and MT structures, suggesting a subaqueous mechanism for their origin.

Cowan and James (1992) suggested that MT structures might be similar to diastasis cracks – subaqueous cracks that result from the mechanical behavior of sand vs. mud during application of mixed shear and tensile stresses produced by wave action at the sediment water interface. In this scenario, liquefaction and oscillatory motion of sand produced by the passage of large waves induces brittle fracturing of typically stiffer and more impermeable mud layers. Fractures are then rapidly filled with sand and later deformed by compaction. That MT structures lack detrital infill and cut across both sand and mud layers, however, suggests that they are not diastasis cracks.

Several authors have proposed a syneresis (subaqueous shrinkage) origin for MT structures, wherein voids were formed by sediment shrinkage, cemented by calcite at an early stage, and then compacted, causing deformation of ribbons (Adshead 1963; Bell 1966; Horodyski

1976; Young and Long 1977; Plummer and Gostin 1981; Calver and Baillie 1990; Knoll and Swett 1990). Two mechanisms are commonly invoked to produce syneresis cracks: 1) shrinkage of clay particles with changing salinity, and 2) compaction-forced dewatering leading to upward injection of pore fluid (Plummer and Gostin 1981; Cowan and James 1992). Support for a clay shrinkage mechanism is provided by laboratory experiments where subaqueous cracks are produced (e.g., Burst 1965), however these shrinkage cracks do not resemble any described occurrence of syneresis cracks within the rock record (Cowan and James 1992; Demicco and Hardie 1994 p. 68-71). If MT structures were produced by clay shrinkage, MT should occur predominantly within clay-rich sediments, however MT structures are typically most abundant within carbonate substrates (Fairchild et al. 1997; James et al. 1998; Pratt 1998; Furniss et al. 1998). If compaction-forced dewatering is invoked as the syneresis mechanism, MT structures should contain brecciated clasts and detrital infill, be traceable into underlying sediment layers, and be associated with mud volcanoes and deformed lamina (Demicco and Hardie 1994 p. 68-71). However, even where MT composes up to 80% of individual beds, implying massive dewatering and injection, none of the above features are observed.

More recently some authors have suggested that MT structures result from seismic shaking (Fairchild et al. 1997; Pratt 1998a). If it is assumed that ribbons were originally linear features, a seismic deformation mechanism might explain the extreme folding and faulting of some vertical ribbons. Measurements of ribbon length vs. bed thickness indicate that beds must have compacted between 70 - 80% in order to generate observed folding (Smith 1968; Fairchild et al. 1997; Pratt 1998a). The assumption of originally straight ribbons is supported by the early work of Smith (1968), who compared, within two layers, total ribbon length vs. present lamina thickness of 23 ribbons and showed statistically that these ribbons might have been originally linear features. Because sedimentologic evidence suggests that MT structures formed near the surface, overburden pressure would be unlikely to produce such extreme compaction.

Fairchild et al. (1997) proposed that MT resulted from earthquake-induced seismic activity and subsequent wave action, producing sub-vertical cracks by brittle failure of mud and sand similar to that occurring during diastasis crack formation. In this case, the distribution of cracks would be controlled by lithology, bed geometry, seismic wave propagation, and ocean wave activity. After fractures formed, water expulsion would keep cracks open until subsequent carbonate precipitation occurred, later compaction would deform crack-fillings. In some cases further seismic activity would result in brecciation and faulting of ribbons.

Pratt (1998*a*; 1998*b*) proposed a similar, seismically induced syneresis origin for MT structures. In this scenario, MT structure would form by seismic shaking, liquefying and compacting the host sediment, thus creating a variety of sheet-like cracks and pockets. MT voids would subsequently be filled by lime mud migrating from the matrix, while clay particles within the surrounding substrate, held together by electrostatic attraction, would remain outside these seismically produced fissures. Continued seismic activity would deform cracks either plastically or brittly, depending on cohesion of the infilled material. In support of a seismic origin, Pratt (1998*a*) cites observations of associated microfaults, fractured and brecciated stromatolites, ball-and-pillow structures, and convolute lamination. Pratt (1998*a*) also noted that some MT fills grade into sedimentary dikelets filled with sand, silt, clay, micrite, and microspar.

However, within the Belt Supergroup, where abundant and diverse MT structures are present, these potential seismites are rare and not directly associated with MT occurrences (Winston et al. 1999). In addition, because seismites may be produced by a variety of processes including mass movement, rapid depositional loading, dewatering, and storm activity (Ettensohn et al. 2002), an origin by seismic activity must be differentiated from other possible causes. According to Ettensohn et al. (2002, and references therein), four criteria may be used to differentiate seismites: 1) deformation is consistent with features of known seismogenic origin, 2) widespread occurrence of deformation occurs in temporally and stratigraphically constrained

horizons, 3) deformation shows an increase in frequency and intensity toward a likely epicentral area, and 4) other possible causes may be reasonably excluded. Although MT distribution can be laterally extensive across individual beds (e.g., O'Connor 1972), neither MT structures or syneresis cracks are associated with the aftermath of known earthquakes (Pratt 1998*b*; Winston et al. 1999). In addition, MT structures do not have a zonal distribution of increasing intensity, and other possible causes, may not reasonably be ruled out, thus suggesting that MT structures are not seismites.

The uniform nature of MT microspar and lack of gradations between MT microspar and partly altered lime mud indicate that MT microspar is cement, and not sediment infill. MT microspar does not fill voids geopetally, rather, it characteristically fills the entire void space and typically lacks any detrital infill. It seems unlikely that lime mud could be preferentially carried into MT voids by seismic shaking without also incorporating significant fractions of clay sediment, or disrupting surrounding lamina. Rather, MT structures commonly occur within substrates composed of many fine laminations, which are characteristically undisturbed except for compactional draping around early-cemented MT voids. It seems difficult to reconcile formation of MT structures by seismically induced syneresis in the absence of widespread occurrences of seismogenically-deformed carbonates (cf. Onasch and Kahle 2002; Ettensohn et al. 2002).

Although MT structures are not likely to result from seismic activity, MT morphologies may have been influenced by seismic activity after their formation. This scenario seems likely for some unusual MT structures within the Atar Group, Mauritania (Bartley et al. 1999), where atypical MT structures, including rosettes and clusters of contorted MT structures, are associated with possible seismic deformation features (microfaults, pillow structures, and liquefied beds) (Moussine-Pouchkine and Bertrand-Sarfati 1997). Bartley et al. (1999) suggested that seismic activity played a role, not in MT formation, but in the post-depositional deformation and resedimentation of MT structures.

III. MOLAR-TOOTH FORMATION BY GAS EXPANSION

Furniss et al. (1998) proposed that MT structures resulted from gas expansion within the host substrate produced by the metabolic activity and/or decomposition of organic material within MT-bearing sediments. A series of laboratory experiments, in which yeast and sugar were added to a water-saturated matrix of kaolinite mud, with or without addition of plaster of Paris as a stiffening agent, demonstrated the viability of a gas expansion hypothesis. In the first phase of experiments, glass aquaria filled with yeast-sugar-kaolinite slurries were left open at the surface to simulate gas production near the sediment water interface. CO₂ gas generated by metabolizing yeast resulted in the formation of spherical bubbles within the mud slurry. Upon continued gas production, bubbles rose through the surface flinging out mud and pulling pore water behind, creating conduits for sediment dewatering and continued gas escape. Dewatering resulted in significant stiffening of matrix sediment and restriction of gas and fluid escape to pre-established pathways. Continued gas production within these more cohesive sediments forced open thin, sinuous sheet cracks projecting from trapped bubbles. In contrast, regions of minimal gas production retained spherical void morphologies. In the second phase of experiments, slurries were capped with Plaster of Paris to simulate gas production beneath a confining sediment layer. Under these conditions, a variety of well-developed horizontal and vertical sheet cracks formed with both straight and sinuous morphologies.

Together, these observations suggest that both blob and ribbon MT morphologies may be produced by a single mechanism, wherein variations in sediment cohesion and surface confinement play important roles in determining migration pathways of early diagenetic gas production. Such a hypothesis is compelling because it provides a common origin for a wide variety of observed MT morphologies and satisfactorily accounts for their early post-depositional formation near the sediment-water interface.

IV. CONCEPTUAL MODEL FOR MOLAR-TOOTH GENESIS BY GAS EXPANSION

Examination of a gas expansion hypothesis can be taken one step further by developing a conceptual model that relates the expansive force of the gas to the cohesive properties of the surrounding substrate. In this model, differing substrate rheologies can be assessed in terms of their sediment cohesion. Sediment cohesion is represented by all those factors that affect how the substrate deforms in response to an applied stress. These factors will include grain size, sorting, compaction, microbial binding, and cementation. Differing MT morphologies can then be modeled as an interaction between the expansive force of the gas and the cohesion of the surrounding substrate. Less permeable substrates, such as a fine-grained, microbial bound, compacted, or early lithified sediment, should be more likely to resist the force of expanding gas and should result in well-defined voids. More permeable substrates, such as well-sorted coarse-grained sediment, will affect void generation by allowing gas to dissipate and diffuse through the sediment pore space, rather than deforming the substrate to create void space. This scenario implies that differing morphologies produced by gas expansion will require a particular level of sediment cohesion, such that the sediment is not so cohesive as to prevent deformation during gas migration, but cohesive enough to prevent gas escape without active substrate deformation. Experiments of Furniss et al. (1998) suggested that a particular range of moderate substrate cohesion interacting with differing amounts of gas is required to produce MT structures.

In this conceptual model, three distinct endmembers arise (Fig. 5). First, if the expansive force of the gas is significantly less than the substrate cohesion, a blob morphology should result. In this case, the surrounding substrate, equally confining in all directions, produces a spherical morphology as the gas expands equally in all directions. Ideally, this endmember should describe the formation of all MT structures during initial gas production, when gas volumes remain low. As an endmember MT morphology, this scenario should arise in fine-grained, non-permeable

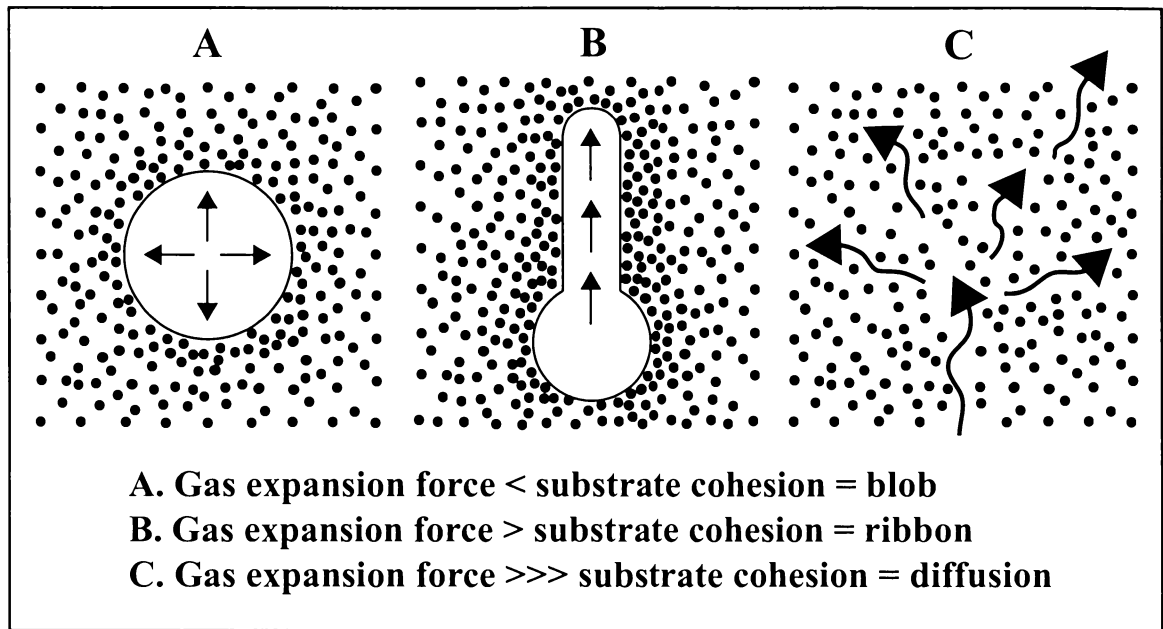


Figure 5. Conceptual model for the origin of different MT morphologies by the interaction between gas production and substrate cohesion. A) If the expansive force of gas is less than the substrate cohesion, expanding gas will be confined equally in all directions, resulting in a blob morphology. B) If the expansive force of the gas is greater than the substrate cohesion, either because there is greater gas expansion or less substrate cohesion, a ribbon morphology should result. Ribbons should propagate upward as gas moves toward the unconfined sediment-water interface. C) If the expansive force of the gas is much greater than the substrate cohesion, the gas should diffuse freely between individual substrate grains, resulting in very irregular or indistinct MT voids.

sediments, or microbially bound or partially cemented substrates where substrate cohesion inhibits gas bubbles from escaping upward. In a second endmember case, if the expansive force is greater than the substrate cohesion, a ribbon morphology should result. In this second case a sheet crack will be produced, either because of increased gas pressure or inhomogeneities in substrate cohesion. Cracks should propagate upward as the gas moves toward the sediment-water interface to escape confining pressures within the substrate. Ribbons should, therefore, show mostly vertical orientation unless an overlying barrier or inhomogeneity (e.g. an impermeable layer) makes lateral crack propagation more favorable. Ribbon formation should arise in fine-grained sediments with higher cohesion (perhaps resulting from surface confinement), such that gas pressure is able to increase past a critical level where more sudden expansion results in sheet crack propagation in a direction of weakness or less cohesion. In a third endmember scenario, if the expansive force is much greater than substrate cohesion, the gas should diffuse through the sediment pore space leaving a very indistinct void or none at all. This scenario will be expected to arise most frequently in coarse-grained sediments, in which gas would preferentially diffuse into pore space rather than pushing grains aside. Less frequently, diffusion may arise in fine-grained sediments that show little cohesion, such as recently deposited, water-laden sediments at the sediment-water interface.

Ultimately, this conceptual model suggests that the morphology of MT structures should differ predictably within substrates of differing rheology. MT structures within less permeable substrates will be more abundant and well developed, whereas MT structures within more permeable substrates will be indistinct or absent as a result of diffusion of crack-forming gasses. In particular, MT structures that cross substrates of differing rheology (e.g., fine- to coarse-grained layers) should show morphological change consistent with this model if gas expansion is the crack forming mechanism. The main focus of this study, therefore, is to test model morphological predictions against observed variations in MT forms.

It is important to note that, because only void space that is cemented by microspar before compaction of surrounding sediment is preserved, MT structures are most easily defined by the presence of characteristic MT microspar cement. Preservation of gas pathways through permeable substrates or irregular void space requires that cementation occurs very rapidly after gas expansion. Early cementation by MT microspar is therefore an assumption of this model. If this assumption holds true, diffusion of gas through substrate pores, if present, may potentially be expressed by the occurrence of MT microspar within substrate pore space.

V. GEOLOGICAL FRAMEWORK

MT structures were observed and described from the Belt basin in western Montana (Figs. 1 and 6), a northwest-southeast trending basin extending from Montana and Idaho into Alberta and British Columbia (Harrison 1972; Horodyski 1983; Winston and Link 1993). Deposition of Belt Supergroup strata occurred between 1470-1401 Ma (Evans et al. 2000), during which time the Belt basin showed variable connection to the open ocean (Frank et al. 1997; Lyons et al. 2000; Luepke and Lyons 2001). Sedimentological data suggest a predominately western source for fine-grained siliclastic sediments (Winston and Link 1993), a provenance believed to be represented by parts of Australia (Ross et al. 1992; Blewett 1998). Uncertainties, however, regarding the boundaries of the Belt basin and the degree of linkage between the Belt basin and the open ocean have led to the interpretation of Belt sedimentation as predominantly lacustrine in nature (Winston et al. 1984; Winston and Link 1993, and references therein). However, recent isotopic data suggest that the at least the Prichard and Helena formations were deposited in a shallow marine environment connected to the open ocean, though perhaps episodically isolated (Hall and Veizer 1996; Frank et al. 1997; Lyons et al. 2000; Luepke et al. 2001).

The Belt Supergroup is subdivided informally into the Lower Belt Group, Ravalli Group, Middle Belt Carbonate, and the Missoula Group (Fig. 6). The 1.45 Ga Helena Formation (Evans et al. 2000) is the eastern facies of the Middle Belt Carbonate and contains abundant and diverse MT forms. The Helena Formation is an approximately 800m thick unit composed of calcitic and dolomitic mudstones with interbedded grainstones, sandstones, and stromatolites, which were deposited in a shallow subtidal to intertidal setting (Horodyski 1983). The present study focuses on the middle to upper Helena, which contains a laterally persistent *Baicalia* and *Conophyton* stromatolitic unit (~200m below top of the Helena Formation; Horodyski 1976; 1983) that aids in

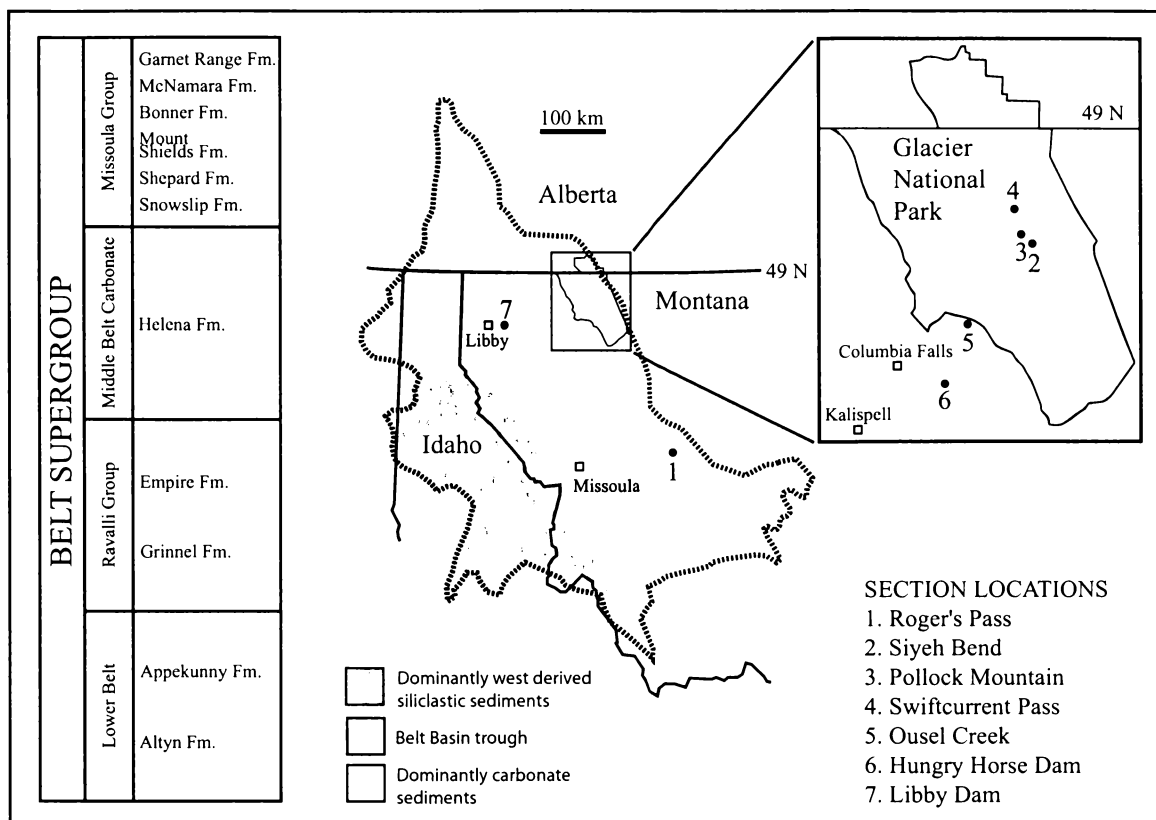


Figure 6. Generalized stratigraphy and location map for the Precambrian Belt basin, northwest United States, with formation names for the eastern Belt basin, including exposures in Glacier National Park (after Winston and Link 1993). Locations of seven measured sections within the middle Helena Formation are shown as numbered dots. In the eastern basin, from the Helena Embayment in the south to Glacier National Park in the north, the Helena Formation is characterized by two part cycles with westerly-derived, fine-grained, siliciclastic rocks at the base, and locally derived carbonates and rare, eastern-derived, cratonic quartz sand. In the central basin, near Libby, cycles become progressively dominated by westerly-derived, siliciclastic rocks.

the correlation of units over large regions of the basin. Fining-upward siliclastic-to-carbonate cycles, 1 to 10m thick, and bounded by scoured surfaces, characterize the Helena Formation (O'Connor 1972; Eby 1977; Winston et al. 1984; Winton and Lyons 1997; Frank and Lyons 1998). To the east, cycles are more carbonate-rich, while westward, cycles become more siliclastic as the Helena Formation grades into the Wallace Formation (Winston and Link 1993). Upward, the Helena Formation shows an increased abundance of stromatolites, oolites, dolomitic mudstone, and desiccation cracks (Horodyski 1976, 1983). Combined with isotopic data showing increasing ^{18}O and ^{13}C enrichment, these features suggest increasingly evaporitic, shallow-marine conditions during Helena deposition (Frank and Lyons 2000; Frank et al. 1997).

The Helena Formation, Belt Supergroup also contains the greatest abundance and largest morphological diversity of MT structures so far described (Smith 1968; O'Connor 1972; Eby 1977; Furniss et al. 1998; Pratt 1998*a*). Both blob and ribbon morphologies are abundant and MT structures show distinct patterns within shoaling cycles (O'Connor 1972; Eby 1977; Furniss et al. 1998; *this study*), suggesting rheologic influences. The Belt basin shows only low-grade greenschist-facies metamorphism (Eslinger and Savin 1973; Hall and Veizer 1996), and is well exposed along its eastern margin within Glacier National Park and the surrounding area, allowing detailed description of MT forms.

VI. METHODS

Seven stratigraphic sections (Appendix A) were measured through the Mesoproterozoic Helena Formation. MT distribution and morphological variation were described within stratigraphic sections and meter-scale cycles noting, in particular, relationships between crack morphology/distribution and substrate facies. Section locales were chosen based on exposure (preferred sections were continuous to the stromatolite marker bed and exposed well enough that MT morphologies could be adequately described), and environment (sections needed to provide differing environmental/substrate conditions that could be used to constrain MT distribution). As best as possible, a shallow-to-deeper water transect of the Helena Formation was made in order to capture a range of depositional environments.

Forty-nine thin sections of MT structures and other carbonate fabrics were made from samples collected from measured sections (Appendix B). All macroscale morphologies were sectioned, including vertical ribbons, horizontal ribbons, blobs, ribbons with halos, and pods. In addition, other coarse-grained facies were sampled where MT structures were not apparent, including oolites and intraclastic grainstones. Thin sections were analyzed for any relationships between MT microspar fill and substrate. Because the goal of this study was to determine substrate controls on MT morphology, intervals of expected rheological change (e.g., alternation of fine- to coarse-grained layers) were preferentially sampled.

VII. FIELD OBSERVATIONS

Helena Formation Lithofacies

MT structures occur in carbonate rocks composed of six interbedded lithofacies: 1) carbonate mud – argillaceous dolomitic mudstone with minor thin graded silt lamina and local mudcracks; 2) fine sand/ mud couples – 3 to 10cm thick graded beds of fine quartz sand to dolomitic mudstone (mudstone layers tending to be thicker than sand layers) with undulose to planar bases, 3) fine sand/mud couplets – < 3cm thick graded beds fine sand/silt to siliclastic mud with planar bases typically lacking a carbonate component, 4) intraclastic grainstone – elongate clasts of MT microspar, dolomitic mudstone, and fine quartz sand in microspar matrix with scoured and planar bases, 5) Oolitic and quartz sand – ooids and well-rounded quartz sand, 6) stromatolites – domal to flat topped stromatolites 3cm to 2.5m thick (Table 1). The lithofacies used here are modified from Winton and Lyons (1997 and references therein) who provide a more detailed discussion of the various lithologies and environmental interpretations.

Lithofacies combine to form overall fining-and shallowing-upward cycles (Fig. 7), 1 to 10m thick, that typically consist of three parts: 1) a coarse basal lag, commonly consisting of MT intraclasts or other coarse-grained facies, 2) a siliclastic-rich unit typically composed of alternating fine sand and mud couplets or couples, and 3) an upper, fine-grained dolomitic unit consisting of carbonate mudstone or carbonate-rich couple facies. In eastern sections stromatolitic facies, when present, occur predominantly atop basal lags; oolitic sand facies show variable distribution and increase in abundance above the *Conophyton* zone; and carbonate mudstone dominates most cycles. Abundance of carbonate mud, couplet, oolitic and quartz sand, intraclast, and stromatolitic facies eastward, result in greater cycle variability (Fig. 7). Western cycles are generally thicker, siliclastic-rich, and composed only of a two-part cycle consisting of a

Table 1. Lithofacies within the Middle to Upper Helena Formation

Facies	Bed Thickness	Characteristics	Molar-tooth structures
Carbonate mud	0.5 - 7m	Fine-grained dolomitic or calcitic mudstone; massive to indistinctly graded beds with fine silt at bases.	Blob to ribbon morphologies common; MT structures cover between 5 to 30% of bed face and locally up to 80%
Fine sand/mud couple	0.5 - 7m	3cm to 10cm thick graded beds of fine quartz and feldspar sand to lime mud and/or clay minerals; planar to undulose bases	Blob to ribbon morphologies common within fine-grained portions of more lime-rich couples with densities similar to carbonate mud facies; ribbons are variously deformed when present across fine- to coarse- grained layers
Fine sand/mud couplet	0.5 - 6m	<3cm thick graded beds of fine quartz and feldspar sand to lime mud and/or clay minerals; planar to undulose bases	MT structures less common; blob and ribbon morphologies present within more lime-rich couplets; ribbons are highly sinuous being affected by lamination; horizontal calcitic pods often present within coarser laminations of more siliclastic rich couplets
Intraclast	1 - 40cm	Elongate clasts ~1-2mm thick by 1-3cm long of MT structures, pods, micrite, and fine sand to silt size quartz and feldspar within a matrix of micrite or MT microspar cement; planar to undulose bases with up to 20cm of relief but typically on the order of 3 to 5cm	Underlying ribbons are truncated at scour surfaces or protrude upward 1 to 3cm into basal portion of intraclast
Oolitic and coarse sand	3 - 80cm	Sand size ooids, peloids, well rounded quartz grains, and elongate MT clasts within matrix of MT microspar cement; ooids are the dominate grain; rare quartzose beds; planar bases	Blob and ribbon MT structures absent
Stromatolite	0.1 - 6m	Domal to flat top stromatolites 3cm to 2.5m high; Columnar <i>Baicalia</i> and <i>Conophyton</i> forms present within 20-30m thick stromatolitic marker bed; basal contact commonly intraclast, oolite, scour or karst surface.	Discontinuous horizontal MT ribbons often make up and merge into microbial lamina; other MT structures cut across stromatolite lamina; laterally stromatolites may grade to beds with abundant MT, while locally some horizontal ribbons may grade vertically into strom lamina; curved elongate pods make up some stromatolite lamina

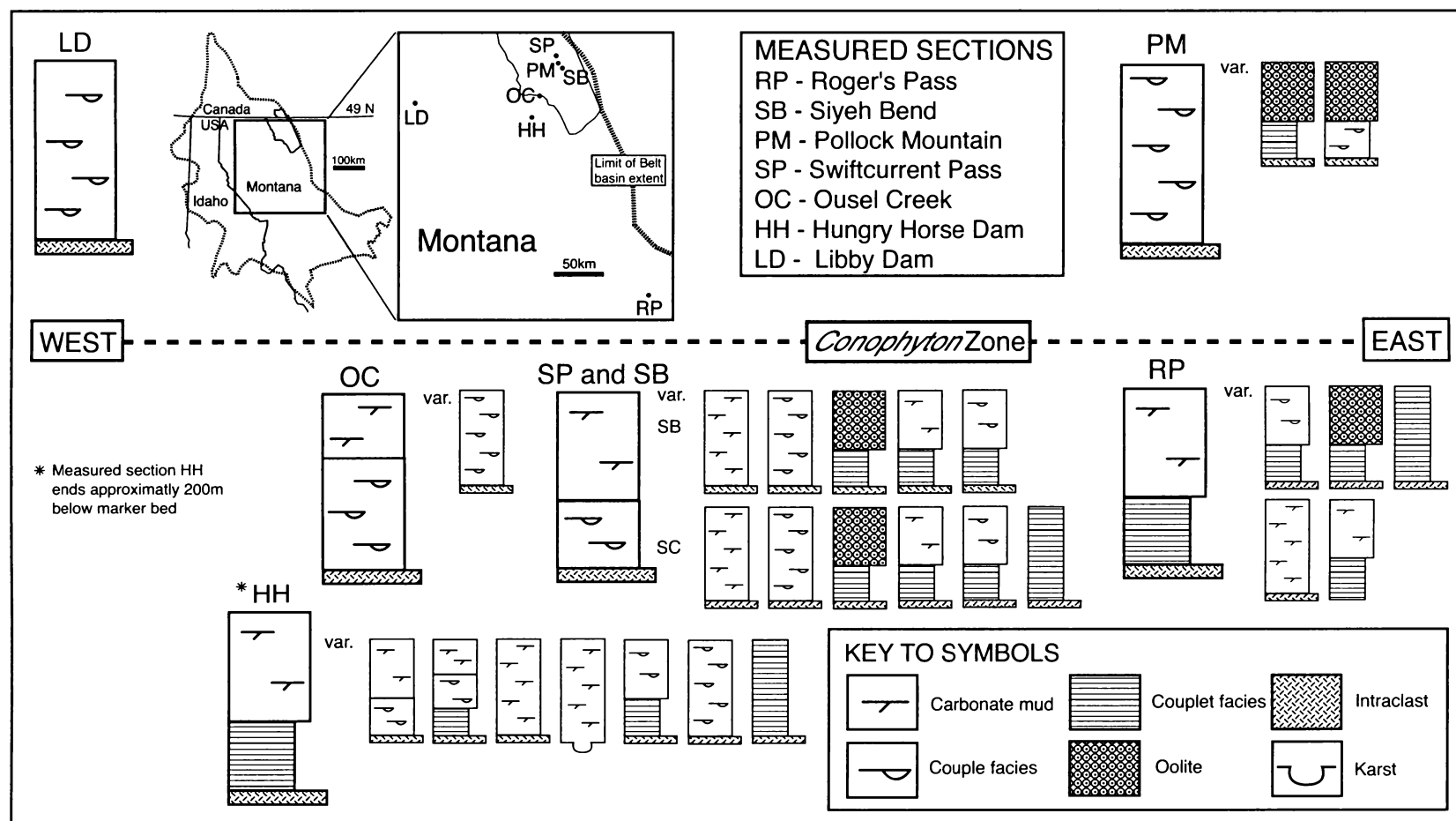


Figure 7. Idealized cycles of the Helena Formation. The dominate cycle type for each section is largest in size, with subordinate variations shown to the left. Sections are shown in terms of their relative geographic distribution and vertical position above or below the *Conophyton* marker bed. Cycles vary between 1 and 10 meters thick, are typically thicker to the west, and consist of variable proportions of carbonate mud, couple, couplet, intraclast, and oolitic facies (see text for description). Eastern cycles are more variable and contain a greater abundance of oolites, intraclast, couplet, and carbonate mud facies, whereas westward cycles are more siliclastic-rich and dominated by couple facies.

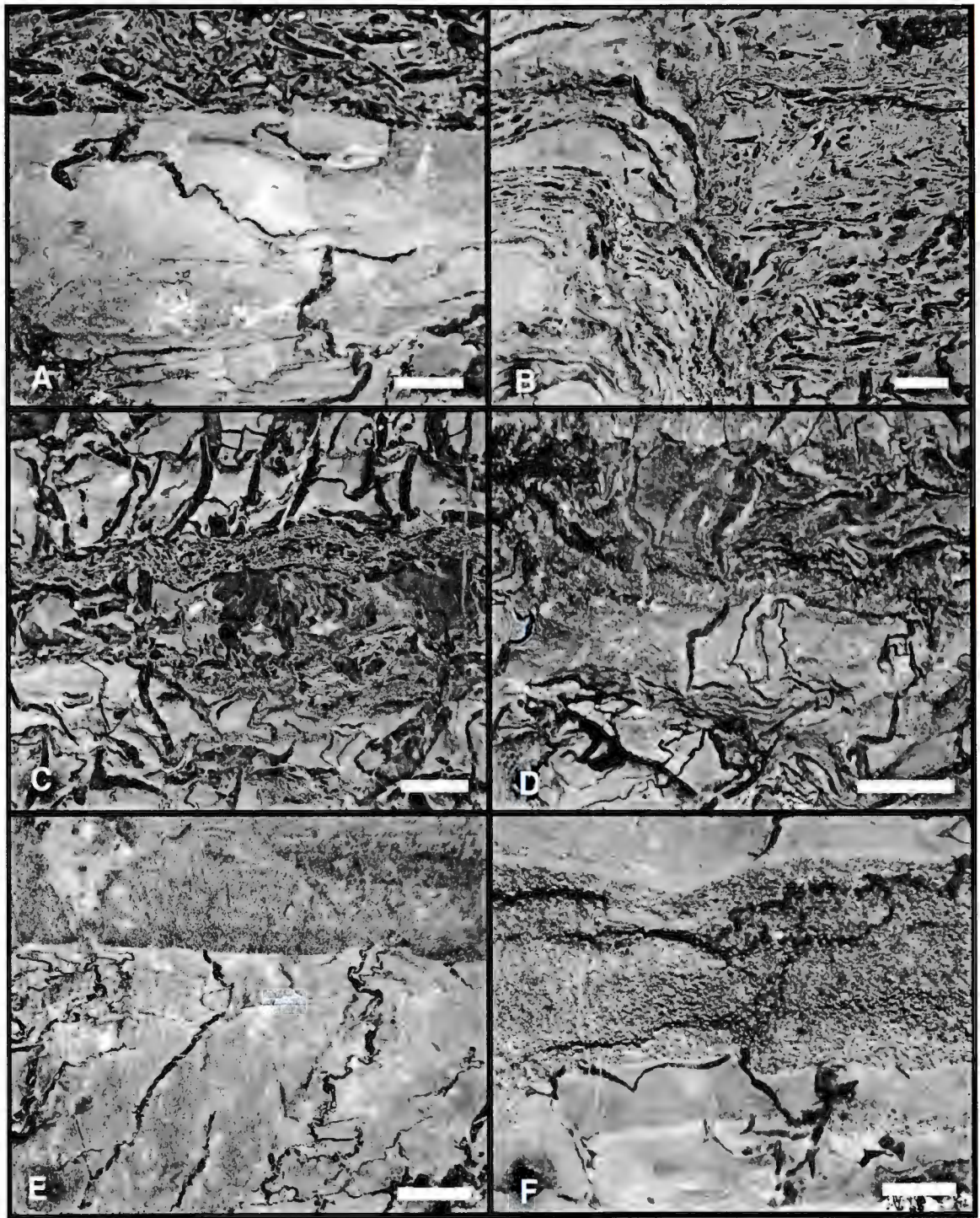
basal MT intraclast lag and an upper sand-mud couple facies that becomes more carbonate-rich upward.

Molar-Tooth Distribution

In the Helena Formation, MT structures are most abundant within fine-grained carbonate facies (i.e., dolomitic mudstones and dolomitic sand-mud couple facies), and rare to absent in coarse-grained facies (i.e., intraclastic grainstones, oolitic and quartz sand facies) and the dominantly siliclastic couplet facies. This apparent substrate preference is also reflected in a regional distribution in which MT structures are more abundant in the eastern Belt basin, where fine-grained carbonate facies dominate, and decrease in abundance westward in the basin, where strata become significantly more siliclastic-rich. Within the eastern Belt basin, MT also increases in abundance upward to the *Conophyton* marker unit, which reflects the most open-marine facies of the Helena Formation (Horodyski 1983; 1976) and gradually decreases in abundance above this marker bed, finally disappearing into the coarser-grained, mudcracked and oolitic beds of the uppermost Helena Formation.

Within single shoaling cycles, MT structures also show distinct changes in abundance. Cycle bases frequently show evidence of erosional scour that truncates MT ribbons within underlying lithologies (fig. 8A). Basal lags are typically composed of elongate clasts of lithified MT microspar, although oolites and quartz arenites may also be present. Discontinuous scours containing MT intraclasts also occur in dolomitic sand-mud couple facies and, more rarely, in dolomitic mudstone facies. These discontinuous intraclastic breccias are interpreted as storm scours. MT structures are not observed in these facies, but in rare cases, more resistant ribbons protrude upward 1 to 3cm into the basal portion of breccias.

Figure 8. Changes of MT morphology with substrate rheology. A) Vertical ribbons are commonly truncated at scour surfaces and reworked into intraclastic breccias composed predominantly of MT microspar. B) MT structures change morphology abruptly as they pass laterally into the stromatolites, where they preferentially follow curved stromatolitic laminae. C) Ribbons become horizontal at substrate boundaries, and appear to merge into and out of regions dominated by microbial laminae. D) Vertical ribbons thin, disappear into, and bend horizontally through or underneath fine sand laminae. E) Vertical ribbons disappear into medium-grained sandstone. F) Well defined vertical ribbons below an oolitic layer, enter coarse-grained layer where ribbons become irregular or diffuse until re-entering overlying finer-grained sediment. Scale is 1 cm in all photos.



In eastern sections, stromatolites commonly overlie scours and basal transgressive lags. Within stromatolitic lithologies, MT structures typically occur as closely packed, horizontally aligned MT ribbons that follow topography of curved stromatolitic lamina (Fig. 8B). Thin stratiform microbial layers can also occur in dolomitic mudstone facies and are commonly marked by abrupt changes in MT crack morphology (Fig. 8C). O'Connor (1972) describes vertical and lateral gradations of stromatolites and MT structures in more detail.

MT structures are generally rare to absent in siliclastic-rich couplet facies, which commonly overly lag deposits. Both MT blob and ribbon morphologies occur in greater abundance in more fine-grained, carbonate-bearing couplets. In these cases vertical ribbons show highly sinuous morphologies as ribbon segments turn laterally for short distances at the interface of each lamina (Fig. 1A and 1B). Thicker ribbons are typically less affected by substrate lamination than thinner forms (Fig. 1A).

Blob and ribbon morphologies are significantly more abundant in dolomitic sand-mud couple facies as long as couples are fine grained and carbonate-rich. Within couple facies MT structures frequently show a banded appearance in outcrop, reflecting preferential formation of MT structures within finer-grained layers of graded couples. Individual MT ribbons are observed to terminate at the interface between fine- and coarse-grained units (Fig. 8D and 8E), become horizontal, at the interface of or within coarser layers (Fig. 8F), or deform (with a decrease in ribbon width) within coarser layers (Fig. 8D). Thinner ribbons (1-2mm width or less) are typically more affected by rheological variation in the substrate, whereas thicker ribbons appear to pass through coarse layers with no morphological change. As a result, multiple ribbons crossing the same coarse-grained lamina show different types of morphological change.

Carbonate mud facies typically cap sedimentary cycles. Here MT structures are very abundant comprising 5 to 30% of bed facies and locally up to 80% of the facies. MT structures are commonly persistent throughout meter thick beds vertically, and laterally extensive across

entire outcrop exposures for 10s to 100s of meters. Both blob and ribbon morphologies are present, occurring as isolated structures or interconnected networks within more dense accumulations. Ribbon morphologies are most abundant comprising denser MT beds, whereas blobs are less abundant and generally occur in distinct laminae. In general, MT morphologies are quite variable. Morphological changes typically occur over a few cm, both vertically and laterally and often coincide with changes in substrate composition.

VIII. PETROGRAPHY

Behavior of MT structures with respect to rheological changes in substrate can be more easily observed in thin section. In most samples, MT structures occur within a matrix consisting of dolomitic microspar containing 5-20% fine-grained quartz, feldspar, and minor clay. A full array of blob and ribbon morphologies, however, can be observed within similar matrix lithologies, suggesting that MT morphologies may have been determined primarily by changes in the volume of gas involved, rather than particular changes in substrate rheology. Minimal gas production within the host sediments unable to overcome substrate cohesion will result in the formation of blob morphologies. However, with increased gas production, ribbon morphologies should be formed where inhomogeneities in the substrate occur. Thin, very sinuous ribbons may represent minimal gas force, such that small variations in substrate cohesion result in changes in the migration pathway wherever inhomogeneities are encountered. Greater gas force may more easily deform semi-cohesive substrates, resulting in formation of thicker and straighter ribbon morphologies. Within the Helena samples, an array of MT morphologies ranging from blobs, to blobs with upward protruding ribbons, to thin sinuous ribbons, to thicker and straighter ribbon forms (Fig. 9A-D) occur within very similar substrates. Although many factors affecting substrate cohesion (e.g., microbial binding, early lithification) may be unrecognizable in thin section, this pattern is consistent with increased volume of gas production within a similar substrate. However, where obvious petrographic changes in substrate occur, such as changes in grain size, significant behavioral differences are observed, including bending/changing of ribbon direction, distribution of MT microspar within pore space of coarser sediments, and collapse and detrital infill of overlying sediment into underlying MT void space.

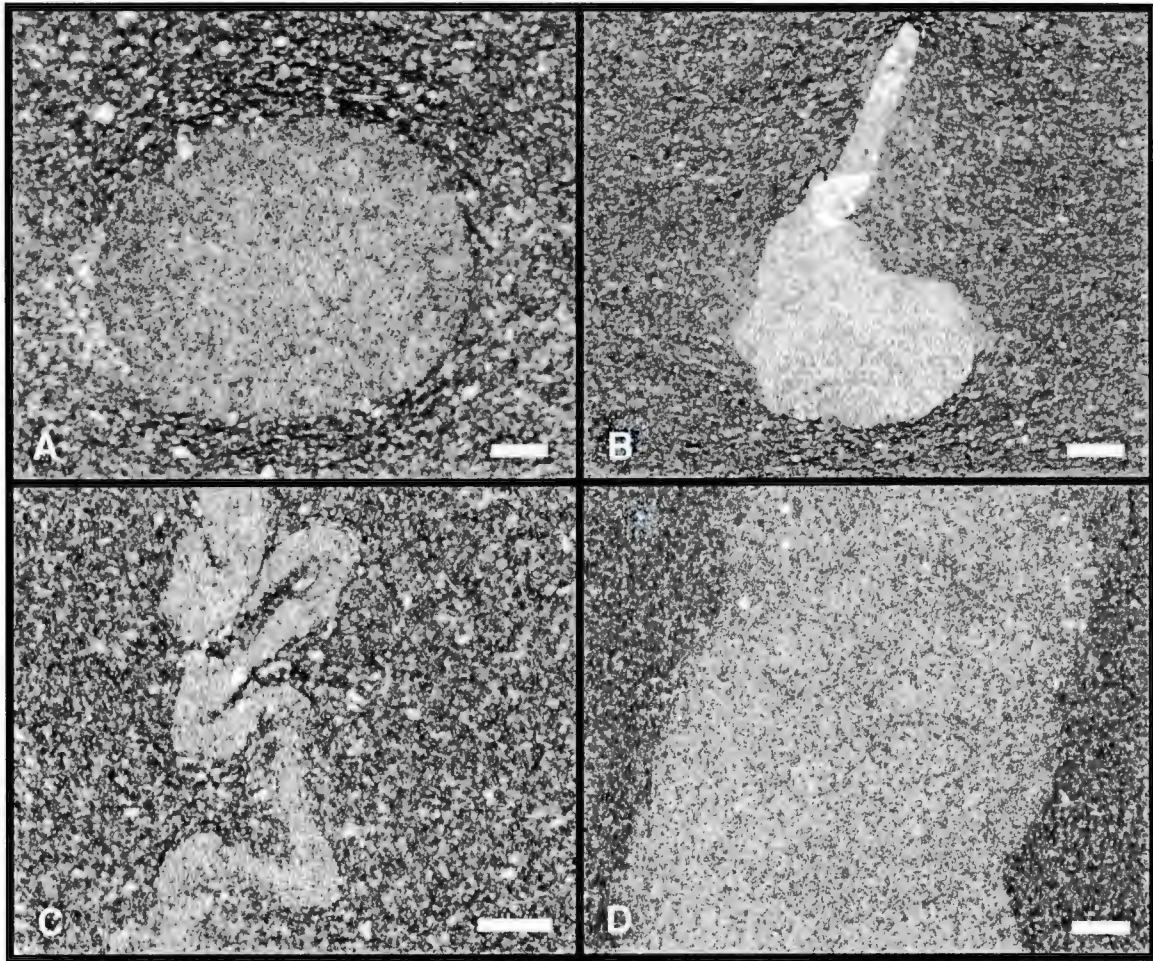


Figure 9. MT morphologies within carbonate mudstone may reflect increased levels of gas production (A to D), assuming that similar substrate lithology reflects similar cohesion in each sample during MT formation. A) Initial or weak gas production where the expansive force is less than the substrate cohesion results in a blob morphology. B) Increased gas production results in ribbon protrusions from bubble walls. Protrusions tend to be vertical as gas migrates toward the sediment water interface. C) Thin, sinuous ribbons result when the pathways of migrating gas is greatly affected by small changes in substrate cohesion. D) Thicker ribbons result when increased gas expansion force is able to overcome smaller substrate effects. Scale bar in all pictures is 200 μm . All photos in plane-polarized light.

Vertical ribbons may pass from fine to coarse layers and show no change in width or direction (Fig. 10A). In terms of a gas model this suggests that the substrate cohesion of both laminae was similar, such that the migrating gas was able to push open a crack of the same diameter within both substrates. This example may seem counterintuitive, because coarser substrates are more likely to have greater permeability and should support gas diffusion. However substrate cohesion will be a function of many different parameters other than grain size.

Vertical ribbons may also become horizontal within coarse layers, tracking them for some distance before resuming a vertical path (Fig. 10B). In terms of a gas model, substrate cohesion of the coarse layer must have been less or more permeable than surrounding layers such that gas flowed preferentially along coarser-grained layers until substrate inhomogeneities allowed vertical gas movement. In a more unusual case of horizontal bending, vertical ribbons are observed to merge into horizontal layers of closely packed pockets of MT microspar, partitioned by wavy, carbonaceous and silty micritic layers (Fig. 10C). This MT morphology is identical to that observed within stromatolites (Fig. 10D), suggesting interaction between gas and microbial laminae. Carbonaceous partitions likely reflect previous microbial laminae that acted as confining layers to the migrating gas.

MT ribbons also disappear upward within coarse layers into diffuse trails of MT microspar which, rather than filling distinct voids, randomly fill pore space (Figs. 11A-E). In the example shown in Figure 11A, the MT ribbon is well defined within the surrounding fine-grained substrate, but within the coarse lamina, MT microspar occupies pore space throughout the sand (see also Fig. 8F). The concentration of microspar cement within pore space typically becomes less dense away from the initial MT structure. In terms of a gas model, this suggests that the coarse layer permeable/non-cohesive, such that gas moved preferentially through pore space rather than pushing grains apart.

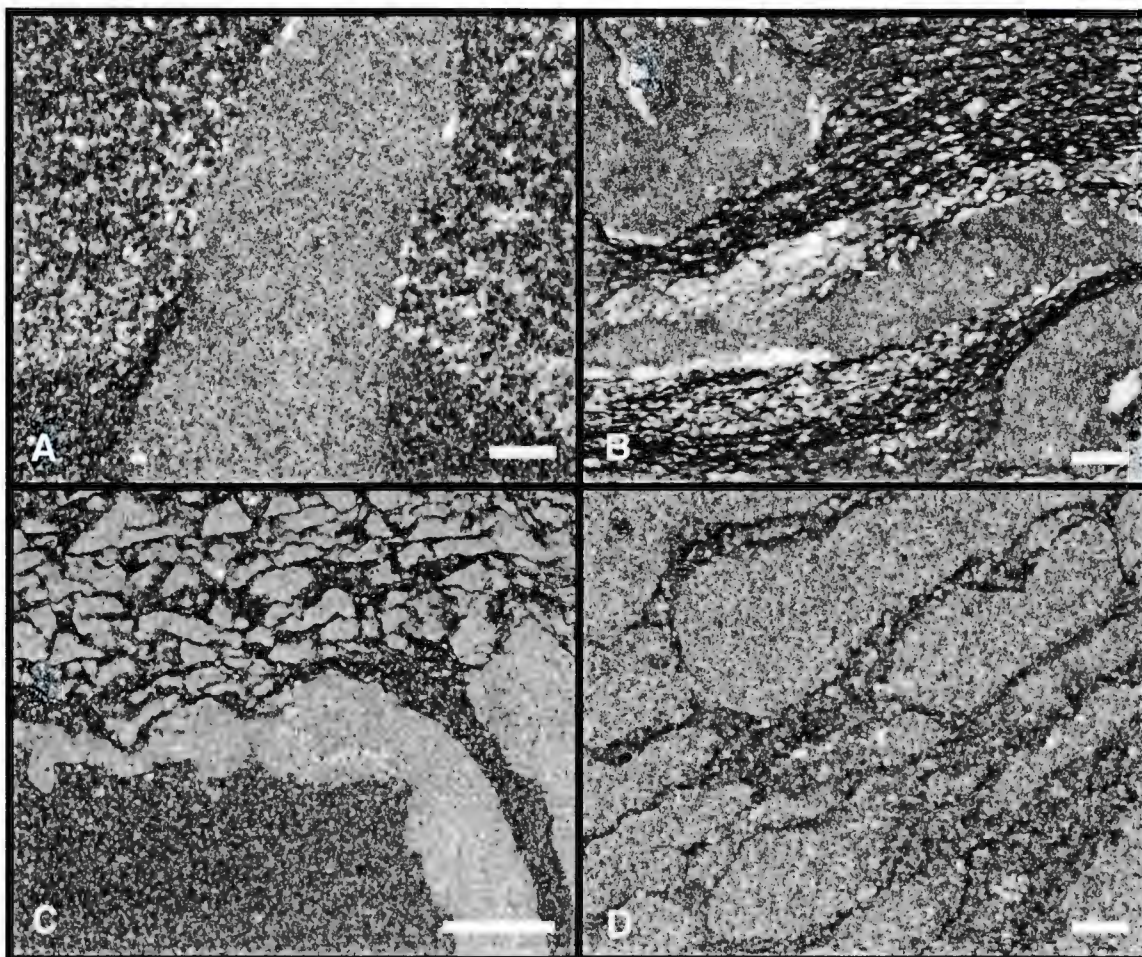


Figure 10. Changes in MT morphology in substrates of differing rheology. A) Vertical ribbon passing from fine to coarse substrate shows little change in morphology, suggesting, in terms of a gas model, that both layers had the same rheology at the time of ribbon formation. In general, coarser-grained substrates should be more permeable, but factors other than grain size may affect substrate cohesion. B) Vertical ribbons can become horizontal within coarse-grained layers, tracking laminae for some distance before resuming a vertical path. In terms of a gas model, the coarser-grained layer must have been more permeable, resulting in preferentially lateral gas flow. (C) Vertical ribbons become horizontal underneath, and appear to merge into microbial laminae, producing somewhat unusual MT morphologies composed of closely packed pockets of MT microspar (see also fig. 8C). In terms of a gas model, microbial laminae must have acted as confining layers, forcing gas laterally, underneath and along organic laminae. (D) Identical MT morphologies, as in C, make up some stromatolitic laminae, also suggesting interaction between gas and organic layers. Scale bar is 200 μm in A,B, and D, and 1 mm in C. All photos are in plane-polarized light.

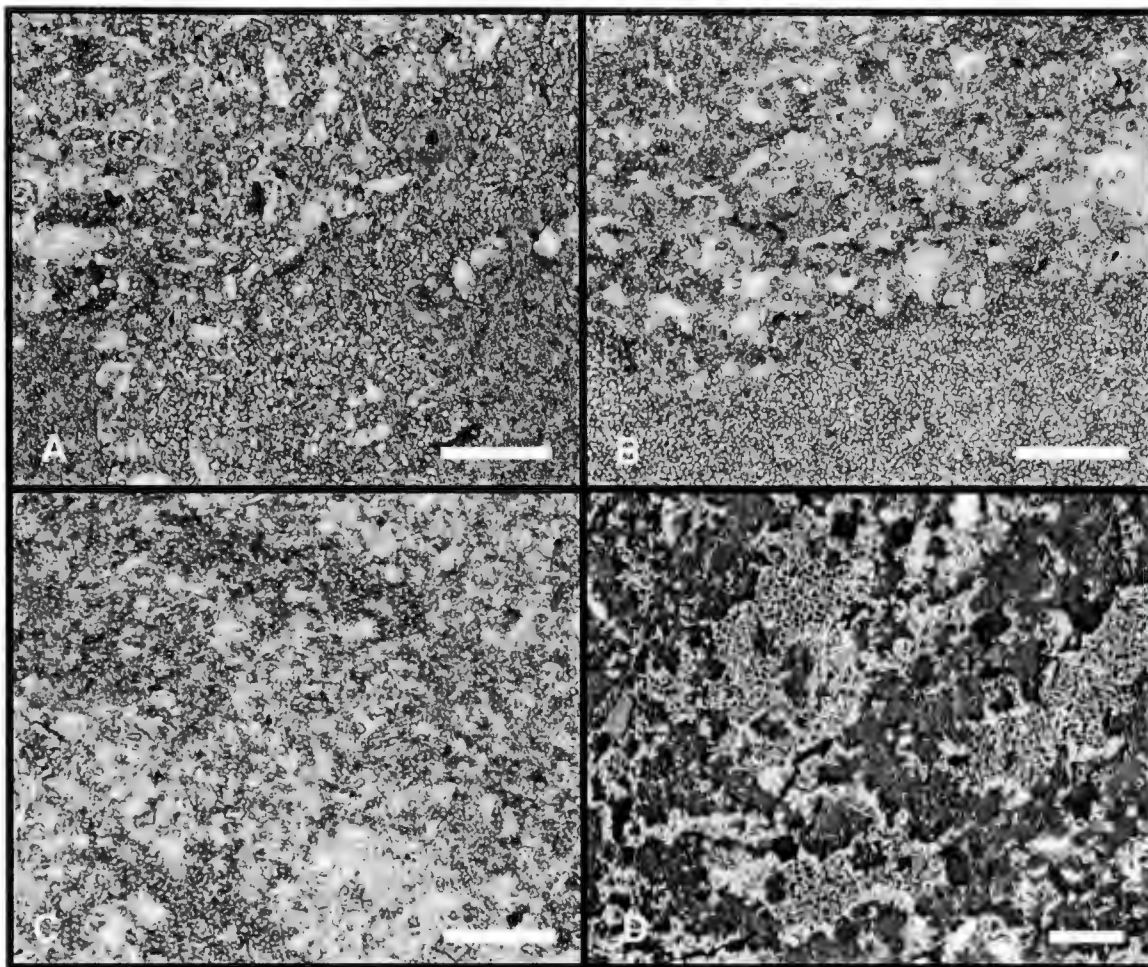


Figure 11. Pore-filling MT microspar within fine sand layers, is consistent with gas diffusion within more permeable substrates. A) MT microspar of vertical ribbons, well defined in the underlying fine-grained substrate, commonly becomes pore-filling when entering coarser-grained laminae. B) Pore-filling MT microspar may occur above horizontal ribbons within coarse-grained lamina. C) Pore-filling MT microspar within a fine sand substrate. D) Cathodoluminescence of pore filling MT microspar shows characteristically dull luminescent round cores and more brightly luminescent polygonal overgrowths, confirming that pore-filling microspar is identical to that filling MT void space. Scale is 200 μm in A,B,C and 100 μm in D. All photos are in plane-polarized light.

Pore-filling MT microspar cement also occurs above horizontal ribbons passing through, or tracking coarse laminae (Fig. 11B). In terms of a gas model, this suggests the substrate cohesion was moderately great, allowing migrating gas to push grains aside, however, still permeable enough that gas was able to diffuse upward through the substrate. That pore-filling microspar is MT microspar can be confirmed by cathodoluminescence (Fig. 11E), which shows characteristic MT microspar luminescence with dullly luminescent, rounded cores and more brightly luminescent, polygonal overgrowths.

Finally, in cases where laminae of coarse sediment were unconsolidated or only weakly bound at the time of MT formation, ribbons are detritally infilled (Fig. 12). In these examples MT microspar occurs throughout pore space in both the coarse-grained lamina and detrital void infilling. In the example shown in Figure 12, gas appears to have continued migrating upwards through the coarse-grained laminae, reforming a distinct MT ribbon in overlying fine-grained sediment.

Interestingly, MT microspar occurs within fine-grained matrix material as well, although in lesser abundance than in previous examples (Fig. 13A). Figure 13A shows a ribbon well defined within fine-grained matrix. MT microspar occurs randomly distributed within the matrix, which is confirmed by cathodoluminescence petrography (Fig. 13B). Although these random microspar crystals may represent initial gas production throughout the matrix (i.e. precursors to larger bleb formation), several examples indicate that the density of MT microspar within matrix sediments is greater near MT ribbons and above horizontal ribbons, suggesting diffusion of gasses away from primary migration pathways.

In a more extreme case of gas diffusion through pore space, MT microspar forms the primary matrix component of oolites (Fig. 13C). Oolites sampled here were not observed to be associated with any underlying intruding MT structures, Pratt (1998a p. 1039 Fig. 9E; 1999 p.

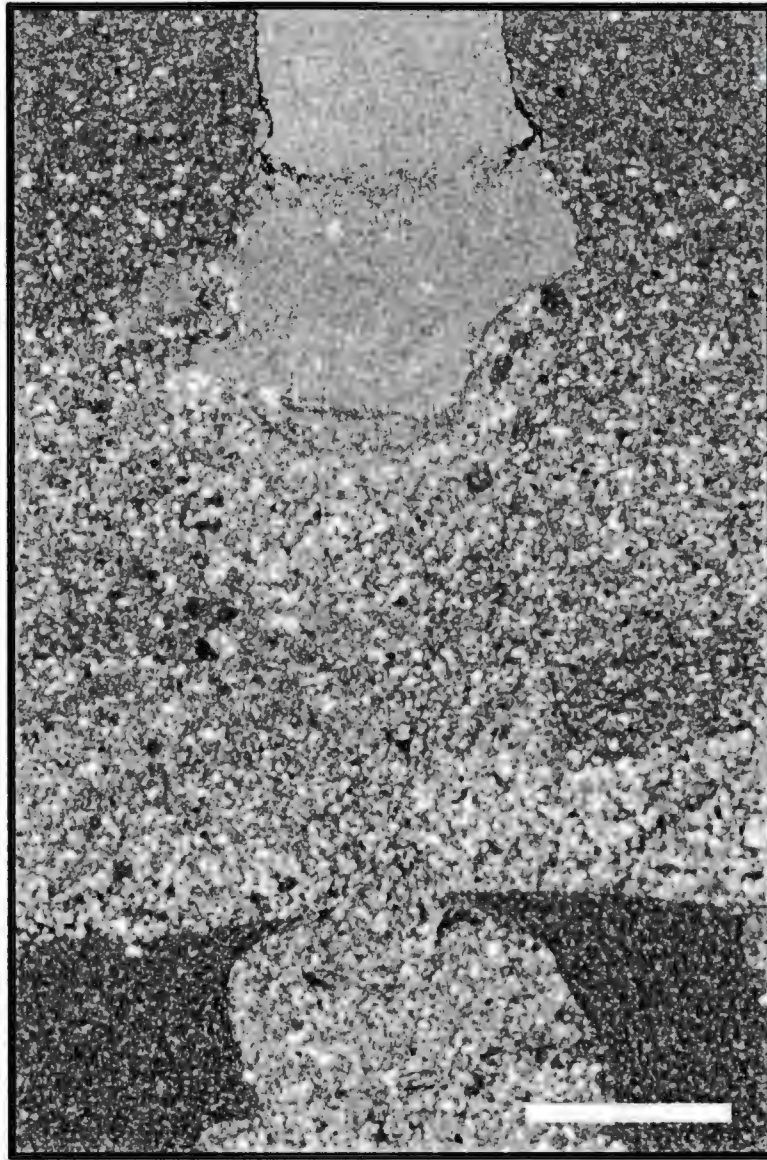


Figure 12. In rare cases vertical ribbons passing through coarse-grained laminae are infilled by detrital sand and show pore-filling MT microspar between detrital grains (see Fig. 11). In terms of a gas model, this would suggest that the coarse-grained layer had very weak cohesion and was significantly disrupted by gas flow, resulting in detrital infill of the lower ribbon segment by quartz sand. However, in the finer, and presumably more cohesive substrate above the coarse-grained layer, a more typical MT ribbon forms. Scale bar is 1 mm. Photo in plane-polarized light.

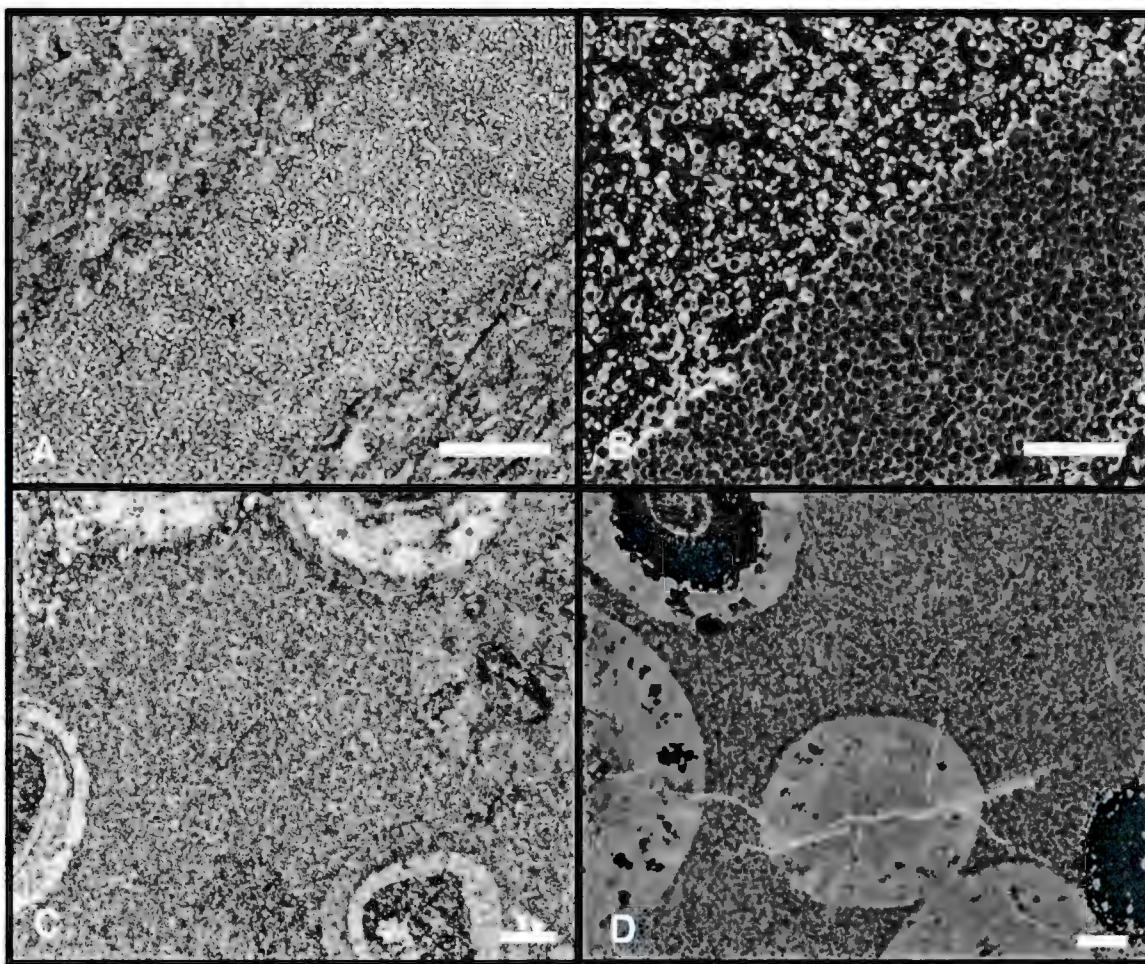


Figure 13. Evidence for gas diffusion within clay- to silt-size sediments and at sediment-water interface. A) Individual crystals of MT microspar are randomly distributed within a fine-grained substrate near a ribbon with well defined boundaries. In terms of a gas model, this suggests either small-scale diffusion of gas within fine substrates, or gas production distributed through the substrate. MT voids may form only when concentrations of gas reach a critical threshold, and are able to deform the surrounding substrate. B) Cathodoluminescence confirms that crystals of microspar within this finer substrate have the same luminescent character as MT microspar. C) MT microspar forms the primary pore-filling cement of oolites, perhaps driven by gas diffusion from the underlying substrate. D) Cathodoluminescence confirms that oolitic, pore filling microspar is identical to MT microspar. No detrital material is observed within oolitic pore space, suggesting that MT microspar precipitated from fluids in contact with overlying seawater. Scale bar is 200 μm in A and C, and 100 μm in B and D. Photos A and C are in plane-polarized light.

IX. SUMMARY AND DISCUSSION

Patterns of change in MT morphology

Patterns of change in MT morphology observed across substrates of differing composition, as defined by the distribution of characteristic MT cement, are consistent with a gas model. Both blob and ribbon morphologies are present predominately within fine-grained carbonate substrates, which are inferred to have relatively high cohesion. Horizontal bending of ribbons occurs where ribbons pass into coarser-grained layers, where gas can presumably travel more readily within these inferred, less cohesive substrates, or where ribbons intersect laminae of greater cohesion, as in microbial examples. Within fine- to coarse sand, diffusion of MT microspar occurs between sediment grains. This pattern of changing morphology with grain size is consistent with model predictions that more permeable/less cohesive substrates will show more diffusive characteristics. Ultimately, however, morphology of MT structures reflects not only substrate cohesion, but the force exerted by different volumes of gas. For example: blobs, blobs with ribbon protrusions, and ribbons may all be observed within very similar substrates, suggesting increasing volume of gas acting on constant substrate cohesion. A continuum of MT morphologies can therefore be defined in terms of the relative gas force and substrate cohesion (Fig. 14), such that with increasing gas force and decreasing substrate cohesion the following MT morphologies will be observed. Under conditions of very high cohesion relative to gas volume MT structures should be absent or very sparse. This scenario may be represented by randomly distribution MT microspar grains within fine-grained substrates, reflecting initial gas production within the substrate. With increasing gas production and decreasing substrate cohesion, blobs and then ribbons will form. Horizontal bending of ribbons will occur within substrates of less cohesion, followed by diffusion, and detrital infill into MT voids by more weakly cohesive substrates. Where substrate cohesion is very weak relative to the force of the migrating gas, gas

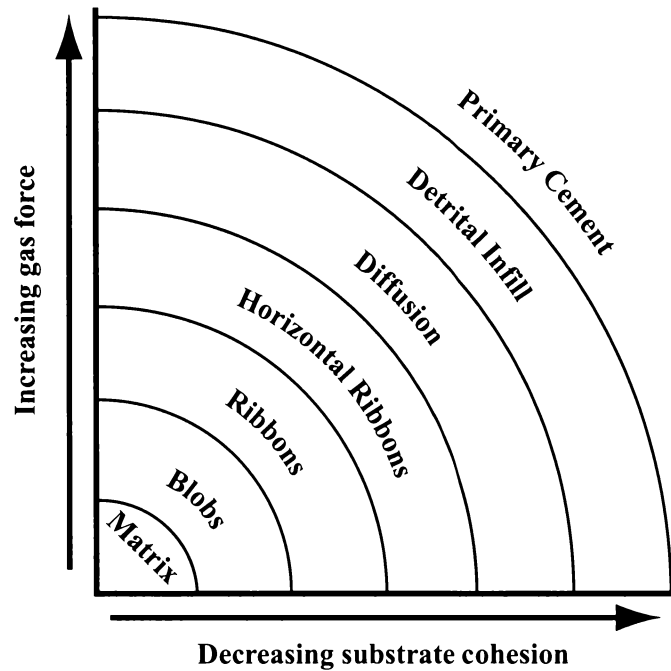


Figure 14. Continuum of MT morphologies with increasing gas production and/or decreasing substrate cohesion. Weak gas expansion force (or little gas production) relative to substrate cohesion results first, in the random distribution of individual MT microspar crystals within the sedimentary matrix. This is followed by formation of blobs, ribbons, horizontal ribbons, pore filling microspar where gas diffusives between sedimentary grains, and by detrital infill of gas produced voids. In cases of significant intraparticle porosity, migrating gases can move freely between grains, in some cases resulting in precipitation of MT microspar as primary, void-filling cement.

should fill the pore spaces resulting in precipitation of MT microspar cement throughout. Assuming that sediment will gradually increase in cohesion after deposition, for example by microbial binding, cementation, or compaction, differing MT morphologies within strata likely reflect multiple episodes of gas production within the substrate. This is suggested by observations of different types of vertical ribbon deformation (e.g., straight ribbon, horizontal, ribbon, diffusion) that are present across a single coarse lamina, often a few mm to cm apart, as well as rarer examples of distinct cross-cutting cement fills (Eby 1977; Pratt 1998), and multiple generations of MT cement within larger voids (cf. Moussine-Pouchkine and Bertrand-Sarfati 1997).

Implications

Formation of abundant ribbons is suggested by experiments of Furniss et al. (1998) to require confinement of the sediment surface. In these experiments confinement of the surface by Plaster of Paris restricted the volume available for gas expansion. When gas pressure then exceeded the strength of the surrounding sediment, sheet cracks formed in a direction of least resistance. Because most MT structures in the Helena Formation have sheet crack morphologies, the gas production that initiated MT cracks likely occurred a few meters below the sediment-water interface. This scenario is consistent with observations that MT structures typically lack detrital infill, but are reworked into intraclasts, and are observed to crosscut sediment-filled shrinkage cracks (O'Connor 1972; *this study*).

Alternatively, confinement of gas may reflect the presence of relatively impermeable microbial biofilms at the sediment-water interface. It has been suggested that microbial mats covered much of the seafloor during the Mesoproterozoic (Narbonne 1998; Seilacher and Pflugner 1994), which may have provided the necessary surface confinement to produce MT

voids (James et al. 1998). Relationships between MT structures and microbially bound layers within the Helena Formation also support this hypothesis. MT ribbons increase in density beneath some stromatolitic lamina (O'Connor 1972; *this study*), and the presence of microbially influenced MT structures at Roger's Pass are associated with the thickest ribbons (2-3cm wide) observed in this study.

MT structures are typically most abundant at cycle tops, which are carbonate-rich, and absent from cycle bottoms, which are siliclastic-rich. If MT structures are dependent on the presence of microbial mats it follows that MT distribution should also be preferential within environments that support mat growth. However, microbial binding of sediments occur in both carbonate and siliclastic rocks (e.g., Noffke et al. 2001). Alternatively, MT preference within carbonate-rich cycle tops may be related to factors controlling chemistry of the overlying water (e.g., water depth, salinity, evaporation, wave induced CO₂ degassing). Both shallow active water conditions, which promote CO₂ degassing and evaporitic conditions, would be conducive to carbonate precipitation. This, combined with the presence of microbes within the sediment, would provide a source for both gas (through microbial decay) and increased cohesion and confinement (through sediment binding and mat formation), thus promoting both blob and ribbon formation.

During interactions between gas and heterogeneities within the substrate, the low viscosity of migrating gasses should result in formation of originally sinuous crack morphologies. Highly sinuous MT ribbons are observed throughout the Helena Formation, even where there is little compaction. For example, sinuous MT ribbons are found within large calcitic pods (*this study*). Compaction of laminae around, but not within, these early-lithified pods indicates that MT sinuosity did not form during compaction. Similar concretions are observed in large early-lithified nodules of the Burovaya Formation (Pope and Bartley, in review) where MT structures occur only inside early-lithified nodules and are not apparent in surrounding, compacted laminae.

It seems unlikely, therefore, that extreme amounts of near surface compaction (70 to 80%) (Smith 1968; Pratt 1998a) is necessary to fold ribbons. However, the many broken ribbon forms suggest that compaction must have affected MT structures to some degree. In addition, given the two phase growth of MT microspar, as discussed above, the possibility exists that some MT structures were deformed plastically perhaps filled with incompletely cemented crystals of subrounded vaterite before complete lithification by overgrowth cement occurred.

Other Models

Regardless of what the mechanism of crack formation is, heterogeneities within the substrate will most likely effect crack morphology and propagation. Inference that gas is the void-forming agent requires that observed morphologic changes can be specifically contributed to gas deformation and not any other type. The most compelling alternative hypotheses for void genesis, seismically induced diastasis (Fairchild et al. 1997), and seismically induced syneresis (Pratt 1998a) imply crack formation via tensional stress and sediment shrinkage. Diastasis cracks form as a result of lateral shifting of an unconsolidated sand by wave action inducing brittle fracturing of an underlying cohesive mud layer (Cowan and James 1992). MT structures are not diastasis the cracks in the strictest terms of Cowan and James (1992) because they also cut across sand layers, however, Fairchild et al. (1997) suggested that partly cemented or microbially bound sand layers may be brittlely fractured at the same time as underlying mud layers by seismic wave propagation. Brittle fracturing, however, cannot explain either the origin of blob morphologies or the diffusion of MT microspar in more unconsolidated rheologies. Although, in the presence of unconsolidated sand layers, more typical diastasis could result from seismic wave propagation, there would be no reason to expect continuation of ribbon morphologies directly in vertical continuity with those in underlying mud layers.

A seismic syneresis hypothesis (Pratt 1998a) suggests that MT structures formed during earthquake-induced lateral shrinkage of sediment and expulsion of fluidized lime mud into sheet- and bubble-like fissures. In this case, rising fluids would be expected to diffuse through more permeable coarse-grained substrates and remain confined within finer-grained sediments, and thus might show crack morphologies that parallel MT formed by gas migration. Fluidization of sediments, however, implies rapid upward expulsion of pore water that overcomes the weight of the sediment grains. The presence of ribbons that intersect coarse-grained layers and are detritally infilled, yet show no evidence of entrained material deforming the upper surface of sedimentary laminae, indicate that upward fluid injection must not have been overly violent. Additionally, in a seismic syneresis hypothesis, fluid and sediment injection must occur very rapidly after seismically induced liquefaction and before any significant vertical compaction, in order to account for 70 to 80% compaction of MT structures. It seems unlikely that rapid injection of both pore water and lime mud would permit detrital infill of sand grains. Furthermore, varying morphologies of ribbons across single coarse-grained laminae (straight, horizontal, diffusive), rare crosscutting relationships observed in MT fill (Eby 1977; Pratt 1998a), and numerous generations of MT cement fill (cf. Moussine-Pouchkine and Bertrand-Sarfati 1997) indicate multiple episodes of MT formation. If multiple episodes of seismically induced liquefaction occurred, ribbons formed in later events might be expected to show less compaction than older structures. However, multiple generations of MT formation are somewhat difficult to explain by a seismic shaking and liquefaction model. Once sediment has been dewatered and compacted by a single seismic event, reduced pore water content, and increased sediment cohesion would make future fissuring significantly more difficult. Finally, it is hard to envision how a seismic mechanism can account for the origin of blob and ribbon morphologies. Brittle fracturing and lateral sediment shrinkage results in the formation of sheet cracks (e.g., Allen 1982 p. 544-556) not spheroidal voids. Implied by both seismic models is that MT structures were

originally linear features, and thus seismic stresses alone cannot account for the origin of blob and interconnected blob and ribbon morphologies.

Although seismic models do not adequately account for MT genesis, this does not exclude the possibility that other extrinsic factors occurring during MT formation may also affect MT morphologies, including overlying wave and current action, slumping, and seismic shaking. While MT forms within the Helena appear to be primarily the result of gas expansion and substrate cohesion, MT found in other localities worldwide do suggest the influence of external factors. For example, as suggest by Sherman et al. (2001), alignment of MT ribbons on bedding planes (e.g. Eby 1977; Sherman et al. 2001) may reflect development of cracks parallel to wave crests (Smith and Winston 1997). In addition, orientation of some MT structures within erosional features (Fairchild et al. 1997) may also reflect modification of MT structures by preexisting stress fields during their initial formation. Unusual occurrences of MT rosettes (Moussine-Pouchkine and Bertrand-Sarfati 1997) may result from the post-depositional modification of MT during seismic activity (Bartley et al. 1999).

Origin of Molar-tooth Microspar

Previous observations suggest that pore-filling MT microspar can be directly related to MT ribbon and blob formation, because pore-filling microspar is commonly associated with underlying intruding MT structures (see also O'Connor 1967 p. 64-65; 1972; Pratt 1998a p. 1039 Fig. 9 E; 1999 p. 1138 Fig. 3A-C). Pratt (1998a; 1999) interpreted MT microspar as geopetal "crystal silt" by analogy with Dunham (1969). However, detailed petrographic analysis indicates that MT microspar is cement and does not fill pore space geopetally. Rather MT microspar forms the primary matrix component of grainstones, and is typically not associated with any overlying blocky void-filling cement. These observations suggest that pore-filling microspar is related to

gas expansion. However, gas production may not have been the catalyst for microspar precipitation. C-isotopic data do not show any compositional difference between MT cement and the surrounding sediments (Frank and Lyons 1998), suggesting that potential sources of microbially produced gas (i.e., sulfate reduction, methanogenesis, or oxidation of organic matter) may not have triggered precipitation. In addition, the morphology of MT cement does not resemble any CaCO_3 precipitates produced by metabolic processes of modern marine bacteria in laboratory experiments (Buczynski and Chafetz 1991). Rather, the strong similarity of MT microspar (morphological and size) to vaterite precipitated in recent experiments (Naka and Chujo 2001), suggests that dissolved organic molecules may have played a critical role in MT cementation. Decaying organic matter within the substrate could have provided a source for both gas and dissolved organic molecules. Rising gas, and fluids pulled behind escaping gas, may have concentrated dissolved organic molecules, which then initiated calcium carbonate precipitation from void filling fluids. These fluids were likely in contact with Mesoproterozoic seawater, as evidenced by the pore filling MT microspar of oolites, which was supersaturated with respect to calcium carbonate at this time (Grotzinger and James 2000). This scenario would promote rapid cementation, and thus favor homogeneous nucleation and precipitation of vaterite crystals (e.g., Dickenson et al. 2002; Kitamura 2002) which may have produced the characteristic texture and morphology of MT microspar. Thus MT structures would be cemented as the upward increased density of dissolved organics came in contact with highly saturated Mesoproterozoic seawater, near and at the sediment water interface, precipitating calcium carbonate in gas expansion voids and permeable pore space (Fig. 15).

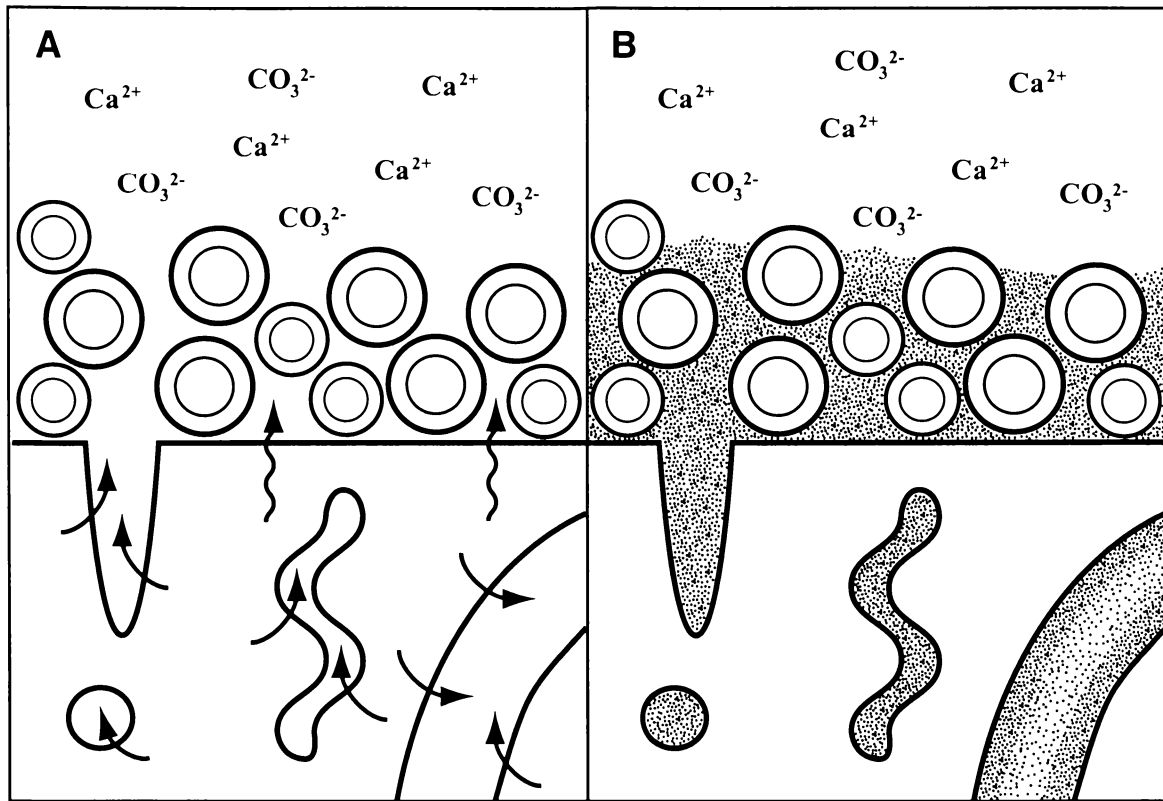


Figure 15. Gas induced migration of dissolved organic material (represented by arrows) results in a void-ward decrease in concentration of dissolved organics. Precipitation of MT microspar cement occurs where dissolved organic material comes in contact with supersaturated Mesoproterozoic porewaters or overlying seawater. Within smaller voids, MT cement typically fills entire pore space. Internal layering of MT cement fill in larger voids (cf. Moussine-Pouchkine and Bertrand-Sarfati 1997) may represent void-ward decrease in concentration of dissolved organics necessary for MT cement nucleation. Cementation by MT microspar may also occur at the sediment-water interface (cf. figs. 13C and D) if concentration of dissolved organics, migrating from underlying sediments, is high enough to induce precipitation.

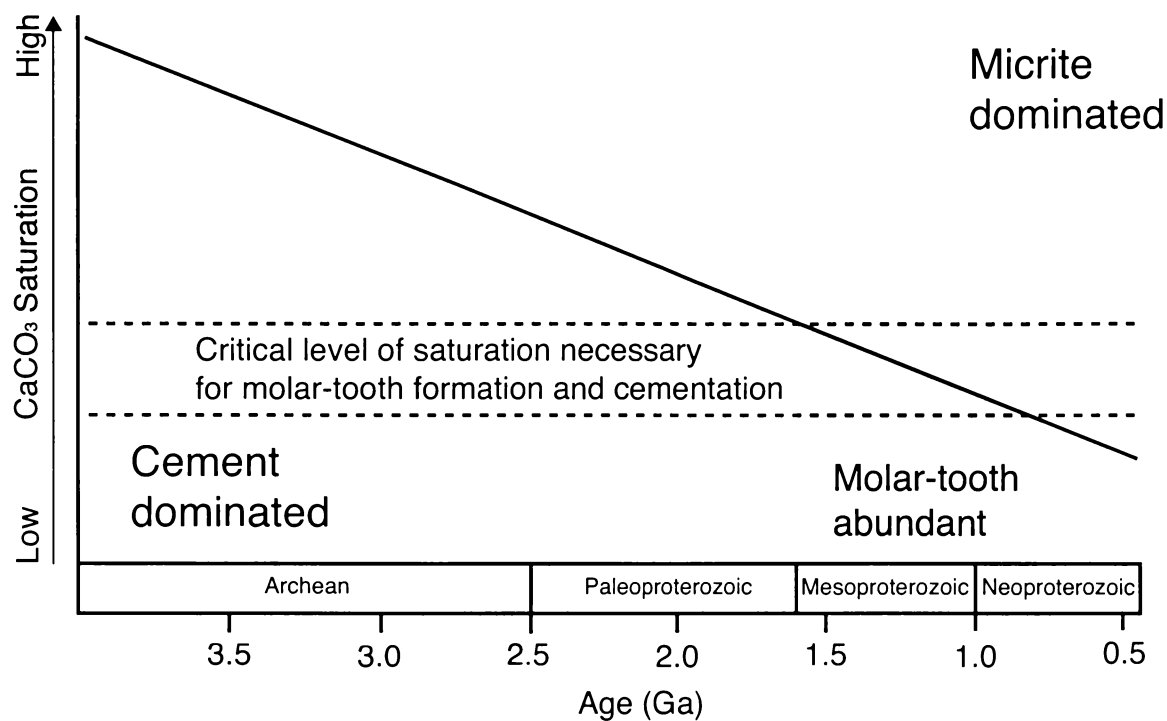


Figure 16. Abundance of MT structures within the Meso- to Neoproterozoic (shaded region) may reflect a critical level of carbonate saturation within seawater. This critical level of saturation was low enough such that immediate substrate lithification was limited, allowing void formation, yet high enough to facilitate precipitation of MT microspar within gas-generated voids and permeable pore space.

present within entirely siliclastic host rocks rather than carbonate substrates. These shales likely cemented less rapidly than is typical for carbonate environments in the Archean, thereby allowing for MT genesis.

Implied by this hypothesis, is that within the Mesoproterozoic, environments promoting rapid lithification of void space, but where immediate substrate lithification is limited, should show a greater abundance of MT structures. Supporting this scenario is the observed environmental restriction of MT structures within the Mesoproterozoic and early Neoproterozoic, wherein MT structures occur predominantly within subtidal to lower intertidal environments (James et al. 1998). Rapid lithification of very evaporitic nearshore substrates and significantly slower lithification in offshore environments (cf. Kah and Knoll 1996; Bartley et al. 2000) may have inhibited formation and/or preservation of MT in these environments, whereas shallow-marine evaporitic environments allowed for MT formation. This environmental control on MT formation may also be observed in the Helena Formation, where MT structures occur within shoaling upward cycles. Here MT structures occur predominantly within dolomitic cycle tops and are rare to absent in deeper water siliclastic cycle bases.

CONCLUSIONS

Variations in MT morphology suggest a strong rheologic control on MT formation. Petrographically observed patterns of morphological change are consistent with a gas expansion model for MT genesis. Cementation of MT voids was likely aided by the presence of dissolved organic molecules and perhaps intimately linked with gas production by decay of organic material within host sediments. Combined observations suggest the following scenario for MT genesis: Gas was generated by decaying organic matter within fine-grained substrates near or at the sediment-water interface. Interaction between the force of migrating gas and substrate cohesion resulted in an array of different void morphologies (Fig. 14). Surrounding pore water containing dissolved organic molecules subsequently filled voids created by migrating gas. In these near-surface environments, pore waters would be highly supersaturated with respect to CaCO_3 , similar to Mesoproterozoic seawater. Increased concentration of dissolved organics, migrating into voids and the overlying water column from pore space, induced homogeneous nucleation and precipitation of subspherical vaterite crystals. Initial vaterite crystals provided nucleation points for later calcium carbonate overgrowths, which cemented the entire void space. Prior to secondary cementation, some MT structures may have been deformed plastically, although sedimentological evidence suggests that most MT structures were completely lithified prior to compaction of surrounding sediment and that folded morphologies resulted largely from interactions between gas and substrate cohesion. Other extrinsic factors including seismic shaking and wave activity may have additionally effected MT morphologies, during or after MT genesis.

Restriction of MT structures within the Mesoproterozoic and early Neoproterozoic was likely related to the level of carbonate saturation in seawater. High levels of carbonate saturation and very rapid lithification of substrates within the Archean and Paleoproterozoic resulted in

substrates too rigid, except within restricted environments, to allow deformation by migrating gasses. In the Mesoproterozoic to early Neoproterozoic, a critical level of carbonate saturation limited immediate substrate lithification, allowing void formation, yet remained high enough to facilitate precipitation of MT microspar within gas-generated voids and permeable pore space, given the presence of an appropriate nucleation mechanism. Carbonate saturation in the late Neoproterozoic may have been so low that environmental catalysts were unable to induce precipitation of microspar into gas-generated void space. Without rapid lithification, MT voids, would have been destroyed during postdepositional compaction.

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APPENDICES

See attached CD ROM (plate 1) for Appendix material.

The CD contains Appendices A-B, where data is stored in Microsoft Excel and Adobe Illustrator format. Simply insert the CD in the CD ROM drive and wait. If the main page does not load automatically it can be opened *via* a file manager.

VITA

Mark D. Pollock was born in Atlanta, GA on January 29, 1977. He was raised in the great southeast, and went to grade school in Knoxville, TN and junior high at Meigs Magnet School in Nashville, TN. He graduated from Hillwood High School in 1995. From there he went to Western Kentucky University, and received a B.S. in geology in 2000. He further pursued his interest in geology at the University of Tennessee, Knoxville where he received a M.S. in geology in 2003. He continues to have interest in higher education and plans to get his doctorate sometime in the near future. Some say he might could be the greatest geologist ever.

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