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# Gas bubble and expansion crack origin of "molar tooth" calcite structures in Middle Proterozoic Belt Supergroup western Montana

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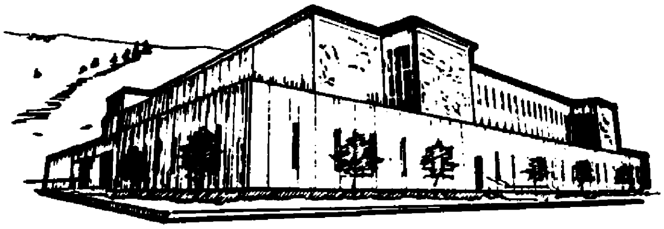

# GAS BUBBLE AND EXPANSION CRACK ORIGIN OF "MOLAR TOOTH" CALCITE STRUCTURES IN MIDDLE PROTEROZOIC BELT SUPERGROUP, WESTERN MONTANA

by

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# GAS BUBBLE AND EXPANSION CRACK ORIGIN OF "MOLAR TOOTH" CALCITE STRUCTURES IN THE MIDDLE PROTEROZOIC BELT SUPERGROUP, WESTERN MONTANA (44 pp.)

Director: Don Winston

"Molar tooth" is a sedimentary structure of interconnecting, thin sheets and small spheroids, composed of uniform, blocky calcite crystals 5-15 um in diameter, and is common in argillitic dolomite of the Middle Proterozoic Belt and Purcell Supergroups of the Rocky Mountains. Experiments that closely replicate "molar tooth" structures suggest that "molar tooth" formed as gas generated voids that filled with blocky calcite. Experimental models using mud, yeast and sugar in glass aquaria produced bubbles and gas expansion cracks which closely mimic shapes of "molar tooth" structures. Mixing $CaCl_2$ and $Na_2CO_3$ solutions precipitated finely crystalline blocky calcite, similar to "molar tooth" calcite. Comparisons of the Belt with the modern Dead Sea, where bacterial decomposition of gypsum is inferred to produce $H_2S$ and $CO_2$ gases suggests a similar origin for "molar tooth" structures and calcite. "Molar tooth" structures in the Belt commonly forms a repeated sequence of shapes in fining upward siliciclastic-to-dolomite cycles. Microfossils and amorphous organic debris in the calcite and host rock suggests "molar tooth" calcite structures resulted from consumption of evaporite minerals such as gypsum by bacterial metabolism and formation of gas bubbles and cracks which were filled by $H_2S$ and $CO_2$ gas which in turn generated pyrite and calcite.

# ACKNOWLEDGMENTS

I thank my advisors Dr. Charles Miller, Dr. Graham Thompson, and Dr. Don Winston for their encouragement, suggestions, and careful, critical review of this manuscript. I extend my gratitude to Don for his infectious enthusiasm for the Belt and all aspects of this project. Thanks to John Rittel for marvelous laboratory ingenuity and skilled SEM techniques. Thanks to John for his talented experimental mind and for the many laughs we shared. Thanks to Jeff Moe for x-ray analysis. Thanks to Don Winston and John Cuplin for drafting the map. Thanks to Patti Furniss for constant encouragement.

## TABLE OF CONTENTS

# LIST OF ILLUSTRATIONS

# INTRODUCTION

This study proposes that during the Middle Proterozoic anaerobic organisms subsisting on organic debris and gypsum, expelled gas into wet calcareous silty clay. The gas formed bubbles and cracks into which calcite precipitated, producing the widespread, enigmatic "molar tooth" structures (Bauerman 1884; Fig. 1B) of the carbonate units within the Belt Supergroup of Montana, Idaho, and Washington and the Purcell Supergroup of Alberta and British Columbia (Fig. 1A).

In this study argillitic dolomite containing "molar tooth" structures is described from samples and outcrops of the Newland Formation in the Helena embayment and the Helena Formation at Rogers Pass, Ravalli Hill, and Hungry Horse Dam (Fig. 1A). Patterns of "molar tooth" structures were compared with very similar gas bubbles and gas expansion cracks produced by yeast grown in mud in laboratory aquaria. Fine grained blocky calcite crystals similar to the fine grained, uniform "molar tooth" calcite were precipitated by mixing $CaCl_2$ and $Na_2CO_3$.

## "Molar Tooth" Structure Description

"Molar tooth" is a field name coined by Bauerman (1884) for calcite concentrations in argillaceous Proterozoic limestones and dolomites from the Canadian Rockies. The structures reminded him of thin ridges of enamel on the grinding surface of an elephant's tooth. "Molar tooth" structure has two basic shapes: "ribbons" and spheroidal "blobs" (O'Connor 1972). Ribbon "molar tooth" structures resemble thin, wrinkled sheets and blades. They measure a few millimeters thick by several millimeters to several decimeters in length and height (Fig 1B-D, 2A, 2F, 3B, 4F, 5D, 5G). The spheroidal blob-like shapes, up to one centimeter in diameter, intersect the sheets and blades, or lie isolated in the host rock (Fig. 1B-D, 2E, 2G, 3B, 4F). The volume of calcite in these structures commonly ranges from 10% to 20%, of the total rock, but reportedly reaches 70% (Smith 1968). Based on the continuity of forms and the uniform composition of the blocky calcite fill, ribbons and blobs are considered genetically related.

## "Molar Tooth" Shape Classification

O'Connor (1972) classified "molar tooth" structures on the basis of shape into (1) vertical ribbons, (2) horizontal ribbons, and (3) blobs. A fourth shape, called "pods" by O'Connor (1972), is probably a form of early carbonate cement, and not the blocky calcite structures of true "molar tooth".

### Vertical Ribbons

The vertical calcite ribbons are 1-5 mm thick and range from 1-30 cm long. They cut bedding at many angles and commonly intersect other vertical and horizontal ribbons forming a network (Fig. 2A) although some also occur alone. Even though most vertical ribbons appear to cut randomly through the host rock, some are regularly spaced 2-4 cm apart and have a marked linear trend on bedding planes. Most appear to have been tightly folded or crenulated before being filled by blocky calcite. Others are crumpled, "S"-folded, broken, or offset, reflecting compression after being filled with blocky calcite (Fig. 2A). Under cathodoluminescence some have wedge-shaped patches of bright, blocky calcite, probably indicating that the ribbons broke and were healed by blocky calcite during compaction of the matrix (Fig. 2F). This relationship indicates that "molar tooth" ribbons were precipitated as rigid calcite from fluids before, or as the clayey dolomitic host sediments compacted.

## Horizontal Ribbons

Horizontal ribbons range from less than 250 um to 1 cm thick (Fig. 1B, 2A). They extend laterally from a few centimeters to several meters. Some are lens shaped. Horizontal ribbons are bounded by sedimentary layers, including organic mats and stromatolites. They commonly intersect vertical ribbons, but appear less deformed than vertical ribbons (Fig. 2A).

## Blobs

The spheroidal calcite blobs range in size from less than 250 um to 1 cm in diameter (Fig. 1C-D, 2E, 2G, 4F). Vertical or horizontal ribbons commonly extend from blobs forming a teardrop or sperm shape. Many blobs interconnect with other "molar tooth" structures through very thin ribbons (Fig. 2E, 2G).

## "Molar Tooth" Lithologies

"Molar tooth" calcite weathers recessively forming light to dark gray etched patterns in tan-weathering outcrops of argillitic dolomite and dolomitic, silty, sericitic argillite (Fig. 1B). The calcite is composed of uniform, equant, polygonal, tightly packed, blocky crystals, from 5-15 um across (Fig. 3C). The contact between the calcite and the host rock is sharp and the uniform blocky texture continues from edge to edge across the "molar tooth" ribbons and blobs.

Although the "molar tooth" calcite appears nearly pure, extremely thin curved bands or stringers of fine-grained host lithology commonly extend from the walls into the "molar tooth" calcite outlining bubble or "froth" shapes (Fig. 3B, 3E, 3H). Scattered aggregates of octahedral, cubic, and framboidal pyrite crystals from 1-15 um across, lie along the edges of some "molar tooth" structures or appear suspended in the blocky calcite (Fig. 3G, 3I). Authigenic quartz and plagioclase have replaced the molar tooth calcite in some samples. Rare samples of "molar tooth" contain terrigenous quartz and feldspar grains (O'Connor 1967). In some cases, filamentous organic material protrudes from the host sediment. Where it crosses the "molar tooth" structure, it appears deflected and reoriented (Fig. 4B,D). Microfossils and amorphous organic debris occur suspended within "molar tooth" calcite (e.g.: Fig. 4A).

## Host Sediment

"Molar tooth" structures are most abundant in uniformly, fine-grained, argillitic microspar, dolomicrospar and silty dolomite, and are rare in siltstone and arenite. Authigenic quartz and feldspar are commonly scattered throughout the host rock. Pyrite crystals similar to those in the "molar tooth" calcite are also common in the host rock. Disseminated waxy, amorphous organic material, filament and sheath-like fragments, and some smooth-walled acritarchs occur throughout "molar tooth" host rock (Fig. 4A). Other features interstratified with "molar tooth" include ooliths, stromatolites, mud cracks, mud chip conglomerates containing fragments of "molar tooth" structures, and halite crystal molds.

"Molar tooth" zones are mostly restricted to stratigraphic intervals less than two meters thick, some of which have been correlated laterally more than 20 kilometers (O'Connor 1967, 1972). Dolomitic layers containing "molar tooth" structures are commonly capped by scoured surfaces that have cut down into the "molar tooth" ribbons. Vertical ribbons commonly protrude above the dolomite, through the scoured surface, and are surrounded by flat mud clasts, and broken, angular to rounded, fragments of "molar tooth" ribbon calcite (Fig. 2A). The conglomerate beds are in turn commonly overlain by finer-grained rocks containing "molar tooth" structures (Fig. 3F, 5G).

## PREVIOUS WORK

"Molar tooth" structure has been described, interpreted and reinterpreted many times since Bauerman (1884) first commented on them over a century ago. Interpretations of their origin range from purely physical and chemical processes to purely biological processes and include combinations of both.

Daly (1912) retained Bauerman's name, "molar tooth" and proposed that "molar tooth" formed by secondary calcite precipitation from fluids moving along joint or cleavage surfaces in the host rock during uplift of Belt strata. For years other Belt workers (Fenton and Fenton 1936; 1937, p. 1927; Rezak 1957, p. 137) supported this explanation.

Other workers (Walcott 1914; Cayeux 1935; Gillson 1930; Ross 1959, 1963; Ross and Rezak 1959; Smith and Barns 1966; O'Connor 1967, 1972) proposed an algal or organosedimentary origin because some "molar tooth" structures intersect stromatolites, or appear in sediments underlying algal structures. O'Connor (1972) proposed that: horizontal "molar tooth" structures "grew" in environments of high waves and strong currents, while vertical structures "grew" in environments of moderate waves or currents, and blobs "grew" in environments of gentle waves or currents.

Many Belt workers proposed chemical origins for "molar tooth" structures. Some (Boyce 1975; Eby 1977; Horodyski 1976, 1985; Young and Long 1977) believed "molar tooth" structures were replaced by calcite. Abundant evidence of hypersaline conditions in the Belt basin when "molar tooth" structures were formed, and the absence of bedded evaporite deposits in Belt rocks, led Boyce (1975) and Eby (1977) to suggest that the "molar tooth" structures were produced by primary precipitation of evaporite minerals such as halite, gypsum, or aragonite and were replaced by calcite. Alternately, Horodyski (1976, 1985), Young and Long (1977), and Eby (1977) suggested evaporite minerals were precipitated into syneresis and shrinkage cracks and pores which were later replaced by calcite.

Another chemical explanation was proposed by Adshead (1963) who concluded that some parallel "molar tooth" sheets were calcite-filled wet sediment slump fractures. From field observations of vertical "molar tooth" ribbons, Bell (1966) proposed that "molar tooth" structures were formed by calcite which precipitated from concentrated solutions that were expelled upward from dewatering sediments. He suggested that the development of voids was controlled by the "granularity and original porosity of the sediments (Bell 1966, p. 42)".

Horodyski (1989) suggested that "molar tooth" structures occurred for a variety of reasons including precipitation of calcite into gas bubbles, pockets, and primary voids caused by the decay of organic matter, fluid evasion stylolite-like voids, and syneresis cracks. Adshead (1963) and Eby (1977) also suggested that the blob structures were perhaps produced by gas pockets.

Without proposing an origin for the structures, Smith (1968) used laboratory models to calculate the mode of deformation of "molar tooth". Because nearly all of the crenulation and shearing of "molar tooth" calcite is in the vertical dimension, Smith proposed that compaction of up to 70% of water-rich silts and clays containing a rigid framework of calcite sheets, formed the sinuous and deformed vertical ribbons.

In many Belt localities "molar tooth"-dolomite strata are interstratified with siliciclastic layers, forming siliciclastic-to-carbonate cycles (O'Connor 1967, 1972; Eby 1977; Grotzinger 1981, 1986). Each cycle consists of the following tripartite lithologic sequence: (1) a basal bed of intraclast conglomerate, (2) graded gray siltite and dark argillite couplets and beds, (3) thinly completed micro-laminated, argillitic stromatolitic or apparently massive dolomicrosparite. "Molar tooth" structures and desiccation cracks are particularly abundant in the upper dolomitic parts of the cycles. These sequences in the eastern Belt basin are more carbonate-rich while equivalent ones in the western Belt basin are more siliciclastic (Grotzinger 1981). The north-eastern Belt basin margin was apparently tectonically stable since no large alluvial fans developed or entered the basin from the east during deposition of the Helena Formation (Eby 1977). Therefore some authors (O'Connor 1967, 1972; Peterson 1971; Eby 1977; Grotzinger 1981, 1986; Winston in press) suggest that oscillations in water level on nearly flat, gently sloping surfaces produced the sedimentary cycles of the eastern Belt basin. Patterns of "molar tooth" structures form cycles which coincide with lithic cycles in the Helena Formation (O'Connor 1967, 1972).

## ANALYTICAL PROCEDURE

### Sample Collection

Outcrops (appendix A) containing "molar tooth" structures were sampled to obtain as wide a variety of structures as possible. Samples were marked to show the stratigraphic up direction.

### Method of Analysis of "Molar Tooth" Structure

In order to study the three-dimensional fabric of "molar tooth" structures, samples were cut into cubes up to 12 cm long. Some cubes were then sawed into thin slabs while others were cut into 8 X 12 cm large thin sections and smaller 2 X 4 cm thin sections for petrographic analysis. Many structures were also photographed under a scanning electron microscope (SEM). The "molar tooth" calcite was dissolved from the host rock with 10% HCl.

## Results

Cavities resulting from calcite dissolution and shapes analyzed in the microscopes were classified as:

(1) blobs (Fig. 1B-D, 2E, 2G, 3B, 4F)

(2) blobs attached to ribbons (Fig. 1B-D, 2E, 2G, 4F)

(3) ribbons (Fig. 1B-D, 2A, 2F, 3B, 4F, 5D, 5G)

(4) blob shapes in ribbons (Fig. 1C-D, 3B, 3E, 3H, 4F,5D)

## Interpretation

Inspection of the "molar tooth" classes led to the following hypotheses:

(1) Blobs may have formed as gas bubble voids (Fig. 1C-D, 2E, 2G, 4F).

(2) Blobs attached to ribbons may have formed as bubble voids connected to bubble trails or bubble

voids split open into cracks, or bubble voids with hairline gas escape cracks (Fig. 1B-D, 2E, 2G).

(3) Ribbons may have been cracks (Fig. 1C-D, 3B, 4F, 5D).

(4) Blob shapes in ribbons may have been gas bubbles or "froth" in cracks (Fig. 1B-D; 3B, 3E, 3H, 4F, 5D).

## Biological Gas Hypothesis

Because these shapes appeared to have developed within the original carbonate mud, removed from the photic zone, and because the shapes appear genetically related, gas from anaerobic organisms was hypothesized to be the agent that produced "molar tooth" void shapes.

If gas was emitted by anaerobic organisms in clayey carbonate mud, it would form throughout the mud. The gas would first accumulate in bubbles forming blobs. The gas bubbles might dilate the sediment until they either moved to the surface, or ruptured, leaking gas to the surface via fractures forming ribbons. Alternately the gas might be re-absorbed into solution, leaving an isolated blob filled with water. Gas bubbles moving through cracks might form the "froth" like that observed in "molar tooth" ribbons since gas generation would be a continual process until the metabolic activity ceased. If the mud dewatered and became firm enough to maintain the void shapes, all four of the above genetic categories of "molar tooth" structures might be preserved at once.

## LABORATORY PROCEDURES

### Phase 1 Procedures

To test the biological gas hypothesis that dispersed gas bubbles formed in mud via anaerobic metabolism, I experimented with water saturated slurries of plaster of Paris and kaolinite (pottery clay), bakers' yeast, and sugar

[yeast + $C_6H_{12}O_6$ ---> 2 $C_2H_5OH$ + 2 $CO_2$ ]

to model the effects of gas development in fine grained, soft sediments. Approximately 1 gram of bakers' yeast and an equal amount of sugar was mixed into each liter of mud. The mud consisted of three parts water and one part clay or plaster. The mixtures were simply pored into boxes, plastic bottles, and vertical tubes and allowed to stand at room temperature from 12 hours to 60 days.

## Phase 2 Procedures

To duplicate mud gas generation and actually observe the formation and movement of gas bubbles, thin aquaria from 2 mm to 2 cm thick, by 30 cm tall and 90 cm wide of plate glass separated by rubber tubing, were filled with a very wet clay slurry, yeast and sugar as in phase 1. These aquaria were observed and photographed each day for up to 14 days. Void shapes in the aquaria were then cast with plaster.

## Phase 3 Procedures

To simulate dewatering of the mud and subaerial exposure forming a salt crust on top of the mud, aquaria as in phase 2 were allowed to expel gas for 7 to 14 days. Then when the mud became dewatered and slightly firm (highly viscous) the top of the system was sealed off by pouring 2-3 centimeters of plaster on the wet clay. These aquaria were observed and photographed for several weeks. Void shapes that formed in these aquaria were eventually cast with plaster.

### Phase 4 Procedures

Because the preservation of "molar tooth" structures requires early formation of uniform, fine-grained, blocky, calcite in the inferred voids, I questioned whether this type of calcite could be produced rapidly by direct precipitation from fluids. To test this idea solutions of approximately 1 mole% $Na_2CO_3$ were combined with solutions of approximately 1 mole% $CaCl_2$ in open beakers at room temperature in the laboratory.

## LABORATORY RESULTS

### Phase 1 Results

When the plaster congealed overnight and the clay dried after many days, these laboratory models were cut open and bubble-shaped voids and some interconnecting cracks were observed (Fig. 4G).

### Phase 2 Results

Stage 1. During the first five hours the water saturated slurry compacted and a centimeter or more of clear water pooled above the surface of the clay sediment. Very small dispersed bubbles formed in the sediment and grew larger indicating the yeast reacted with the sugar producing $C_2H_5OH$ and $CO_2$ gas.

Stage 2. As some ovoid gas bubbles expanded they nearly touched each other, but remained separated by a thin wall of clay (Fig. 4C).

Stage 3. Small horizontal expansion cracks propagated from bubbles as the gas pried mud farther apart (Fig. 5F, left side).

Stage 4. Gas bubbles continued to grow, join, and migrate upward, pushing and slightly compacting the sediment sideward and in front of them. The pathway immediately behind the rising bubbles was quickly filled with a mixture of sediment and water. After each bubble rose to the sediment-water surface, its track was followed by subsequent bubbles that entered the track from the sides and then moved upward. Each bubble reaching the sediment-water interface, flung mud to either side as the bubble rose through the water (Fig. 3A). This activity riled the water pooled above the sediment. When many bubbles exited the sediment at one location, flinging mud to either side, the accent of other nearby bubbles was halted for several centimeters. An equally spaced network of "open" bubble pathways, a few centimeters apart, consequently developed. The resulting pathways became chaotically stirred by bubbles and filled with sediment suspended in water. Away from these pathways the sediment remained essentially undisturbed (Fig. 2B-D, 3A). Water appeared to move up or was pumped up and out of the sediment with the bubbles. These processes continued from 5 hours to 14 days.

Stage 5. Eventually, as the clay stiffened after about seven days, mobile bubbles were restricted to the pathways. Gas bubbles that formed outside of these previous escape routes remained as ovoid-shaped voids, which filled with water when the carbon dioxide gas finally escaped through hairlike cracks or was absorbed into the water (Fig. 5F).

Stage 6. After several weeks, when clay in the aquaria dewatered and became firm, and voids were cast with plaster, bubble path networks were evident (Fig 2B-C).

## Variations to the Sequence

Aquaria with more than 3 1/2 parts water to 1 part clay forming a very wet slurry mixed with 1 gram of yeast and more than 3 grams of sugar per liter, developed regularly spaced bubble degassing pathways (Fig. 2B-C). One aquarium with mud and yeast, but no sugar, developed only a few scattered bubbles which filled with water.

## Phase 3 Results

When the plaster congealed and sealed the top of the aquaria, gas was trapped. Within one hour, the increased pressure formed expansion cracks in the clay. The expansion deformed the walls of the cracks so that the walls no longer matched (Fig. 4E). Within several hours cracks became diffuse and haphazard responding to local differences in gas generation (Fig. 4E, 5A-C, 5E). Cracks propagated upward or downward or horizontally in the sediment. Some cracks wedged through earlier bubble voids and bubble trails. One set of nearly parallel cracks a few centimeters apart focused toward a gas escape vent in the top of a sealed aquarium (Fig. 5E). Some cracks never reached the sediment surface. Water mixed with gas bubbles in some voids forming bubble "froth". After about 10 hours this mixture of bubbles and water indicated a network of movement of gas through an unseen, connected permeability in the aquarium, but the bubble void shapes and the expansion cracks otherwise remained unchanged. Figure 5C typifies a cast of an expansion crack.

### Phase 4 Results

Upon mixing the solutions of $Na_2CO_3$ and $CaCl_2$, small blocky calcite crystals, verified by x-ray diffraction, precipitated within seconds. The crystals are equant, and about 2-10 um in size (Fig. 3D).

## DISCUSSION

### Summary Comparison of Experiments and Belt "Molar Tooth"

These laboratory mud experiments produced a great variety of void structures all similar to the size and range of shapes and spacing displayed in Belt "molar tooth" rocks (Fig. 4C, 4E, 4G, 5A-C, 5E, 5F). The gas bubble voids appear to match the "molar tooth" blobs and the expansion cracks appear to match the vertical and horizontal ribbons. In addition, the expansion cracks were intermingled with ovoid-spherical bubble voids which is a common association in the "molar tooth" rocks. All of the voids in the experiments maintained their shapes for several weeks until desiccation cracks cut them when the aquaria dried completely. By analogy with the experimental results, the blob shapes are early stages of development of "molar tooth" structures. They were gas pockets and bubbles. "Molar tooth" ribbons are interpreted as expansion cracks, some of which followed bubble trails with connecting pathways that were degassing networks. Bubbles rising up through these networks may have pumped water from the sediment by first compacting the sediment near them as bubbles passed upward and secondly by drawing fluids into their track as the sediment lost water and they moved toward the surface with the water. The sediment stiffened, becoming too viscous to form more bubbles.

The "molar tooth" void shapes were probably constrained by factors such as sediment rate, type, viscosity, temperature, depth, and the volume and rate of gas production, similar to the conditions in the experimental aquaria. The aquaria conditions connote warm temperatures (20-40 degrees C), shallow depths, and slow but steady, dispersed anaerobic production of gas in fine grained sediment. Optimum conditions for biological gas generation probably occurred as a result of changing environments during the cyclic Belt sedimentary regimes suggested by O'Connor (1967, 1972), Eby (1977), and Grotzinger (1981, 1986). Solutions saturated with calcium carbonate must have filled the gas voids and rapidly precipitated uniform, blocky calcite into them when favorable permeability developed. The calcite crystals produced in Phase 4 Procedures are morphologically similar to the "molar tooth" calcite and demonstrate that fine-grained, blocky calcite can form by rapid, direct precipitation (Fig. 3D).

## Dead Sea Gypsum Metabolism - A Modern Analogy

A modern sulfate-reducing environment possibly analogous to the Belt basin is the Holocene Dead Sea. Neev and Emery (1967) noticed that large amounts of gypsum precipitated from the surface waters were not preserved below the depositional interface. They sought to explain the disappearance of gypsum by inferring that anaerobic sulfate-reducing bacteria in Dead Sea sediment decomposed gypsum and organic material. They suggested bacterial reduction of sulfate as follows:

$3(CaSO_4 - 2\ H_2\ O) + C_6H_{12}\ O_6 \text{ ---> } 3\ CaCO_3 + 3\ H_2S + 3\ CO_2 + 9\ H_2O$

The $CaCO_3$ generated by this process precipitated as calcite in the sediment (Neev and Emery 1967). The hydrogen sulfide from the reaction readily combined with iron oxides in suspended or deposited sediments to form black iron monosulfides, which were later converted to pyrite (Neev and Emery 1967). Most of the hydrogen sulfide returned to the oxygenated surface water where it quickly combined with calcium to form more gypsum, which sank to the bottom, maintaining a continuous cycle.

### Application to the Belt

While gypsum and anhydrite pseudomorphs do not occur in Belt carbonate containing "molar tooth" structures, the presence of organic material and pyrite indicates that the mud was anaerobic and is strong evidence that sulfate was reduced by organisms. This process requires organic material and results in pyrite if iron oxide is present in the water.

The Belt water was populated by prokaryote unicellular and multicellular cyanobacteria (Horodyski 1989). Gaseous byproducts generated by anaerobic metabolic reactions would have been expelled into muddy sediment wherever favorable conditions existed (e.g.: Neev and Emery 1967). This mechanism may have released sufficient $CO_2$ and $H_2S$ gas to create the "molar tooth" gas bubbles and expansion cracks.

The cycle boundaries capping the carbonate half-cycles record emergence of enormous areas of Belt "sea floor" (O'Connor 1967; Eby 1977). The exposed carbonate mud may have dried to form a stiff carbonate mud or salt crust which sealed off the mud beneath and kept it wet and plastic for long periods of time. Metabolism of sulphate-reducing organisms may have continued during exposure, creating "molar tooth" bubbles (blobs) and cracks (vertical and horizontal ribbons) until either: (1) all the sulfate was consumed, (2) all of the organic material was consumed, (3) the mud dehydrated and oxidized, or (4) the organisms died.

Blocky calcite could precipitate rapidly into the "molar tooth" porosity when the connate waters became supersaturated with $CaCO_3$. The reduction of sulfate (e.g.: Neev and Emery 1967) may have produced sufficient $CaCO_3$ for the process. The "molar tooth" calcite textures indicate that it is a primary, unreplaced, authigenic precipitate that filled voids rapidly, in wet carbonate mud. Evidence to support this interpretation include: (1) The "molar tooth" calcite has a uniform texture with no evidence of partial replacement (Fig. 3C); (2) Cathodoluminescence of the "molar tooth" ribbons show evidence of wet-sediment fracture repairs that would not have survived replacement recrystallization (Fig. 2F); (3) The calcite-host rock boundary is sharp suggesting the calcite grew in voids and was not replaced; (4) "Molar tooth" calcite contains fossils and acritarchs that probably would not have survived replacement (Fig. 4A); (5) Calcite with a similar size and crystal shape to the "molar tooth" calcite was produced in the laboratory by rapid precipitation from solutions (Fig. 3D); (6) Easily recognized "molar tooth" calcite ribbon fragments are found with dolomite mud chip fragments in intraformational conglomerates (Fig. 2A). It seems unlikely that replacement processes would be this selective.

## CONCLUSION

I propose that "molar tooth" structures in Belt rocks were produced by gas expansion voids which filled with uniform, finely crystalline, blocky calcite, while the silty, clayey carbonate mud was wet. The voids formed as gases were released into fine grained sediments by metabolic activity of anaerobic sulfate-reducing bacteria. As in the Dead Sea, anaerobic bacteria in the mud digested gypsum crystals precipitated from the Belt "sea" or "lake" water during falling water levels.

Gases generated in watery clay in laboratory aquaria using yeast and sugar yielded bubble voids similar to the "molar tooth" structures in Belt rocks. Some bubbles in the experiments rose toward the sediment-water interface, pumping water from the sediment and setting up a network of wet bubble trails. When these experimental bubble degassing systems were sealed off trapping the gas, expansion cracks propagated through most of the previous bubble voids and networks. These cracks are similar to "molar tooth" ribbons in Belt rocks.

On the basis of these experiments, I propose that dewatering of the Belt carbonate mud began with gas bubbles forming in the mud and continued during episodes of regression or contraction, and increasing salinity of the Belt water. When the mud became too firm and plastic to allow the bubbles to form it began to dilate and crack. As metabolic activity continued to generate gases in the mud, cracks expanded from previous, isolated gas voids propagating through the mud until a network of cracks reached the sediment surface. Solutions filled the voids, similar to the process observed in experimental aquaria. Finally, degassing and changes in sediment water chemistry caused by cyclicity in Belt basin water depth, and shore line geochemistry, triggered the precipitation of blocky calcite from solutions in the enclosing mud into the expansion voids. Thus the "molar tooth" ribbon and blob structures were preserved by rapid precipitation of fine-grained, blocky calcite similar to the calcite precipitated in laboratory experiments. Further compaction and dewatering of the Belt sediments after the calcite structures had formed, folded and broke some of the "molar tooth" calcite vertical ribbons. During episodes of transgression or expansion of Belt water some of the sediment containing the structures was scoured, breaking, reworking, and re-depositing "molar tooth" fragments in intraformational conglomerates.

This model for the origin of "molar tooth" structures in Belt rocks differs from previous hypotheses in that it easily explains the abundant bubble-shaped blob forms of "molar tooth" as well as the abundant ribbon structures.

This model for the origin of "molar tooth" structures suggests that we should find post-Belt or even modern examples unless these structures are now obliterated by bioturbation, or they exist but have not been recognized.

****

FIGURES

Fig. 1.-(A) Geologic map of Middle Proterozoic Belt rocks; Sample locations in Montana: (HH) Hungry Horse Dam area, (RH) Ravalli Hill between Ravalli and Saint Ignatius, (RP) Rogers Pass area, (NL) Newland Formation from Helena embayment south of Neihart; (B) "Molar tooth" ribbons and blobs in outcrop showing argillitic dolomicrospar beds from Helena Fm., Rogers Pass area, MT; (C) "Molar tooth" ribbons and blobs etched in HCl from Newland Fm. south of Neihart, MT; (D) "Molar tooth" ribbons and blobs etched in HCl, from Newland Fm., south of Neihart, MT.

All solid white scale bars = 1 cm.

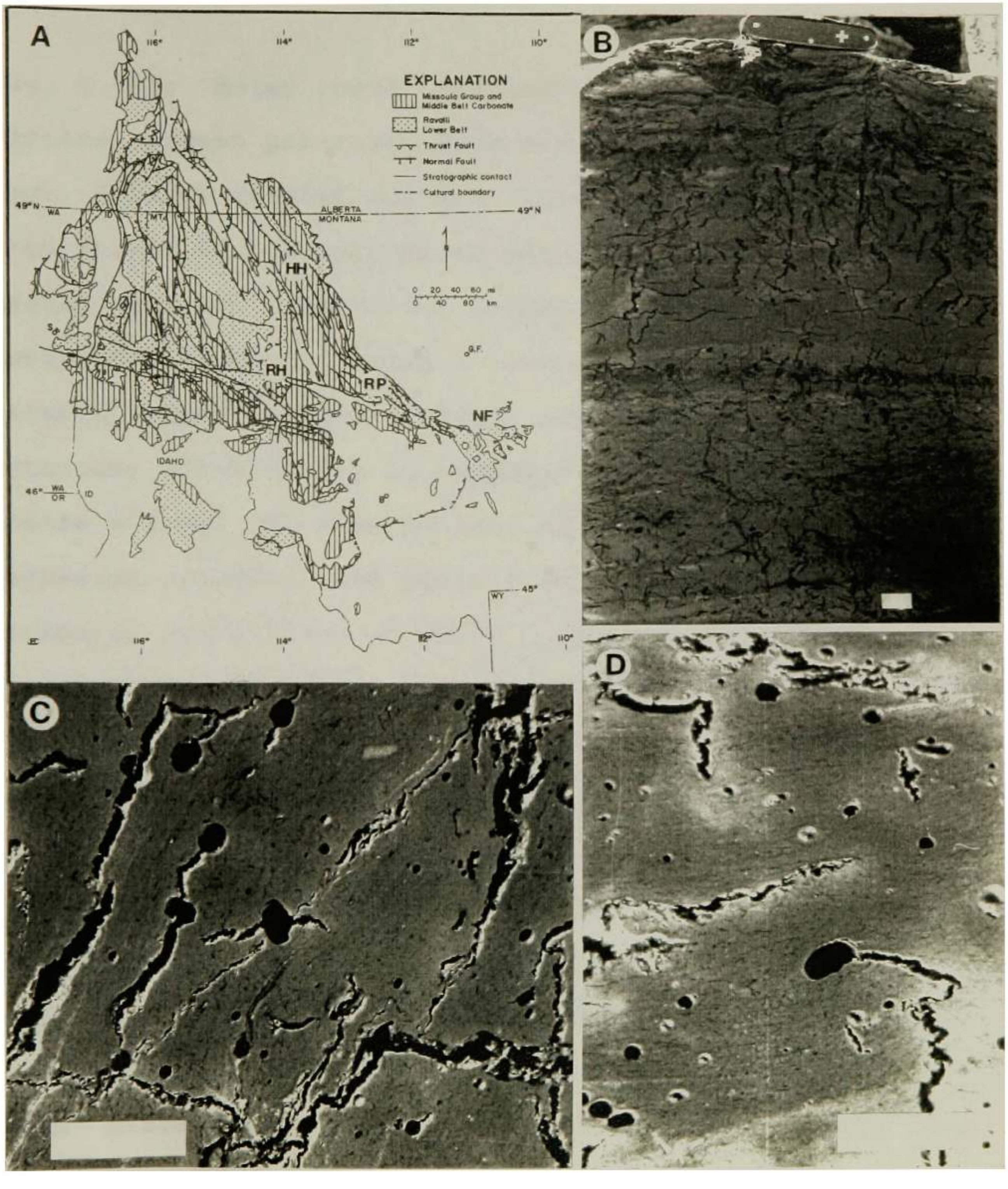
A
116°
114°
112°
110°
EXPLANATION
Missoula Group and Middle Belt Carbonate
Ravalli Lower Belt
Thrust Fault
Normal Fault
Stratographic contact
Cultural boundary
49° N
WA
ID
MT
ALBERTA
MONTANA
49° N
HH
0 20 40 60 mi
0 40 80 km
S
G.F.
RH
RP
NF
IDAHO
46°
WA
OR
ID
B
WY
45°
JEC
116°
114°
112°
110°
B
C
D

FIG. 1.

Fig. 2.-(A) "Molar tooth" horizontal and vertical ribbons; vertical ribbon protrudes from argillitic dolomite host rock, through scoured surface, into conglomerate (arrow), from Helena Fm., Hungry Horse Dam area, MT; note folded and broken vertical ribbons and interconnected vertical and horizontal ribbons forming a network; (B) Plaster cast of network formed by bubble trails preserved in phase 2 aquarium; scale at top in inches and white scale bar at bottom = 1 cm; (C) Plaster cast of evenly-spaced bubble degassing networks from phase 2 aquarium; (D) Photo showing irregular mud surface of phase 2 aquarium after evenly-spaced bubble degassing networks formed; scale bar = 1 cm; (E) "Molar tooth" ribbons and blobs in slab un-etched, from Helena Fm., Hungry Horse Dam area, MT; white scale bar = 1 cm; (F) "Molar tooth ribbon under cathodoluminescence showing bright wedges of calcite (arrows) that filled tension cracks in rigid "molar tooth" calcite during compaction of the enclosing mud; sample from Rogers Pass area, MT; black scale bar = 2 mm; (G) HCl-etched "molar tooth" blobs interconnected with thin ribbons; sample from Helena Fm., Hungry Horse Dam area, MT.

All solid white scale bars = 1 cm.

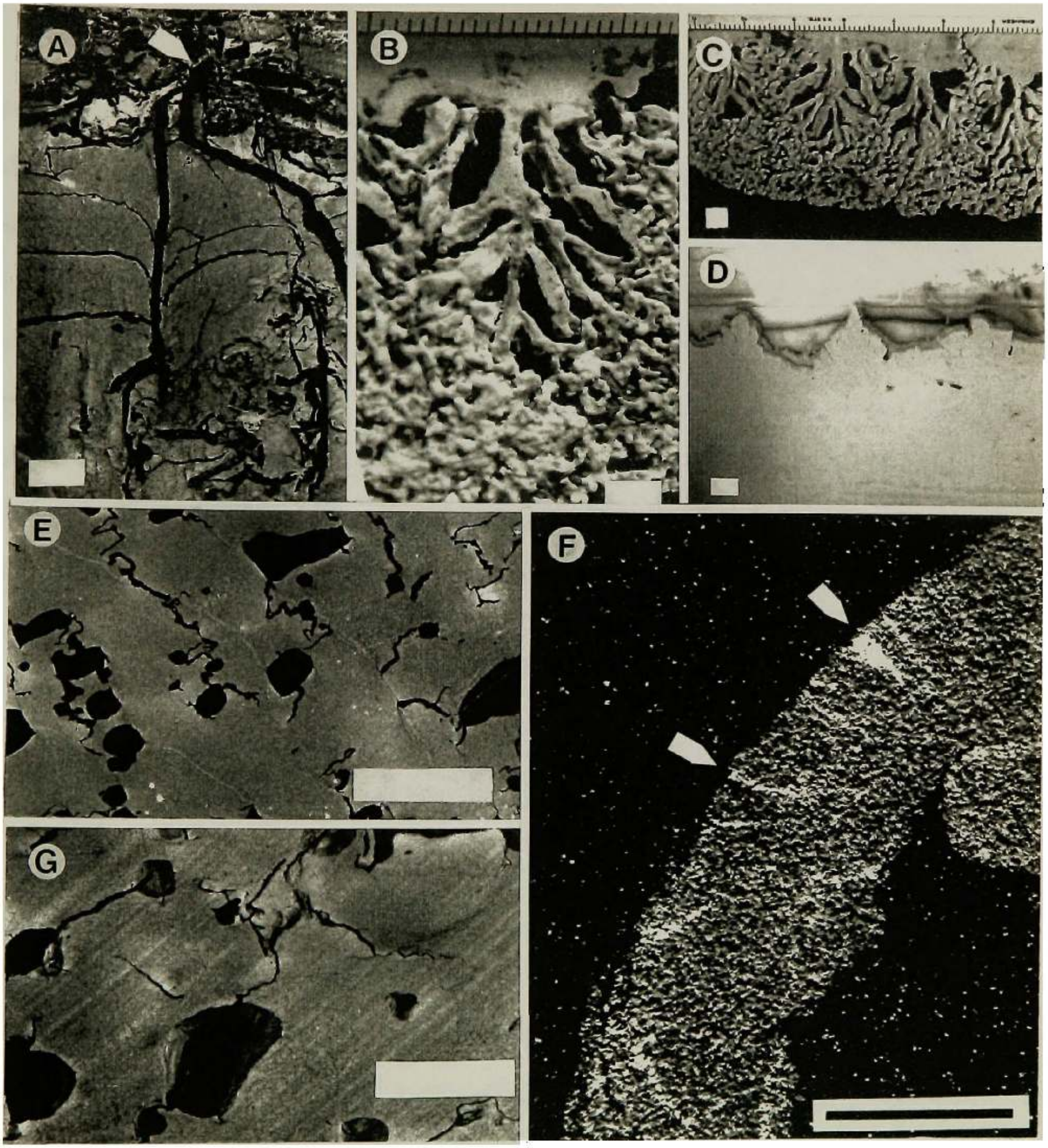

FIG. 2.

Fig. 3.-(A) Sketch of bubble activity in phase 2 aquaria; bubbles shown forming a network of pathways to mud surface and rising through water, flinging sediment to either side which blocks accent of nearby bubbles; no scale; (B) HCl-etched "molar tooth" ribbons and blobs from Newland Fm. south of Neihart, MT; note enclosed "bubble shapes"; scale bar = 1 cm; (C) SEM photo of "molar tooth" calcite from Ravalli Hill area, MT; white scale bar = 10 microns; (D) SEM photo of blocky calcite precipitated in the laboratory, white scale bar = 10 microns; (E) SEM photo of "molar tooth" bubble outlines or "froth" entering ribbon structure from host rock of HCl-etched sample; sample from Newland Fm. south of Neihart, MT; white scale bar = 200 microns; (F) Stylized sketch of "molar tooth" zones interstratified with conglomerate beds containing fragments of re-worked "molar tooth" structures; no scale; (G) Photomicrograph of "molar tooth" ribbon calcite (white) mixed with pyrite crystals (black) from Rogers Pass area, MT; black scale bar = 100 um; (H) Photomicrograph of "molar tooth" ribbon structure with thin band of host rock outlining a "bubble" or "froth"; black scale bar = 400 um; (I) SEM photo of pyrite crystals obtained from HCl-etched "molar tooth" calcite; sample from Hungry Horse Dam, MT; scale bar = 4 um

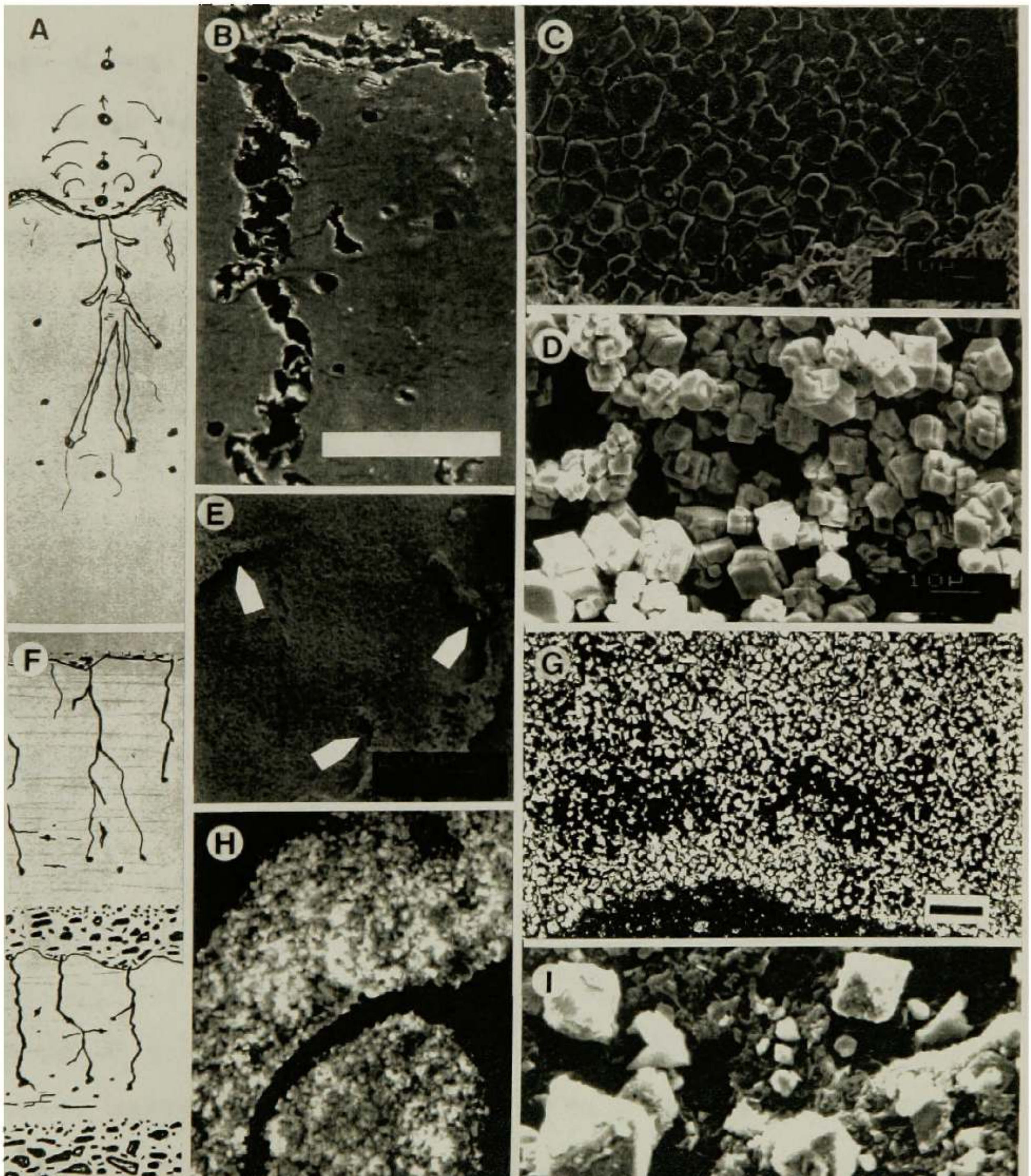

FIG. 3.

Fig. 4.-(A) Photomicrograph of "smooth-walled" arcritarch in "molar tooth" calcite from Hungry Horse Dam area, MT; black scale bar = 20 um; (B) Photomicrograph showing organic laminae crossing into "molar tooth" calcite from host sediment; sample from Hungry Horse Dam area, MT; black scale bar = 200 um; (C) Gas-caused bubble and crack voids filled with water in phase 2 aquarium; note thin clay laminae separating the two large bubble voids, center; compare with "molar tooth" bubble "froth"; (D) Photomicrograph showing organic laminae displaced by "molar tooth" structure; sample from Helena Fm. near Hungry Horse Dam, MT; black scale bar = 200 um; (E) Gas-related expansion cracks caused by sealing off phase 3 aquarium containing active bakers' yeast and sugar; white scale bar = 1 cm; (F) HCl-etched "molar tooth" ribbons and blobs in arigillitic dolomite from the Newland Fm. south of Neihart, MT; (G) Gas bubbles (black) and some cracks in phase 1 block of plaster (white) and clay (gray) that contained active bakers' yeast and sugar while drying and congealing; scale bar = 1 cm.

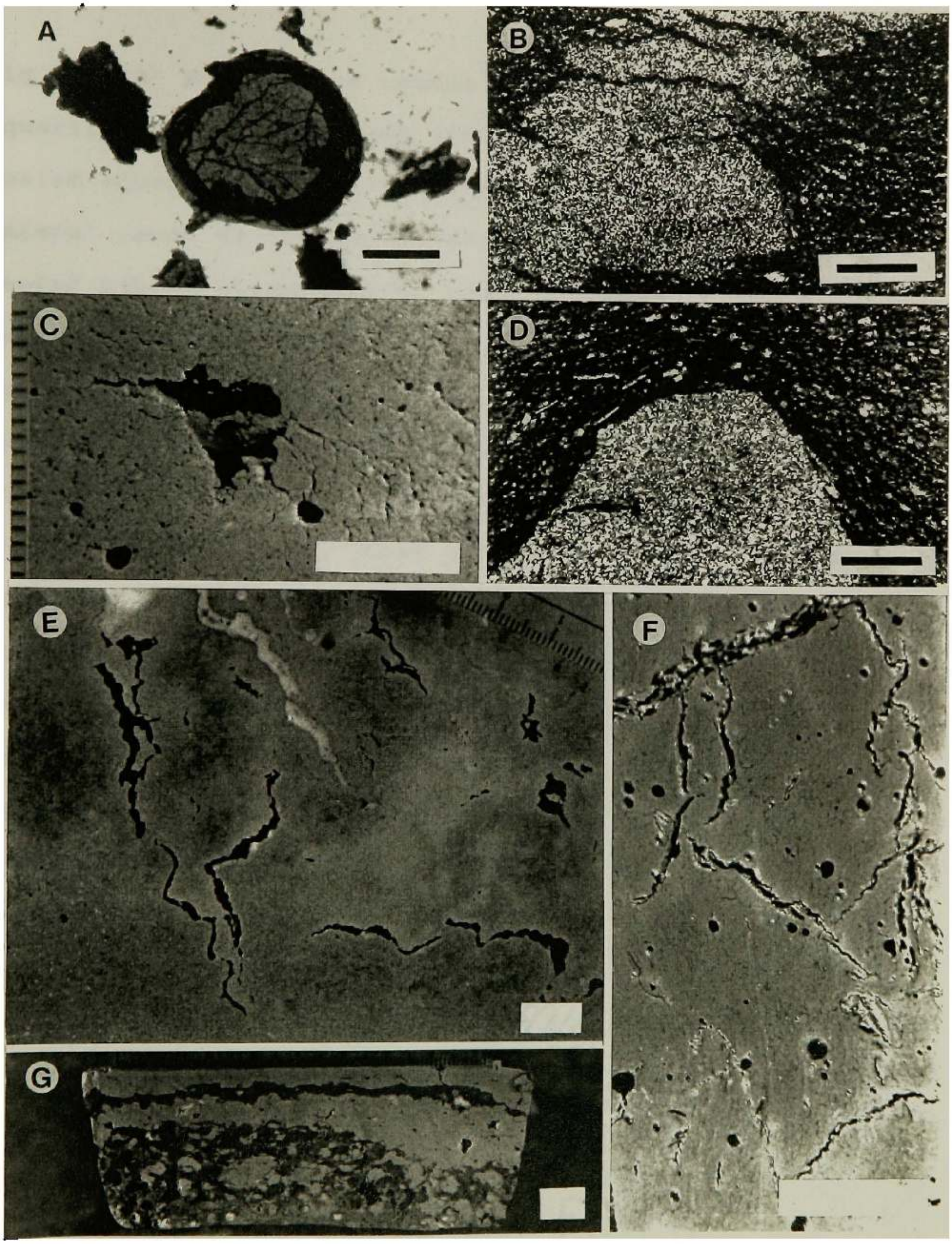
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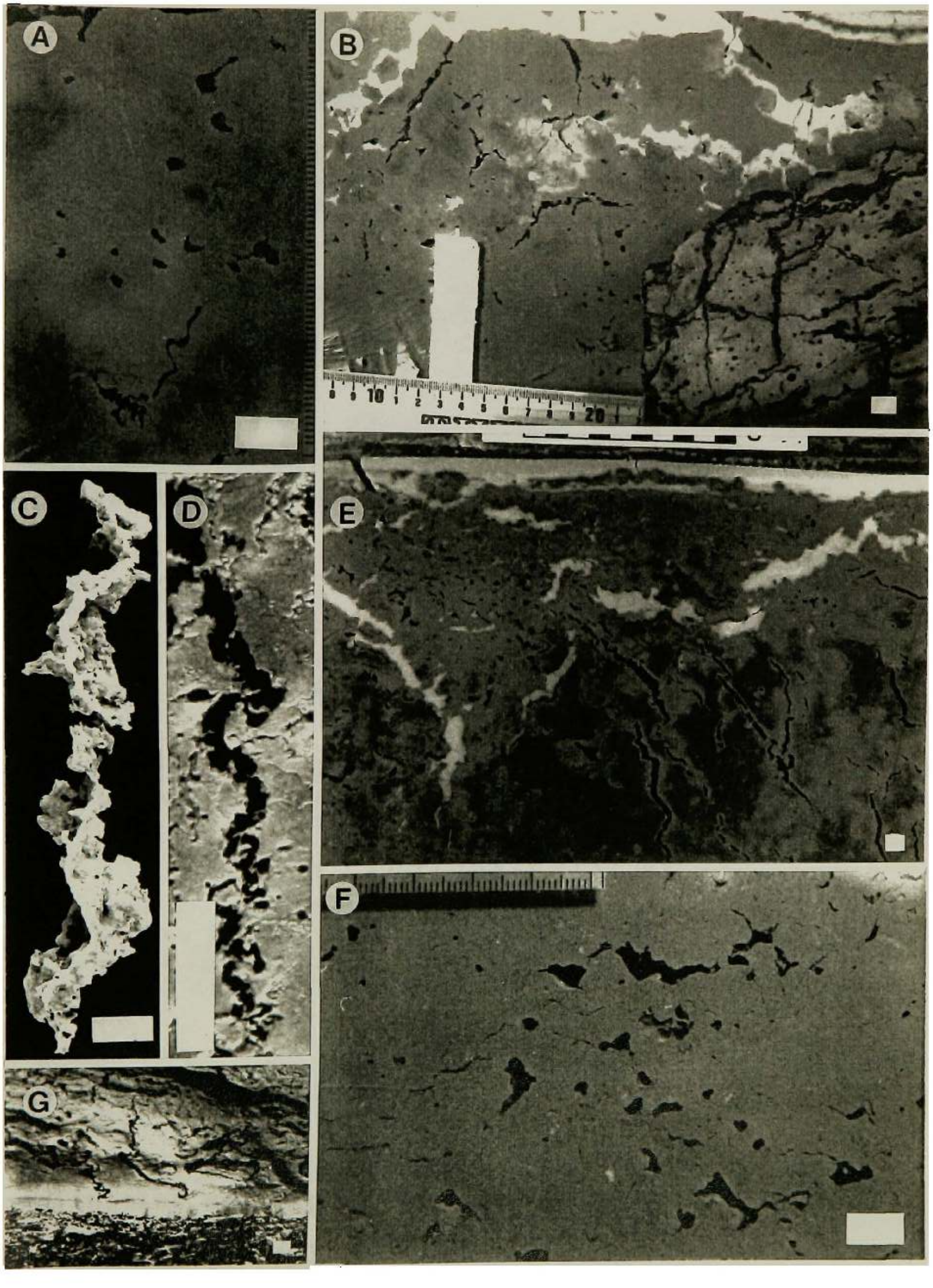
Fig. 5.-(A) Bubbles and cracks formed by gas in phase 3 aquarium; (B) Bubble voids and expansion cracks in phase 3, sealed aquarium containing water, clay, sugar, and active bakers' yeast as source of gas; note the sample of Belt "molar tooth" structures in argillitic dolomite from Newland Fm. south of Neihart, MT, lower right for comparison; (C) Plaster cast of expansion crack formed in phase 3 aquarium; note irregular walls and overall sinuous shape and compare with "molar tooth" ribbons; (D) HCl-etched "molar tooth" ribbon structure from Newland Fm. south of Neihart, MT; (E) Bubble voids and expansion cracks formed in phase 3, sealed aquarium containing mud, sugar, and active bakers' yeast; note gas escape hole (dark colored) in plaster (white) seal upper left and bulge in seal, top center; (F) Gas bubbles and small horizontal cracks in phase 2 aquarium containing mud, sugar, and active bakers' yeast; (G) "Molar tooth" ribbons and blobs in light colored argillitic dolomite above dark colored intraformational conglomerate (bottom) containing fragments of re-worked "molar tooth" structures; sample from Rogers Pass area, MT.

All white scale bars = 1 cm.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# APPENDIX A

Detailed Sample Locations

Newland Formation:
Collected south of Neihart, Montana in the Helena Embayment.

Helena Formation:
Rogers Pass-Several strata sampled along west roadcut of Highway 20, approximately one Kilometer northeast of summit.

Ravalli Hill-Several strata sampled along north roadcut of Highway 93 east of summit between Ravalli and Saint Ignatius, Montana.

Hungry Horse Dam-Several strata sampled along roadcut of Highway 2, approximately 0.2 kilometer east of Hungry Horse townsite and many strata sampled between visitor's center at Hungry Horse Dam and one kilometer north of visitors center along east roadcut of access road.