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Petrographic observations of stromatolites in the late Cambrian to early Ordovician Knox Group, Northwest Georgia and their relationship to stromatolitic fabrics over geologic time

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Petrographic observations of stromatolites in the late Cambrian to early Ordovician Knox Group, Northwest Georgia and their relationship to stromatolitic fabrics over geologic time

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Abstract:

Silica deposits are common in Proterozoic carbonate platforms and are interpreted to form early in the diagenetic history of the carbonate strata. Black early diagenetic chert deposits are often associated with evidence of ancient microbial mats, or stromatolites. Proterozoic chert nodules can contain well-preserved microfossils, because silicification occurs rapidly; however, silica deposition has changed over time and it is unclear if similar deposits exist in the Cambrian period after silica-utilizing organisms evolved. The Copper Ridge Dolomite in the Knox Group, northwest Georgia, which was deposited in the late Cambrian to early Ordovician, contains black chert nodules that follow the structure of stromatolitic fabrics. Unlike Proterozoic stromatolites, the Copper Ridge stromatolites do not preserve many individual microfossils, but the patterns observed in the silicified stromatolites provide insight into the silicification process and later diagenetic processes. Petrographic analysis of the Knox Group stromatolites performed in this study identifies the preservation of stromatolitic layers through the precipitation of silica, and multiple episodes of alteration by diagenetic fluids. In an effort to better understand the silicification patterns observed, silicification experiments aimed at recreating silicification in the lab were begun with the aim of comparing the Knox Group stromatolitic fabrics to the fabrics of lab-created silica rock. Correlating these two fabrics can help identify the geochemical environment of silicification of the Knox Group stromatolites during the late Cambrian and early Ordovician.

Introduction:

Stromatolites are fossilized microbial mat structures found across the world and throughout geologic time. The oldest known stromatolites indicate that life had evolved during the Archaean approximately 3.49 billion years ago (Allwood, et al., 2018). These fossils accumulate vertically in tidal and subtidal environments by the precipitation of laminae as mineral layers, or the trapping and binding of sediment (Tewari and Seckbach, 2011). During the Mesoproterozoic, stromatolite diversity reached its peak, as the conditions of Earth's habitats during that time were not conducive to the survival of more complex forms of life. During the transition into the Phanerozoic, more diverse and sophisticated organisms evolved which could graze on algal mats. This resulted in the decline in stromatolite diversity we see in the rock record. (Tewari and Seckbach, 2011). Stromatolites can still be found today in highly saline environments with low amounts of nutrition such as the Bahamas and Shark Bay, Australia.

Stromatolites donated to the Tellus Museum in Cartersville, Georgia were found in the late Cambrian to early Ordovician strata of the Knox Group in northwest Georgia. Although these stromatolites have been found and studied in Knoxville, Tennessee (Montenez and Read, 1992) to our knowledge, this is the first description and analysis of the Knox Group stromatolites and their associated fabrics from Georgia.

Geologic Setting:

The Knox Group represents a carbonate ramp deposited on the passive margin of Laurentia during the Late Cambrian to the Early Ordovician. This unit is characterized by shallowing-upward peritidal cycles and is identifiable through what is now western Virginia, Tennessee, Georgia, and Alabama (Montanez and Read, 1992). This passive margin, once flat, was faulted and deformed into giant folds from compressional forces originating from the southeast (Cressler 1963). Cressler (1963) (see Fig 1) divided the Knox group in Northwest Georgia and southeastern Tennessee into the Copper Ridge formation, the Chepultepec formation, and the Longview formation. The Copper Ridge Dolomite forms the lower 200 feet of the Knox Group and is composed of light and dark layers of thinly laminated chert (Oder, 1934). The Chepultepec Dolomite is fossiliferous and consists of dull porous chert and makes up the middle 800 feet of the Knox Group. The Longview Limestone is 350 feet thick and made up of highly cherty gray and olive gray limestone and dolomite. These three dolomite deposits form the resistant ridges found in the Valley and Ridge province (Oder, 1934).

Ordovician	Chickamauga Limestone		1,400-2,300	Limestone, clayey and silty, and siltstone.
Ordovician	Knox Group	Longview Dolomite	350	Thick-bedded limestone and dolomite
Ordovician	Knox Group	Chepultepec Dolomite	800+	Thick-bedded dolomite; little limestone.
Cambrian	Knox Group	Copper Ridge Dolomite	2,500	Thick to massive-bedded dolomite; some thin-bedded dolomite at base.
Cambrian	Conasauga Formation		1,500-4,000	Impure limestone, calcareous siltstone, and claystone.
Cambrian	Rome Formation		4,000-5,000	Shale and sandstone.

Fig 1: Stratigraphic section of the Cambrian and Ordovician in NW Georgia. From Cressler (1963)

The several orogenies that created the Appalachian Mountain chain caused significant structural changes in the carbonate rock hosting the Knox Group stromatolites. As a result, diagenetic fluids were introduced leaving behind chemical alteration signatures. (Montanez and Read, 1992). Geochemical analyses of similar ancient dolomites to the Knox Group record a complex diagenetic past of numerous episodes of dolomitization (Montanez and Read, 1992).

The Knox Group was found to record both the chemistry of its original precipitation, as well as the following episodes of dolomite modification after burial (Montanez and Read, 1992).

Samples were collected from two outcrops of the Copper Ridge formation in northwest Georgia. The first location was on private property in Chatsworth, GA where the ridge-forming Knox Group was identified by the presence of silica nodules found alongside laterally linked hemispheroid and stacked digitate stromatolites (Chowns and O'Conner, 1992). The silica nodules found in Chatsworth were similar to micro-fossiliferous chert of the Proterozoic in color, ranging from light gray to dark black (Manning-Berg et al., 2019). The second location was on private land in Adairsville, GA where the Knox Group was identified by the presence of gray to black silica nodules containing stromatolitic fabrics, and its association with oolitic limestone.

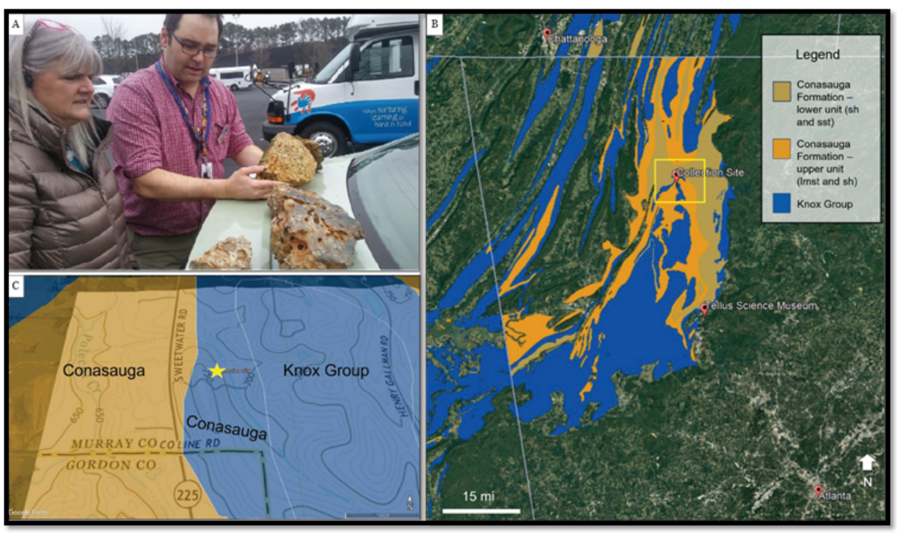

Fig 2: The location of sampling sites in NW Georgia (A). Sampling was completed in tandem with the Tellus Museum. (B) Map of the Knox Group (blue) and Canasauga Formation (orange) NW Georgia (C) Samples were collected on ridge bounding the Knox and Conasauga groups in Murray County, GA.

Materials and Methods:

Petrographic Analysis

Petrographic analysis was performed using a Leica DM6 B microscope at the University of Tennessee at Chattanooga. Thin sections made by Wagner Petrographic and six were cut to a standard thin section thickness of 30µm. Four larger thin sections were cut to 90µm for the preservation of possible microfossils. Lieca's LAS X software was used to create large photomicrograph mosaics by stitching hundreds of smaller photomicrographs together. This allowed for the rapid transition between larger scale features of the rock fabric such as stromatolitic structure and silica infilled fractures to the minute thin section details such as grain size and laminae thickness. The same software was used to measure crystal size and laminae within the thin sections. 63 measurements of the thicknesses and spacings between the dark and light laminae as well as 360 measurements of the sizes of dark and white crystals were collected.

CL at UTK

Cathodoluminescence (CL) microscopy was completed using a CITL MKS Optical Cathodoluminescence Microscope Stage connected to an Olympus BX6 at the Department of Earth and Planetary Sciences at the University of Tennessee in Knoxville. CL was used to find remanant carbonate crystals and identify known diagenetic elements such as Mn, Fe, and Sr within individual carbonate crystals.

Stromatolites were analyzed following the acquisition procedure from Krainer and Spotl (2006), using 15-20 kV beam potential and 500 MA beam current and a wavelength of 460 nm (blue light).

XRD

Two samples of the Copper Ridge chert were crushed and powdered in a ball-mill for analysis by X-ray diffraction (XRD) to determine whether any compositional differences exist between the black and white chert of the Knox Group. The analyses were completed at The University of Tennessee at Chattanooga using a PW 1830 X-ray generator made by Philips Analytical (rebranded today as PANalytical). Analyses were performed using Cu radiation at Ka1, l=1.54056 Å focused through a PW2273 long fine-focus X-ray tube. The generator was set to an accelerating potential of 40kV and a filament current of 40mA. The incident beam slits used were 1 degree divergence slits while the diffracted bean slits were composed of a 0.2mm receiving slit, soller slits, and a 1-degree anti scatter slit. The sample was scanned from a range of 18° to 70° with a step size of 0.015°. A counting time of 1 second was used resulting in a total scan time of 58 minutes.

Silica-gel Experiments

Ongoing silica-gel experiments are being performed in the Biogeochemistry lab at the University of Tennessee at Chattanooga. Silica gel experiments will allow us to compare the fabric of the Knox Group stromatolites to a lab grown fabric. This will tell us the significance of the crystal size difference between more organic and less organic laminae in the stromatolite samples.

Artificial Sea Water (ASW) and stock solutions were created following the procedure from Moore, K.R. et al, (2020). Throughout the experiment, several variations of the Mg:Ca solution will be added to ASW that is spiked with a sodium silicate solution (NaSiO2(OH)4) bought from Sigma Aldrich ranging from 90 ppm to 120 ppm; 120 ppm. For our first experiment, a 1:7 ratio of Mg:Ca solution was used. In our experiment, 40 ml of spiked ASW was poured into 50 ml centrifuge tubes. Small amounts of this water was allowed to evaporate.

We will also introduce two microbial species, *Chlorella* and *Oscillatoria*, purchased from UTEX, to explore the silicification process in the presence of microorganisms (Fig.3). These organisms will be transferred into the silica saturated seawater medium and allowed to grow for 30 days. Samples will be checked on day 0, 1, 15 and 30. Once precipitated and dried fully, the samples will be cut from their holders and thin sectioned. Comparison between the fabrics of the

Knox Group stromatolites and the lab grown silica gel will be conducted using the Leica DM6 B microscope located in the Biogeochemistry lab.

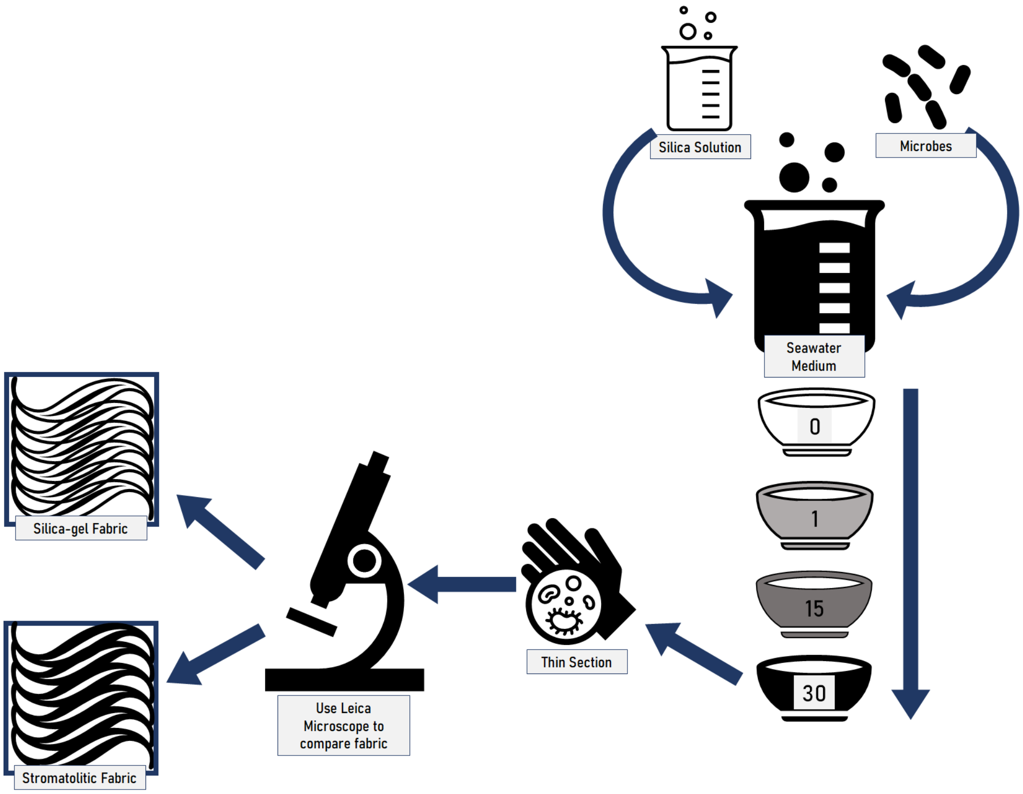

Figure 3: Diagram of the silica-gel experimental design. Microbes and silica solution are added to seawater medium and observed for 30 days. Once dried and subsequently thin sectioned, comparison of the silica-gel fabric and Copper Ridge stromatolitic fabric will be done using a Leica DM 6 B microscope.

Results:

Rock Descriptions

Silicified stromatolites occur within carbonate strata, many of which resembled nodules. In most occurrences, the silica follows the shape of the stromatolitic layering. The chert color ranges from jet black, dark gray, light gray, to milky white. Our focus for this project was on the dark black chert. Most of the preserved stromatolitic fabrics are coalesced and cumulate or pseudo columnar, but some oncolytic forms were found. Stromatolite samples range in size from 5cm long to 18.7cm long at their longest length.

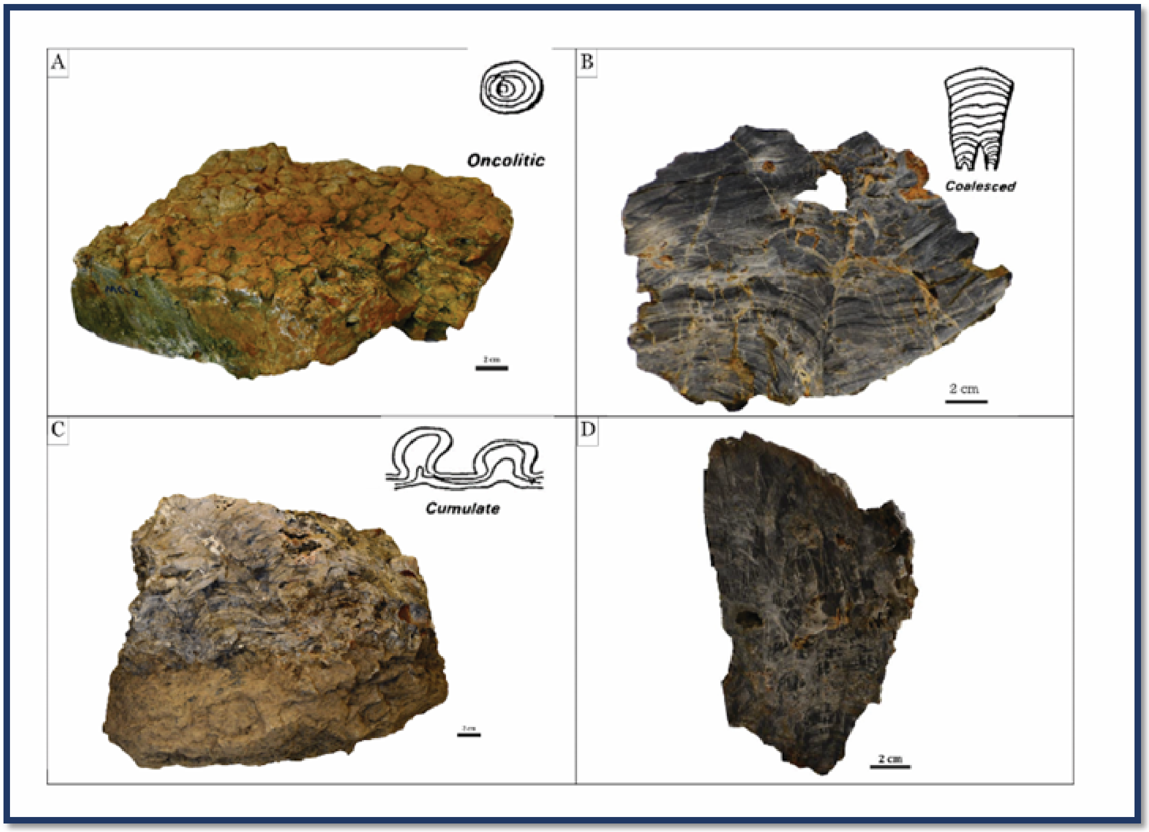

Fig 4: Structures associated with Knox Group stromatolites collected in NW Georgia.

Petrography

All samples, including those that displayed black and white layering, are composed of silica. Under plane-polarized light (PPL) the samples are homogeneous with respect to texture and composition. However, under crossed-polarized light (XPL), laminae are visible and vary in thickness and crystal size. Laminae associated with organic staining, referred to here as dark laminae, have an average width of 250.45µm, with a maximum width of 501.43µm and a minimum width of 93.20µm. These laminae are made up of smaller quartz crystals with an average crystal size of 11.03µm ± 4.4µm.

Laminae formed between organic staining (referred to here as light laminae) have an average width of 290.37µm, with a maximum width of 643.09µm and a minimum width of 123.47µm and are composed of larger crystals (average size of 52.45µm ± 27.27 µm). The laminae were also examined with the gypsum plate, as described by Dunham (2018), which shows a rectilinear pattern of silica crystals within the lamina, common in early chert samples (Gauvey and Kah, 2021). The organic staining of the samples did not fluoresce with fluorescence microscopy, and the crystals did not fluoresce under CL.

Fractures are common and are all infilled with silica. Fractures are commonly infilled with either flamboyant quartz or quartz with undulatory extinction. Dolomite rhombs ranging in size from 45µm to 450µm are commonly found near fractures. When viewed in XPL, the dolomite rhombs display undulose extinction indicative of quartz recrystallization. Some samples contained a small amount of opaque minerals, which are likely small pyrite crystals.

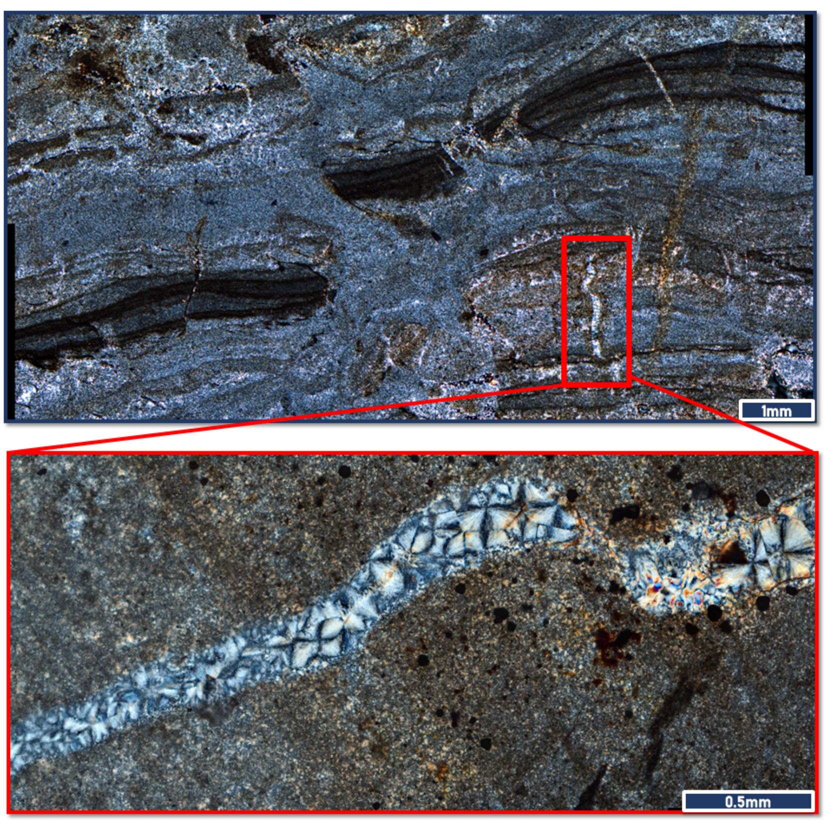

Fig 5: Photomicrograph showing the highly fractured stromatolitic fabric. Fractures are infilled with chalcedony and flamboyant quartz.

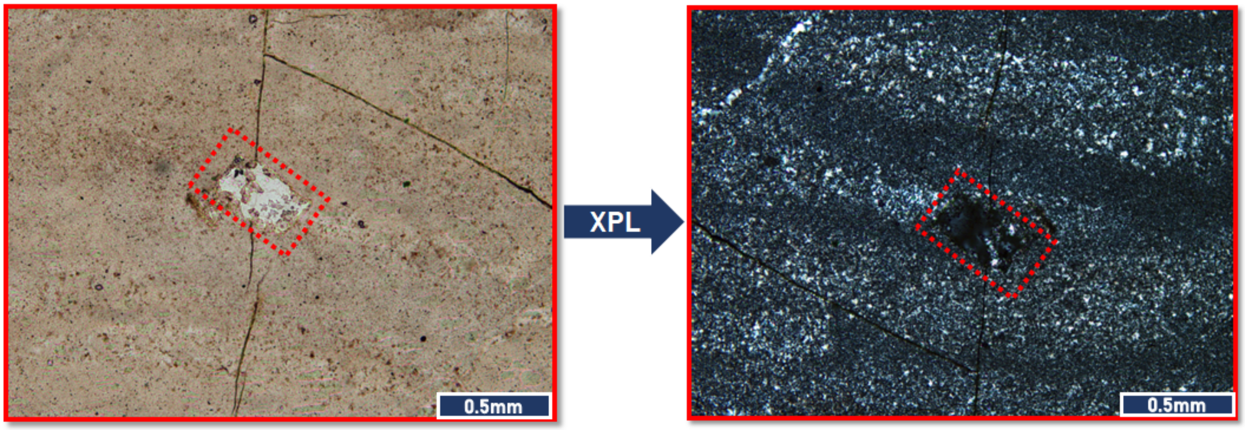

Figure 6 shows the presence of dolomite rhomb growing near a fracture. The crystal has undulose extinction when viewed under XPL, consequently showing it has been recrystallized as quarts.

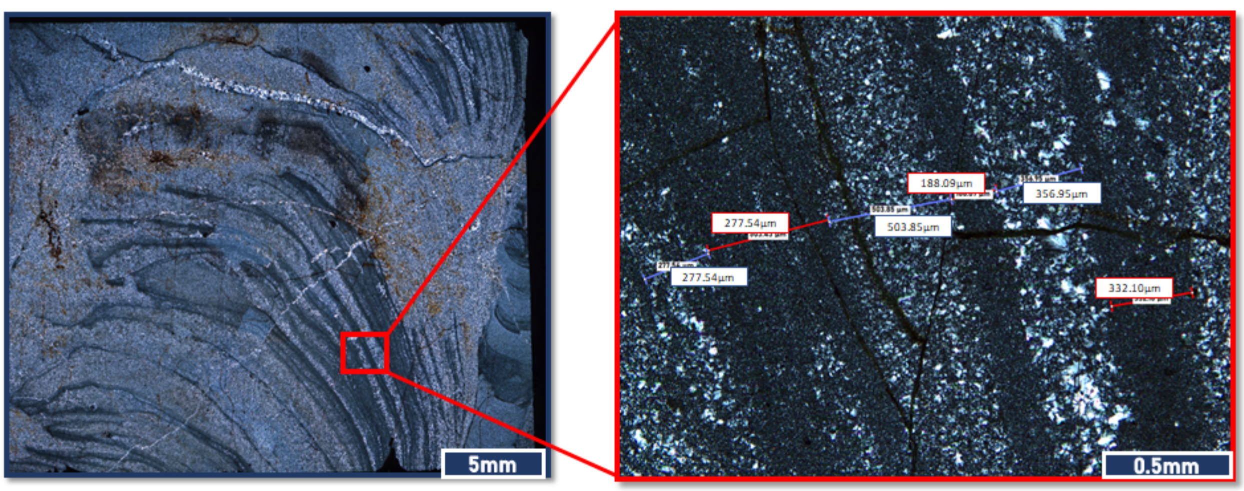

Fig 7 shows stromatolite laminae are only visible in XPL. Crystal sizes vary between laminae and are smaller near organic layers and larger in less or non organic layers.

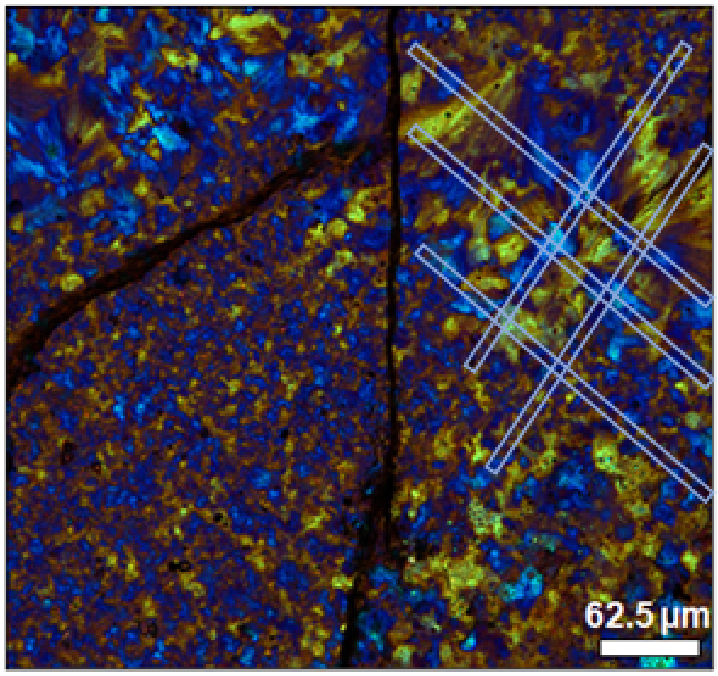

Fig 8: Inserting the gypsum plate reveals the rectilinear pattern identified by Dunham, (2018) and Guavey and Kah, (2021) as a texture indicative of a silica gel precursor.

XRD

X-ray analysis for both samples identified silica (SiO_2) as the only mineral. The presence of an anomalous peak appearing at 31° was found in MC-11 (black chert sample) and originally was thought to be attributed to the presence of graphite. Subsequent search matching identified no link to graphite and no other known causes for the peak were found.

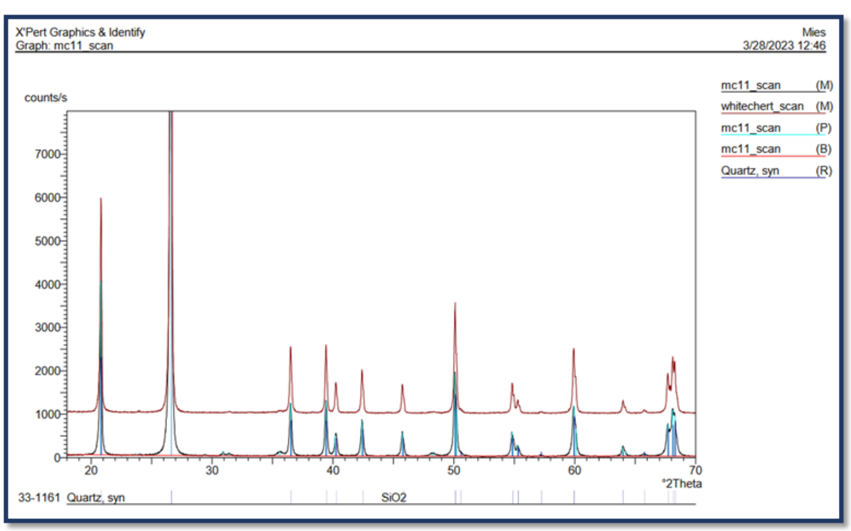

Fig 9: XRD patterns of both black and white chert nodules. Both are composed entirely of silica. (Sample MC-11 is black, White chert sample is red)

Raman Spectroscopy

Raman spectroscopy was collected in the Paleobiology lab at the University of Cincinnati. Sample preparation and data collection were done previously by a former student (Jones et al., 2021). Poorly preserved microfossils were occasionally identified in the solidified stromatolites. Raman spectroscopy revealed quartz peaks around 400 cm-1 and a D- and G-band between 1400-1600 cm-1.

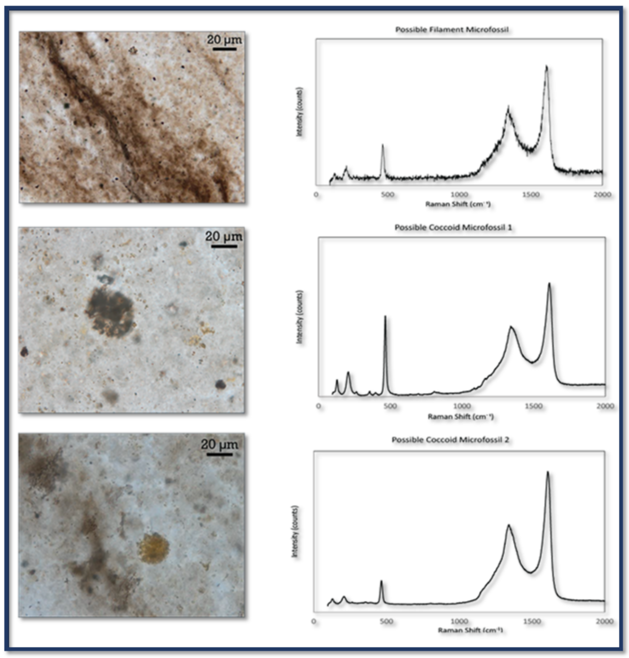

Fig 10: Raman spectroscopy of possible microorganisms in black chert nodules. The two peaks around 1500 (cm−1) represent the presence of organic matter.

Silica-gel Experiment

Silicification experiments are in progress; however, there is no data to share at the time of writing this thesis.

Discussion:

Proterozoic peritidal carbonate environments are associated with black chert nodules that can contain well preserved microfossils. The silicified stromatolites of the Copper Ridge dolomite were deposited in a peritidal environment and resemble older chert deposits of the Proterozoic. Early diagenetic chert deposits of the Proterozoic are often dark black in color; these are the deposits in which microfossils are observed. During this time period, seawater was saturated with dissolved silica because organisms that remove silica from seawater had yet to evolve. This meant that silicification occurred in shallow marine environments. The location of silica deposits moved deeper into the ocean basin after the evolution and diversification of radiolaria in the Ordovician (Maliva, 2005).

Similar to Proterozoic chert samples, the chert within the Copper Ridge dolomite records black and white layers in outcrop and hand samples. These cherts offer an opportunity to investigate the fabrics and potential changes in silicification after the Proterozoic, but prior to the major transition caused by silica-utilizing organisms. Previous petrographic investigation and data collected with Raman spectroscopy concluded that the microfossils preserved in these chert samples have a poor morphology, but the pattern of the D- and G- peak region indicate that the organic matter is relatively immature (Jones et al., 2021). Raman spectroscopy was also performed on crystals that included brown staining, and identified the staining as carbon-rich (Jones et al., 2021).

Petrographic analysis found diagenetic features, including mineralized fractures cross-cutting the stromatolitic fabric, silicified dolomite rhombs found around fractures, rectilinear pattern reflecting primary precipitation of a mineral gel, and crystal size variation between organic rich and organic poor laminae. The fabrics of the Knox Group stromatolites may not have been formed predominantly by trapping and binding and may suggest a different formation mechanism than the Phanerozoic analogs of Shark Bay and the Bahama (Guavey and Kah, 2021).

Distinct laminae of the stromatolites can also be identified at the microscale when observing the samples under XPL; however, petrographic and XRD analysis indicate there is no chemical or crystallographic variations in between black and white layers observed on the macroscale. Petrographic observations agree with the XRD analysis, although there is evidence for secondary diagenesis in the laminae that can be seen in thin sections. Two key differences observed between the light laminae and the dark laminae include crystal size variation and the presence of organic matter or organic staining. The lighter laminae have larger crystals than the darker laminae and contain little organic matter. In contrast, the darker laminae have smaller crystal sizes, form in areas that are organic-rich, and tend to be narrow laminae. We interpret these laminae to represent the primary fabric of the stromatolites. Chalcedony spheres present in both types of laminae are better observed when using a gypsum plate. These samples show a rectilinear pattern that has been interpreted to be evidence of silica formation from a gel phase (Dunham, 2018; Gauntly and Kah, 2021), which is the phase expected to form during the silicification of ancient microbial mats in seawater saturated with respect to silica (Manning-Berg and Kah, 2017; Moore et al., 2020). This indicates that the stromatolites of the Knox Group did not form like the structures we see growing in Shark Bay today. Instead the silicified mats resemble their Proterozoic counterparts that formed by mineral precipitation.

Secondary dolomite rhombs are observed in the silicified stromatolites, which likely formed as a result of diagenetic fluids. These dolomite crystals are found within the primary fabric and along fractures. Petrographic and Raman spectroscopy confirm, however, that the rhombs have been replaced by silica. This indicates that the stromatolites have experienced at least two episodes of diagenetic fluids (one that promoted dolomitization and a second that promoted silicification). However, we are unable to determine how many episodes of diagenetic fluids interacted with these samples.

To determine whether the chalcedony spheres are a primary feature that results from the precipitation of a silica-gel phase, silicification experiments are being performed in the lab. Silica concentrations in the modern ocean are low, due to the evolution of silica-utilizing organisms; therefore, there are no modern analogs for this type of chert formation. Our goal is to replicate the patterns observed in Proterozoic and these Cambrian silica deposits through evaporative conditions likely responsible for increasing dissolved silica concentrations in marine water. Evaporation would allow for precipitation of silica from a supersaturated solution. The resulting fabrics of the lab-created "rock" can then be explored using the methods outlined in this thesis. Microorganisms analogous to those documented in early diagenetic chert will also be introduced to these silica-rich fluids to precipitate a lab-created "fossil." Through the introduction of an organic substrate, we can observe nucleation processes and identify textures of fabrics that may resemble the dark laminae observed in early diagenetic chert. Future work will focus on this experiment.

Conclusions

Proterozoic early diagenetic chert deposits inform much of what we know about early microbial life and their preservation as stromatolites. These deposits are common in peritidal carbonate strata and are interpreted to form close to, or at the same time as, the surrounding carbonate rock. Petrographic observations of early diagenetic chert samples reveal chalcedony spheres interpreted to form from a primary silica-gel. However, during the mid-Paleozoic, silica concentrations in seawater decreased as silica-utilizing organisms evolved, which pushed the location of silica deposition deeper into the ocean.

Silica nodules, which often preserve stromatolitic textures, are an identifying feature of the carbonate rocks in the Knox Group, southeastern US. These strata have been interpreted as a peritidal carbonate platform, and despite being late Cambrain to early Ordivican in age, the silicified stromatolites indicate that they formed through mineral precipitation similar to those in the Proterozoic. This is opposed to trapping and binding established in the mid-Paleozoic and in “modern analogs” of stromatolites. The Knox Group stromatolites are completely silicified with chalcedony spheres similar to those observed in chert deposits from the Precambrian. Although diagenetic alteration is evident through the silicification of late dolomite rhombs, indicating more than one diagenetic fluid interacted with these rocks, these chert deposits may help constrain silicification processes across the Precambrian-Phanerozoic boundary.

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