Origin of Large Carbonate Concretions in the Huron Member of the Ohio Shale (Devonian), Central Ohio

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TABLE OF CONTENTS

Abstract

Large carbonate concretions are a prominent feature of the lower Huron Member of the Ohio Shale, a classic Devonian black shale, of Ohio. The origin of the carbonate concretions, and their growth history, has long remained largely unknown. The purpose of this study was to determine the mineralogy and interpret the early diagenesis of the concretions, with the ultimate aim of gaining insight into the early taphonomic history of organisms preserved in them. Specimens studied are from Franklin and Delaware counties, Ohio. Concretions were studied in the field, and in the laboratory using Scanning Electron Microscopy/Electron Dispersive Spectroscopy (SEM/EDS), and X-ray Diffraction (XRD) technology. XRD analysis reveals that the concretions are differentiated into three parts by distinct mineralogical differences. The inner core region consists largely of barite and calcium phosphate. The outer core is formed mostly of calcite and notable amount of quartz, and the outer rings (non-core zone) are composed largely of ankerite. The concretions thus seem to have experienced multiple growth phases. SEM analysis shows that some concretions have fossils resembling algae. The fossils are preserved in silica, which may be secondary after carbonate. The fossils were likely responsible in part for nucleating the concretions. The presence of calcium phosphate in the inner cores of concretions suggests that decaying animals also may have played a role in nucleating the Ohio Shale carbonate concretions.

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I thank my parents for their selfless mental and financial support throughout my college life as I pursued knowledge in geology. Although a bit skeptical about my choice at first, they still respected my choice and helped me from the beginning to the end.

Finally, I want to specially thank my high school Earth science teacher, Xie Fang. She revealed this amazing world of Earth science to me and encouraged my academic pursuit in this wonderful direction.

LIST OF FIGURES

Introduction

Carbonate concretions are relatively common in certain organic-rich black shales of Paleozoic age. The presence of carbonate concretions in black shales seems counterintuitive. In general, carbonates precipitate under well lit, well oxygenated, shallow, alkaline aqueous conditions, whereas organic-rich black shales commonly require anoxic to dysoxic, acidic conditions for deposition. A commonly used hypothesis is that decay processes created local alkaline conditions, allowing for carbonate precipitation, but many factors remain uncertain. The study of concretions and carbonate layers in black shales is stimulated in part because such sedimentary features often contain exceptionally preserved fossils. Figuring out the mechanisms by which these carbonate deposits formed will have the benefit of furthering our understanding of fossilization processes.

Carbonate concretions are a major sedimentary feature of the lower part of the Huron Shale Member of the Ohio Shale (Devonian: Famennian). The concretions are enclosed in organic-rich black shale. The concretions are enormous, and have a compressed-spheroidal shape. Some have diameters of around 1.5 meter. Such concretions resemble the celebrated ‘Orsten’ of Cambrian age in Scandinavia. Orsten concretions are famous not only because of their size, but also for exceptionally preserved fossils contained within them. Some dark colored, small fossils with morphologies resembling algae were observed in this work in the ‘Orsten’-type concretions from the Huron Member.

In the Huaqiao Formation (Cambrian), Hunan, China, dark limestone layers are interbedded with organic-rich black shale. Here, fossils of a calcifying brown alga, *Padina*, have been recognized in the carbonate and considered responsible in part for the origin of the carbonate mud (Babcock et al., 2012). Holocene *Padina* secretes carbonate needles and, when it dies, those needles scatter to form carbonate mud (Babcock et al., 2012). One hypothesis developed during this project is that the algae-shaped fossils in the carbonate concretions of the Huron Member are also *Padina*, or perhaps another carbonate-secreting alga, and that the algae have served as source of calcium. Furthermore, decay of the algae might create local alkalinity necessary for precipitation (or reprecipitation) of carbonate in concretionary form.

The process of nucleating carbonate concretions in the Huron Member may be analogous to the process inferred for the nucleation of pyrite concretions from the Ledyard Shale Member of the Ludlowville Formation (Devonian), New York. Those pyrite concretions preserve fossils of fungal-bacterial webs (or ‘halos’) that, with evidence from lab experiments, evidently formed around decaying organismal remains, ultimately leading to precipitation of pyrite (Borkow and Babcock, 2003).

Thus, another hypothesis developed during this research is that nucleation of carbonate concretions in the Huron Member of the Ohio Shale was triggered by the decay of organic remains.

GEOLOGIC SETTING

The studied carbonate concretions are from the lower part of the Huron Member of the Ohio Shale (Devonian: Famennian). Specimens of concretions and surrounding shale were studied in the field in Camp Mary Orton, northern Franklin County, and Shale Hollow Park, southern Delaware County, Ohio. Specimens collected for lab analysis are from both localities. Details of the geologic setting were recently provided by Meyer (2019).

Concretion Morphology

Concretions in the field are commonly observed to be separated into layers of a core zone (including inner core and outer core), and a non-core zone (including an inner ring and an outer ring) by differences in appearance.

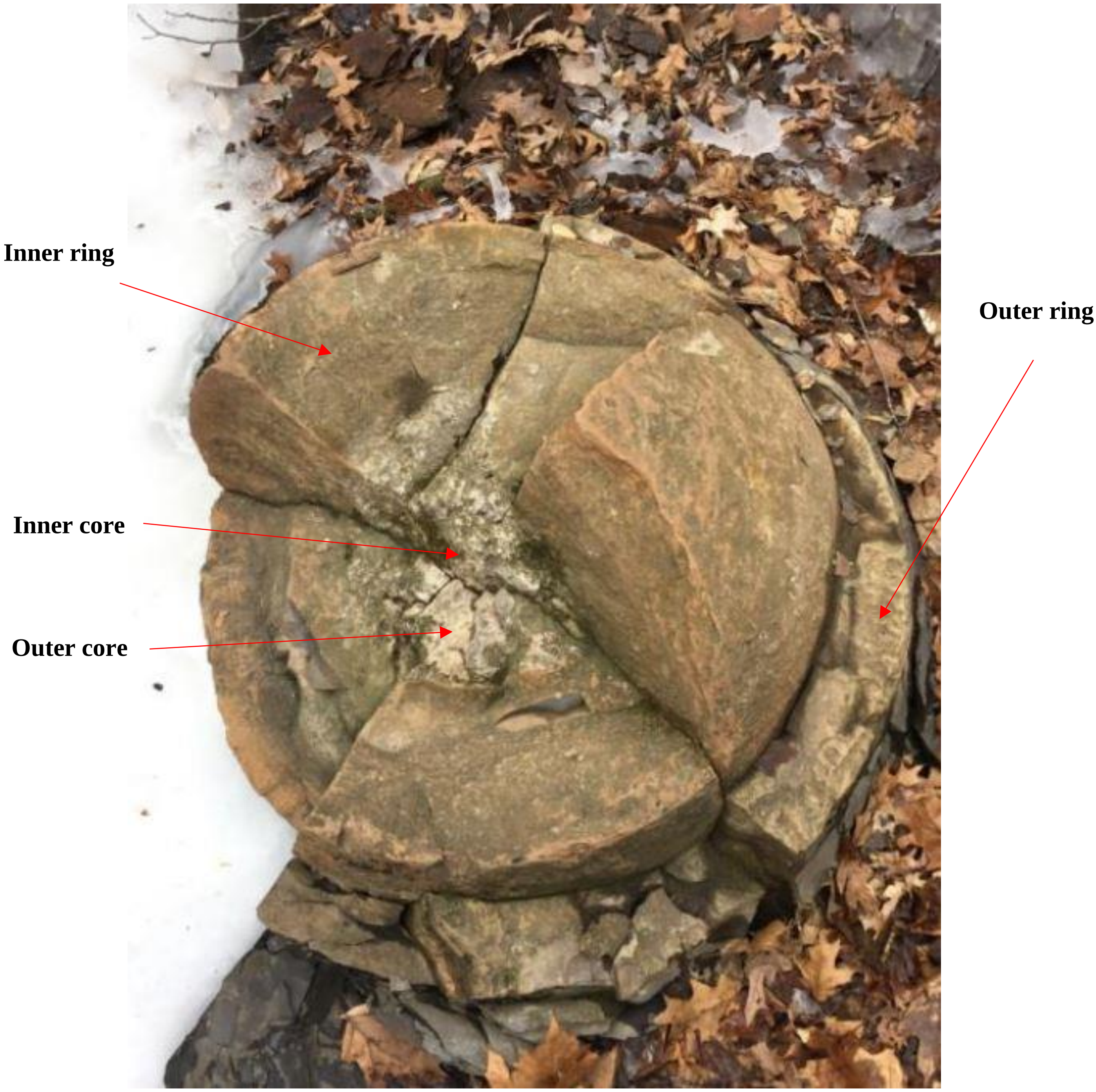

Figure 1. Field photograph of a concretion showing layered structure.

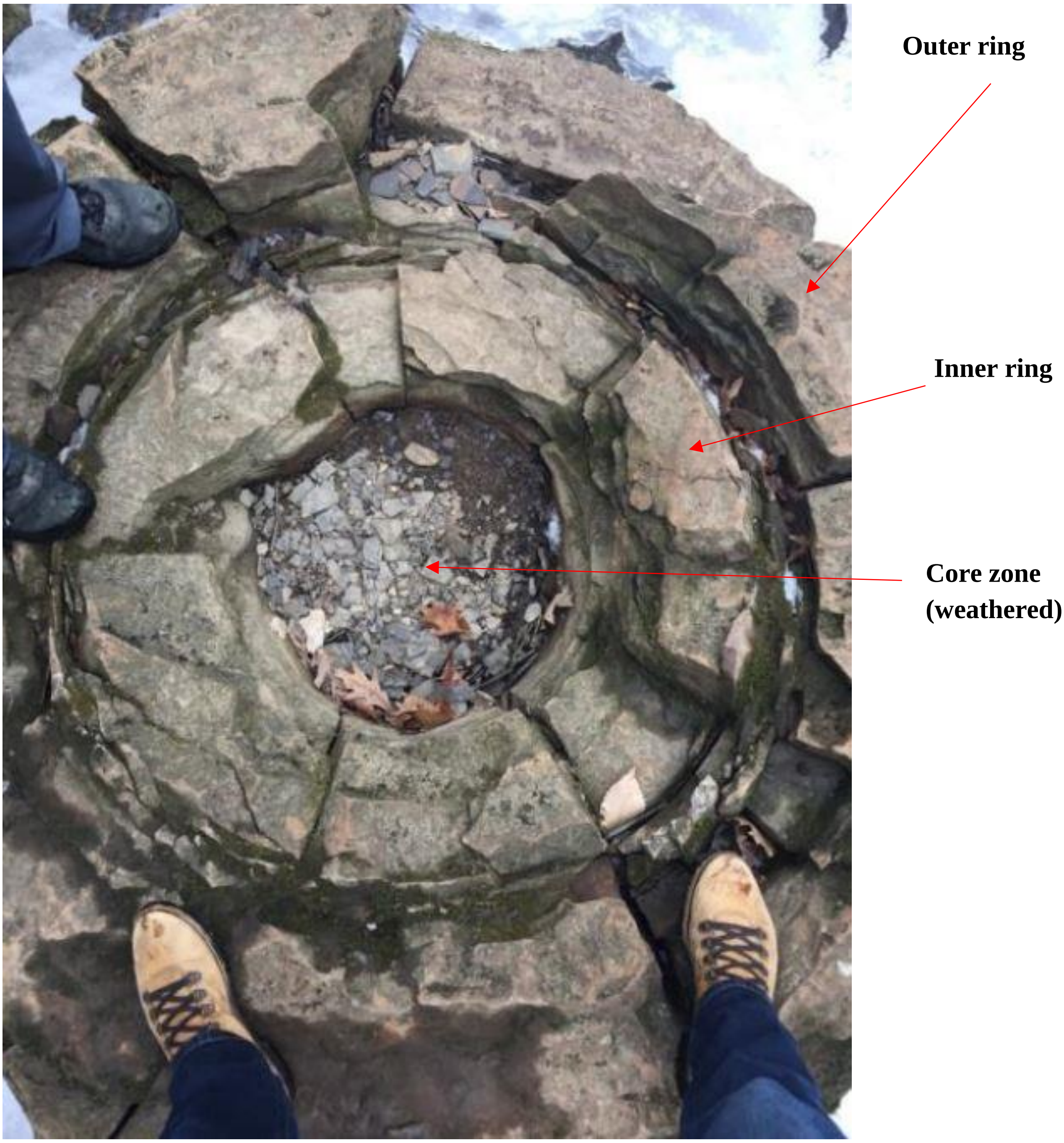

Figure 2. Field photograph of a concretion showing layered structure, and with a weathered core zone.

METHODS

Sampling methodology

Concretion and shale samples analyzed in this research were collected from the Huron Member of the Ohio Shale in Camp Mary Orton and Shale Hollow, Ohio. Samples were collected either as naturally broken pieces from concretions or they were separated from concretions using a geologic hammer.

Light Microscopy

Samples were first examined using light microscopy under a Wild MP-5 microscopy. Some samples in which fossils were discovered were later subjected to SEM analysis.

SEM Microscopy

Small samples collected from Camp Mary Orton were separated into groups representing the inner core, inner ring, and outer ring regions of concretions. Small samples of shale from rock surrounding the concretions were also broken into small chips. Specimens from each group were observed under the Scanning Electron Microscope (SEM) housed in the SEMCAL lab of the School of Earth Sciences of The Ohio State University. The SEM was used to identify the morphology and composition of certain features, such as fossils. Observations on uncoated samples were made using a Back Scattered Electron Detector (BSED) and, to generate high-resolution topographic images of features, using an Everhart-Thornley Detector (ETD). Elemental maps of these features were generated with the data collected by a BSED detector. Some samples were coated with gold (Au) for further observation under high resolution. The model used is a ThermoFisher Quanta 250 field emission gun (FEG) SEM.

XRD analysis

Samples collected from Shale Hollow were divided into groups of the outer core, inner ring and outer ring. Three samples from each group, together with one sample from the inner ring of a concretion collected from Camp Mary Orton, were crushed into powders and examined by X-ray diffraction equipment housed in the SEMCAL lab. Data on two-theta angles of the samples tested by the equipment were then analyzed by comparison with data from mineral databases to determine the mineral composition of the concretions. The model used is a PANalytical X’Pert Pro X-ray diffractometer.

Results

Silica fossils preserved in the non-core zone of a concretion

Microfossils (Figure 3) in the non-core zone of a concretion were scanned under the SEM. Some fossils show compositions differing from that of the surrounding matrix of the concretion. The fossils illustrated in Figure 3 are composed of Si and O (Figure 4), whereas the matrix is mainly composed of Ca, Mg, C, O, and Fe (Figure 5). An SEM image made using higher magnification (Figure 6) and a different detector, taken at the boundary of a fossil and the matrix, shows the obvious contrast in composition. An elemental map was plotted to show the major element differences between carbonate matrix of the concretion and the fossils at this boundary (Figure 7). This observed fossil-rich region is in the inner ring of the concretion.

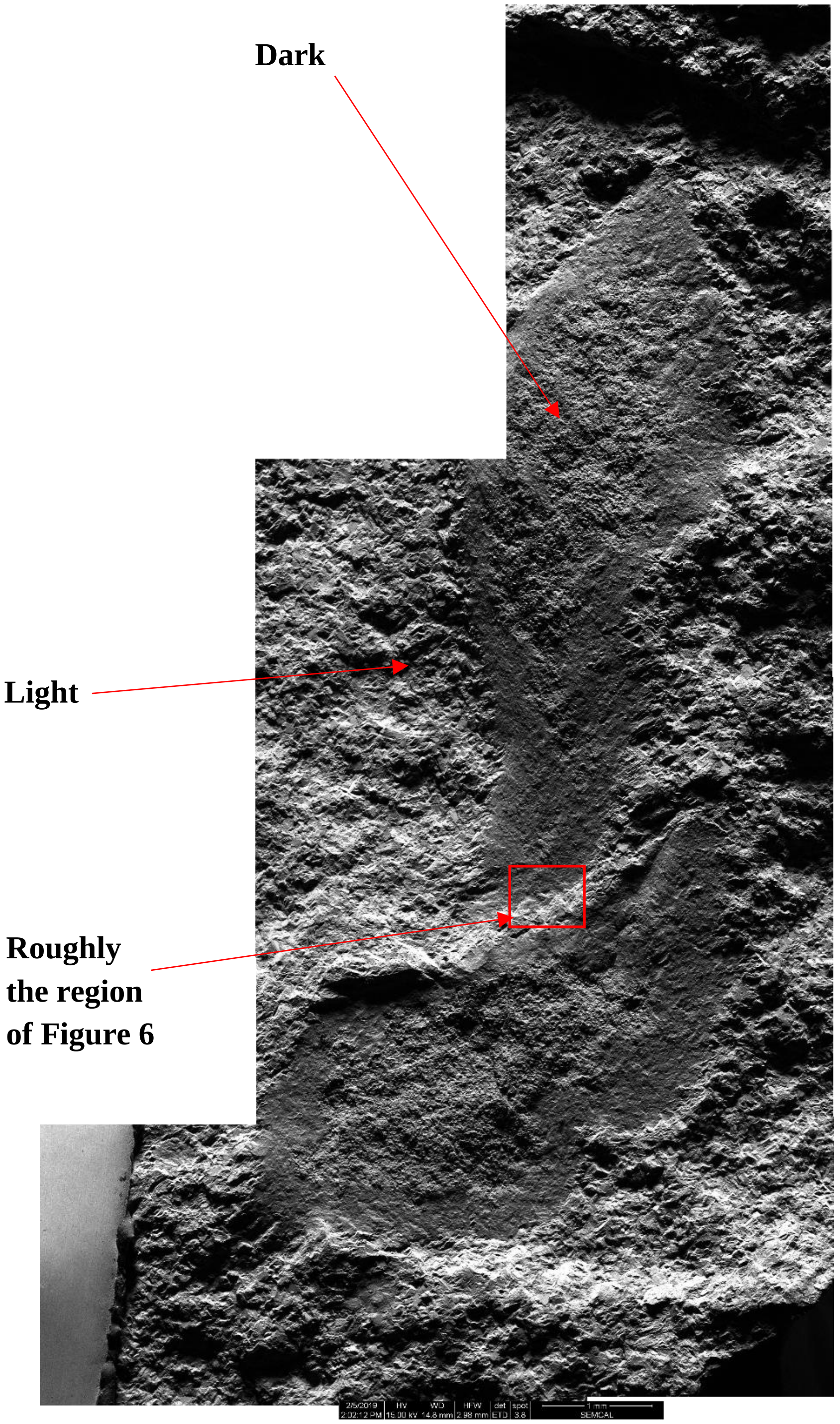

Figure 3. Stitched images of fossils from the inner ring of a concretion under Everhart-Thornley detector (ETD). The fossils are darker, and located centrally. The surrounding lighter colored region is matrix.

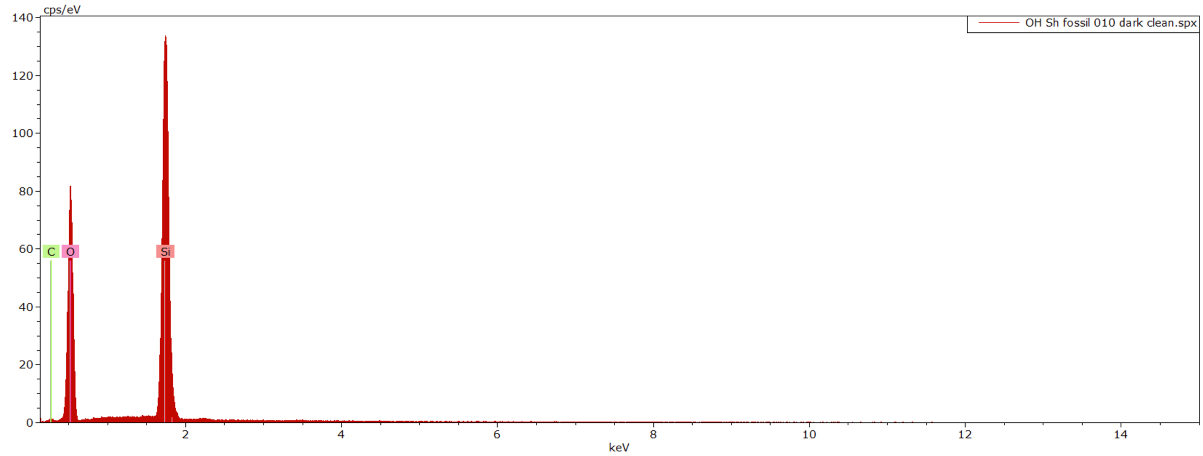

Figure 4. SEM/EDS spectrum of the chemical composition of a fossil in Figure 3. The fossil is composed mainly Si and O.

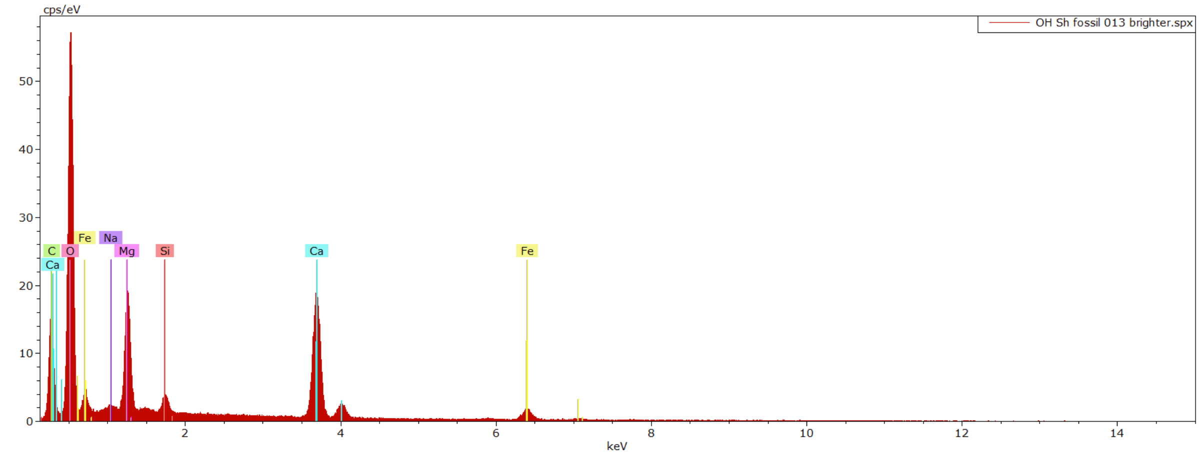

Figure 5. SEM/EDS spectrum of the chemical composition of the matrix in Figure 3. The composition is mainly Ca, Mg, C, O and Fe.

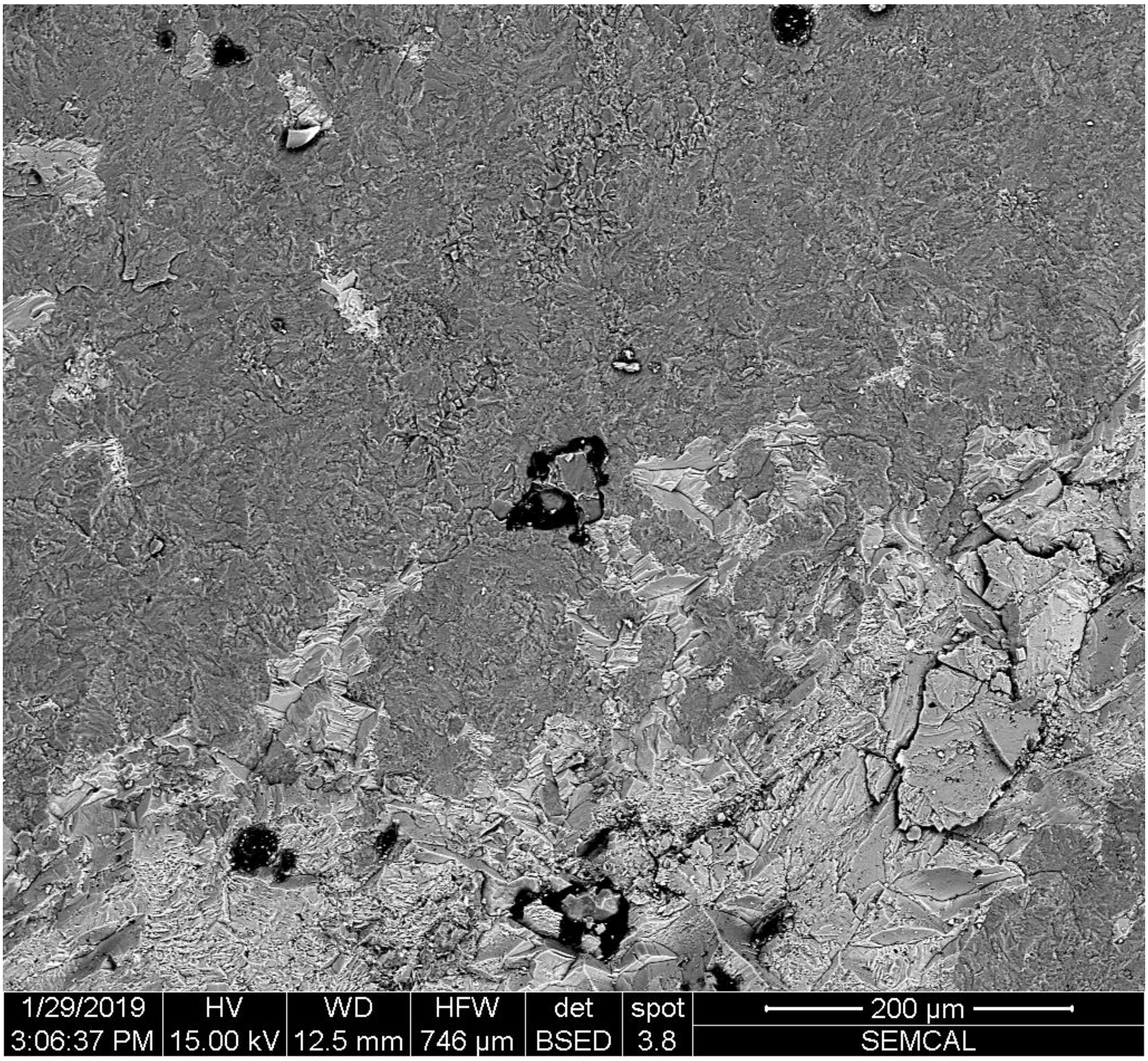

Figure 6. SEM image of the boundary between a fossil and concretion matrix under a Back Scattered Electron Detector (BSED), showing compositional differences. The region is located near the central area of the Figure 3, with a higher magnification. The darker colored region is fossil. The lighter colored region is the matrix.

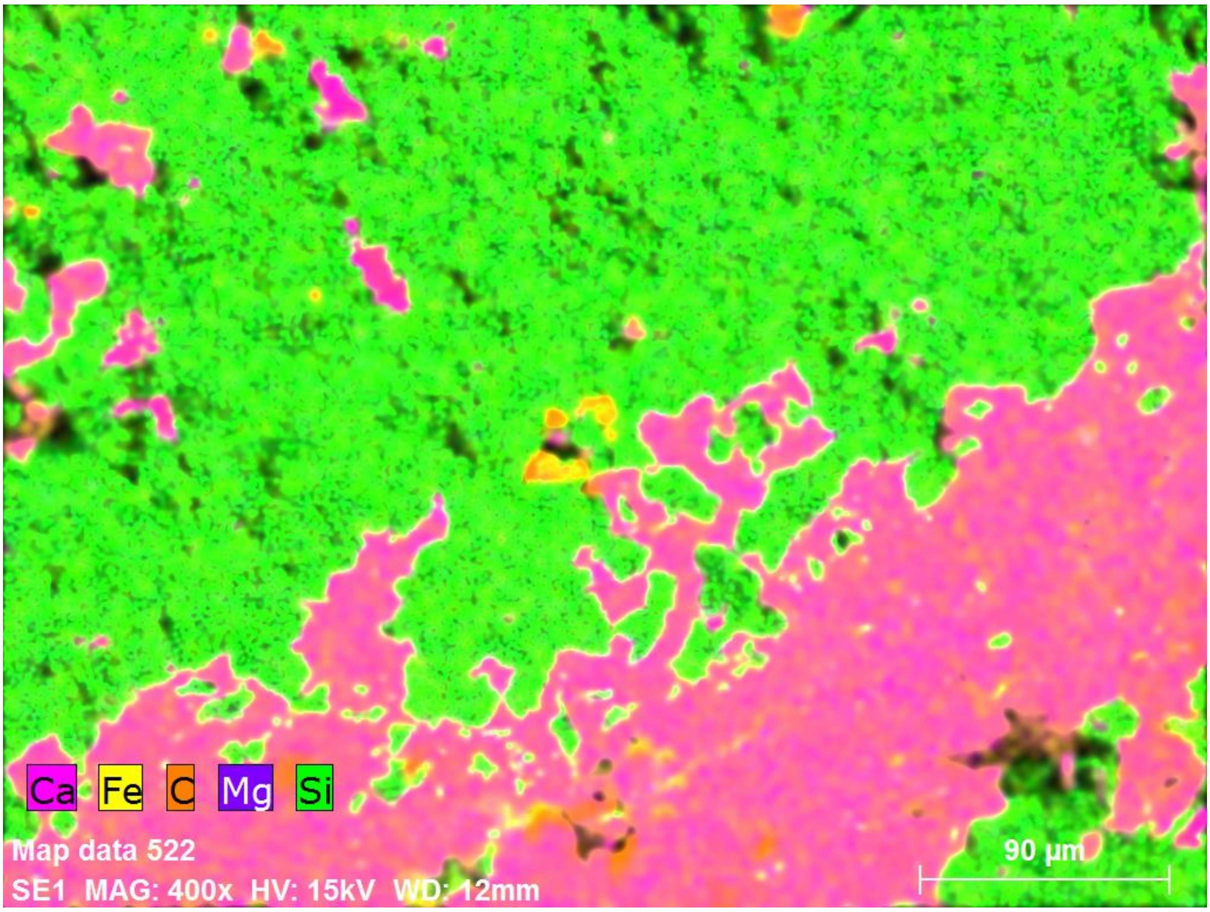

Figure 7. Elemental map of the boundary between a fossil and the concretion matrix shown in Figure 6.

Inner core region of the concretion

Following weathering, cores of the concretions are commonly hollow, with large euhedral minerals on the inner walls. SEM scanning was applied to some crystals sampled from the inner part of the core zone of some concretions. Background signals included Ca and other elements. In addition, euhedral crystals were shown to be composed of elements such as Ba, S, and P. Minerals inferred to be present include barite, and possibly apatite.

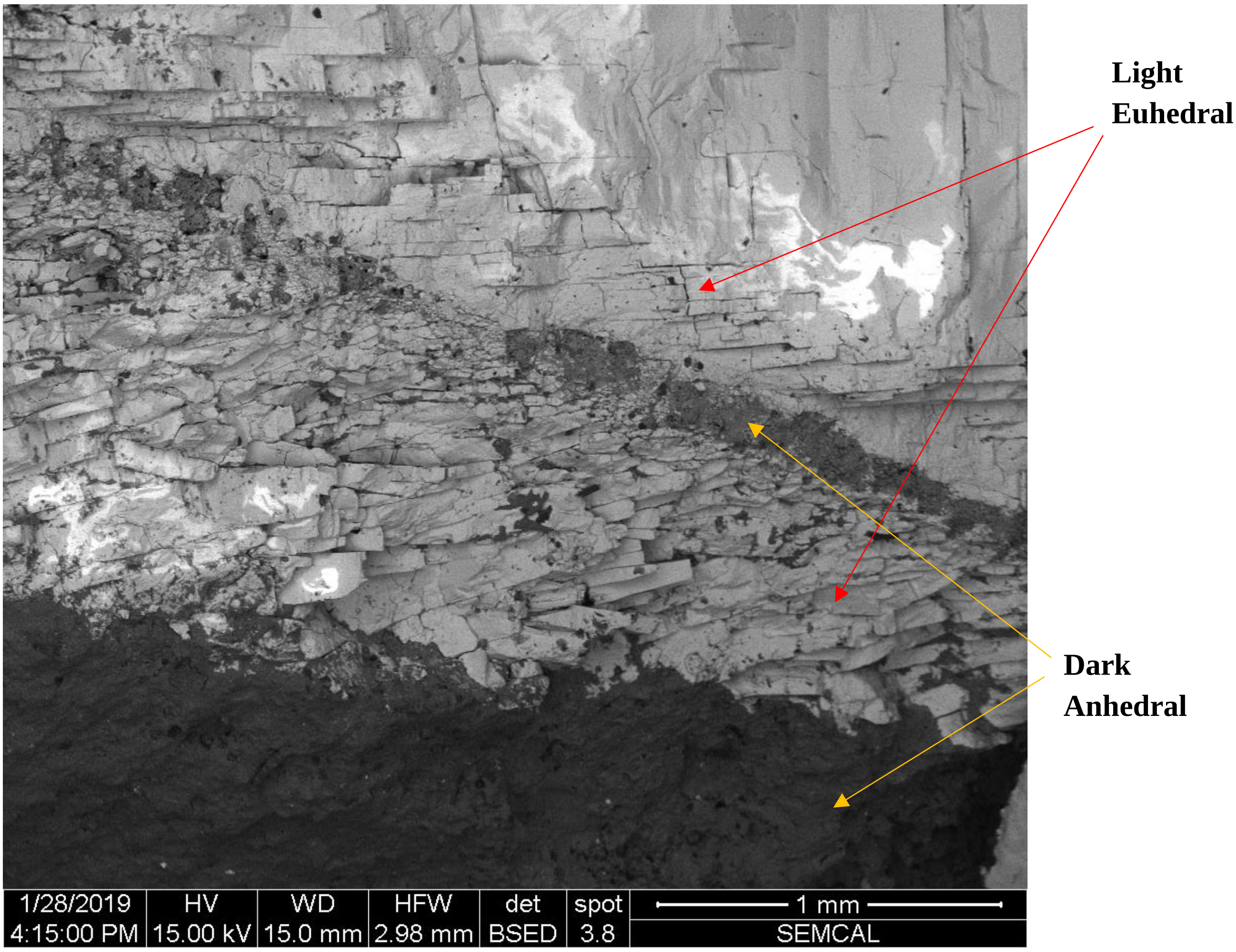

Figure 8. SEM image (BSED detector) of the boundary between an euhedral mineral crystal (light color) and anhedral minerals (dark color).

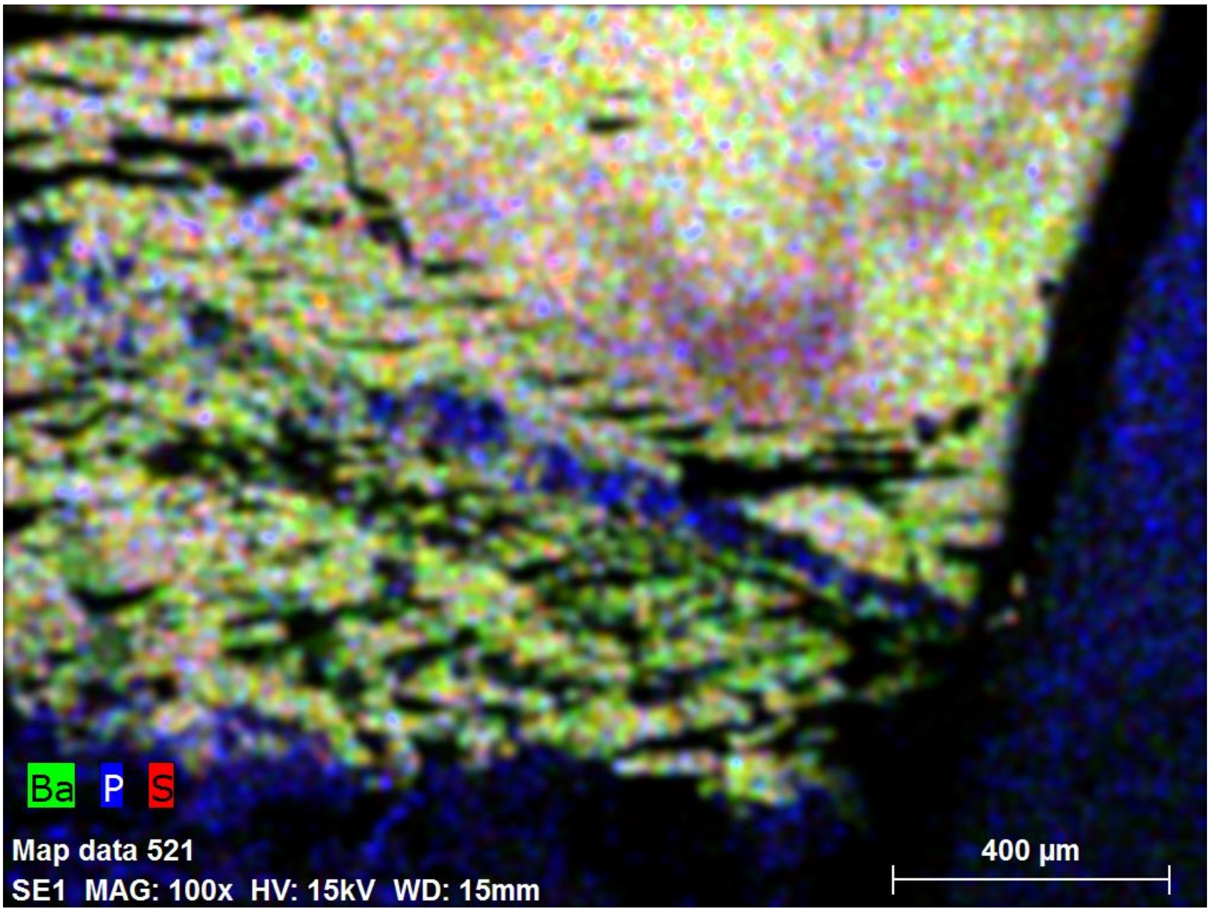

Figure 9. Elemental map of the boundary illustrated in Figure 8.

XRD analysis for mineral composition

XRD analysis was applied to determine the mineral composition differences between carbonate parts of the concretion. The carbonates in the outer core are composed mainly of calcite, whereas the carbonates that are further away from core zone are mostly composed of ankerite.

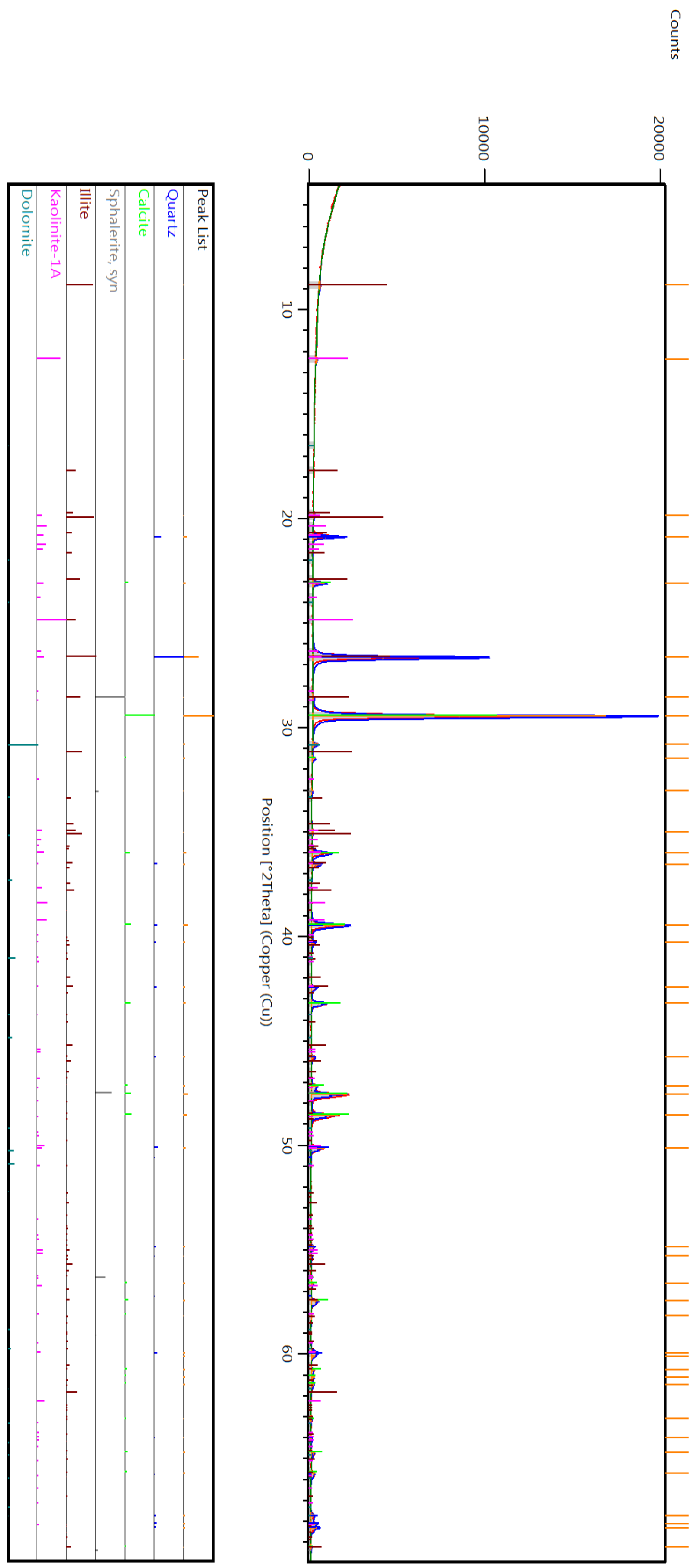

Figure 10. Two-theta angle data and mineral compositions of the carbonate part of the outer core of a concretion. Inferred composition: mainly calcite, with a little ankerite.

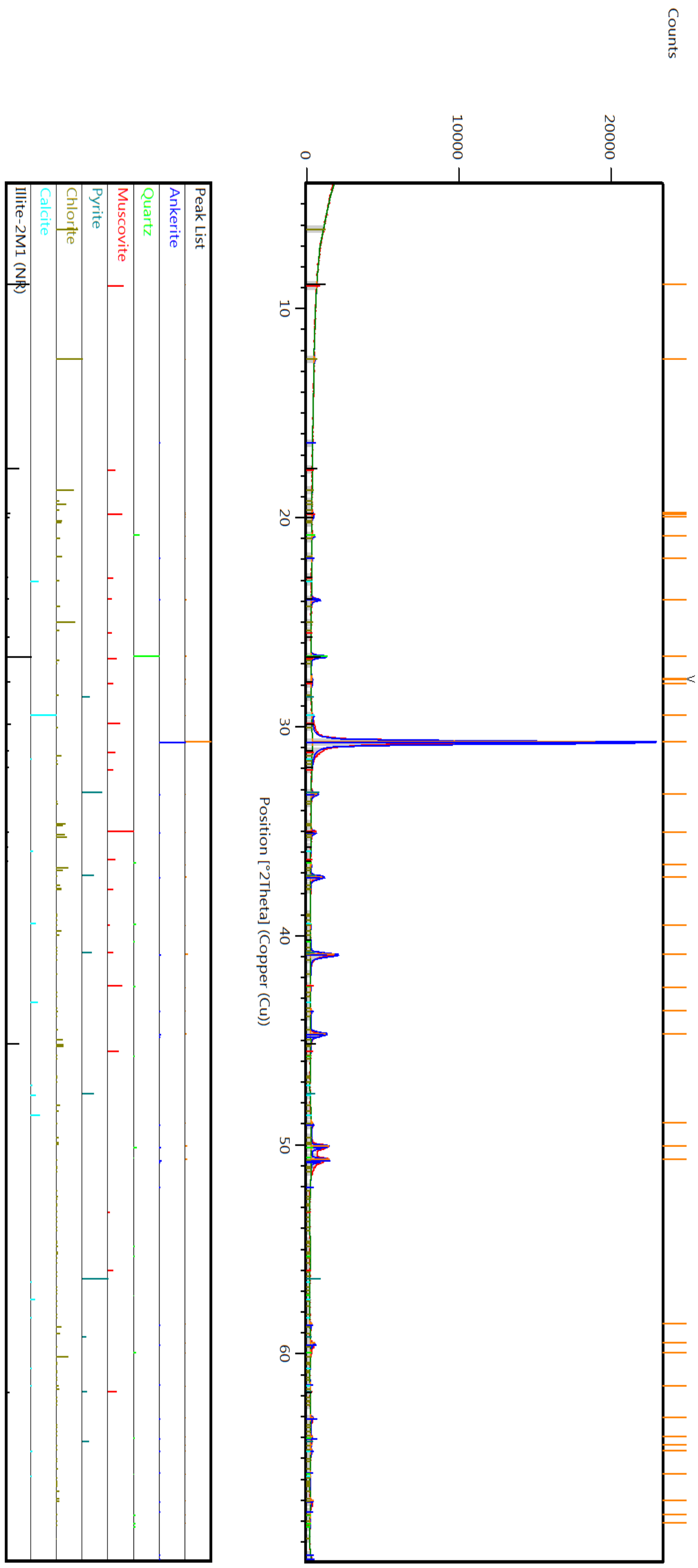

Figure 11. Two-theta angle data and mineral compositions of the carbonate part that is the inner ring of a concretion. The sample that contains silica fossils were found in this layer. Inferred composition: mainly ankerite, with a little calcite.

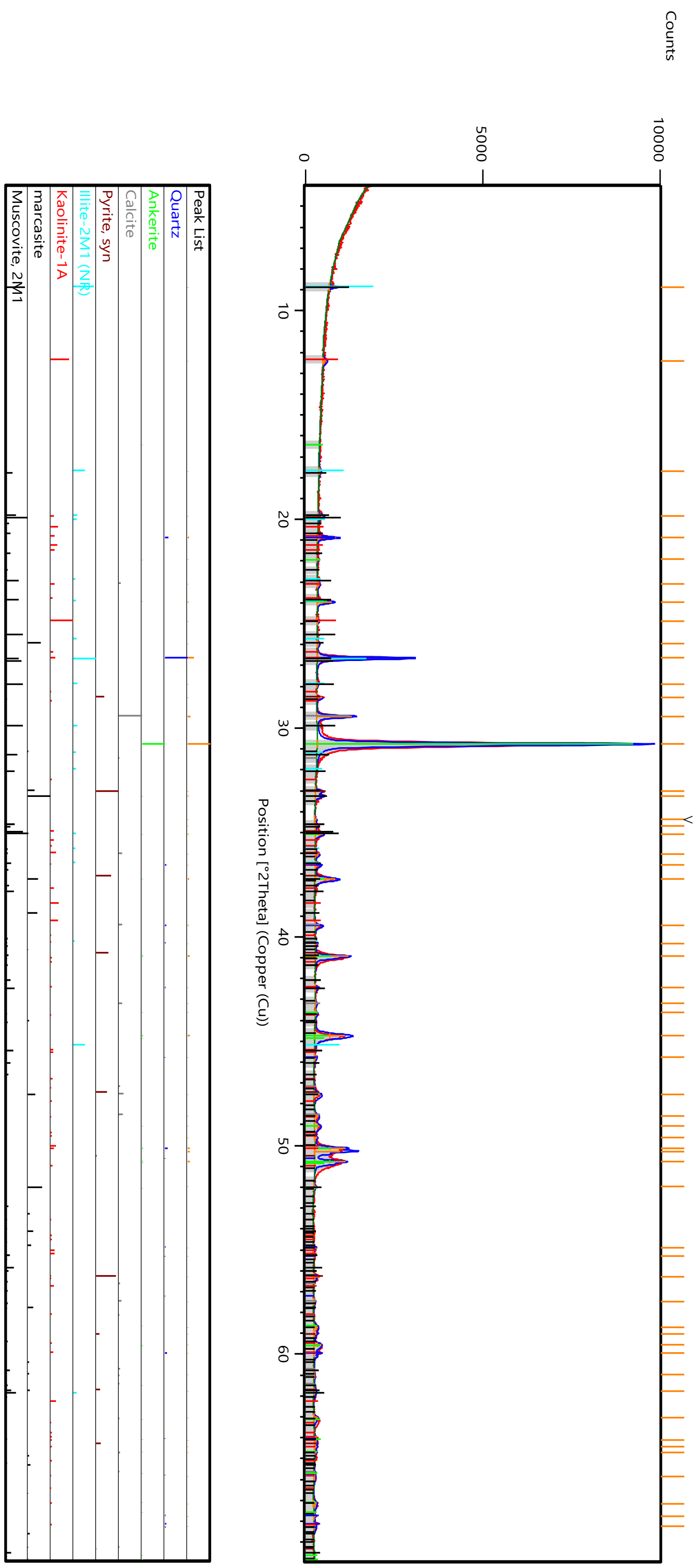

Figure 12. Two-theta angle data and mineral compositions of the carbonate part that is the outer ring of a concretion, next to the surrounding shale. This sample has more clay minerals and quartz than the inner ring shown in Figure 11. Inferred composition: mainly ankerite, with a little calcite.

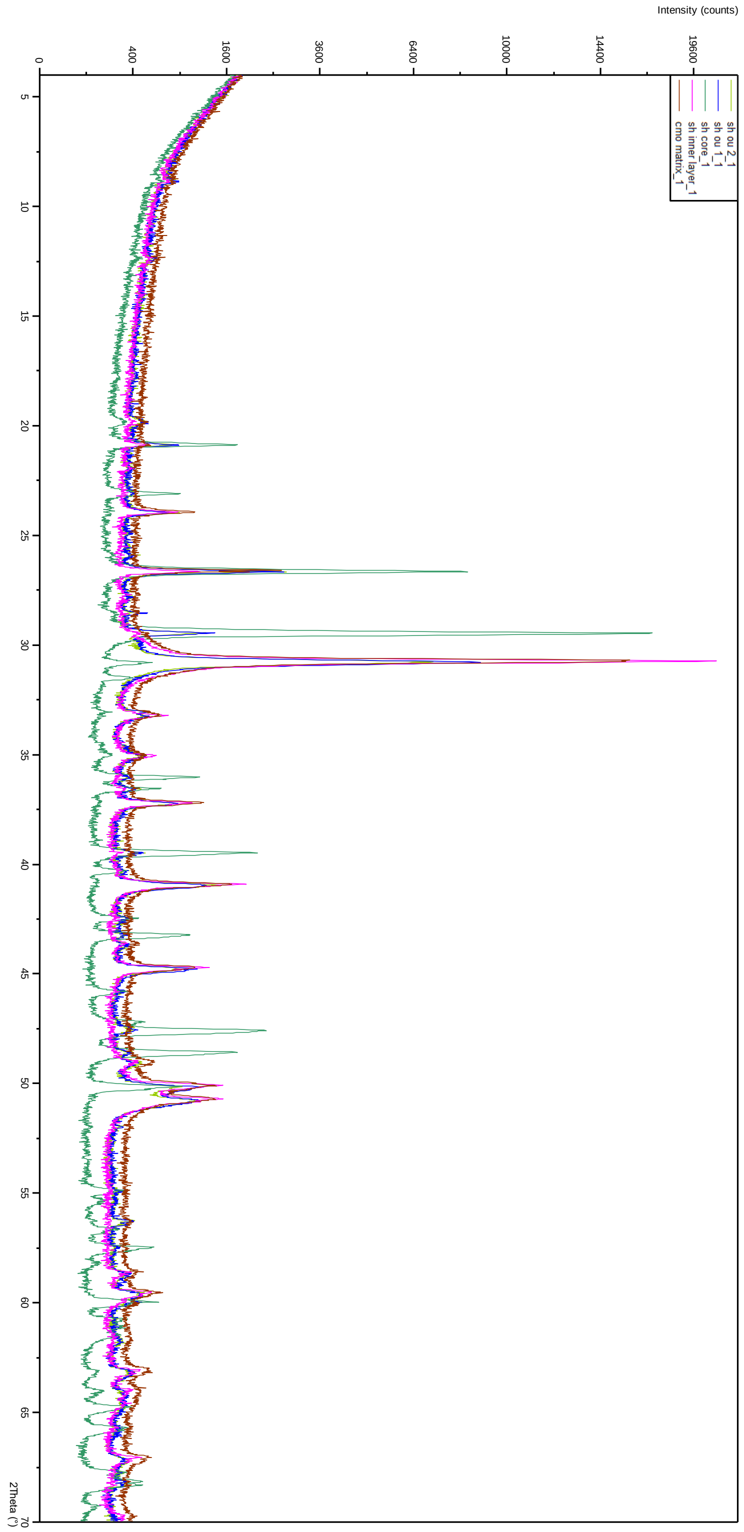

Figure 13. Comparison of two-theta angle data of all the concretion samples tested with XRD. "Sh ou 2_1" and "sh ou 1_1" are two samples from the outer ring (see Figure 12). "sh inner layer_1" and "cmo matrix_1" are two samples from the inner ring (see Figure 11). "Sh core_1" is the sample from the outer core (see Figure 10). The peak of calcite from the outer core (green) is different from the rest of the non-core layers, which are mainly composed of ankerite.

Discussion

Fossil content

The hypothesis that 'Orsten'-type carbonate concretions from the Huron Member of the Ohio Shale have an origin analogous to black limestone beds in the Huaqiao Formation (Cambrian of South China), is not fully supported by the research. Fossils of carbonate-secreting *Padina* algae were found in black limestones of the Huaqiao Formation (Babcock et al., 2012). Fossils having an algal shape are present in carbonate concretions from Huron Member. They do not, however, appear to be *Padina*, as they have a rather different morphology, including a more elongate thallus. Furthermore, the Ohio Shale algae are preserved in silica (which may be of secondary, but early diagenetic, origin). The fossils are surrounded by carbonate matrix materials, mainly ankerite, so it is unlikely that silica replacement occurred after formation of the concretion.

An alternative explanation is that the fossils in the concretions could be some sort of siliceous sponges or radiolarians, but morphological evidence rules this out. The silica may be a mineral coating mediated by microbes early in the early process of nucleating the concretion. Similar phenomena have been inferred for the Waukesha Biota (Silurian), where fossils were coated in phosphate (Wendruff, 2019), and in siliceous concretions from the Conasauga Formation (Cambrian), where fossils were preserved in silica (Kastigar, 2016). It must be emphasized, though, that the analysis of fossil content was done for samples from a limited number of concretions. In future work, multiple concretions should be tested to search for the existence of similar fossils in other carbonate concretions in the Huron Member.

Inner core minerals

Euhedral barite crystals are present in the inner core area of the carbonate concretions from the Huron Shale Member. The precipitation of barite commonly requires an anaerobic environment and the presence of organic matter (Graber and Chafetz, 1990). This finding tends to strengthen the inferred environment for the early growth of these concretions. An anaerobic environment needed for barite precipitation is consistent with the inferred background environment for black shale deposition in the Huron Member. An environment rich in organic matter is also supported by both the presence of barite and organic-rich black shale. From Figures 8 and 9, it appears that barite crystals grew following the growth of calcium phosphatic minerals. Considering that calcium phosphate commonly originates with organic materials (animal remains), the growth of the concretions might have begun around dead and decaying animals.

Multi-stage growth history yielded by XRD

XRD analysis shows that mineralogic differences the concretion into two major regions, outside the barite- and calcium phosphate-rich inner core. The outer core is the carbonate layer that is closest to the inner core (Figure 10). The non-core zone includes carbonate extending from the inner ring to the outer ring (Figures 11 and 12). From Figure 13, it is clear that the two samples from the non-core zone are composed mostly of ankerite, whereas the sample from the outer core is composed of mainly calcite. Such a difference in carbonate composition suggests multiple (at least two) growth stages of the carbonate concretions in the Huron Member. Other research on the septarian carbonate concretions in Huron Member using structural tools pointed to a similar conclusion of multi-stage growth (Meyer, 2019). The apparent difference in silica signal between the outer core and the non-core zone is also worth noting. The outer core has significantly more quartz than the non-core zone. According to SEM/EDS data, the major Si contributor is from fossil content. In addition, the outer ring differs from inner ring by having relatively higher quartz and clay mineral contents

CONCLUSIONS

The algae-shaped fossils in the carbonate concretion from Huron Member of the Ohio Shale are most likely algal remains that have undergone silica coating or replication early in the diagenetic process. The algal fossils probably played a major role in the early stages of concretion growth.

Barite and calcium phosphate occur in the inner cores of Huron Member concretions. They are evidence of the existence of organic remains in the earliest stages of concretion nucleation. Fossils of bacteria and fungi were not observed, but it is nevertheless likely that dead and decaying organismal remains influenced the nucleation of the concretion.

XRD analysis supports differentiation of the concretions into three major regions according to mineral composition. From inside to outside, the concretions are composed of an inner core, an outer core, and a non-core zone, which can be divided into an inner ring and an outer ring. The inner core is distinct, as barite and calcium phosphate are present. The outer core differs from the non-core zone in being calcite-rich, whereas the non-core zone is ankerite-rich. The non-core zone can be furthered divided into an inner ring and an outer ring. The outer ring has a relatively higher quartz and clay mineral contents than the inner ring. Such mineralogic differences suggest multiple growth stages for the concretions.

Considering the available evidence, it is concluded that the large, ‘Orsten’-style carbonate concretions in the Huron Member of the Ohio Shale have organic origins for their nucleation. Completion of concretion growth, however, must be more complex, and at this time it is unknown how the non-core zone, especially the outer ring of the concretions, developed.

Recommendations for Future Research

The samples of fossils analyzed in this research are limited in number. Future researchers might consider collecting samples from multiple carbonate concretions from different locations in the Huron Member to examine if the conclusions about the fossils are more universal.

Future researchers might consider using different sampling methods. Drilling cores from whole concretions would be a more efficient method for collecting samples than is separation of samples using geologic hammers or natural fracturing.

As some fossils are composed of silica, whereas the matrix is carbonate, acid preparation could be applied by future researchers to dissolve the matrix and obtain complete fossils to study their three-dimensional morphology.

Lab work could be done to simulate the depositional environment of the carbonate concretion with organismal remains to study the mechanics of carbonate concretion nucleation under organic-rich mud conditions.

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