Origin of Pyrite Concretions from the Huron Member of the Ohio Shale (Devonian), Central Ohio, USA

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By

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Abstract

Concretions in sedimentary deposits form through chemical processes mediated by the decay of organic matter. Concretions often contain conspicuous macrofossils (Maples, 1986; Borkaw and Babcock, 2003). Use of X-ray computerized tomography (XTC) and scanning electron microscopy (SEM) reveals body fossils of microscopic organisms and pyrite framboids (Borkow and Babcock, 2003), which may be secondary to organic material, in some concretions. By exploring the biological origins of the concretions we can learn how concretions form, develop insight into the processes of exceptional preservation, and enhance understanding of the environmental conditions at the time of sedimentation. A field emission gun (FEG) SEM, EDX, and XCT have been used to study pyrite concretions from black shale layers of the lower Huron Shale Member of the Ohio Shale (Devonian) from central Ohio, USA. Pyrite occurs in the concretions in three forms: 1, small pyrite framboids evidently formed around bacterial cells; 2, cone-in-structure; and 3, large euhedral crystals. Studied concretions contain remains of spores referred to *Protosalvinia*. Two sizes classes, probably reflecting individual spores (50-100 μm in diameter) and spore capsules (~200 μm in diameter), have been observed. Pyrite framboids are commonly present on the spores, whereas more extensive pyritization and cone-in-cone structure is associated with the presence of spore capsules. A consistent pattern of occurrence of euhedral crystals was not observed. Unrecrystallized bacterial cells and fungal hyphae were not observed. The black shale matrix surrounding the concretions is composed of primarily illitic clay. *Protosalvinia* spores are present in the matrix, and normally have small pyrite framboids on their surfaces. Studied pyrite concretions show no evidence of an origin with traces in sediment or the decay of animals.

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I would also like to extend my gratitude to my fiancé, Adam Bridenstine, for assisting in many ways during this project and through the hectic years of pursuing dual degrees in Earth Sciences and Evolution, Ecology, and Organismal Biology. He offered encouragement and stability in all aspects of my education. His curiosity and questions provided me with a sense purpose and determination in my own pursuit of knowledge.

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Introduction

Pyrite concretions are typically small sedimentary concretions that occur in dark grey or black shales (Berner, 1984; Carstens, 1985; Babcock and Speyer, 1987). Various shapes are known, but many are round or ovoidal. Some are formed around burrows in sediment (Schieber, 2002; Ahn and Babcock, 2012). Pyrite concretions are known from many localities and formations globally. Some classic examples include the Niutitang Formation (Cambrian), South China (Goldberg *et. al*., 2006), the Ledyard Shale Member of the Ludlowville Formation (Middle Devonian), New York, USA (Babcock and Speyer, 1987), and the Huron Member of the Ohio Shale, Ohio, USA (Hellstrom and Babcock, 2000).

A relationship between the formation of concretions and the decay of biological material has long been known. In an experiment by Berner (1968), observed increased amounts of dissolved bicarbonate, carbonates, and ammonia were associated with small fish decaying in seawater-filled jars. Ca++ ions involved in decay may have contributed to the growth of $CaCO_3$ concretions. More recent work by Borkow and Babcock (2003) demonstrated that concretions nucleate around decaying organisms through the activities of microbial biodegraders (detritivores), which are organisms that break down organic matter. Microbial biodegraders involved in taphonomic processes include fungi and bacteria, some of which are autolithifiers (Pineiro *et. al.*, 2012; Borkow and Babcock, 2003). Borkow and Babcock (2003) showed that concretions can be experimentally initiated by the growth of a fungal-bacterial biofilm “halo” around organic matter. Fungi seem to have played a major role in decay, and formed the framework for the fungal-bacterial halo. Bacteria may have also contributed to decay but played a leading role in mediating early diagenetic mineralization. Borkow and Babcock (2003) showed that Devonian pyrite from New York was formed around fungal hyphae and bacteria, and illustrated pyritized examples of these microorganisms. In the New York material, clusters of presumably autolithifying coccoid bacteria apparently served as the nuclei for microscopic clusters of pyrite crystals, which are termed framboids. A similar scenario for the pyritization of burrows in sediment has been documented. Ahn and Babcock (2012) showed that *Planolites* burrows from the Cambrian of Nevada, USA also formed through early diagenetic processes mediated by fungal hyphae and bacteria.

Most pyrite concretions described from the Devonian of New York, and most pyritized burrows that have been described are three-dimensional in shape, whereas pyrite concretions from the Ohio Shale of Ohio tend to be rather flattened in appearance. This observation led to questions about the origins of pyrite concretions in the Ohio Shale.

The purpose of this study was to investigate the origins of the pyrite concretions that are common along certain bedding planes in the lower part of the Huron Member of the Ohio Shale in central Ohio. In studying the morphology and mineralogy of the concretions I found that they contain fossilized spores composed mostly of organic material and pyrite in varied crystal habit. Organic breakdown associated with the spores and spore cases seems to have contributed to the precipitation of pyrite. Depending on the availability of organic material, pyrite framboids, euhedral crustals, or larger concretions having cone-in-cone structure, were formed. Pyrite precipitation preceded the time of sediment compaction.

GEOLOGIC SETTING

Geology

The Ohio Shale is an organic-rich shale that crops out in a north-south band through Ohio from the Ohio river to lake Erie where the outcrop belt can be traced eastward into Pennsylvania (Hellstrom and Babcock, 2000). The Ohio Shale contains the members Cleveland, Chagrin and Huron (Figure 1). The Cleveland member is black shale which also contains some grey shale. It has flattened carbonate concretions that contain many of the fossils known from the member (Carr and Jackson, 2008) of which some of these concretions exhibit cone-in-cone. The Chagrin Member, underlain by the Cleveland Member, is exposed along the Chagrin River and is made up of grey mud stones and siltstones. The Three Lick Bed occurring in Southern Ohio and Kentucky may be a distal tongue of the Chagrin Shale Member (Hellstrom and Babcock, 2000). The Huron Member, the oldest of the Ohio Shale's members, extends into eastern Kentucky, through Ohio and into Canada (Foreman, 1959). It overlies the Olentangy Shale and is overlain by the Chargin Member. The Huron member is a fissile black shale and includes concretions ranging from large calcareous concretions (Foreman, 1959) to pyrite concretions. Due to the presence of concretions the Huron member is traceable over large distances, but individual concretionary beds are traceable only to a few km (Hellstrom and Babcock, 2000).

Depositional Environment

The Ohio Shale is located in the Appalachian Basin and was deposited in the Catskill delta of the Devonian. The environment was a warm epicontinental sea located 15º to 20ºS latitude (Scotese and McKerrow, 1990) and associated with transgressive event (Johnson *et. al.* 1985). The clastic sediment and presence of terrestrial input (Rimmer *et. al.* 2004) are a result of Acadian Orogeny to the East. The Ohio Shale, particularly the Huron Member, is typically associated with low oxygen conditions. The formation of the Member's pyrite concretions required anoxic conditions for the pyrite crystals to form. This anoxia could have occurred in the water column or in the sediment. A deep, poorly mixed, water column would support water column anoxia. The deeper poorly mixed water column would suggest a strong pycnocline and depths greater than 200m (Hellstrom and Babcock, 2000). However a study by Murphy *et. al.* (2000) and a study by Werne *et. al.* (2002) found evidence of storms making a pycnocline to be unlikely. Shallower models were supported by the preservation of hummocky cross stratification which would have been formed marginally above the storm weather wave base (Schieber 1994).

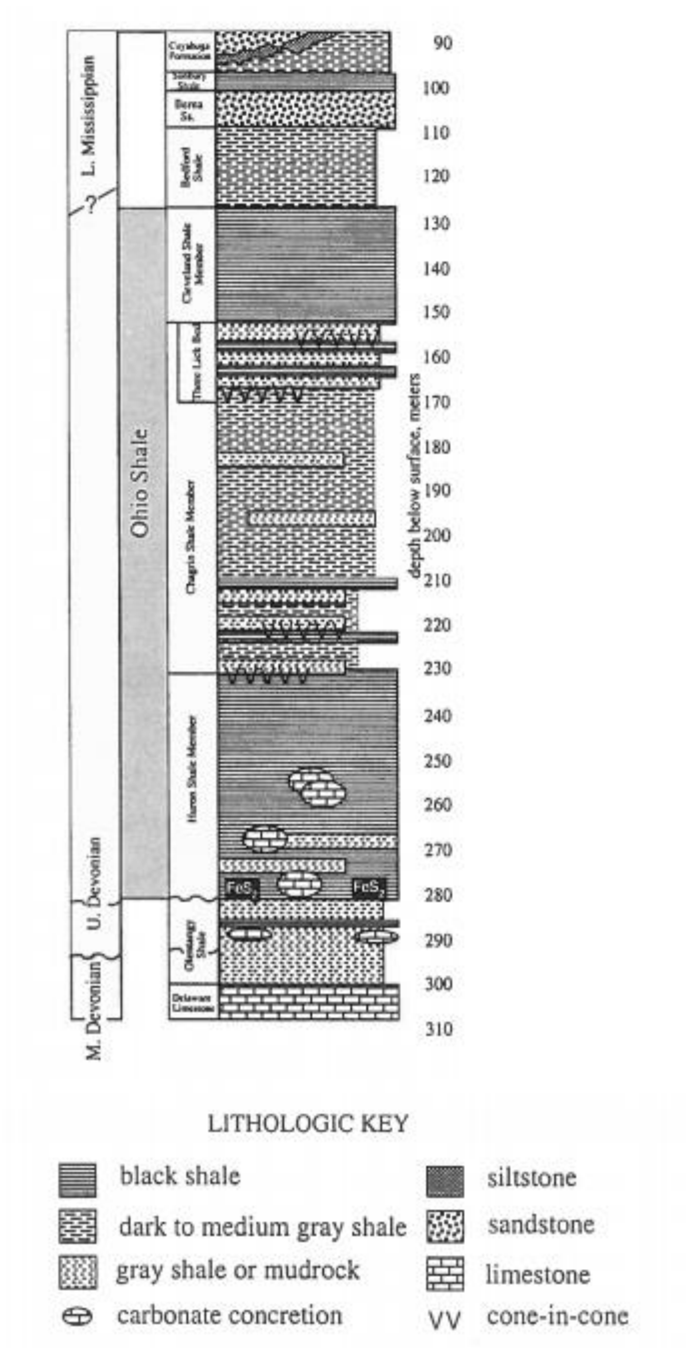

Figure 1. Stratigraphic column for central Ohio (modified from Hellstrom and Babcock, 2000) FeS_2 indicates location of samples.

Methods

Collecting

Studied samples were collected from Flint Run, Camp Mary Orton, Columbus, Franklin County, Ohio (Figure 2), where the Huron Shale Member of the Ohio Shale (Upper Devonian: Famennian) is well exposed. The samples are from a rock slabs in the lower part of the member. Individual concretions were broken from the rock with some care so as to preserve them in matrix, as oxidized halos surrounding them were also of interest. All illustrated specimens are from this site.

Figure 2. Outcrop of Olentangy and Huron Shale Members in Ohio. Star indicates the position of Camp Mary Orton, Columbus, Ohio. Modified from Hellstrom and Babcock (2000).

Microscopy

Often in the research of the origin of concretion the shape of the crystals is important. Cubic crystals imply slow diffusion and spherical, framboid crystals could indicate early diagenesis around another object. Initially the samples were viewed with a dissection scope to see general morphology and associated features. With a low power microscope the shapes of pyrite crystals surrounding the concretion could be viewed and there was evidence of dense areas of organic matter.

Morphology of the pyrite and organic matter was studied using a Scanning Electron Microscope (SEM) in the School of Earth Science at The Ohio State University. Samples were initially viewed by being attached to a sample holder with copper conductive tape to help control charging when placed into the electron beam. The mount was inserted into the specimen chamber of a FEI Quanta field emission gun (FEG) SEM and observed using an accelerating voltage of 15 keV and a spot size of 4.0. The samples were uncoated and run in high vacuum mode using a water pressure of 0.6 mbar. Energy-dispersive X-ray spectroscopy (EDX) was used to better investigate the mineralogy.

XCT Scanning

X-ray computed tomography was used as a non-destructive means of gaining insight into the morphology of the concretions. Four concretions were scanned to find areas of variable density and to look for evidence of concentric growth stages. The concretions were each placed in sand to reduce edge effects and artifacts.

RESULTS

General Morphology and Distribution

The studied pyrite concretions were collected a float block in the lower part of the Huron Shale Member of the Ohio Shale. Most were collected from a single bedding plane on a large slab approximately 75 cm^3. Others were collected from smaller slabs of rock. In most cases, the concretions were closely clustered together. Studied concretions range in size from 2 to 10 cm and most are ovoid in outline and flattened parallel to bedding. In the field, shale layers were sometimes observed to bend over or around the pyrite concretions, leading to the conclusion that they were formed prior to shale compaction and lithification.

Light Microscopy

When viewed under light microscopy, halos were observed to surround the samples that were still in matrix. These halos radiated in a circular pattern around the central mass up to several centimeters and contained pyrite crystals. Broken concretions all show cone-in-cone structure internally.

XCT Scans

Four concretions were placed into the XTC scanner to scan for areas of variable density. There were areas of lower density within each concretion scanned. The areas of lower density were found off-center of the concretions and in irregular patterns within. The density values were not diagnostic for mineral identification, but their signatures were less dense than that of the pyrite and denser than would have been expected for calcite or air.

SEM Analysis

Four samples were analyzed using Scanning Electron Microscopy to evaluate surface morphology. On three of the samples only the surface could be observed, but one sample was broken in half while being freed from the matrix so the cross section was also scanned. Chemical analyses of the samples using EDX were taken to analyze the chemistry of three substances: crystalline matter, organic matter, and the matrix.

Crystalline Matter

In using scanning electron microscopy the most common minerals discovered within the shale matrix were pyrite (FeS_2), and platy muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$. Anhydrous sulfides, probably the result of weathering, were also identified. Less commonly observed minerals included barite ($BaSO_4$), sphalerite (ZnS_2). Inside pyrite concretions, pyrite, clay minerals, and minor siderite ($FeCO_3$) were identified. Much of the pyrite shows cone-in-cone structure (Figure 3), but framboids (Figures 4, 5) and euhedral crystals are present (Figure 6). Shale matrix often caps the chevron shapes of the cone-in-cone structures.

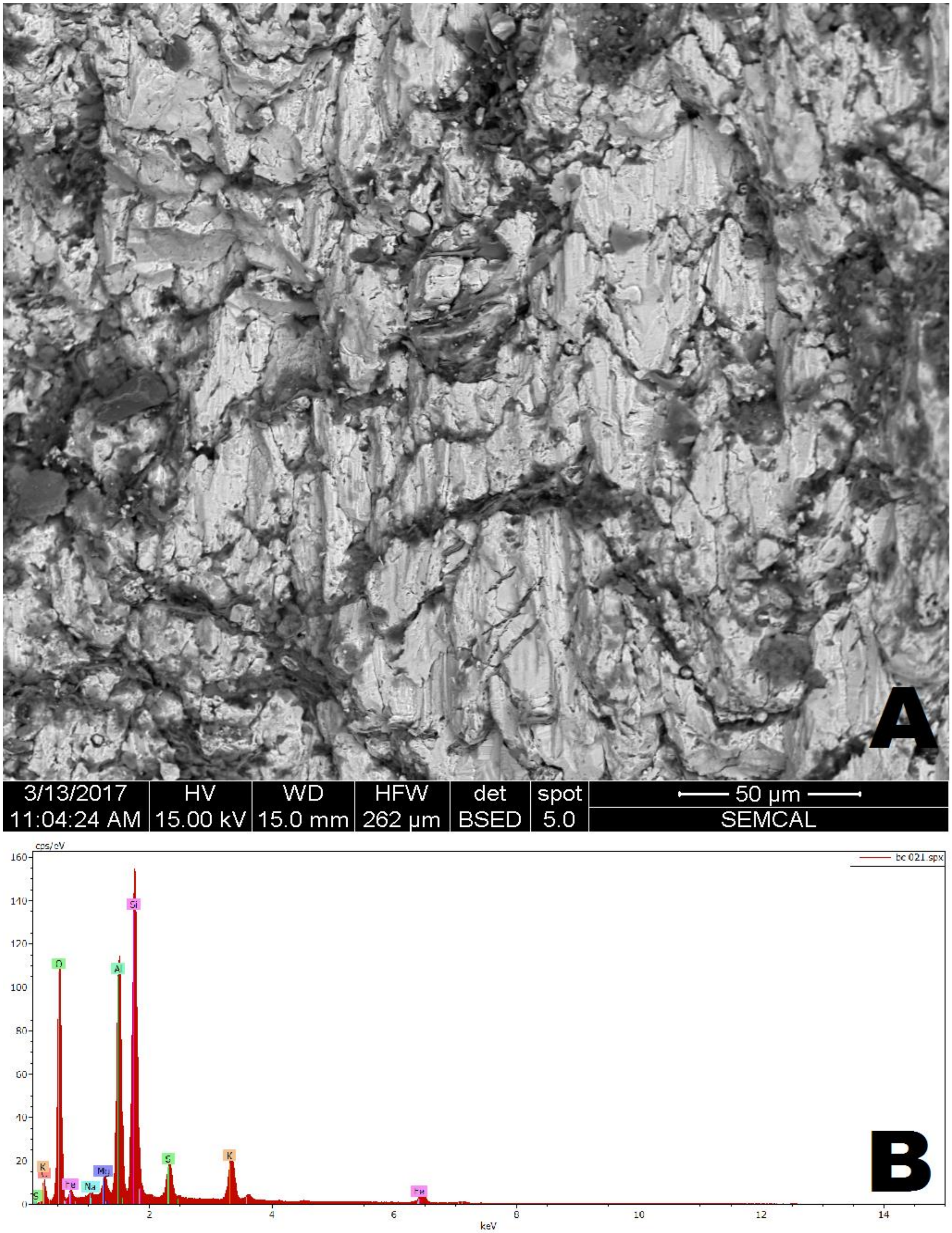

Figure 3. A. Cone-in-cone crystal habit of pyrite shown in a broken pyrite concretion. B. EDX data taken from cone-in-cone structure.

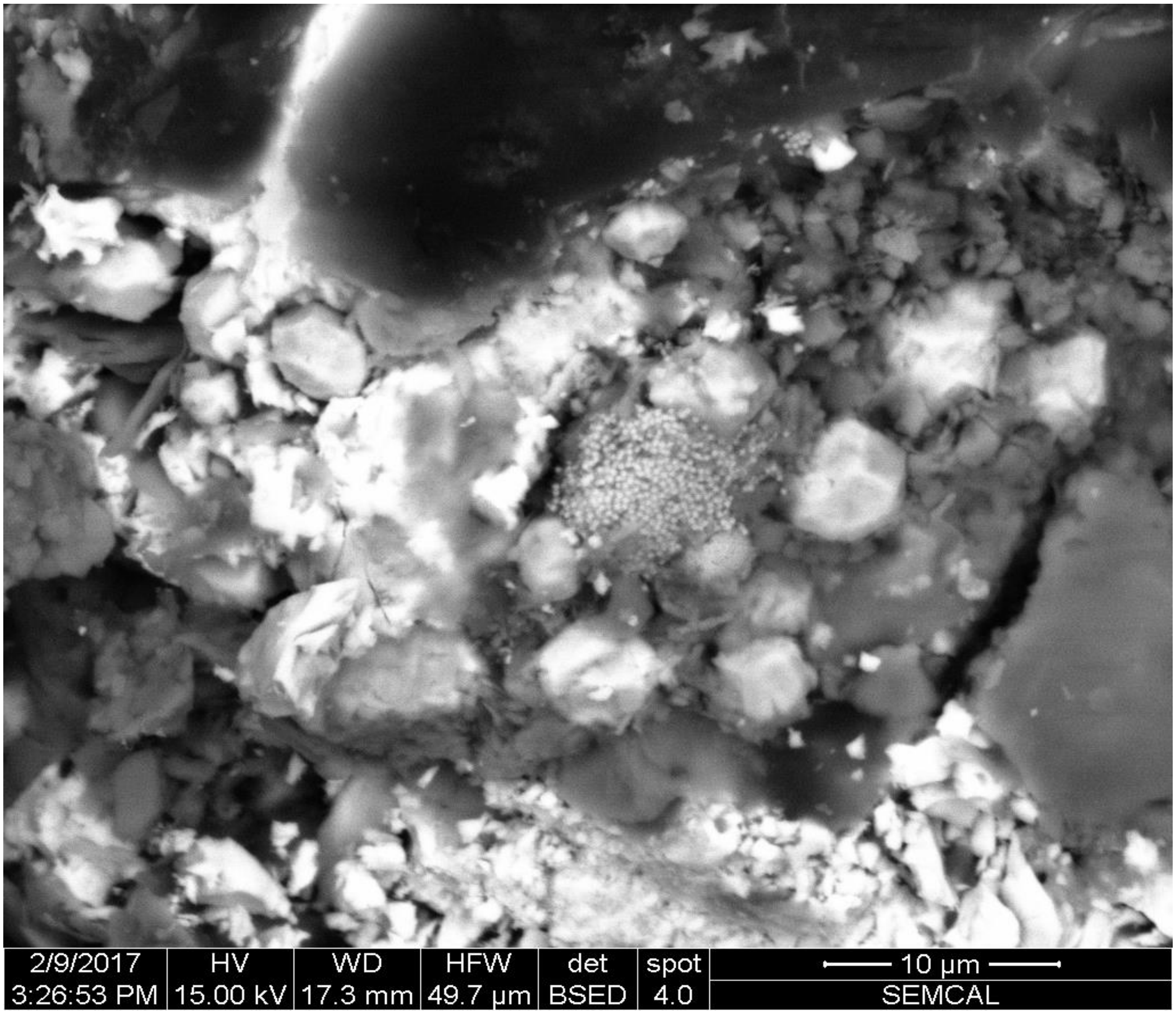

Figure 4. Pyrite framboids (clusters of small crystals) and larger euhedral crystals present within an inferred spore capsule of *Protosalvinia*.

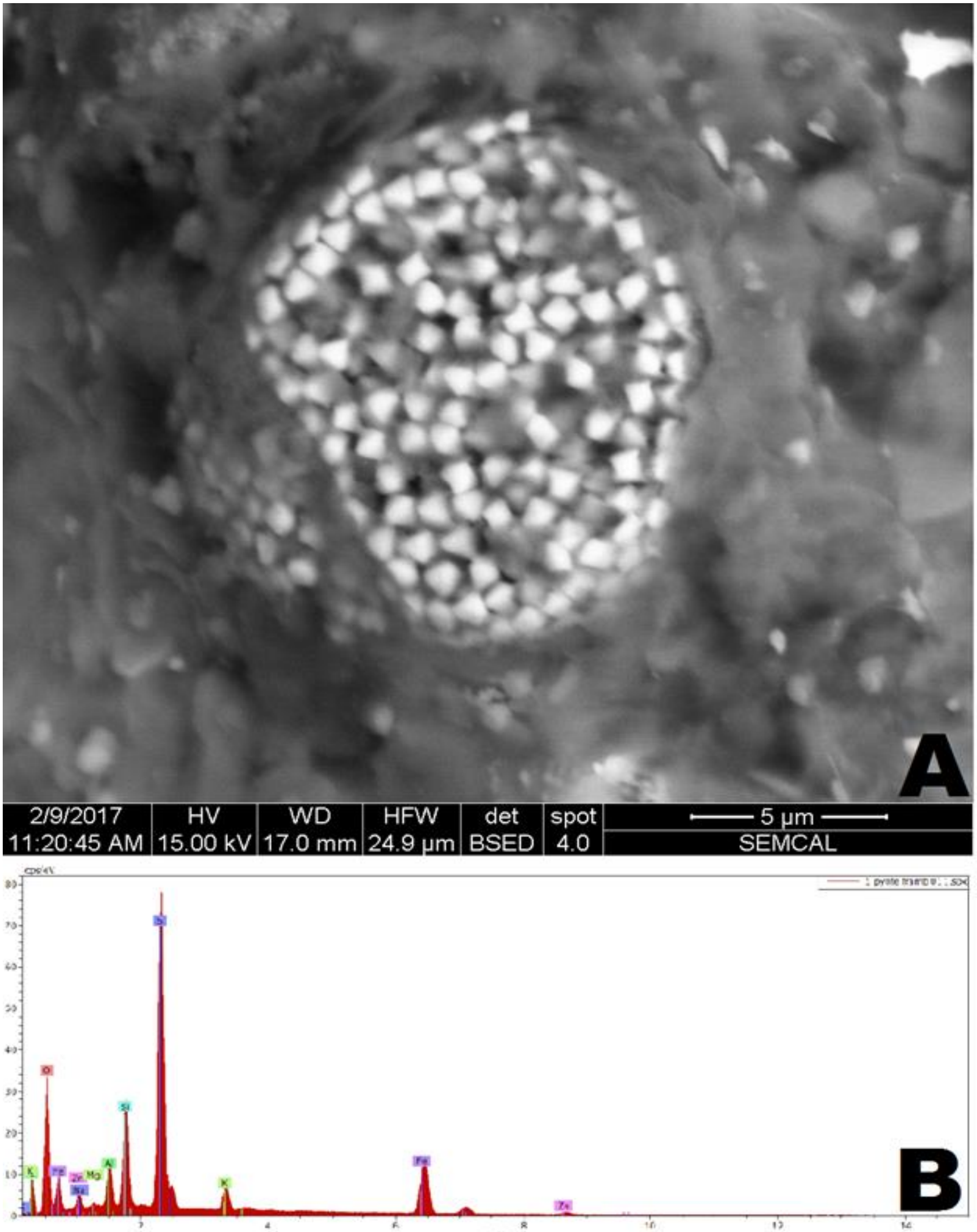

Figure 5. A. Close up of a pyrite framboid on the surface of a pyrite concretion. Each individual euhedral crystal of pyrite may represent an autolithified bacterial cell whereas the entire framboid may represent a colony. B. EDX data from the same framboid.

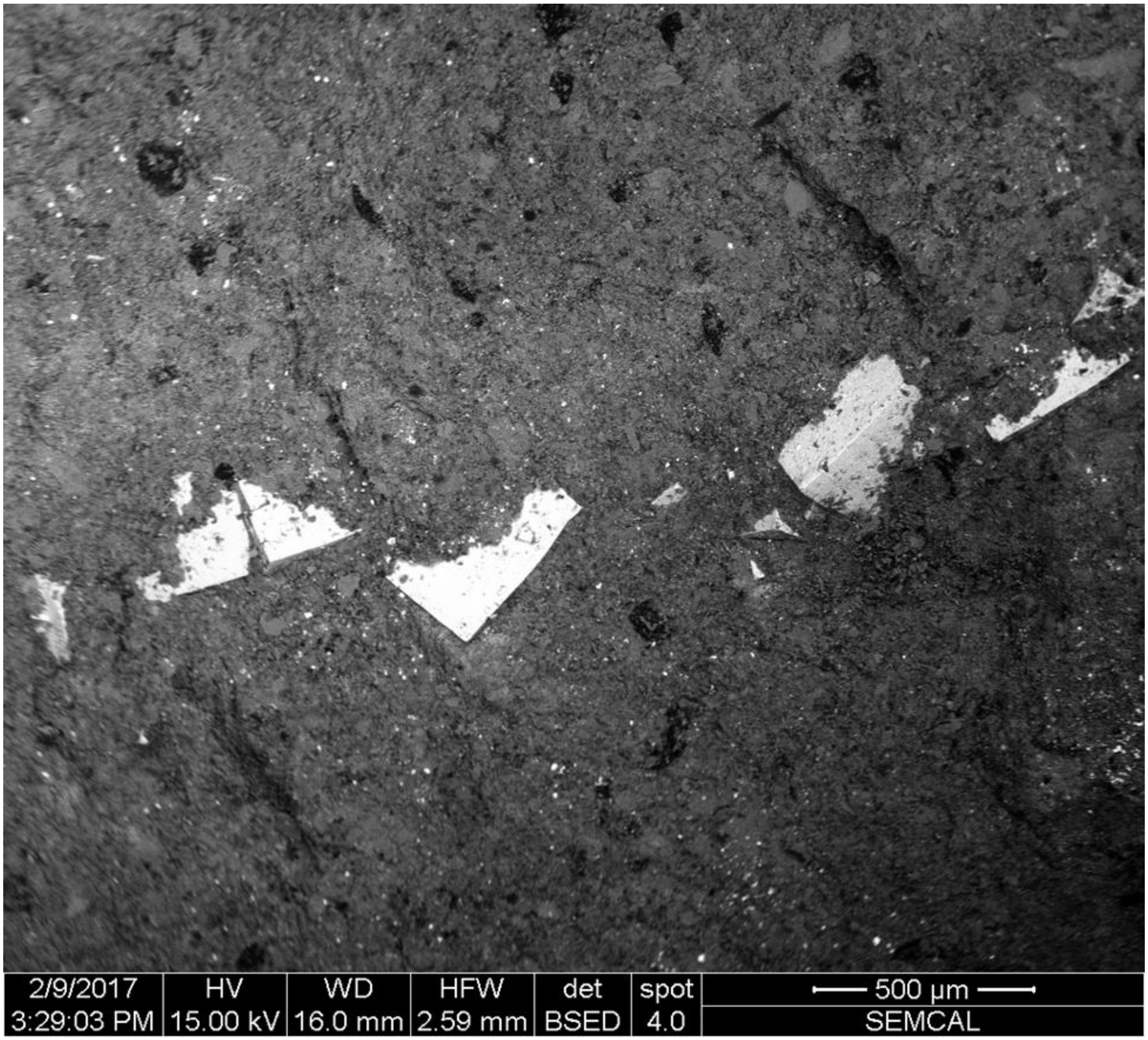

Figure 6. Large euhedral crystals of pyrite protruding from the surface of a pyrite concretion.

Organic Matter

The concretions contain organic matter of two size classes (Figure 7), and both are referred to as the organic microfossil *Protosalvinia*. Round spores, some of which show trilete morphology (Figure 8), ranging from 50 to 100 µm were found distributed through each concretion studied. This organic matter showed high carbon and oxygen levels with some iron and sulfur present. Specimens assigned to the other size class of organic matter, approximately 200 µm in diameter, are rounded in outline, similar to the smaller spores, and often have associated pyrite. These specimens contain framboids (Figures 4, 5). The larger specimens may represent spore capsules.

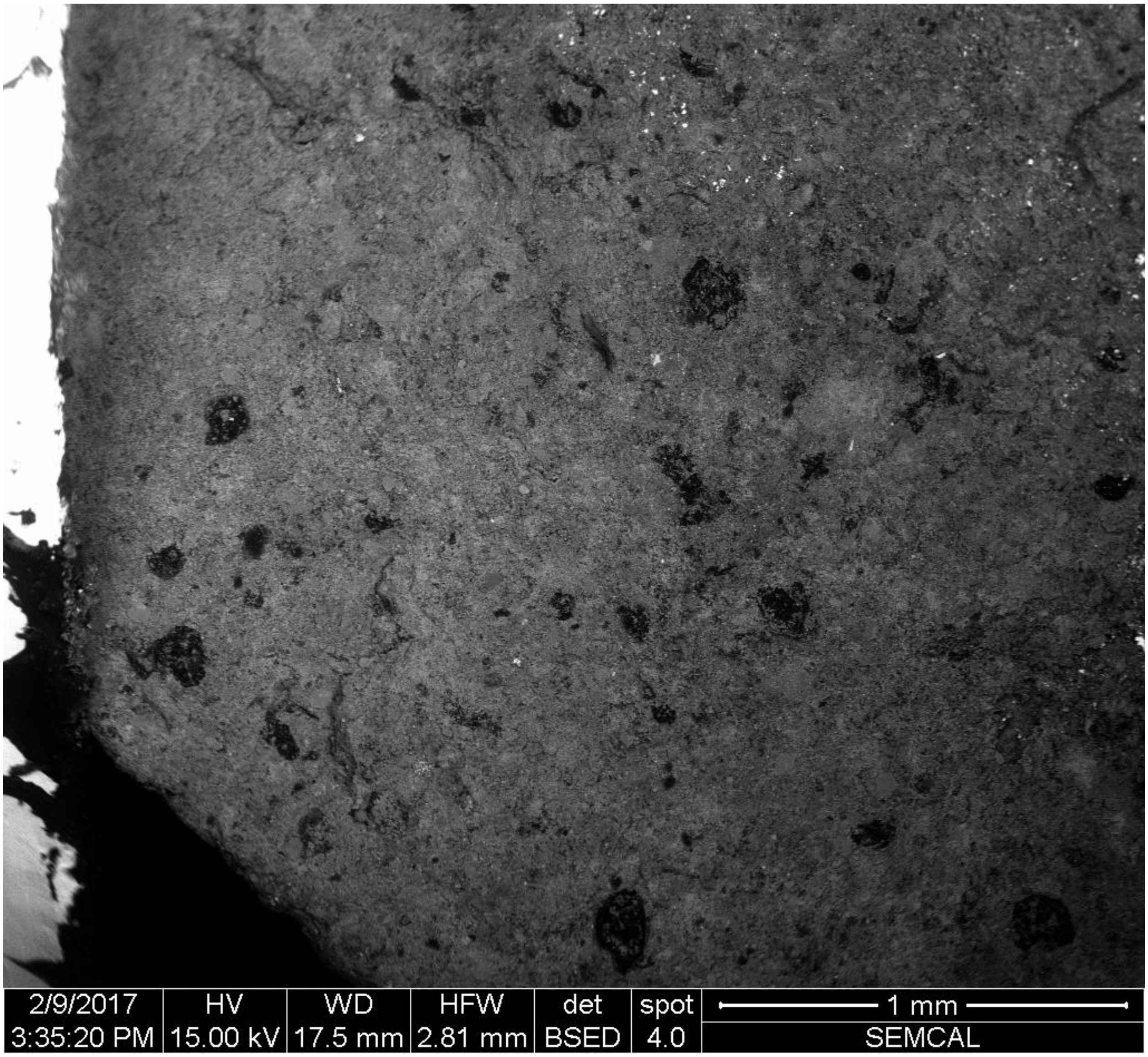

Figure 7. Large and small spores (in black) identified on the upper surface of a pyrite concretion.

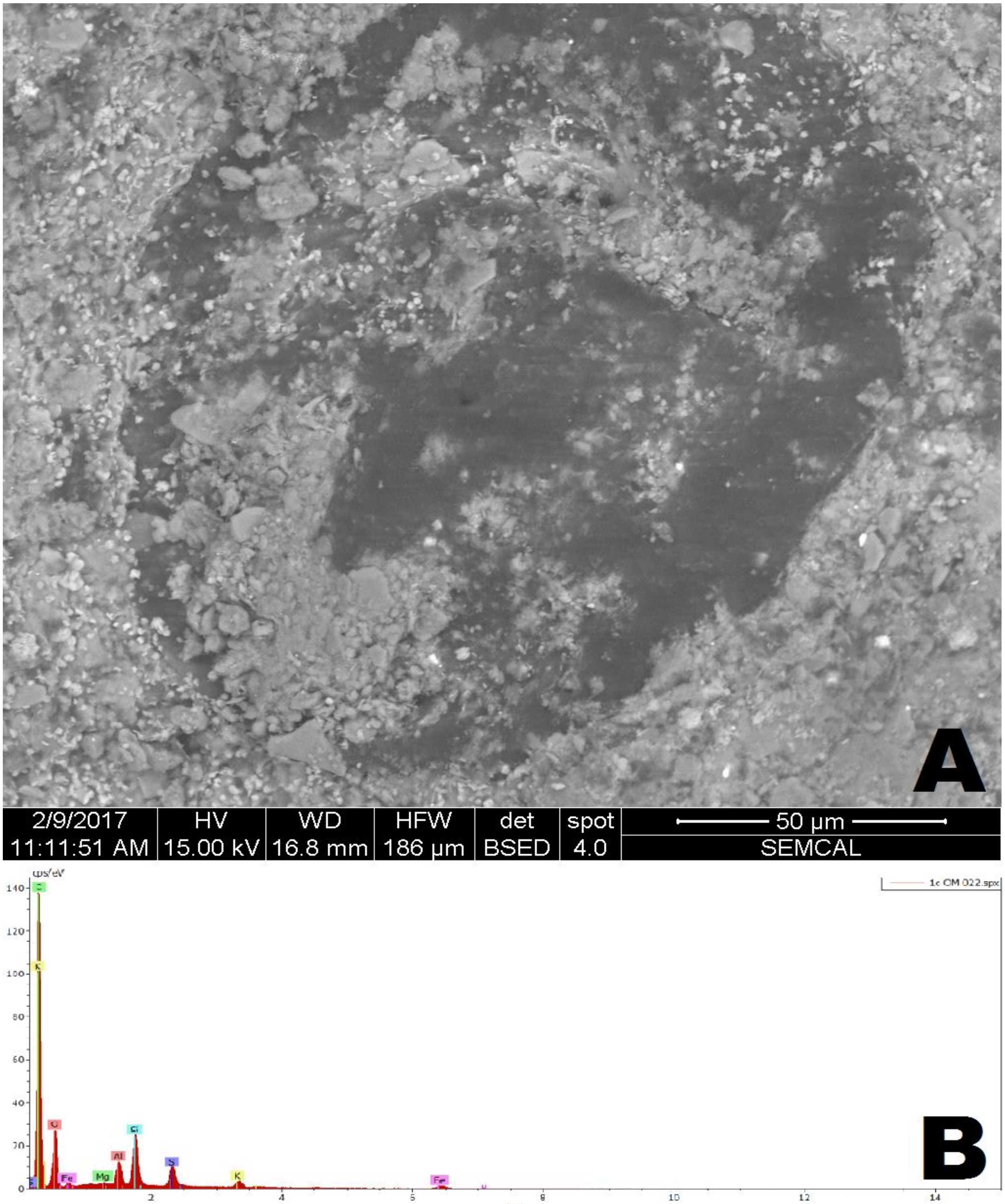

Figure 8. A. SEM view of a small *Protosalvinia* spore showing trilete pattern. B. EDX data corresponding with the center of the spore.

Rock Matrix

The composition of the black shale matrix was determined to be illitic clay with platy crystals of muscovite and perhaps feldspathoids (Figure 9), 5 to 20 μm in maximum dimension. Within the matrix, carbon, iron, sulfur, and oxygen were found in abundance. Anhydrous sulfides were found in elongate crystals, often in association with the pyrite on a weathered surface.

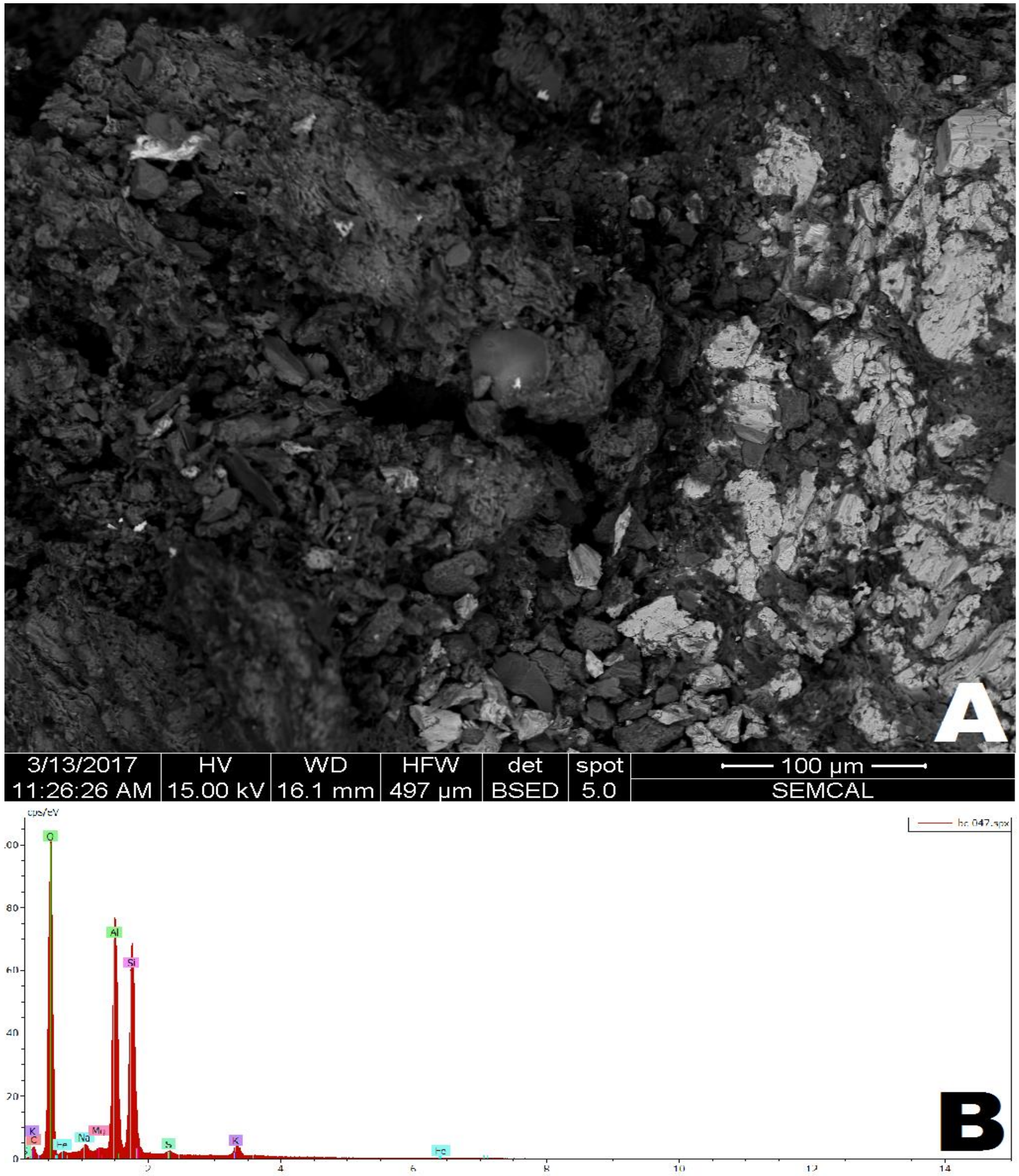

Figure 9. A. SEM view of black shale matrix (darker grey portion). B. EDX data taken suggest felspathoid minerals.

Discussion

Shape and Distribution of Pyrite in Concretions

Scans of several of the pyrite concretions reveal irregular areas of less dense material and no concentric growth. The composition of the less dense material could not be determined from the scan, but these areas are less dense than pyrite and more sense than calcite. The irregular pattern and small size of these less dense areas does not suggest that these are the initial points of nucleation. The distribution of the concretions suggests a related origin for each group, but many common related origins such as a disseminating, dead pelagic organism, fecal matter from pelagic organisms, benthic organisms or their activity (Schieber 2002) have been ruled out as likely origins.

An important and pervasive morphological feature of the pyrite concretions is the presence of cone-in-cone structure. Cone-in-cone structures have been observed in varied localities, and always in association with organic-rich, dark grey or black shales/black limestones (Carstens, 1985). Some classic occurences are in the Wheeler and Marjum formations (Cambrian) of Utah (Robison and Babcock, 2011), and in Alum Shale (Cambrian-Lower Ordovician) of Scandinavia (e.g., Carstens, 1985).

Bacterial Origins for the Pyrite Crystals

Much of the recent literature (Borkow and Babcock, 2003; Ahn and Babcock, 2012; Wilson and Brett, 2013) on concretions points to microbial biodegraders as having a central role in early diagenetic mineralization around decaying organic matter. Whereas the larger areas of cubic pyrite may represent secondary crystallization and are not associated with particular features that could be discerned in this study, the smaller framboidal pyrite was found in association with the organic matter. The size of the framboids present, 0.3 to several µm, coincides with the size and shape of bacterial cells (Portillo et. al., 2013) and occur in colonial bunches. Bacteria have been known to autolithify, becoming encased in minerals (Melendez et. al., 2013) and are likely to be found in these raspberry-like bunches (Borkow and Babcock, 2003). These bacteria may have provided the sulfur for the production of pyrite. While breaking down organic material the sulfur reducing bacteria supplied sulfur to the associated seawater and the pyrite also may have nucleated around the bacterial bodies. The iron was provided by Fe oxides, FeS compounds (Virtasalo et. al., 2013) or the clay minerals found in abundance in the matrix.

Anoxic conditions

The presence of bacterial framboids confirms the presence of anoxic conditions, in the sediment, at the time of deposition. The growth of euhedral crystal shapes, such as those that make up framboids (Figure 1), requires restricted access to oxygenated seawater and access to a supply of iron (Raiswell, 1982).

Organic Structures

The studied concretions show no macrofossil remains, nor do they have morphologies suggestive of burrows or other trace fossils. The only organic material identified in them is spore material referred to the genus *Protosalvinia*. Two size classes of this material are present. The smaller specimens seem to represent spores, whereas the larger specimens likely represent spore capsules from which the smaller specimens emerged, or perhaps spores of another species. The phylogenetic affinities of the organism that released the *Protosalvinia* spores are uncertain. Three hypotheses have been postulated: 1, a non-calcifying, marine brown alga (Schopf, 1978); 2, a non-vascular, terrestrial plant such as a bryophyte (Niklas and Phillips, 1976); and 3, an emergent aquatic (terrestrial) plant of uncertain taxonomic position but with 'tracheid-like' tubes identical to those of the Nematophytales (Gray and Boucot, 1979).

The spores fall into two class sizes. The circular organic bodies of 50-100 µm may represent the denser or more resistant areas of algal bodies. These were found distributed throughout the concretions and not often found in association with pyrite framboids. The persistence and lack of association with framboids indicates that these small organic bodies are unlikely to have provided the organic matter for the origin of framboids in the concretions. One consideration for these small dense, non-degraded spores is that they represent microspores. Microspores develop into the male gametophyte and are associated with land plants.

Larger circular organic matter of 200 µm (Figure 6) was discovered to be associated with pyrite framboids (Figures 3, 4) found inside the spores. The larger spores could represent *Protosalvinia* (Niklas and Phillips, 1976) spore capsuales. The fossil is known from the upper Devonian and is typically around 200 µm. If the *Protosalvinia* represents a land plant (hypotheses 2,3) these larger spores could represent megaspores in relation to the microspores. Larger megaspores would be associated with more biodegradable material and may explain their association with framboids. The minimal amount of organic matter available to be degraded could explain the lack of fungal hyphae. There may not have been enough organic material to cause the growth of fungus. Another potential cause for the limiting degradation and microbial growth would involve burial in seawater if the spores are not of marine origin. In a study by Babcock (1998) terrestrial organisms buried in marine settings had reduced decay.

CONCLUSIONS

Concretion nucleation is understood to be related to the decay of organic matter. In pyrite concretions from the lower Huron Shale Member of the Ohio Shale (Upper Devonian: Famennian) of central Ohio, early (pre-compactional) pyrite diagenesis is shown to be related to the presence of organic material in the form of spores identified as *Protosalvinia*. Distinct bacterial cells and fungal hyphae were not observed in these pyrite concretions. The concretions exhibit cone-in-cone structure in cross section. Two size classes of spore material are present, and cone-in-cone-bearing concretions are preferentially associated with the larger spores (spore capsules?). However, smaller spores are also contained in the concretions.

Recommendations for Future Work

This study raised many questions, primarily about the organisms involved. Whereas it added confidence to bacterial origins of concretions, the process of the bacteria autolifying is poorly understood. It is not apparent why living organisms would become encased in minerals after a period of growth. This process would prevent future reproduction so is unlikely to be mediated by bacterial cells, but the cells had a period of growth making it unclear how the environment would have changed to lithify the cells. More investigation of modern marine sediment could advance our understanding of concretion origins. Sampling the detritivores currently in anoxic marine sediment might help to better understand the microbes in the concretions.

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