

**METHODS FOR DETERMINING BIOGENICITY IN ARCHEAN AND OTHER ANCIENT ROCKS.**

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**Introduction:** Microscopic structures in terrestrial sedimentary rocks may not be easily identified as either biogenic or syngenetic with the deposition of the rocks. Both Schopf [1] and Knoll [2] have established criteria for determining biogenicity and syngenicity in ancient samples. Schopf's criteria were directed specifically towards identifying Archean fossils: 1. the rocks must be of unquestionable Archean age; 2. the structures must be indigenous to the Archean sediments; 3. the structures must occur in clasts that are assuredly syngenetic with deposition of the sedimentary unit; 4. the structures must be biogenic; and 5. replicate sampling of the fossiliferous outcrop firmly demonstrates the provenance of the fossil. Knoll's criteria are more general: 1. the structures must be compatible with formation by known biological processes; and 2. The structures must be incompatible with formation by physical processes.

Most previous studies of ancient fossils have relied primarily on petrographic sections studied by optical microscopy. The use of petrographic sections ensures that the possible microfossils are actually included within the rock. Surface techniques, particularly scanning electron microscopy (SEM), have not been widely utilized in the study of ancient fossils.

We believe that the SEM is an extremely useful tool for addressing questions of biogenicity in ancient samples, particularly if the SEM is used in conjunction with optical microscopy. A modern SEM, with resolution <2nm, usable magnifications to 250,000X and the ability to image uncoated samples at low kV, allows study of features that would otherwise be undetectable. In conjunction with SEM imaging, energy dispersive X-ray spectrometry (EDS) can be used to analyze submicron structures for important biogenic elements. These capabilities, combined with specialized sample preparation techniques, provide new insights into the biogenicity of ancient rocks.

**Methods:** We are examining samples originally studied by the Precambrian Paleobiology Research Group [3]. These samples include the following: 002 PPRG - chert with stromatolitic fabric, ~3.3-3.5 GA (Archean), Towers Formation, Warrawoona Group, Pilbara Block, Australia; 412 PPRG - stromatolitic carbonate ~1.790-2.170 GA (Proterozoic), Taltheilei Formation, Pethei Group, east arm of Great Slave

Lake, N.W.T. Canada; and 435 pprg - carbonate, ~1.6-1.7 GA (Proterozoic), Kulele Creek Limestone, Earaheedy Group, Nabberu Basin, western Australia.

Freshly fractured chips, and petrographic thin sections were analyzed with an Oxford ISIS energy dispersive spectrometer (EDS) and a Phillips SEM XL 40 field emission (SEM).

Selected samples were prepared as petrographic sections and initially studied by optical microscopy. In some of these sections we observed possible biogenic features similar to those previously described in the same rocks [3]. These sections were etched in HF vapor for less than an hour, and the exposed features were analyzed with an SEM [4,5].

**Results:** Previous studies of Archean and other ancient rocks have identified a variety of microbial remains that include spheres, rods, filaments and possible biofilms [3,6,7,8]. Based on optical microscopic examination and criteria established by earlier investigators, some microstructures are now suspected to be contaminants, dubiofossils, or inorganic facsimiles [1,2,9].

Our optical and SEM examination of Early Proterozoic carbonate rocks (PPRG 412, 435) clearly indicates the presence of contaminant microbes. All of the contaminants, which includes rods, spheres, and film-like deposits, are found on surfaces that have dissolution features.

In addition, EDS spectra show that these samples contain titanium, which is not present at detectable levels in the groundmass. The absence of titanium within the groundmass indicates that it probably entered the rock through a crack or fissure and it is not syngenetic.

Weathering profiles probably account for the restricted distribution of titanium. Weathering processes, whether biogenic or abiogenic, produce secondary minerals in solution that subsequently precipitate [10,11,12,13]. Secondary products in solution can move downward through underlying rocks through cracks and fissures. Bacteria can concentrate ionic species either by acting as nucleation surfaces or by metabolic processes [10,11,12,13]. Thus, these latter day microbes can be identified because they are utilizing immigrant ions and not syngenetic ones. These immigrants, even after fossilization, would retain a

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different geochemical signature from the groundmass.

There appear to be several syngenetic, biogenic inclusions in the Proterozoic carbonates, however, including filaments (412 PPRG), rod shaped microbes (435 PPRG), and a helical filamentous structure that may represent the fossil prokaryote *Heliconema* (435 PPRG). The syngenetic inclusions are either imbedded in the rock (and exposed by etching) or broken by fracturing the rock. The geochemistry reflects that of the groundmass, (i.e. calcium carbonate), usually with an elevated carbon content, which is a good signature for biogenicity.

The Warrawoona carbonaceous cherts are Archean in age, and although dominated by SiO<sub>2</sub>, they also contain barite, iron oxide, siderite, and possibly magnesite. Unlike carbonates, cherts do not readily demonstrate dissolution surfaces, but some fractures or crevasses can be identified by weathering features such as pitting on quartz crystal surfaces. Mineralized films appear to be abundant on many of the fractured surfaces and seem to be superficial. In addition, they possess a chemistry that is different from the groundmass. EDS spectra and elemental maps of the films indicate the presence of N, Cl, K, Ca, Na, Si, C, and occasionally Fe. Similar signatures have been identified from the remains of modern microbes that were collected near hydrothermal vents [12]. We suggest that although these are probably biogenic, they are also fairly modern, and therefore contaminants.

Some rods and spheres within the Warrawoona are probably both biogenic and syngenetic. Our lines of evidence for accepting the syngenicity are that they occur in more than one area of the sample, and similar sizes and shapes are identifiable within petrographic thin sections. Representatives have been found partially to nearly completely embedded within the groundmass and etching with HF indicates enclosure within the ground mass.

As for the Proterozoic carbonates, biogenicity of spheres, filaments, and possibly some rods, is suggested by elevated carbon levels. Elevated levels of iron have also been detected. Elemental mapping indicates that both of these elements are present, albeit at very low levels, within the groundmass. Iron silicates and oxides can nucleate on cell membranes, and metallic ions such as iron can enhance preservation of microbes [12, 14].

**New Methods and Criteria:** Based on the results of our studies we suggest the following as a set of criteria for identifying biogenic, syngenetic structures using SEM and EDS:

1. Fresh samples: It is important to use freshly fractured chips that have been obtained from the inte-

rior of the sample. The sample should also be examined with an optical microscope to determine that there are no visible cracks or crevices. 2. Replicate sampling: Schopf's criterion #5 should be applied on an electron microscope scale, in order to identify syngenetic features. Contaminant microbes are usually restricted to areas encompassing a few millimeters, and are superficial. In contrast, although syngenetic structures may be exposed due to the fracture pattern, many are partially to completely embedded in the groundmass, and some will indicate fracturing that follows that of the groundmass. Contaminants also appear to be restricted to surfaces, and these surfaces often indicate dissolution or other evidence of weathering. 3. Chemical compositions: EDS spectra and elemental mapping indicates that syngenetic structures reflect groundmass chemistry. Additionally, biogenicity would be implied within rods, spheres and filaments by elevated signatures of ionic species that are known to be utilized metabolically, nucleated on microbial membrane surfaces, or precipitated by bacteria changing redox and/or pH conditions through their metabolic activity. Contaminants, whether abiogenic or biogenic, usually have compositions very different from the groundmass.

**Conclusions:** The issue of identifying biogenicity and syngenicity in ancient rocks can be aided with SEM and EDS. Although rods and spheres can be formed by physical processes, biogenic processes appear to leave unique geochemical signatures. If these organic residues are ancient, the chemical signature will reflect the groundmass, albeit some of the signatures, particularly metallic ions, may be elevated within suspected microbes. Syngenetic forms are partially to completely embedded, while nonsyngenetic forms are restricted to surfaces.

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