

# Phosphate Biomineralization of Cambrian Microorganisms

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## ABSTRACT

As part of a long term study of biological markers (biomarkers), we are documenting a variety of features which reflect the previous presence of living organisms. As we study meteorites and samples returned from Mars, our main clue to recognizing possible microbial material may be the presence of biomarkers rather than the organisms themselves. One class of biomarkers consists of biominerals which have either been precipitated directly by microorganisms, or whose precipitation has been influenced by the organisms. Such microbe-mediated mineral formation may include important clues to the size, shape, and environment of the microorganisms. The process of fossilization or mineralization can cause major changes in morphologies and textures of the original organisms. The study of fossilized terrestrial organisms can help provide insight into the interpretation of mineral biomarkers. This paper describes the results of investigations of microfossils in Cambrian phosphate-rich rocks (phosphorites) that were found in Khubsugul, Northern Mongolia.

## 1. INTRODUCTION

Unusual Cambrian phosphate-rich rocks (phosphorites) are found in Northern Mongolia. [1]. Specialists have long studied these phosphatized rocks from Khubsugul because they were believed to be a classical example of inorganic phosphate precipitation [2]. The formation of phosphorites interbedded with carbonates, cherty shales and cherts from the Khesen Formation was originally related to abiotic deposition beneath upwelling zones. However, recent SEM studies of HCl-etched samples revealed phosphatic bacteriomorphs which had been preferentially preserved with respect to the more carbonate-rich matrix. The bacteriomorphs presented a variety of shapes and sizes and were interpreted as fossil bacteria representing communities consisting of consortia of different types of bacteria [1]. The filamentous (cyanobacteria), coccoid and rod-shaped microbes have been fossilized in different ways. This paper presents further SEM studies of this interesting microfossil assemblage.

## 2. METHODS

We used the same technique for sample preparation as Rozanov and Zhegallo [1]. A freshly broken rock chip was etched in 10% HCL for 2 minutes, then cleaned in distilled water and alcohol. The sample was coated with a thin Pt conducting layer (30 sec coating time) and was observed with a Philips FEG-SEM XL-40 at the Johnson Space Center.

## 3. RESULTS AND DISCUSSION

The etched surface revealed two major types of material. The calcite matrix was clearly etched by the acid revealing more resistant Ca phosphate or apatite which was distributed over most of the surface as recognizable fossil microbes or microbialites. The predominant structure consists of relatively large spherical or ovoid microbialites ranging from 10  $\mu\text{m}$  to 1 mm in diameter (Fig. 1). These frequently show both complex concentric and radial structures similar to microoncolites or microoolites. Both microbialites and calcite matrix contain several types of microfossils:

(1) Large, cyanobacteria-like filaments occur as hollow moulds (Fig. 2) in a phosphate precipitate which may consist of stacked discoidal apatite crystals (Fig. 3), more isometric crystals, or a complex texture consisting of overlapping hemispherical to nearly spherical globules having diameters ranging from 0.1 to 0.5  $\mu\text{m}$  (Fig. 4). This latter texture is tightly packed, overlapping, and non-porous. At the end of some filaments, the apatite crystals grade to porous network of discrete tubular forms which may be the shape and size of the original bacteria. By contrast, another apatite texture

which makes up the walls of some filaments consists of porous network of isometric equant crystals have a very narrow size distribution .

(2) The encrusted casts of cyanobacteria (Fig. 5) consist of a robust 400-500 nm thick crust what appears to be blocky calcite, the outer wall of which is lined by a 50-100 nm thick coat (probably of apatite), and an inner cast of amorphous phosphate. The crust represents the mineralized sheath whereas the inner cast represents the trichome. The whole structure ranges from 3-4  $\mu\text{m}$  in diameter. Sometimes a number of filaments are associated, as in Figure 5 in which two filaments are enveloped in a common, hourglass-shaped sheath. In other examples, the apatite crystals make up the body of the filament and fill in the volume, or the apatite crystals may grow perpendicularly to a central core or cylinder.

(3) Smaller bacteriomorphs include rod-shaped and coccoid structures of heterotrophic bacteria which abound in the phosphorite. Figure 6 shows large numbers of small, "rice-grain" -like, rod-shaped bacteria about 1  $\mu\text{m}$  in length. These colonies form wavy, garland-like mats embedded in the calcite matrix (Fig. 7) and weave around the larger crusts and moulds of the cyanobacteria fossils.

(4) The calcite matrix is permeated with curved and circular voids which cross-cut the etched crystal cleavage pattern (Fig. 8). The curved moulds are of two types: fine, filamentous structures with diameters of 0.5  $\mu\text{m}$  and lengths of a few micrometers, and thicker filaments 1  $\mu\text{m}$  in diameter with lengths  $> 5 \mu\text{m}$  . Given the abundance of fossil bacteria and moulds of cyanobacteria trichomes in this material, these filamentous moulds in the calcite probably also represent fossil bacteria moulds.

Cyanobacterial mats, their mineralization and the subsequent implications for the rock record have been intensely studied [3-6]. Stromatolites of various kinds were, and still are, dominated by mucus-producing cyanobacteria, although other bacteria also form part of the community [*op. cit.*]. In an analysis of cyanobacterial calcification, Pentecost and Riding [7] noted that calcification can occur as the impregnation of the interior of the sheath and /or the external encrustation around the sheath. Défarge *et al.* [8] documented

the initiation of calcification in modern cyanobacteria using cryo-SEM whereas Merz [9] documented the same process with the light microscope and normal SEM. Gerasimenko *et al.* [6] experimentally studied the phosphatization of cyanobacteria, showing that inorganic phosphate assimilation in the living organism resulted in the phosphatization of

the sheaths upon the death of the organism. Phosphatized non-cyanobacteria have previously been described from very differing environments. Liebig *et al.* [10] documented phosphatized rod-shaped and coccoid bacteria in reducing volcanic lake sediments from the Eocene Lake Messel Formation in southern Germany. From the continental shelf off Peru Miocene-Quaternary phosphorite nodules are attributed to bacterial mediation by Lamboy [11] who shows photographs of phosphatized rod-

shaped and coccoid bacteria, although he does not name them as such. The mineralization of microbial mats as a result of bacterial activity is well known [3-6, 12]. Less well known, however, are phosphatized microbial mats and stromatolites. Phosphatized stromatolites of Jurassic age have been described from the Upper Jurassic of Southern Spain [13]. Phosphatized microbial mats are also implicated in the preservation of the soft parts of fossil organisms [10, 14,15].

The microfossils from the Cambrian Khesen Formation that we describe occur both in phosphate and in calcite, both minerals apparently intermixed and contemporaneous. Their co-precipitation probably has to do with the different species of microorganisms within the microbial mat and their control of the immediate chemical environment. The particular morphology of the apatite crystals fossilizing these microbial mats may be constrained by the presence of organic matter and an organic template on which to nucleate. The crystal morphology may, perhaps, be further linked to precipitation mediated by specific microorganisms.

## CONCLUSIONS

There is, thus, a growing body of evidence for the implication of bacterial activity in the formation of phosphorite deposits via the phosphatization of microbes and microbial mats in the experimental and in the rock record. This sample from the Khubsugul Basin documents a very good example of the differing modes of preservation of the variety of organisms that makes up the microbial consortium in a mat environment. The mat builders, the cyanobacteria, are preserved as hollow crusts, encrusted casts and as moulds whereas the heterotrophic bacteria are replaced casts as well as moulds. The variety of fossil microorganisms and modes of fossilization very much resembles that of the Early Archean microbial mat communities from the Barberton greenstone belt of South Africa [16].

The assemblage described in this paper adds valuable information to the rapidly enlarging database of terrestrial microfossils and biomarkers, such as microbial mats and biofilm, which can be used as analogues for possible extraterrestrial life forms. It also suggests that the morphology of biogenically-precipitated phosphate may be directly related to specific microorganisms. If this is the case, then crystal morphology may be another, valuable biomarker.

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## FIGURE CAPTIONS

Figure 1. General view of the phosphate sample from the Cambrian Khesen Formation of the Khusugul Basin, Mongolia showing oncolitic to ooid-like, phosphatic microbialites embedded in calcite.

Figure 2. Moulds of cyanobacteria filaments embedded in an apatite matrix.

Figure 3. Detail of the discoidal apatite crystals forming the mould of the cyanobacteria filaments.

Figure 4. Biogenically-precipitated apatite in the form of coalescing nanometer-sized globules.

Figure 5. Double cyanobacteria filaments, replaced by phosphate, enclosed in a calcified (?) sheath, forming an encrusted cast structure. The calcified (?) sheath appears to be lined by a thin coat of phosphate.

Figure 6. Small, 1 $\mu$ m-sized, phosphatised rod-shaped bacteria in the phosphate deposit. Scale 5  $\mu$ m.

Figure 7. Phosphatised cyanobacteria filament (large arrow) in a calcite matrix with a garland-like mat of small, phosphatised, rod-shaped bacteria (small arrows).

Figure 8. Rounded and curved hollows (arrows) representing bacteria moulds in the calcite matrix.

Figure 1

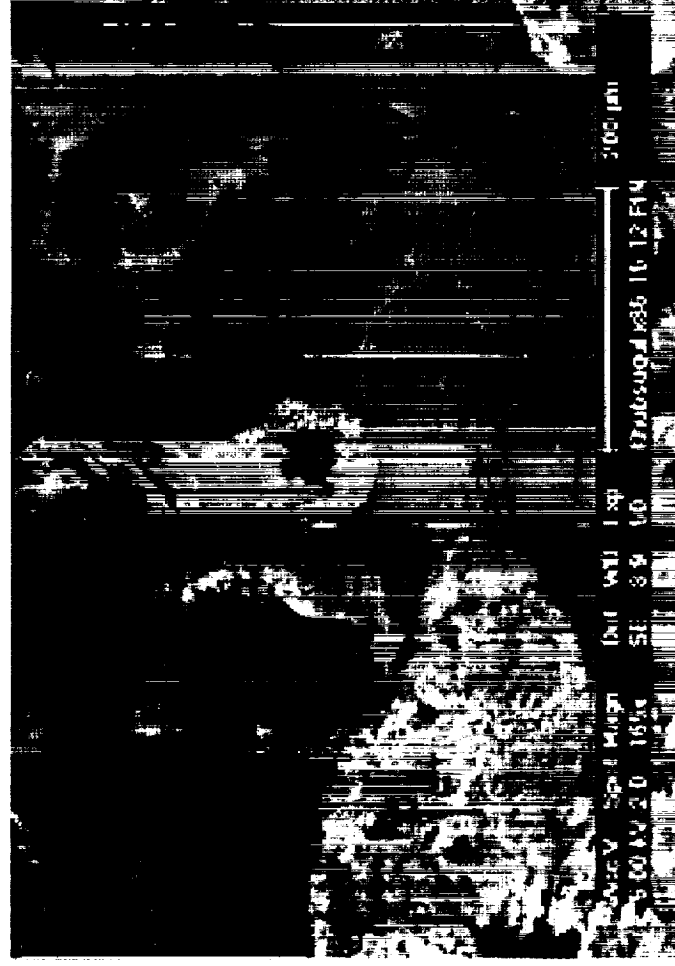


Figure 2



Figure 3

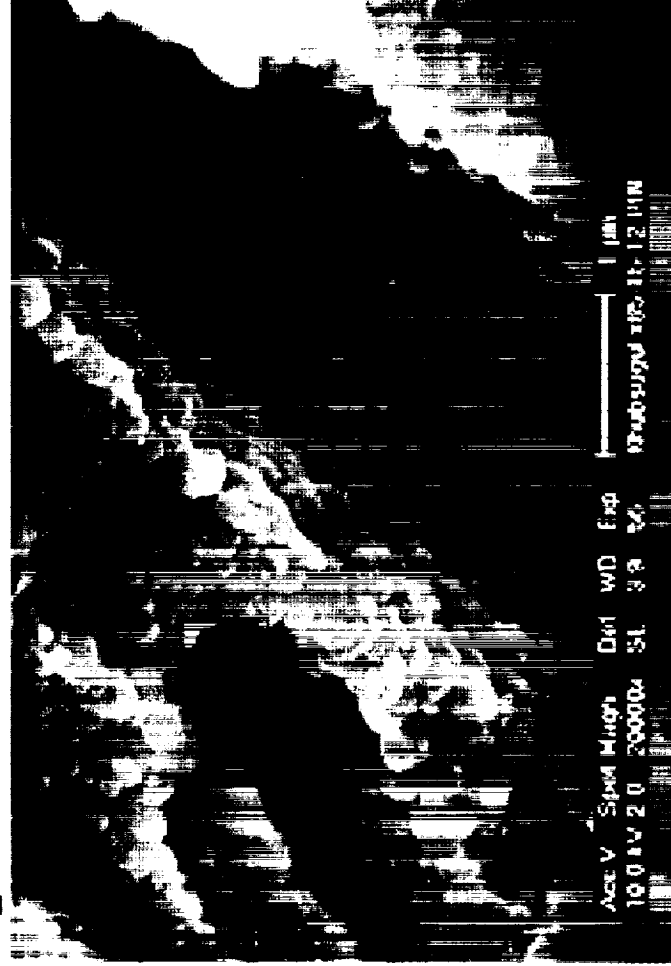


Figure 4



Figure 5



Figure 6

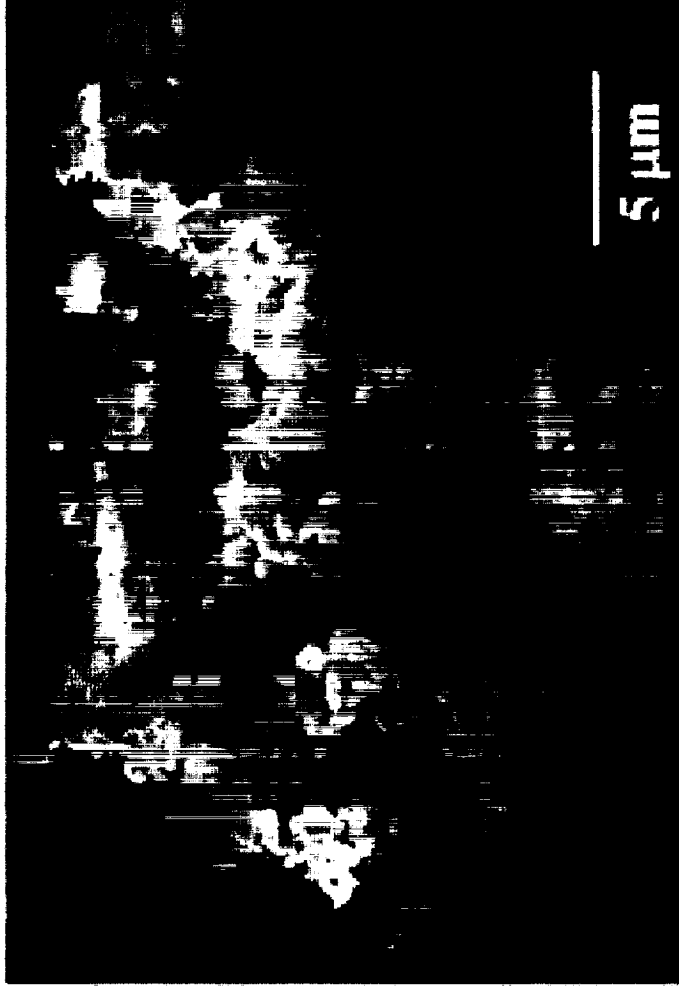


Figure 7



Figure 8

