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# Implications of *in situ* calcification for photosynthesis in a ~3.3 Ga-old microbial biofilm from the Barberton greenstone belt, South Africa

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ABSTRACT

Timing the appearance of photosynthetic microorganisms is crucial to understanding the evolution of life on Earth. The ability of the biosphere to use sunlight as a source of energy (photoautotrophy) would have been essential for increasing biomass and for increasing the biogeochemical capacity of all prokaryotes across the range of redox reactions that support life. Typical proxies for photosynthesis in the rock record include features, such as a mat-like, laminated morphology (stratiform, domical, conical) often associated with bulk geochemical signatures, such as calcification, and a fractionated carbon isotope signature. However, to date, *in situ*, calcification related to photosynthesis has not been demonstrated in the oldest known microbial mats. We here use *in situ* nanometre-scale techniques to investigate the structural and compositional architecture in a 3.3 billion-year (Ga) old microbial biofilm from the Barberton greenstone belt, thus documenting *in situ* calcification that was most likely related to anoxygenic photosynthesis. The Josefsdal Chert Microbial Biofilm (JCMB) formed in a littoral (photic) environment. It is characterised by a distinct vertical structural and compositional organisation. The lower part is calcified *in situ* by aragonite, progressing upwards into uncalcified kerogen characterised by up to 1% sulphur, followed by an upper layer that contains intact filaments at the surface. Crystallites of pseudomorphed pyrite are also associated with the biofilm suggesting calcification related to the activity of heterotrophic sulphur reducing bacteria. In this anoxygenic, nutrient-limited environment, the carbon required by the sulphur reducing bacteria could only have been produced by photoautotrophy. We conclude that the Josfsdal Chert Microbial Biofilm was formed by a consortium of anoxygenic microorganisms, including photosynthesisers and sulphur reducing bacteria.



## 1. Introduction

The earliest traces of photosynthesis occur in well-preserved sedimentary rocks of Early–Mid Archaean age (4.0–3.3 Ga) in the Barberton (South Africa) and Pilbara (Australia) greenstone belts (see review in Westall, 2010). In the commonly accepted understanding of the evolution of life, anoxygenic photosynthetic microorganisms appeared first in the Early–Mid Archaean (Tice and Lowe, 2004; Westall et al., 2006)

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while the more sophisticated and more efficient oxygenic photosynthesisers appeared in the Late Archaean (Altermann and Schopf, 1995; Brocks et al., 1999; Buick, 1992; Summons et al., 1999).The most common expression of photosynthesis in the rock record is fossilised photosynthetic microbial mats. These are finely laminated structures that are formed by photosynthetic microorganisms in generally oligotrophic environments where the primary producing microorganisms have access to sunlight that they can use as an energy source. These mats are highly complex consortia of different kinds of microorganisms living off the organic biomass produced initially by the photosynthetic microorganisms (Dupraz et al., 2009; Møller et al., 1998; Ramsing, et al., 1993). The preservation of photosynthetic microbial mats is serendipitous because they often form in ephemeral, littoral environments that are active and subject to physical destruction (Knoffke, 2009). Moreover, early diagenetic processes may also lead to complete degradation of the mats or blurring of their signatures. A concatenation of events is therefore required to preserve them, such as burial by fine detritus to produce recognisable, microbially-influenced sedimentary structures (MISS, Knoffke, 2009), or impregnation of the layered photosynthetic structure by minerals, such as carbonate or silica (Cady and Farmer, 1996; Jones et al., 2001; Konhauser et al., 2001; Walter, 1976). The latter process will concomitantly dilute any organic or geochemical proxy signature.

Given the vagaries of the taphonomic process, identification of the remains of photosynthetic microbial mats in ancient rocks needs to be based on a range of complementary data that support its formation within the photic zone, as well as identifying proxies that indicate that the mat was formed by photosynthetic microorganisms. Proxy features that are commonly used to identify fossil photosynthetic microbial mats include (1) a mat-like, laminated morphology (planar or three dimensional, as in domical or columnar stromatolites), (2) the presence of fossil microorganisms of known photosynthetic affinity (*e.g.*, the later-evolved oxygenic photosynthesising cyanobacteria, many species of which have readily identifiable morphologies), (3) a carbon isotopic signature consistent with photosynthesis, (4) evidence of *in situ* calcification as a by-product of photosynthetic activity (Supplementary Fig. 1). It should also be demonstrated that these combined characteristics do not occur in microbial mats formed by non-photosynthesising microorganisms. Bailey et al. (2009) note that almost all of the physical and chemical characteristics used for identifying fossil photosynthetic mats can also be produced by non-photosynthetic mats, such as those formed by sulphur/sulphate or methane oxidisers in cold seep, hydrothermal or other types of environments. Table 1compares the characteristics of modern photosynthetic and non photosynthetic microbial mats, underlining the similarities between them in terms of environment of formation, structure, composition and metabolic signatures.

Both types of mats can be formed in the photic zone but non-photosynthetic mats can also form in caves or deep water. Both can form on sediment surfaces but non-photosynthetic mats also form within the sediment. Both mat types can be laminated (chemical mineral precipitates, such as calcareous travertines can also be laminated, Pentecost, 2005). Whereas non-photosynthetic microbial mats have also been described as being sediment stabilising and having crenulated, contorted and wrinkled surface (Bailey et al., 2009) interlayering with chemically-precipitated evaporite deposits in littoral/sabkha environments seems to be restricted to photosynthetic mats. Certain biomarkers distinguish the microbial composition of photosynthetic and non-photosynthetic microbial mats. For example, Summons et al. (1999) describe 2-methylhopanes from 2.7 Ga-old oil shales from the Pilbara of Australia as being the degradation products of phototrophic bacterial lipids. Lipid biomarkers of sulphate reducing bacteria include mono-O-alkyl glycerol ethers (Arning et al., 2008). However, biomarkers have a limited life time (albeit very long) and even at 2.7 Ga the syngenicity of the 2-methylhopanes is questioned (Rasmussen et al., 2008). Elemental sulphur deposits are associated with mats formed by sulphur-oxidising bacteria (Nelson and Castenholz, 1981) but not with photosynthetic microbial mats. Phosphorite deposits are also characteristic of non-photosynthetic microbial mats, such as those formed by the sulphur-oxidisers *Beggiatoa* (Reimers et al., 1990) and *Thiomargarita* (Schulz et al., 1999). Calcification, on the other hand, occurs in non-photosynthetic microbialites, such as carbonate mud mounds formed around cold seeps (Barbieri and Cavalazzi, 2005), as well as in photosynthetic microbial mats (Dupraz et al., 2009).

Although many species of cyanobacteria are readily recognisable in the fossil record when well preserved (*e.g.*, Hofmann, 1976; Knoll, 1985), not all photosynthetic microorganisms possess distinct morphological attributes and not all microorganisms can be/are fossilised (Orange et al., 2009; Westall, 1997). Carbon isotope signatures are not sufficiently distinctive of photosynthesis since photosynthetic microorganisms are characterised by a wide range of $\delta^{13}C$ values (*e.g.*, −3 to −28‰ for oxygenic photosynthesisers and −9 to −36‰ for anoxygenic photosynthesisers) that overlap with those of other non-photosynthetic microorganisms (Schidlowski, 1988, 2001), as well as those of carbon formed by non-biogenic processes (van Zuilen et al., 2002). However, bulk carbon isotope signatures from photosynthetic microbial mats will be heavier than those for mats produced by sulphur/sulphate oxidisers or methane oxidisers. Moreover, carbon isotopic measurements are generally made on bulk rock samples that contain traces of the hypothetical photosynthetic microbial mats, as well as traces of any other microorganisms in that particular habitat. The resulting isotopic signature will, thus, be mixed.

Purported photosynthetically metabolising microorganisms and their macrostructures (microbial mats, stromatolites) have been identified in the oldest, well-preserved sedimentary rocks known. Dunlop et al. (1978), Schopf and Walter (1983), and Lowe (1980, 1983) first described stromatolites and/or the possible remains of cyanobacteria in well-preserved sediments (cherts) dating from the Early Archaean (3.5–3.3 Ga) in the Pilbara region of NW Australia. Similar interpretations were made in Early Archaean cherts from the Barberton greenstone belt in South Africa (Byerly et al., 1986). Further studies have been undertaken since the 1990s in both Early Archaean terrains (*e.g.* Allwood et al., 2006, 2009; Hofmann et al., 1999; Schopf, 1993; Tice, 2009; Tice and Lowe, 2004, 2006; Walsh, 1992; Westall et al., 2006; see reviews by Westall, 2004, 2010) using structure (laminated and/or domical), and fractionated carbon isotopic signatures as proxies for photosynthesis. Indeed, the carbon isotope signatures of highly metamorphosed sediments from the Isua Greenstone belt in Greenland (3.8 Ga) were also interpreted as indications of photosynthesis (Mojzsis et al., 1996; Rosing, 1999; Schidlowski, 1988, 2001). However, the remains of the photosynthetic primary producing organisms are rarely preserved (*cf.* Altermann and Schopf, 1995), Critiques of some of these studies have concentrated on the biogenicity of the laminated structures (Brasier et al., 2002; Lowe, 1994) and the hypothetical photosynthetic isotopic signatures (*e.g.*van Zuilen et al., 2002). More recent investigations have addressed the importance of environmental habitat and the effects of local variations on the distribution of the ancient photosynthetic structures. For instance, Allwood et al. (2006, 2009) demonstrated by detailed field mapping and macro to microscopic analyses that several varieties of domical structures in a 3.5 Ga-old formation in the Pilbara in Australia formed in a variety of localised habitats on a shallow water carbonate platform. They argued that their environment of formation and their physical and chemical characteristics of the domical structures could only have been produced by photosynthetic microorganisms. Similarly, Tice and Lowe (2004, 2006) and Tice (2009) made a detailed microscopic and isotopic study of laminated structures in the 3.4 Ga-old Kromberg Formation in the Barberton Greenstone Belt, interpreted in terms of a diversity of mats related to specific local environments in a littoral environment.

Among all proxies, *in situ* calcification, which is a common signature of modern, lithifying photosynthetic microbial mats (Supplementary Fig. 1; Défarge et al., 1994, 1996; Dupraz et al., 2009), is one feature