Precambrian Research 298 (2017) 530–551

Contents lists available at ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

Iron mineralization and taphonomy of microfossils of the 2.45–2.21 Ga Turee Creek Group, Western Australia

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ARTICLE INFO

Article history:
Received 21 June 2016
Revised 30 June 2017
Accepted 4 July 2017
Available online 5 July 2017

Keywords:
Microfossils
Siderite
Iron oxidation
Chert
Turee Creek Group
Great Oxidation Event

ABSTRACT

We report a new assemblage of carbonaceous microfossils intimately associated with siderite and Fe-silicates, from a black chert nodule included in iron formation of the ca. 2.45–2.21 Ga Turee Creek Group, Western Australia. This chert comprises microbial fabrics dominated by filaments preserved in matrix of nano- to micrometric quartz. Filaments occur in clumps and in a cobweb-like fabric interspersed with coarse crystalline, void filling quartz granules. We studied this chert with optical microscopy combined with Scanning Transmission Electron Microscope observations of Focused Ion Beam sections of microfossils. This distinguished three types of well-preserved fossil interpreted as polysaccharide sheaths that usually do not preserve chains of cells (trichomes): Type 1 comprises narrow filaments with thin continuous kerogen sheaths, Type 2 comprises narrow filaments with thick granular sheaths, and Type 3 comprises broad filaments with thin sheaths. Type 4 filaments are poorly preserved as granular kerogen. Organic ultrastructures of Type 2–4 microfossils are variably replaced by siderite crystals, associated with minor Fe-silicates. Iron isotope analyses on bulk powder and reactive iron fraction show indistinguishable and highly positive δ^{56}Fe values (+1.45‰ relative to the reference IRMM-014), indicating that the bulk of siderite derives from reduction of Fe(III)-oxides. This provides indirect evidence that the microbial community was originally associated with Fe(III)-oxides. Siderite and Fe-silicates are found with Type 2–4 but not Type 1 filaments, suggesting that only the former were encrusted by Fe(III)-oxides, which may have been reduced *in situ*. Siderite and Fe-silicates could result from oxidation of organic matter in filaments coupled with microbial and/or thermal reduction of Fe(III)-bio(?)minerals. The increasing abundance of siderite correlated with decreasing organic matter preservation in filaments supports that this reaction occurred to variable extents, *in situ* on each microfossil. Type 2–4 microfossils may thus represent iron-oxidizing bacteria. These microbial mats display strong similarities with those associated with immediately overlying carbonate rocks of the Turee Creek Group, where filaments were interpreted as sulfur-oxidizing bacteria. Some filamentous bacteria can oxidize both iron and sulfur. Such metabolic versatility could have enabled benthic microbial mats to thrive in the drastically changing chemical conditions of the Great Oxidation Event.

1. Introduction

Although the timing of the first emergence of O_2 producing photosynthesis is unresolved (Lyons et al., 2014; Schopf, 2014), several geochemical tracers recorded the production of free O_2 by photosynthetic cyanobacteria as early as 2.9 Gyrs ago (Anbar et al., 2007; Crowe et al., 2013; Farquhar and Wing, 2003; Frei et al., 2009; Garvin et al., 2009; Kendall et al., 2010; Partin et al., 2013; Planavsky et al., 2014; Reinhard et al., 2013; Thomazo et al., 2011). The disappearance of mass-independent fractionation of sulfur isotopes (MIF-S) indicates the rise of O_2 in the upper layers of the atmosphere at least ca. 2.45 Ga ago (Farquhar and Wing, 2003; Reinhard et al., 2013). This marks the beginning of a substantial rise of free O_2 in the atmosphere named the Great Oxidation Event (GOE, Holland, 2002) and coincides with the end of the Archean eon and a paucity in the deposition of Banded Iron Formations (BIF) (Van Kranendonk, 2010). This GOE was observed for the first time in the Huronian Supergroup, Southern Canada (Hoffman, 2013; Roscoe, 1968). The Huronian Supergroup contains three

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http://dx.doi.org/10.1016/j.precamres.2017.07.003
0301-9268/

formations with diamictites indicating that glacial episodes coincided with the rise of O_2 in the atmosphere during a widespread shutdown of magmatic activity (Condie et al., 2009) associated with a possible drop of biological CH_4 (Konhauser et al., 2009). The development of sulfidic water formed by sulfate reduction also induced a decrease of Fe concentrations (through Fe-sulfide precipitation) in the ocean and likely represent the main cause for the absence of BIF deposits between 1.8 and 0.8 Ga (Anbar and Knoll, 2002; Canfield, 1998; Rasmussen et al., 2012).

The Turee Creek Group (2.45–2.20 Ga) of Western Australia was deposited during the GOE. It conformably overlies BIFs of the Boolgeeda Iron Formation (Van Kranendonk, 2010). The Turee Creek Group contains diamictites recording a glaciation (Martin, 1999; Van Kranendonk, 2010) that could correspond to one of the two lower Huronian glaciations (Hoffman, 2013). In the Turee Creek Group, S isotope compositions of pyrite in shales that directly overly the Boolgeeda BIF show a 90‰ range (δ^{34}S from −45.5‰ to +46.4‰), suggesting microbial sulfate reduction under non-sulfate limiting conditions (Williford et al., 2011). This result implies significant oxidative weathering of sulfides on the continents, due to atmospheric O_2 accumulation. Small MIF-S are, however, preserved in these shales, suggesting that pO_2 remained low enough to produce MIF-S (Williford et al., 2011), although this may reflect a time lag between atmospheric oxygenation and MIF-S disappearance in the sedimentary record (Reinhard et al., 2013).

Gunflint-type microfossil assemblages dominate the post-GOE fossil record between 2.1 and 1.7 Ga (Barghoorn and Tyler, 1965; Knoll et al., 1988; Knoll and Barghoorn, 1976; Lepot et al., 2017). Gunflint-type microfossil assemblages are dominated by filamentous microfossils (*Gunflintia*) of ca. 1–5 μm in diameter, spherical microfossils (*Huroniospora*) ca. 1.5–12 μm in diameter, and generally comprise uncommon star-shaped microfossils (*Eoastrion*) and scarce umbrella-shaped microfossils (*Kakabekia*). This assemblage has been exemplified by the Gunflint Iron Formation (Canada) occurrence discovered in the 1950 (Barghoorn and Tyler, 1965). The Paleoproterozoic era is dominated by Gunflint-type assemblages (Awramik and Barghoorn, 1977; Barghoorn and Tyler, 1965; Knoll et al., 1978). Moreover, the characterization of nanoscale textures of fossil cell walls or fossil polysaccharide sheaths and the textures of associated entombing quartz provided criteria of biogenicity for the identification of much older microfossils (Moreau and Sharp, 2004; Wacey et al., 2012). The metabolism of filamentous microfossils in the Gunflint-type assemblages is, however, ambiguous (Shapiro and Konhauser, 2015) and could correspond to oxygenic photosynthetic cyanobacteria (Barghoorn and Tyler, 1965) as well as iron-oxidizing bacteria (Cloud, 1965; Planavsky et al., 2009). Microfossil assemblages dominated by filaments have been found in blacks cherts of the Kazput Formation in the upper part of the Turee Creek Group (Schopf et al., 2015; Van Kranendonk et al., 2012). In contrast to many Gunflint-type assemblages that formed stromatolitic mats of microfossils in shallow-water (*e.g.* Barghoorn and Tyler, 1965), the Turee Creek microfossils formed cobweb-like structures in relatively quiet, possibly deeper water similar to the assemblages of the 1.8 Ga Duck Creek Formation (Schopf et al., 2015). Based on environment, isotope ratios of organic carbon and pyritic sulfur, and the morphological similarity between the observed filaments and modern S-oxidizing and/or S-reducing bacteria, it has been proposed that the Duck Creek and Turee Creek microfossil assemblages are dominated by filamentous sulfur-metabolizing organisms of a sulfuretum, a microbial community using sulfur by oxidation and reduction metabolisms in a cyclic fashion (Schopf et al., 2015; Van Kranendonk et al., 2012).

The mineral assemblage associated with microfossils may provide important constraints on the nature of the microfossils and on diagenetic processes. Some Gunflint-type microfossils are intimately associated and/or replaced by hematite (Knoll and Simonson, 1981), which has been used to support iron metabolism (Cloud, 1965; Planavsky et al., 2009). However, association of hematite with microfossil may reflect taphonomic processes rather biomineralization induced by the microorganisms (Shapiro and Konhauser, 2015). Similarly, replacement of organic matter by pyrite in Gunflint-type microfossils is a common taphonomic process (Wacey et al., 2013). In contrast, intra-microfossil Fe-silicates (greenalite) and Fe-carbonates (siderite, $FeCO_3$) were observed in specific morphospecies of the Gunflint Iron Formation (Lepot et al., 2017). The Fe-minerals were interpreted as products of reductive recrystallization of intracellular Fe-biominerals and used to infer that these morphospecies were cyanobacteria performing oxygenic photosynthesis (Lepot et al., 2017).

Here we report Turee Creek Group microfossils that are well preserved to fully replaced by siderite and associated with iron silicates. This study characterized their ultrastructures and the associated mineralizations by nanoscale petrography. Based on textures, mineralogy, elemental composition and bulk-rock isotope ratio of iron (δ^{56}Fe), carbon (δ^{13}C), and oxygen (δ^{18}O), we discuss the metabolism, the environment, the taphonomy and the diagenetic and metamorphic histories of these microfossils.

2. Geological setting

The Turee Creek Group reaches a maximum of 4 km in thickness in the Hardey Syncline (Fig. 1). It comprises, in ascending stratigraphic order: the Kungarra Formation (that contains the Meteorite Bore Member), the Koolbye Formation and the Kazput Formation (Fig. 1D). The Kungarra Formation is composed of approximately 3 km of clastic sediment grading from siltstone, mudstone and shales with minor dolomite that are interpreted as distal turbidites at the base, to grained sandstones with stromatolitic carbonates deposited in shallow water setting (Martindale et al., 2015; Van Kranendonk et al., 2015). The Meteorite Bore Member of the Kungarra Formation consists of 270 m of glaciogenic diamictites and siltstones that have been correlated with the Huronian glaciations (Eriksson and Condie, 2014; Lindsay and Brasier, 2002; Martin, 1999; Martin et al., 2000; Van Kranendonk et al., 2015). The Koolbye Formation that conformably overlies the Kungarra formation, includes 130 m of quartzarenite, siltstone and minor conglomerate deposited in coastal–fluvial setting (Mazumder et al., 2014; Van Kranendonk et al., 2015).

The Kazput Formation, the final stage of the Turee Creek Group displays two mains units (Fig. 1D). The lower unit is mainly composed of dolomite and mudstones, while the upper unit consists mainly of siltstones and fine-grained sandstones (Barlow et al., 2016; Lindsay and Brasier, 2002; Martin et al., 2000; Martindale et al., 2015). Finally, the Lower Wyloo Group succeeds the Turee Creek group above an erosional unconformity and is composed of the Beasley River Quartzite and the Cheela Springs Basalt (Fig. 1D) (Eriksson et al., 1999; Martin, 1999; Martin et al., 2000). The age of the Turee Creek Group is constrained by the underlying Woongarra Rhyolite (2449 ± 3 Ma, (Barley et al., 1997) and the overlying Cheela Springs Basalt (2209 ± 15 Ma, Martin et al., 1998). Detrital zircons in the Meteorite Bore Member indicate a maximum age of deposition of ca. 2420 Ma (Takehara et al., 2010). Hence, the microfossiliferous cherts of the overlying Kazput Formation are 2209 to 2420 Ma old.

The black chert samples studied here were collected within the lower, carbonate-dominated unit of the Kazput formation in the Kazput Syncline locality, at S22°29.748′, E116°31.817′ (see Fig. 1C) (Barlow et al., 2016), distinct from the locality of chert reported by Schopf et al. (2015) and Van Kranendonk et al. (2012). There, the sequence consists in shallow-water (domical,