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Evidence of biogeochemical processes in iron duricrust formation

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ABSTRACT

Canga is a moderately hard iron-rich duricrust primarily composed of goethite as a result of the weathering of banded iron formations. Canga duricrusts lack a well-developed soil profile and consequently form an innate association with rupestrian plants that may become ferruginised, contributing to canga possessing macroscopic biological features. Examination of polished canga using a field emission scanning electron microscope (FE-SEM) revealed the biological textures associated with canga extended to the sub-millimetre scale in petrographic sections and polished blocks. Laminae that formed by abiotic processes and regions where goethite cements were formed in association with microorganisms were observed in canga. Biological cycling of iron within canga has resulted in two distinct forms of microbial fossilisation: permineralisation of multispecies biofilms and mineralisation of cell envelopes. Goethite permineralised biofilms frequently formed around goethite-rich kaolinite grains in close proximity to goethite bands and were composed of micrometre-scale rod-shaped, cocci and filamentous microfossils. In contrast, the cell envelopes immobilised by authigenic iron oxides were primarily of rod-shaped microorganisms, were not permineralised and occurred in pore spaces within canga. Complete mineralisation of intact rod-shaped casts and the absence of permineralisation suggested mineralised cell envelopes may represent fossilised iron-oxidising bacteria in the canga ecosystem. Replication of these iron-oxidising bacteria appeared to infill the porous regions within canga. Synchrotron-based Fourier transform infrared (FTIR) microspectroscopy demonstrated that organic biomarkers were poorly preserved with only weak bands indicative of aliphatic methylene (CH_2) associated with permineralised microbial biofilms. High resolution imaging of microbial fossils in canga that had been etched with oxalic acid supported the poor preservation of organic biomarkers within canga, indicating mineralogical replacement of organic biomarkers.

1. Introduction

The increased demand for steel as a base metal in the construction industry has resulted in an exponential increase in the production of iron ore, with over 300 million tons produced from Brazil each year (Yellishetty et al., 2010). Iron ore is extracted from vast opencast mines that impact the natural landscape and associated biome. Pre-mining, these iron ore systems are capped by canga, a ferruginous duricrust. Canga is composed of detrital fragments of hematite and itabirite cemented together by secondary goethite that forms a moderately hard, permeable layer with a typical thickness of approximately 10 metres (Dorr, 1964). Insect bore holes and root structures are commonly associated with canga and contribute to the macroscopic biological features that are routinely observed (Fig. 2A).

Canga is enriched in iron oxides via the extensive weathering of banded iron formations (BIFs), which results in the dissolution of the silica-rich layers and precipitation of relatively stable iron oxides in the void spaces between resistant hematite crystals (Dorr, 1964). Canga forms a relatively chemically and mechanically resistant layer that protects the underlying friable high-grade iron ore in the weathering profile of iron ore systems (Dorr, 1964, 1973; Melfi et al., 1988; Shuster et al., 2012).

Canga hosts an astonishing ecosystem containing hundreds of rupestrian plant species, several of which are naturally rare and endemic to canga-associated habitats (Jacobi et al., 2007; Gibson

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et al., 2010; Jacobi and Carmo, 2011; Yates et al., 2011; Messias et al., 2013). Iron ore mining operations in Brazil pose a threat to the biodiversity associated with canga ecosystems. Despite an iron content of up to 60%, canga is typically removed as a waste by-product of iron ore mining due to the compositional variation as well as high phosphorus and alumina concentrations compared with the underlying high-grade iron ore (Dorr, 1964). Canga has a phosphorus concentration of approximately 0.1% $_{(wt/wt)}$ (Dorr, 1964), which is likely to be adsorbed within the structure of goethite (Fontes and Weed, 1996; Monteiro et al., 2014). Canga is customarily removed and stock piled prior to the commencement of iron ore mining, destroying the vegetation and severely impacting the associated ecosystem (Toy and Griffith, 2001).

Hillslope stabilisation, soil erosion and long-term revegetation programs have been identified as key targets in the remediation of iron ore mines in Brazil (Griffith and Toy, 2001). Concerted rehabilitation efforts involving iron ore mining companies, the government, ecologists and environmental geologists must be made to protect the remaining native biome and to overcome challenges with the restoration of canga-associated habitats post-mining (Skirycz et al., 2014). Re-cementation of canga is the first stage towards the successful rehabilitation of areas mined for iron ore. Canga re-cementation will restore the landscape, prevent erosion and provide a natural platform for the revegetation of plant species following the removal of high-grade iron ore. Understanding the chemical and biological processes that contribute to canga genesis is imperative for the accelerated re-cementation of canga.

Canga ecosystems are considered to be dynamic, formed via the continued dissolution and precipitation of secondary goethite, which contributes to their complex textures (Fig. 2A) and self-healing properties (Monteiro et al., 2014); however, the mechanisms responsible for the cycling of iron that contribute to canga genesis are poorly understood. Dorr (1964) stressed the need to determine the role of bacteria in the formation of canga. A detailed geochronological, petrographic and geochemical study conducted by Monteiro et al. (2014) indicated that biological processes were likely to be the major mechanism driving the reductive dissolution of iron oxides in canga. Parker et al. (2013) also supported the hypothesis that microbial reductive dissolution of Fe(III) oxides is critical to the transport and cycling of iron in canga. Conversely, processes responsible for the precipitation of several goethite generations and textures in iron systems (Ramanaidou, 2009) require investigation. Evidence of increased near-surface cycling of iron in biological regions (Monteiro et al., 2014), highlights the need to determine the role of microorganisms in the genesis of canga.

Iron-oxidising and iron-reducing bacteria are essential to the environmental cycling of iron (Schröder et al., 2003; Emerson et al., 2010). In anoxic environments, iron-reducing bacteria respire using ferric iron as a terminal electron acceptor, resulting in the production of ferrous iron (Reaction 1; de Castro and Ehrlich, 1970). Conversely, a wide range of neutrophilic iron-oxidising bacteria enzymatically oxidise ferrous iron, producing ferric iron (Reaction 2; Emerson and Revsbech, 1994). Iron-oxidising and iron-reducing bacteria have been cultured in close juxtaposition at the redox boundary, which may result in rapid cycling of iron in circumneutral environments (Roden et al., 2004). Therefore, iron-oxidising and iron-reducing bacteria may significantly contribute to the cycling of iron, driving the continued dissolution and precipitation of iron oxyhydroxides, identified to be critical to the formation of canga (Monteiro et al., 2014).

$$CH_2O + 4\,Fe^{3+} + H_2O \rightarrow 4\,Fe^{2+} + CO_2 + 4\,H^+ \quad (1)$$

$$Fe^{2+} + \tfrac{1}{4}\,O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\,H_2O \quad (2)$$

Iron-oxidising bacteria are most likely to play a key role in microaerobic niches within canga, a circumneutral environment, to avoid the loss of their energy source via abiotic ferrous iron autooxidation (Sobolev and Roden, 2001; Rentz et al., 2007). In aerobic circumneutral environments, ferric iron produced via iron-oxidising bacteria (Reaction 2) is unstable and rapidly hydrolyses to form amorphous 2-line ferrihydrite (Reaction 3) that can precipitate on the cell envelope of iron-oxidising bacteria (Hallberg and Ferris, 2004; Corbari et al., 2008), and which has been demonstrated to resist recrystallisation to goethite in the presence of bacteria (Kennedy et al., 2004). The phase stabilisation of ferrihydrite by bacteria is possibly a result of the inhibition of crystal rotation, preventing the transformation of ferrihydrite to goethite (Banfield et al., 2000). Salama et al. (2013) suggested heavily encrusted bacterial filaments may coalesce to form goethite. The diagenetic controls on the transformation of biogenic iron oxides together with potentially preserved biosignatures continue to be areas of active research. Extensive encrustation of iron-oxidising bacteria may contribute to cell fossilisation, which can be utilised to identify the presence of biomolecules including organic functional groups that may be precursors to cellular components, termed biomarkers (Kennedy et al., 2004; Miot et al., 2009).

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_3 + 3\,H^+ \quad (3)$$

To investigate the role of bacteria in the formation of canga, the present study aimed to determine the occurrence and distribution of microbial fossils in canga using scanning electron microscopy and to employ Fourier transform infrared (FTIR) spectroscopy to identify the presence of organic biomarkers within hotspots of paleobiological activity. Acid dissolution experiments have previously exposed microbial remnants in carbonates (Power et al., 2011). Using a similar approach, iron oxides were dissolved using oxalic acid, a powerful iron chelator (Panias et al., 1996), to release cell components from canga. Insight into the hypothesised role of microorganisms in the formation of canga (Dorr, 1964; Monteiro et al., 2014) is important to the development of an accelerated canga restoration program following the removal of the underlying iron ore.

2. Materials and methods

2.1. Site description and sample collection

The Carajás mineral province of northern Brazil has a tropical climate with an approximate annual rainfall of 1800 mm largely falling in the wet season (November–March) and a consistent average annual temperature of 26 °C. Geological, petrographic and geochemical studies of the Carajás mineral province have demonstrated that canga occurring above weathered banded iron formations is composed of goethite cements (Tolbert et al., 1971; Figueiredo e Silva et al., 2011). Hand-samples of canga were collected from the Vale S.A. N1 site located in the eastern aspect of Carajás mineral province in the State of Pará, Brazil (Fig. 1). Canga samples were in close proximity to surface water and vegetation and contained macroscopic biological inclusions, including an association with plant roots and insect bore holes, as well as goethite bands, which indicated the circulation of soluble iron. A rock hammer was used to collect canga hand samples, which were highly consolidated and exposed at the surface, with the notable absence of a soil layer (Fig. 2A).

2.2. Microscopy

Canga samples were prepared as: petrographic thin sections for