



Theoretical effects of industrial emissions on colour change at rock art sites on Burrup Peninsula, Western Australia



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ABSTRACT

Burrup Peninsula in northwest Western Australia, with an estimated one million petroglyphs, has the world's largest concentration of ancient rock art. It is one of a few places in the world where a continuous history of people living with a changing environment for over 40,000 years is recorded through rock art. The art is under threat due to high concentrations of acidic and nitrate-rich pollution from nearby industrial complexes. Maintenance of the outer, rock or desert varnish, layer of the rocks is essential for preservation of the art. An increase in acidity of rock surfaces through acid rain and organic acids from nitrate-stimulated microbial growth may alter the mineral composition, integrity and colour of the rock varnish. This paper describes analyses of distilled water washings from rocks on Burrup Peninsula compared with rocks collected prior to industrialisation. Acidity of rock surfaces has increased from near neutral to a pH just above 4. The increasing acidity has been associated with a logarithmic increase in solubilisation of manganese (Mn) and iron (Fe) compounds from the rock surfaces. A theoretical evaluation using electrochemical equilibrium principles confirms that increasing acidity will increase the solubilisation of Mn and Fe compounds. Removal of darker Mn and Fe mixed M(II)/M(III) compounds from the outer, rock varnish layer and the relative increase in ferrous oxide and illite/kaolin compounds will result in the rock surface layers becoming thinner, lighter, redder and more white/yellow over time. The impact on engraved surfaces would be expected to be greater because the rock varnish is thinner than on the non-engraved surface rock. Pollution from industry on Burrup Peninsula is likely to destroy the rock art over time.

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1. Introduction

The rock engravings (petroglyphs) on Burrup Peninsula in north-west Western Australia comprise one of the most significant archaeological sites in the world (Bird and Hallam, 2006; Donaldson, 2009; Mulvaney, 2011). The area contains over 1,000,000 engravings documenting the lives and spiritual beliefs of the first Australians (Fig. 1) through a rapidly changing environment and extending over > 40,000 years. The oldest known images of the human face, dating back at least 30,000 years, are found on this Peninsula. Engravings depict extinct animals, including mega fauna, Tasmanian tiger (*Thylacines*), fat-tailed kangaroos, as well as many different species of birds, land and marine animals. There are numerous geometric forms and intricately carved standing stones with large and small circular engravings within separated compartments; perhaps being a form of calculation or navigation. The art is extraordinary in its beauty and its diversity. Its hidden symbolism is only now being decoded.

Petroglyphs on Dampier Archipelago are carved into the weathering rind of the parent granophyre and gabbro igneous rock types (Fig. 2). The weathering rind varies in thickness from a few microns to around 10 mm, depending on the time from fracture of the rock and other conditions (Bednarik, 2007; Donaldson, 2011). The rind has a hard, dark-coloured outer coating, or patina, often called rock, or desert varnish. This patina is thin, from <1 to 200 µm thick (Liu and Bröcker, 2000). Petroglyphs are formed by breaking through the patina into the softer and lighter coloured partially weathered rock consisting largely of kaolinite clays formed from decomposing feldspars (Bednarik, 2002; Pillans and Fifield, 2013). The petroglyphs rarely penetrate the hard, unaltered parent rock. The petroglyphs are visible, initially, because of a colour and contour contrast. However, rock varnish forms over the engraving and after 20,000 to 30,000 years the colour contrast becomes small as seen in Fig. 2.

Rock varnish forms in desert environments under low rainfall, arid conditions. It is extremely slow forming, at a rate of <1 to 10 µm per thousand years, but under some slightly wetter circumstances the rate can be as high as 40 µm per thousand years (Dorn and Meek, 1995; Liu and Bröcker, 2000; Dorn, 2009a). The layer is formed by the extraction of clay and minerals through inorganic and organic, lithobiont,

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Fig. 1. Examples of petroglyphs on Burrup Peninsula.

processes from ambient dust particles deposited on the rock (Engel and Sharp, 1958; Dorn, 2009a). Rock varnish is composed of approximately 70% clay minerals, primarily as montmorillonite and kaolinite, 25% manganese (Mn) and iron (Fe) oxides and hydroxides, with the remainder being oxides and hydroxides of several dozen minor and trace elements (Potter and Rossman, 1977; Garvie et al., 2008; Dorn, 2009a).

A unique feature of rock varnish is the high concentration of Mn, which is 50 to 300 times greater than the source dust material (Engel and Sharp, 1958; Dorn, 2004; Dorn, 2009b). The ratio of Mn to Fe in surrounding soil is around 1:40 to 1:60, but the ratio in rock varnish is approximately 1:1 (Dorn, 2004). Concentrations of Mn and Fe are enhanced in rock varnish through activity of an extremely small number of bacteria and micro-colonial fungi, thought to be as low as five per hundred years (Flood et al., 2003; Dorn, 2009b). These microorganisms deposit Mn and Fe compounds in their outer sheath as a means of protection from the extremely harsh environment and lay dormant for long periods between wetting events. The Mn and Fe compounds concentrated in bacteria and fungi become chemically bound in the crystalline structure and external coating of the clay minerals, which cements the clays to rock surfaces (Dorn, 2009a). Fossils of these Mn and Fe rich microorganisms have been observed within the structure of rock varnish (Flood et al., 2003).

The ratio of Mn to Fe in the rock varnish varies with climatic conditions (Broecker and Liu, 2001). Fe concentrations rise relative to Mn in dryer more alkaline conditions, whereas Mn deposition is relatively greater in more moist conditions when bacteria and fungi produce organic acids. Colour of rock varnish varies with the proportion of dark

Mn compounds relative to the proportion of redder ferrous oxide compounds.

A man-made land bridge formed Burrup Peninsula on the southern end of Dampier Archipelago. Burrup Peninsula is the site of a large petrochemical industrial complex including two liquefied natural gas (LNG) plants, a fertiliser plant producing ammonia and urea, and a recently constructed ammonium nitrate plant. Acidic emissions, primarily as NO_x (nitric oxide and nitrogen dioxide) compounds, from the LNG and fertiliser plants were approximately 36,000 t in 2014 (Woodside, 2016; Yara Pilbara, 2016). The new ammonium nitrate plant is proposed to release a total acid load into the atmosphere of 200 meq/m²/year, primarily as NO_x compounds (which equates to 20 t of nitrate over an area of 100 km²/year) as well as 25.2 t/year of ammonium nitrate PM₁₀ dust particles. These industrial plants are situated amongst the world-significant rock art sites. The emissions will cause acid rain and increase the acidity of the Burrup rocks and the deposition of nitrogen on the rocks will stimulate growth of adventitious organisms including bacteria, yeasts, fungi and lichens (MacLeod, 2005; Giesen et al., 2014). These growing organisms release their metabolites which are organic acids onto the rocks. Acids from the rain and microbial activity dissolve the Mn and Fe compounds in rock varnish and both varnish composition and colour will change when varnish erosion from acids is faster than varnish formation (Gordon and Dorn, 2005).

Colour measurements have been made by CSIRO at seven rock art sites on Burrup Peninsula from 2004 to 2014 (Lau et al., 2007; Lau et al., 2013; Markley et al. 2015). These authors claimed there have been no consistent trends in colour change in either an increasing or

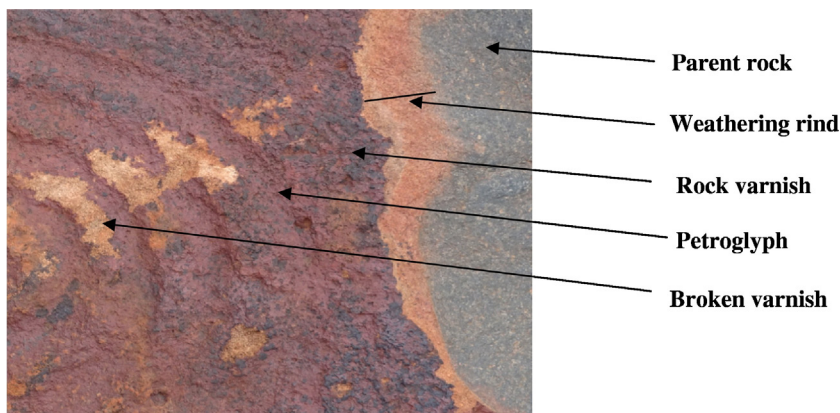


Fig. 2. Burrup rock with petroglyph showing parent rock, weathering rind and the rock varnish patina.

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