



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-western 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 Brøecker, 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 Brøecker, 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

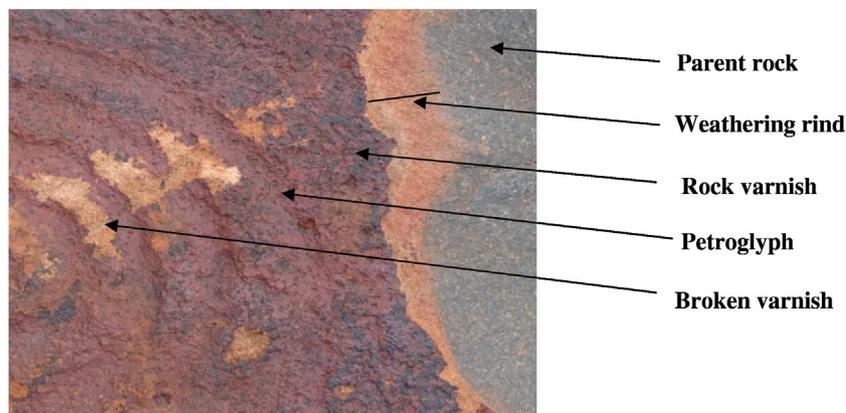


Fig. 2. Burrup rock with petroglyph showing parent rock, weathering rind and the rock varnish patina.

decreasing direction over the 11 years of measurement. The claim was made without statistical analyses of colour change over time. However, these reports are being used by government and industry to justify the placing of additional industry, particularly the ammonium nitrate plant, on Burrup Peninsula (EPA, 2011). Colour measurements on complex and deeply fissured surfaces that characterize the rocks on which the engravings have been made are difficult and need a high degree of experimental rigour to gain accurate results. This paper provides results from a previous study on the impact of acidity on solubilisation of Mn and Fe compounds from the surface of rocks on Dampier Archipelago (MacLeod, 2005), plus a theoretical assessment of changes in mineral compounds and likely colour changes based on Pourbaix Eh-pH electrochemical equilibrium principles.

2. Methods

MacLeod (2005) described methods used to measure pH, salts (including chloride, nitrate, nitrite, sulphate and oxalate) and Mn and Fe compounds on the surface of rocks at a wide range of sites across Burrup Peninsula and adjacent islands. A standardised area of 200 cm² of rock surface was washed with double distilled water. Soluble salts collected in the wash were measured by ion chromatography and metal ions were determined by inductively coupled plasma-mass spectrometric (ICP-MS) methods. Washings from rock surfaces were obtained in June 2003, August 2003 and February 2004. Although a wide range of salts and ions were measured, this paper deals only with the various Mn and Fe ionic compounds. There were insufficient concentrations of Mn and Fe ionic species in some washings for reliable measurement and these were not included in the analyses. A similar process was used to obtain washings from samples of Burrup Peninsula rocks collected prior to industrialisation of the region. These rocks would have minimal contamination because they were stored in a controlled environment, in infrequently-accessed, museum compactus shelves at the Western Australian Museum.

The concentration of Fe₀₂, Fe₀₄, Mn₀₅, Mn₀₃ and Mn₀₂ in the rock washings were related to pH to assess the effect of pH on solubility of ions from various rock varnish compounds using standard regression analysis techniques. The data were log₁₀ transformed for 'normalisation' so pM (−log₁₀[Mⁿ⁺] or [Feⁿ⁺]) versus pH plots could be used to determine the nature of the species undergoing dissolution.

The Pourbaix Atlas of Electrochemical Equilibria in Aqueous Solutions (Pourbaix, 1974) was used to evaluate the theoretical impacts of changes in pH from preindustrial times on the likely solubilisation of various Mn and Fe compounds in the patina from rocks on Burrup Peninsula. The changes in Mn and Fe compound concentrations were used to estimate the trend in patina colour changes that may be expected as acidity increases on the surface of rocks on Burrup Peninsula.

3. Results

3.1. Burrup rock measurements

Solubilisation of both Mn and Fe compounds increased logarithmically as acidity of the rock surface increased (Fig. 3). The regression analysis results for Mn and Fe ionic groups, expressed as log₁₀ ppm (Table 1), shows these relationships were strong with R² values of 0.97 or above, except for Mn₀₅ where R² was 0.82. Substantially more iron was mobilised from rock surface compounds than manganese as acidity increased. The mean slope of the relationship was approximately −2.0 for Fe ions and approximately −0.75 for Mn ions.

Washings from the rocks collected pre-industrialisation provided a mean pH value of 6.8 ± 0.2. Extrapolation of the regression relationships to neutral pH (7) shows the inherent solubility of metal ions on the surface of rocks collected prior to industrialisation. The consequent molar concentrations of the different minerals at pH 7 were: Fe₀₄, e^{−6.15}; Fe₀₂, e^{−5.43}; Mn₀₅, e^{−4.38}; Mn₀₃, e^{−4.22}; Mn₀₂, e^{−4.08}. These higher concentrations of Mn ion compounds than Fe compounds at pH 7 show that Mn compounds are approximately 100 times more soluble than Fe₀₄ compounds, which are approximately 5 times less soluble than Fe₀₂ compounds.

3.2. Theoretical changes in Mn and Fe compounds with pH

The Pourbaix electrochemical equilibrium diagram for Mn (Fig. 4) shows, at alkaline pH found on rocks in many desert environments, Mn compounds within the aqueous range of Eh voltage values consist of Mn(OH)₂, Mn₃O₄, Mn₂O₃ and MnO₂. As pH falls with increasing acidity, these Mn compounds will be solubilised in approximately the same order, with the darker black-brown hydroxides and higher oxides dissolving before the browner MnO₂. Solubilised manganese species consisting of Mn²⁺ and Mn³⁺ ions will be washed from the surface

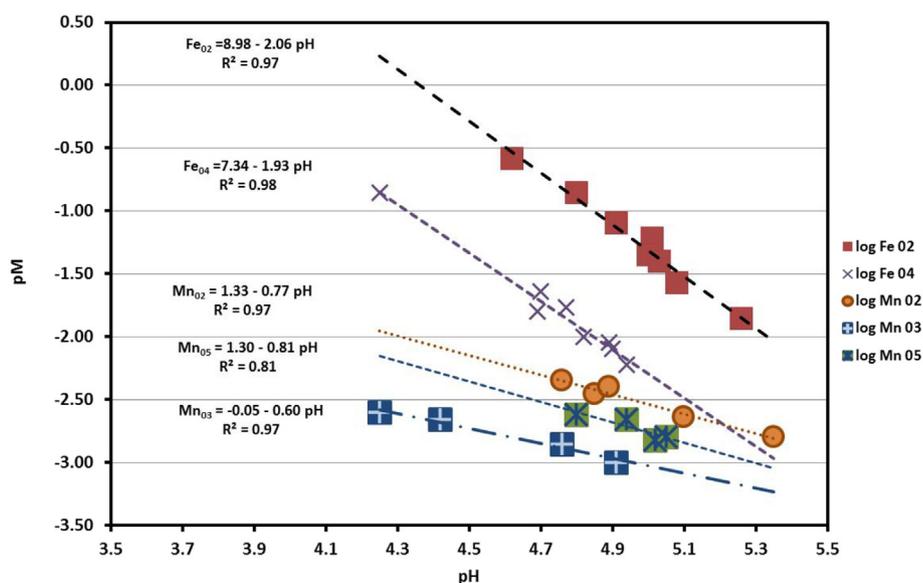


Fig. 3. Relationship between pH and concentration (PM, log₁₀ ppm) of iron and manganese minerals in the washings from rocks on Burrup Peninsula. The slope of the relationships indicates the increase in solubility of rock varnish compounds as acidity increases.

Table 1

Linear regression of the relationship between pH and \log_{10} ppm concentration of iron and manganese minerals in washings collected from rocks on Burrup Peninsula.

Metal ion	Slope	Intercept	R ²
Fe ₀₄	-1.93 ± 0.12	7.34 ± 0.56	0.98
Fe ₀₂	-2.06 ± 0.14	8.98 ± 0.70	0.97
Mn ₀₅	-0.81 ± 0.27	1.30 ± 1.36	0.82
Mn ₀₂	-0.77 ± 0.08	1.33 ± 0.42	0.97
Mn ₀₃	-0.60 ± 0.07	-0.05 ± 0.32	0.97

of the rock when rain is sufficient. As pH falls from pre-industrial values to the lowest measured values of approximately 4, Mn compounds will dissolve from the rock varnish. The pM vs pH slope of -0.75 for manganese (Fig. 3) shows that this reaction involves dissolution of the mixed oxidation state of manganous-manganic oxide, Mn₃O₄.

A similar Pourbaix diagram for Fe compounds (Fig. 5) shows as pH falls within the aqueous range of Eh values, magnetite (Fe₃O₄) solubilises before iron oxide (Fe₂O₃). Solubilised Fe²⁺ and Fe³⁺ ions will be washed from the surface of the rock when rain is sufficient. As pH falls from pre-industrial values to the lowest measured values of approximately 4, Fe compounds will dissolve from the rock varnish.

4. Discussion

Results from analyses of the washings from rocks collected on Burrup Peninsula show that acidity of rock surfaces has increased significantly during the period of industrialisation. A reduction in pH has resulted in an increase in the solubilisation of both Mn and Fe compounds on a logarithmic scale. Mn compounds are more soluble

at neutral pH than Fe compounds. This finding is supported by Krauskopf (1957) who found that Fe compounds are less soluble than corresponding Mn compounds under naturally occurring Eh-pH conditions. However, the rate of dissolution of Fe compounds is greater than for Mn compounds as acidity increases. Solubilisation of Mn and Fe compounds in rock varnish would lead to removal of important compounds required to bind clay minerals to form the hard outer layer of the varnish and to bind it to rock inner surfaces. A predominant Mn compound in rock varnish is birnessite ((Na_{0.3}Ca_{0.1}K_{0.1})(Mn⁴⁺,Mn³⁺)₂O₄·1.5H₂O) with hexagonal structured sheets binding with clay minerals. Lefkowitz et al. (2013) demonstrated that birnessite sheets were disrupted when pH was <7.0. The varnish would become thinner and softer with removal of these Mn and Fe compounds. Composition and colour of rock varnish changes whenever varnish erosion from acids is faster than varnish formation (Gordon and Dorn, 2005).

Acid fog in the Santa Monica Mountains of southern California has been reported to dissolve rock varnish (Dorn, 1998), while erosion of rock varnish by acid rain has been reported in several locations in America (Microbe Wiki, 2016; National Park Service, 2016). Other evidence for the destruction of rock varnish with increased surface acidity comes from the observations of Bednarik (1979) with the dissolution of rock patina under bird droppings where the average pH was 5.9 across 30 sites in an area adjacent to Burrup Peninsula. Similarly, Engel and Sharp (1958) and Dragovich (1986) showed that rock varnish in arid environments was not present beneath growing lichen, presumably because of accumulation of organic acids.

Erosion of the rock varnish would destroy the petroglyphs on Burrup Peninsula. Once this hard outer layer of the weathering rind is eroded, the softer inner component would breakdown rapidly and petroglyphs would become indistinguishable on the rocks.

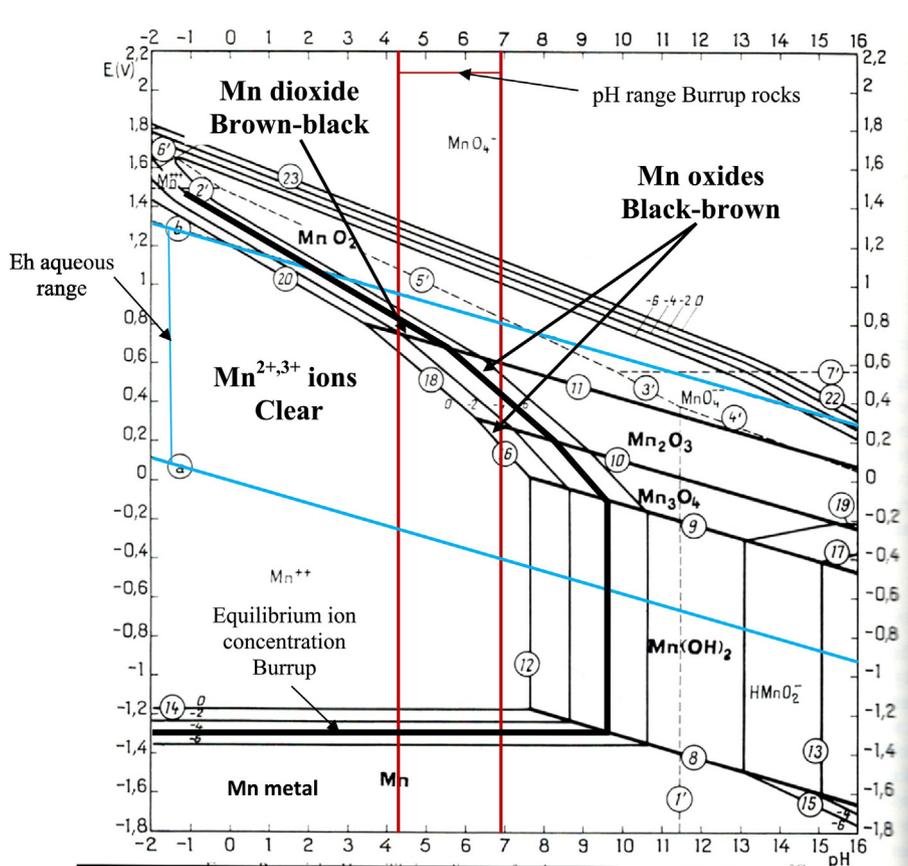


Fig. 4. Pourbaix electrochemical diagram for Mn compounds showing the effect of pH and Eh voltage on the solubility of Mn compounds. Red vertical lines represent the range of pH measured on Burrup rocks from pre-industrialisation. Blue sloping lines represent the range in aqueous solution Eh values. The very heavy black line represents the approximate molar concentration of Mn ionic compounds extracted from rocks on Burrup Peninsula. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

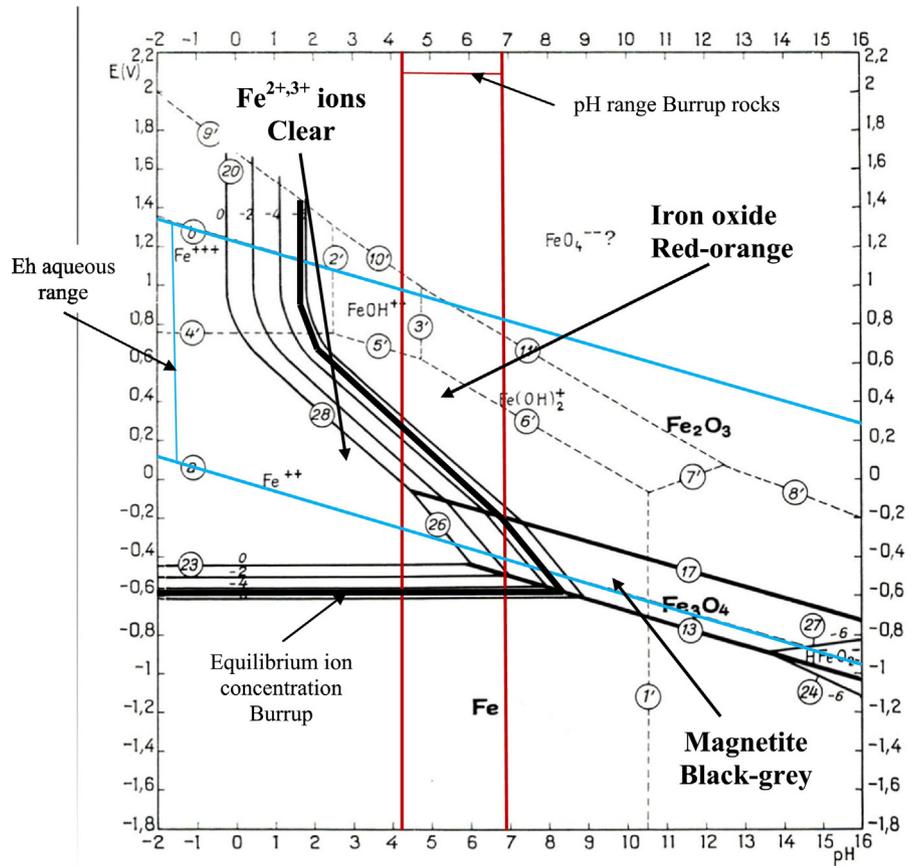


Fig. 5. Pourbaix electrochemical diagram for Fe compounds showing the effect of pH and Eh voltage on the solubility of Fe compounds. Red vertical lines represent the range of pH measured on Burrup rocks from pre-industrialisation. Blue sloping lines represent the range in aqueous solution Eh values. The very heavy line represents the approximate molar concentration of Fe ionic compounds extracted from rocks on Burrup Peninsula. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The Pourbaix diagrams show how the composition of rock varnish will change over time to a new equilibrium as pH falls. The darker coloured Mn oxides and hydroxides and the dark colour of magnetite (Fe_3O_4) will dissolve from the rock varnish leaving a higher proportion of the white/yellow illite and kaolinite clays. An increase in acidity will, therefore, lighten the colour of the rock surface. Similarly, the Pourbaix diagram suggests iron oxide will become relatively more abundant than the dark coloured magnetite and Mn compounds as pH falls tending to make the redder varnish redder in colour. An increase in acidity on the surface of rocks on Burrup Peninsula through acid rain from industrial emissions and increased microbial activity through greater nitrogen deposition will, from this theoretical analysis based on electrochemical principles, make the rock surfaces lighter, redder and more white/yellow in colour. The impact of acid on the engravings would be expected to be faster than for background rock because the varnish on engravings will be more recent, thinner and more easily eroded. [Bednarik \(2009\)](#) and [Mulvaney \(2015\)](#) observed a correlation between age of patination of Burrup rocks and colour, with rocks becoming darker over time.

[Bednarik \(2002\)](#) reported 'bleaching' of rocks on Burrup Peninsula from pre-industrial times to 2002, due to removal of the ferruginous surface crust caused by increasing surface acidity. Based on the International Federation of Rock Art Organisations standard colour assessment system, [Bednarik \(2002\)](#) predicted the petroglyphs would disappear during the second half of the 21st century at the then current levels of acid emissions and around 2030 if emissions were trebled.

The impact of windborne sea salts has previously been reported ([MacLeod, 2005](#)) as a natural way in which the alkalinity of the drying carbonate and borate solutions will tend to neutralise acidity from the metabolic activities of yeasts, moulds and fungi. However, the ability of the sea salt evaporates to neutralise the acidity coming from natural

rain events during severe thunderstorms is limited. Increasing nitrogen deposition on the surface of rock varnish results in proliferation of adventitious microorganisms that out compete the slow growing varnish forming organisms ([Dorn, 2009a](#)). Microbes on rock surfaces preferentially colonise along crevices and cleavages and would be concentrated in the rock engravings ([Barker et al., 1998](#)). Hyphae from fungal organisms will invade the softer clay layers of the weathering rind and erode the edges of the petroglyphs. Additional impact on the loading of micronutrients as the amount of soluble nitrate increases cannot be sourced from natural events and so there is a high probability of the previous equilibria not being able to be restored until the increased acid and nitrate loading from industry is abated.

5. Conclusions

Analysis of washings from rock surfaces on Burrup Peninsula showed acidity has increased from neutral pH pre-industrialisation to pH near 4. The increase in acidity resulted in a logarithmic increase in solubilisation of Mn and Fe compounds from the varnish layer of the rocks. A theoretical evaluation using electrochemical equilibrium principles confirms that increasing acidity will remove darker Mn and magnetite compounds from the rock varnish and increase the proportion of red ferrous oxide and lighter-coloured clay minerals. These changes will make the rock surfaces lighter, redder and more white/yellow in colour over time. The changes are expected to be greater on engravings than on background rock because the rock varnish will be more recent and thinner on the engravings. Destruction of the rock varnish will lead to destruction of the rock art archaeological treasure on Burrup Peninsula. Whilst the conclusions by [Lau et al. \(2007\)](#), [Lau et al. \(2013\)](#), [Markley et al. \(2015\)](#), that there have been no consistent colour changes at

rock art sites on Burrup Peninsula can be contested because of lack appropriate statistical analyses, the outcomes from this paper provide irrefutable evidence that the levels of pollution being emitted from industry on Burrup Peninsula will, over time, cause significant deleterious changes to the integrity and colour of the petroglyphs. The analyses also refute claims by government and industry that industrial emissions from the new ammonium nitrate production facility will not damage rock art on Burrup Peninsula.

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