Current Assessment of the Impact of Pollution on Murujuga Rock Art

John L Black in collaboration with Stéphane Hoerlé and Ron Watkins

Summary of a presentation in Karratha at the Murujuga World Heritage Summit – 6 August 2018

Summary

The petroglyphs of Murujuga are unique in the world. The Dampier Archipelago is the only known place where at least 45,000 thousand of years of human culture and spiritual beliefs through a changing environment are captured in rock engravings. Murujuga is also the location for a major petrochemical industrial complex which is served by one of the largest bulk handling ports in the world. Emissions from industry have increased acidity of rock surfaces at some rock art sites by more than 1000-fold from near neutral pH of 6.8 ± 0.2 pre-industry to as low as 3.8 ± 0.15 in 2017. Maintaining integrity of the outer rock patina is essential for survival of the petroglyphs. The patina is formed at an extremely slow rate of around 10 microns per 1000 years through biological and chemical processes under neutral to weakly alkaline conditions of desert environments. Acid dissolves the manganese and iron oxides in the patina. Theoretically, petroglyphs at some locations on Murujuga are now being degraded by acids emitted from industry and shipping. However, there has not been credible research to determine whether this is occurring. Research is needed urgently to show whether the combined emissions from industry, shipping and the environment are dissolving the patina, the concentrations needed for dissolution and the rate it is occurring. The research must also examine the impact of nitrogenous emissions on the growth of microorganisms and fungi and the role of their organic acids in degrading the petroglyphs. A full understanding of the chemical reactions involved in degradation of the patina and its attachment to the underlying weathering rind is required to develop simulation models for predicting the likely impacts of future industrial emissions and to identify potential methods to arrest patina degradation. In the meantime, the Western Australian Government should invoke the Precautionary Principle from the Environmental Protection Act 1986 by restricting further industrial development on Murujuga and by setting regulations that limit industrial emissions to near zero.

Significance of rock art (petroglyphs) on Murujuga

The Dampier Archipelago, which includes the island Murujuga ('Burrup Peninsula'), is estimated to contain more than one million rock art images in the form of petroglyphs (JMcD CHM 2011). These petroglyphs capture at least 45,000 thousand years of human culture and spiritual beliefs through a changing environment (Bednarik 1979; Donaldson 2009; JMcD CHM 2011; McDonald and Veth 2009; Mulvaney 2011). The rock art is believed by some to contain the oldest known representation of the human face (Mulvaney 2015). Other petroglyphs include elaborate geometric designs, extinct mammals such as megafauna, the fat-tailed kangaroo and Thylacines, as well as existing animals, birds and sea creatures (Bird and Hallam 2006; JMcD CHM 2011; Mulvaney 2009, 2013, 2015; McDonald 2015). Examples of the petroglyphs are shown in Figure 1. The Murujuga inhabitants created this rock art until 1868, when the Yaburara indigenous population was almost exterminated in the 'Flying Foam Massacre' (Bednarik 2006; Gara 1983). The petroglyphs on Murujuga are a priceless, irreplaceable, historical and archaeological treasure of global significance.

Figure 1. Examples of the petroglyphs on Murujuga.

Industrial development of Murujuga

Murujuga is also the site of a large industrial complex (Figure 2). An iron ore export terminal was established in 1964 and a salt production facility in 1970. Natural gas processing facilities commenced in the early 1980s and were followed by liquefied natural gas (LNG) production plants in 1995 and 2007. An ammonium fertiliser plant commenced production in 2006 and an ammonium nitrate production facility in 2017. The National Pollution Inventory shows that in 2016 -17 Woodside Energy Limited Burrup gas plants produced 8,000 tonnes (t) oxides of nitrogen, 97 t sulphur dioxide and 16,000 t of volatile organic compounds, while the Yara Pilbara fertiliser plant produced 13,600 t of sulphur dioxide equivalents in 2014. There are not yet annual figures available for the Yara ammonium nitrate plant.

The Port of Dampier is one of the busiest bulk-handling ports in the world. During the year 2017-18, 3,173 vessels entered the port with exports approaching 180 million tonnes (Pilbara Ports Authority 2018). A single bulk cargo ship burning high-sulphur fuels has been estimated to release 5200 t of sulphur oxides into the atmosphere annually (Vidal 2009). The sulphur dioxide combines with water to form sulphuric acid. The shipping, liquefied gas, fertiliser and ammonium nitrate plants are in close proximity to the rock art motifs.

Figure 2. Examples of industrial development and emissions from industry and shipping.

Murujuga rocks and petroglyph formation

To assess the potential impact of industrial emissions on the petroglyphs, it is important to understand the nature of the rocks on Murujuga and the way the petroglyphs were formed. Rocks on Murujuga are igneous and crystallised at high temperatures to produce extremely hard granophyre and gabbro types (Hickman 2001; Donaldson 2011). The now exposed rocks rarely exfoliate and produce little soil. Temperature changes cause splitting of the rocks over time producing large flat surfaces. The new rock faces degrade extremely slowly (Pillans and Fifield 2013), producing an orange/yellow coloured weathering rind comprising a mixture of feldspar and clays that can attain a thickness of 5 - 10 mm in 30,000 years depending on the rock type (Bednarik 2007; Donaldson 2011). The weathering rind is overlayed by a hard, thin dark, red/brown/black, patina or rock varnish from <1 to 200 microns thick (Liu and Broecker 2000). The petroglyphs are created on the flat surfaces by breaking through the patina to expose the underlying pale weathering rind, which results in a colour and contour contrast (Vinnicombe 2002). The rock structure and petroglyph formation are illustrated in Figure 3, where the rock varnish has covered the contours of an ancient petroglyph.

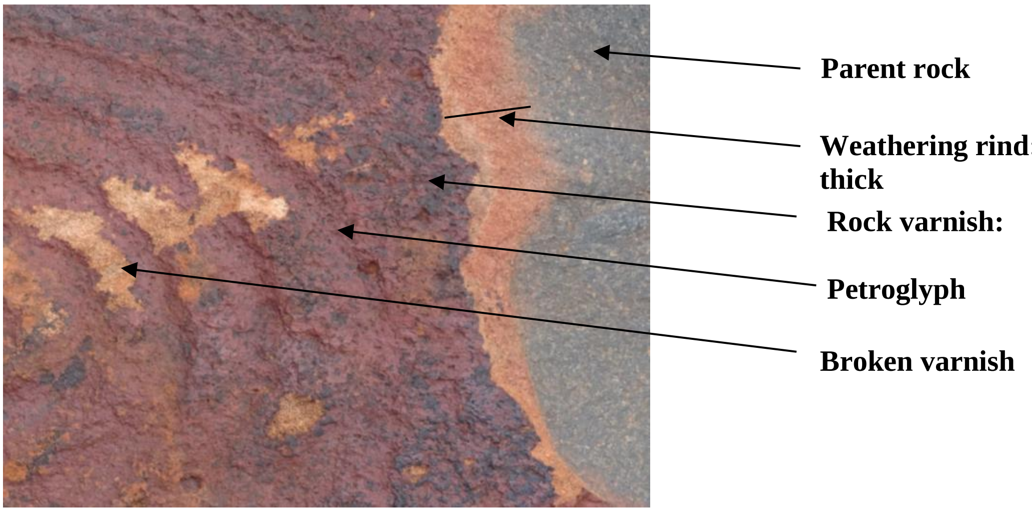

Figure 3. The photograph shows to the right a relatively recent fracture, which is likely to be several 1000 years old due to the slight colouration compared with the blue-grey of a new fracture. The weathering rind of an ancient fracture is the yellow-orange area, which is covered by the rock varnish patina. The petroglyph is likely to be more than 20,000 to 30,000 years-old because the rock varnish has covered the underlying weathering rind to leave only a contour contrast.

Integrity of the patina is crucial for preservation of a petroglyph. Figure 4 provides two examples where removal of the patina results in destruction of the petroglyph.

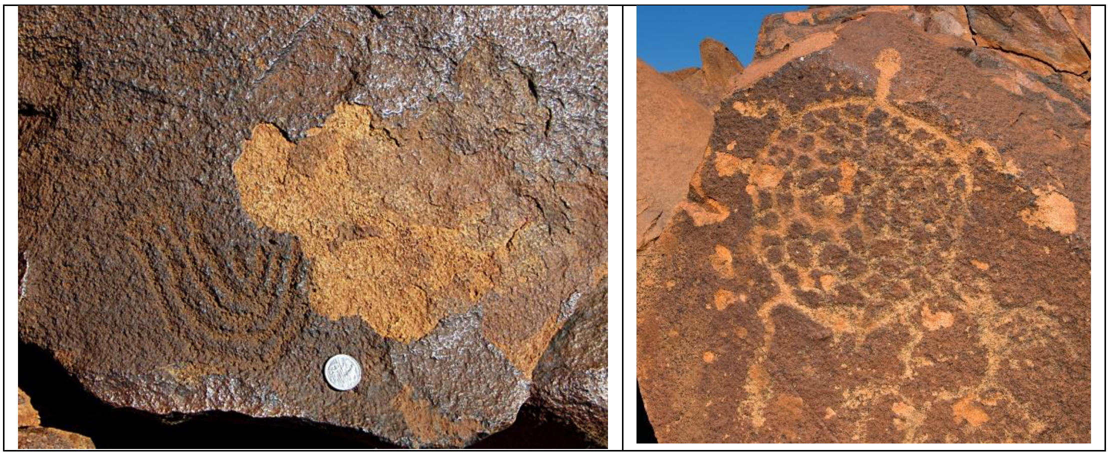

Figure 4. The left photograph from Pillans and Fifield (2013) shows an ancient petroglyph being destroyed by flaking of the patina and weathering rind. The right photograph from Donaldson (2009) shows partial loss of a petroglyph through patina flaking.

Formation of the rock varnish patina

Studies of patina formation have not been conducted for Murujuga rocks. However, evidence for the formation of rock varnish (syn. "desert varnish") in similar environments in the Arizona and New Mexico deserts suggest the varnish forms at the rate of less than one micron to 10 microns in 1000 years (Dorn and Meek 1995; Liu and Broecker 2000; Dorn 2009a). This is an extremely slow rate of accretion as, by comparison, the average human hair is around 100 microns in diameter. The patina is believed to be formed by both biological and chemical processes. Specialised bacteria and fungi are believed to have evolved to survive in the extremely dry, harsh environment of rock surfaces, with temperatures exceeding 70°C (Flood et al. 2003; Dorn 2009b; Esposito et al. 2015; Krinsley et al. 2017). These organisms extract and concentrate many-fold manganese and iron compounds in dust to form a hard, protective sheath. The microbes are thought to live for up to 100 years, being dormant most of the time and multiplying only when conditions are sufficiently moist. The microbes are finally incorporated with clay from the dust in a chemical reaction to form the patina, where the remains of the organisms are found (Krinsley et al. 2017). The patina is approximately 70% clay, 25% manganese and iron oxides and hydroxides and 5% other mineral compounds (Potter and Rossman 1997: Garvie et al. 2007).

The manganese and iron oxides in the patina are formed only under near neutral and alkaline conditions with the ratio of manganese to iron compounds varying with climatic conditions and resulting small differences in acidity (Broecker and Liu 2001). Proportionately more iron compounds form in drier conditions with a more alkaline environment. Colour of rock varnish varies with the proportion of darker manganese compounds relative to the proportion of redder ferrous oxide compounds (Figure 5).

The manganese and iron compounds in the patina are subject to dissolution by acids (Black et al. 2017b).

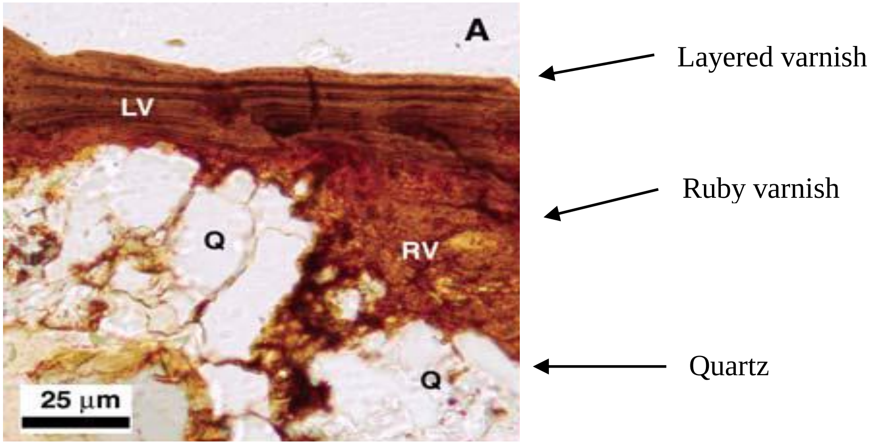

Figure 5. Cross sectional view of rock varnish (Garvie et al. 2007).

Changes to the acidity of Murujuga rock surfaces since industry establishment

Rocks collected pre-industrialisation from Murujuga and stored at the Western Australian Museum were found to have a rock surface with circum-neutral pH (pH of 6.8 ± 0.2; MacLeod 2005), similar to that suggested by Bednarik (2009). MacLeod (2005) placed 10-15 drops of distilled deionised water on a 20 cm square area of rock and found that the pH of rock surfaces at 30 sites across Murujuga ranged from 4.25 to 5.74 when measured in 2003/4. More recent measurements in 2017 of the same rocks showed continuing decline in pH with individual sites being as low as 3.81 ± 0.15. The lowest individual measurement was pH 2.89. At the extreme, these measurements suggest the acidity of rock surfaces has increased by more than 1000-fold following industrialisation of Murujuga.

Natural rainfall precipitation in equilibrium with an atmosphere uncontaminated by industrial and transport emissions has a pH of approximately 5.6 (Appelo and Postma 2005). Reaction with minerals in rock surfaces usually increases the pH to circum-neutral values (7.0 ± 1.0), as found on Murujuga rocks pre-industrialisation. Organic acids from biological activity will lower the pH of rock surfaces. However, in well-oxygenated environments such as the Murujuga, organic acids will not normally reduce pH of rock surfaces below 4.2, which is the buffering point of aluminium oxide (Appelo and Postma 2005). The recorded pH values as low as 2.9 on petroglyph-bearing rock surfaces of Murujuga are indicative of the influence of strong mineral acids, such as may be produced by anthropogenic generated sulphur and nitrogen oxides.

Potential effects of emissions on petroglyphs

Electrochemical theory dictates that lowering of pH will promote dissolution of the manganese and iron oxides from the patina (Black et al. 2017b). Macleod (2005) observed a log increase in the concentrations of free manganese and iron ions in solution with decreasing pH (Figure 6) in the water samples collected following equilibration in distilled deionised water placed on rock surfaces. The same trend was confirmed at specific rock art sites during the 2017 measurements (Figure 7). The Eh:pH values lie in the field of soluble Mn^{2+} and Fe^{2+} ions for dilute Mn-Fe-H_2O systems, indicating the propensity for the dissolution of solid manganese and iron compounds comprising the patina. Detailed geochemical analysis of the surface water irrigations is required to define better the chemical system (e.g. influence of S and NO_3 surface deposits) and the rate of the solubility of Mn and Fe.

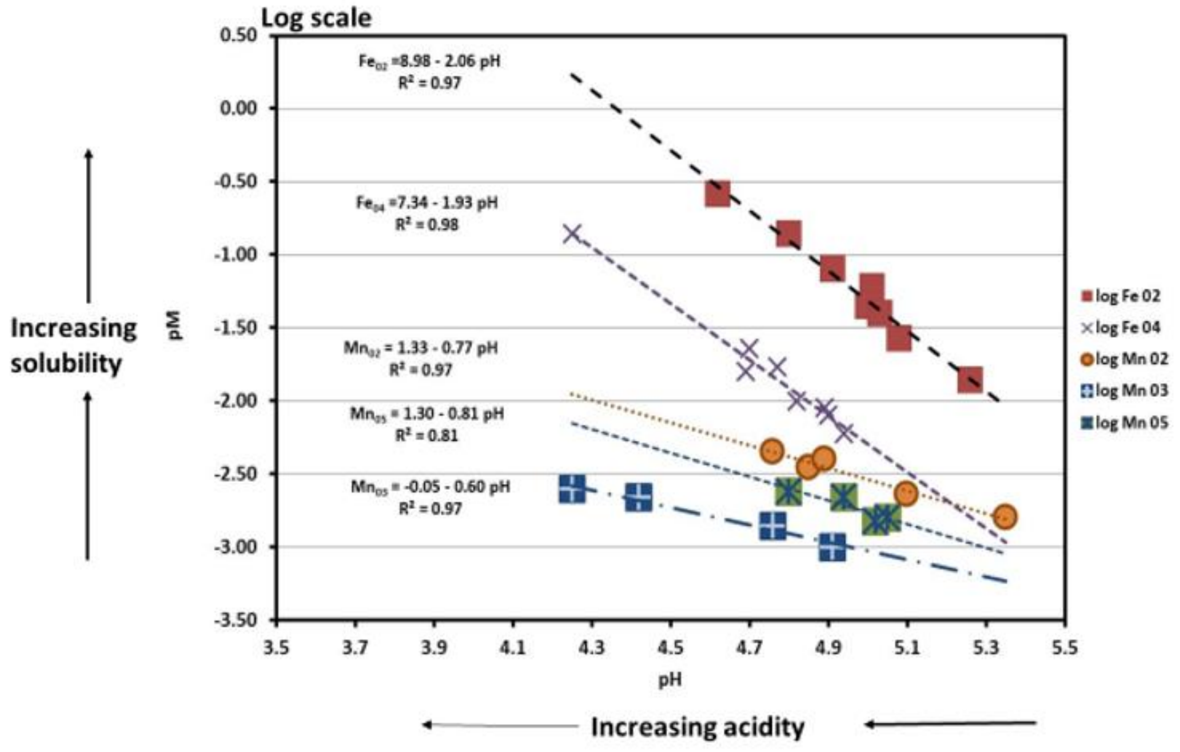

Figure 6. Relationship between solubility of iron and manganese compounds with decreasing pH of rock surfaces on Murujuga (data from MacLeod 2005). pM is the negative value of the log concentration of Fe and Mn ions in solution following equilibration in water on rock surfaces.

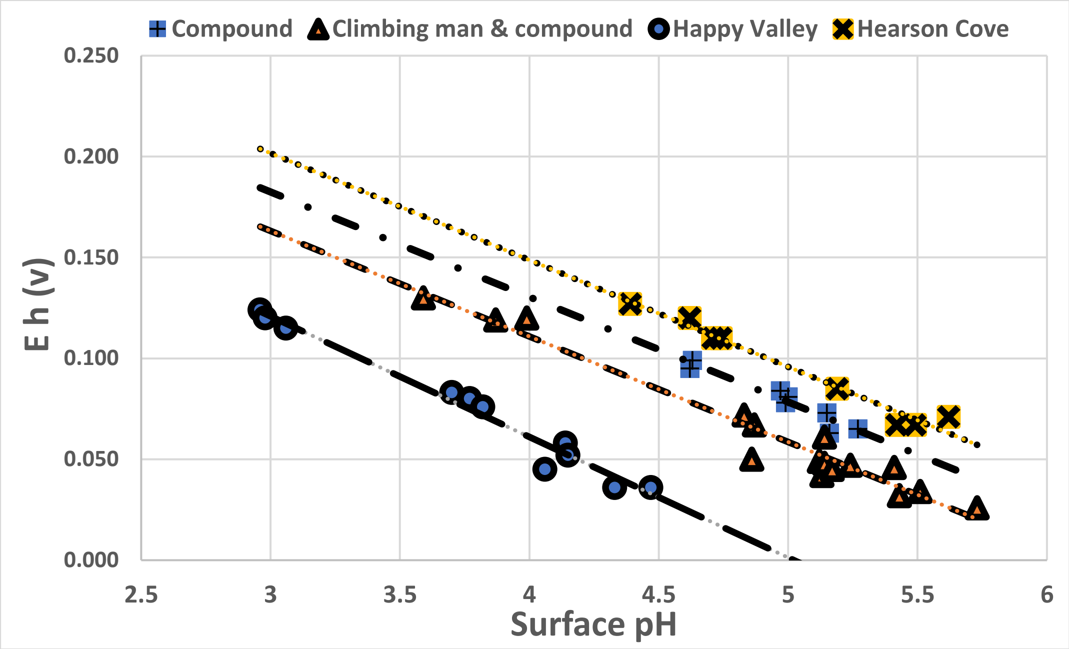

Figure 7. pH and Eh (redox potential) values recorded from individual rock surfaces at several locations on Murujuga in 2017 (MacLeod, unpublished). The compound refers to an area where rocks containing petroglyphs removed during construction of the Woodside Energy gas facilities are located.

Nitrogen emitted from industry on Murujuga, including an estimated 25 t/year of ammonium nitrate dust-sized particles from the ammonium nitrate facility (EPA 2011), will increase nitrogen available for adventitious microbial and fungal growth. MacLeod (2005) showed a log increase in microbial mass with increasing nitrate in rock surface water. There is evidence that organic acids from trees (Bednarik 2009) and acidic bird droppings (Duffy et al. 2017) dissolve the patina from rocks on Murujuga. Microbes, fungi and lichen produce organic acids which further increase the acidity of rock surfaces and dissolve rock patina (Dragovich 1986).

Dissolution of the darker manganese, magnetite and associated iron compounds and an increase in the proportion of red ferrous oxide and lighter-coloured clay minerals as surface acidity increases will make the rock surfaces lighter, redder and more white/yellow in colour over time. A possible example of colour changes to a rock with a petroglyph is shown in Figure 8. The patina is also likely to become thinner and more porous as the manganese and iron compounds are dissolved. Increased porosity is likely to facilitate the passage of acidic solutions to the patina-weathering rind interface and to weaken the chemical bonds holding the patina to the rock. In addition, on drying, the crystallisation of nitrate and sulphate compounds at this interface may further encourage flaking of the patina.

Figure 8. A petroglyph near sites where rock surface pH has fallen to less than 4 showing increases in red and light clay colouration as is predicted with dissolution of darker manganese and iron compounds.

Conclusions

Acidity of rock surfaces, as measured by an increase in the concentration of H^+ ions, has increased up to 1000-fold since the introduction of industry at some sites on Murujuga. Theoretically, an increase in acidity of this magnitude can leach the manganese and iron compounds from the rock patina over time.

There is no proof yet that the patina on Murujuga rocks is dissolving. Dissolution of the patina may not become visually evident until the majority has been removed. However, whenever the patina is dissolved or flaked away from the weathering rind, the petroglyphs will be disfigured or destroyed.

Research projects examining the possible damaging effects of industrial emissions on petroglyphs have been restricted to either measuring colour and mineralogy changes to petroglyphs and background rock surfaces over time (Lau 2007; Markley et al. 2015) or measurement of rock surface pH (MacLeod 2005; unpublished). Unfortunately, the results of colour and mineralogy change measurements have been discredited because of lack of effective design, effective statistical analysis and interpretation (Black et al. 2017a; WA Government report 2018).

As for the rock surface pH measurements, a low pH simply means that there is a higher proportion of H^+ ions to OH^- ions in the solutions when distilled water is allowed to equilibrate with materials of the rock surface for two minutes. The rate of leaching to reach an equilibrium of theoretical dissolution of the manganese and iron compounds in the patina is unknown. This rate of patina dissolution will depend on the type and concentration of acid compounds and how long they are effective in a solubilised state. Much of the acid will land upon the rocks in the form of dry deposition, to become reactive when dissolved in water. Measurements are needed of the time acids may be effective on the rock surfaces and the relative effects of dew compared with the flushing effects of heavier rains.

Laboratory research is required to determine whether the combinations of chemicals emitted from industry and shipping, in conjunction with those from the natural environment, will dissolve the Murujuga rock patina and, if so, the concentrations required for dissolution. Estimates must be made of the rate of patina dissolution to assess when destruction of the petroglyphs through industrial emissions may occur.

Research is needed to confirm the results of MacLeod (2005) showing that the increase in nitrogen compounds on rock surfaces stimulates adventitious microbial growth, the types of organisms and quantities of acids produced. In addition, comprehensive understanding of the chemical reactions involved must be obtained so that simulation models can be constructed to predict likely impacts of future emissions on the petroglyphs, and to elucidate the means of arresting negative impacts.

The proposed research is needed urgently. The University of Western Australia through the Centre for Rock Art Research + Management has established a research project to undertake the needed measurements. However, in the meantime, the Precautionary Principle in the Western Australian Environmental Protection Act 1986 should be invoked with the prevention of new industry and strict regulations to ensure emissions are near zero for existing industries and shipping.

References

Appelo, C.A.J. and Postma, D. 2005. *Geochemistry, groundwater and pollution. 2dn Edition.* CRC Press, Florida, USA.

Bednarik, R.G. 1979. The potential of rock patination analysis in Australian archaeology - part 1. *The Artefact* 4:14-38.

Bednarik, R. G. 2006. *Australian apocalypse: the story of Australia's greatest cultural monument*. Occasional AURA Publication 14, Australian Rock Art Research Association Inc., Melbourne.

Bednarik, R.G. 2007. The science of Dampier rock art - Part 1. *Rock Art Research* 24:209–246.

Bednarik, R.G. 2009. Experimental colorimetric analysis of petroglyphs. *Rock Art Research* 26:55–64.

Bird, C and Hallam, S.J. 2006. A review of archaeology and rock art in the Dampier Archipelago. A report prepared for the National Trust of Australia (WA). Retrieved 7 May 2016 from http://www.burrup.org.au/2006-10-20%20Technical%20Report%20Final%20draft%202.pdf

Black, J.L., Box, I. and Diffey, S. 2017a. Inadequacies of research used to monitor change to rock art and regulate industry on Murujuga ('Burrup Peninsula'), Australia. *Rock Art Research* **34**, 130-148.

Black, J.L., MacLeod, I.D. and Smith, B.W. 2017b. Theoretical effects of industrial emissions on colour change at rock art sites on Burrup Peninsula, Western Australia. *Journal of Archaeological Science: Reports* **12**, 457-462.

Broecker, W.S and Liu T. 2001. Rock varnish: recorder of desert wetness? *Geological society of America (GSA) Today* 11:4-10.

Donaldson, M. 2009. *Burrup rock art: Aboriginal rock art of Burrup Peninsula and Dampier Archipelago, Western Australia*. Perth: Wildrocks Publications.

Donaldson, M. 2011. Understanding the rocks: Rock art and the geology of Murujuga (Burrup Peninsula). *The Journal of the Australian Rock Art Research Association* 28:35–43.

Dorn, R.I. 2009a. Desert rock coatings. In "*Geomorphology of Desert Environments*". Second Ed. Eds A.J. Parsons & A.A. Abrahams. Springer Science+Business, Media B.V. pp. 153-186.

Dorn, R.I. 2009b. Rock varnish and its use to study climate change in geomorphic settings. In "*Geomorphology of Desert Environments*". Second Ed. Eds A.J. Parsons & A.A. Abrahams. Springer Science+Business, Media B.V. pp. 657-672.

Dorn, R.I. and Meek, N. 1995. Rapid formation of rock varnish and other rock coatings on slag deposits near Fontana. *Earth Surface Processes and Landforms* 20:547-560.

Dragovich, D. 1986. Weathering of desert varnish by lichens. In: *Readings in Australian geography: proceedings of the 21st Institute of Australian Geographers' Conference, Perth, 10-18 May 1986,* Edited by Arthur Conacher. Published by Institute of Australian Geographers (WA Branch) and Dept. of Geography, University of W.A Perth [W.A.]

Duffy, N., Ramanaidou, E., Alexander, D. and Lau, D. 2017. *Burrup Peninsula Aboriginal petroglyphs: colour change and spectral mineralogy*. CSIRO, Australia: EP161761, June 2017.

Environmental Protection Authority 2011. Technical Ammonium Nitrate Production Facility, Burrup Peninsula. Burrup Nitrates Pty Ltd. Report 1379. January 2011.

Esposito, A., Ahmed, E., Ciccazzo, J., Sikorski, J., Overmann, J., Holmström, S.J. and Brusetti, L. 2015. Comparison of Rock Varnish Bacterial Communities with Surrounding Non-Varnished Rock Surfaces: Taxon-Specific Analysis and Morphological Description. *Microbial Ecology* 70(3): 741-750.

Flood, B.E., Allen, C. and Longazo, T. 2003. Microbial fossils detected in desert varnish. In *Annual Lunar and Planetary Science Conference* **34**, Abstract 1633.
Gara, T. 1983. The Flying Foam massacre: an incident on the northwest frontier, Western Australia. Paper presented to the Archaeology at ANZAAS 1983, 53rd ANZAAS Congress, Perth, Western Australia.
Garvie, L.A.J., Barr, D.M. and Buseck, P.R. 2008. Nanometer-scale complexity, growth, and diagenesis in desert varnish. *Geology* 36:215-218.
Hickman, A.H., 2001. Geology of the Dampier 1:100 000 Sheet. In: *Western Australia Geological Survey 1:100 000 Geological Series Explanatory Notes*, p. 39.
JMCD CHM, Jo McDonald Cultural Heritage Management Pty Ltd 2011. Study of the outstanding universal values of the Dampier Archipelago site, Western Australia. Unpubl. report to the Australian Heritage Council, Canberra.
Krinsley, D.H., DiGregorio, B., Dorn, R.I., Razink, J. and Fisher, R. 2017. Mn-Fe-Enhancing Budding Bacteria in Century-Old Rock Varnish, Erie Barge Canal, New York. *Journal of Geology* 125(3): 317-336.
Lau, D., Ramanaidou, E, Furman, S, Cole, I, Hughes T. and Hoobin, P 2007. *Field studies of rock art appearance, final report: fumigation & dust deposition, Progress report: colour change & spectral mineralogy*, CSIRO Manufacturing and Materials Technology, viewed 9 January 2017, *http://web.archive.org/web/20091002111652/http:/www.dsd.wa.gov.au/documents/BI_BurrupRockArtCSIROFieldStudies.pdf*.
Liu, T. and Broecher, W.S. 2000. How fast dos rock varnish grow? *Geology* 28:183-186.
MacLeod, I. D. 2005. Effects of moisture, micronutrient supplies and microbiological activity on the surface pH of rocks in the Burrup Peninsula. *In 14th Triennial Meeting, The Hague, 12-16 September 2005*: Preprints (ICOM Committee for Conservation), Isabelle Verger, ed. pp. 385-393, Earthscan Ltd.
Markley, T., Wells, M, Ramanaidou, E, Lau, D. and Alexander, D. 2015. *Burrup Peninsula Aboriginal petroglyphs: colour change & spectral mineralogy 2004–2015*, No. EP1410003, CSIRO, viewed 15 January 2017, *https://www.der.wa.gov.au/images/documents/our-work/programs/Burrup-Penninsula-Aboriginal-Petroglyphs-Report-2004-2014.pdf*.
McDonald, J. 2015. I must go down to the seas again: Or, what happens when the sea comes to you? Murujuga rock art as an environmental indicator for Australia's north-west. *Quaternary International* **385**: 124-135.
McDonald, J. and P. Veth 2009. Dampier Archipelago petroglyphs: archaeology, scientific values and National Heritage listing. *Archaeology in Oceania* 44(S1): 49–69.
Mulvaney, K. 2009. Dating the Dreaming: extinct fauna in the petroglyphs of the Pilbara region, Western Australia. *Archaeology in Oceania* 44(S1): 40–48.
Mulvaney, K. 2011. About time: toward a sequencing of the Dampier Archipelago petroglyphs of the Pilbara region, Western Australia. *Records of the Western Australian Museum*, Supplement 79 ['Fire and hearth' forty years on: essays in honour of Sylvia J. Hallam. Bird, Caroline and Webb, R. Esmee (eds).]: 30–49.
Mulvaney, K. 2013. *Burrup and beyond: a short guide to the area's cultural heritage and history*. Rio Tinto Mining Company of Australia, Perth, Western Australia.
Mulvaney, K. 2015. *Murujuga Marni: rock art of the macropod hunters and mollusc harvesters*. UWA Press, Perth.
Pilbara Ports Authority 2018. Annual Report. https://www.pilbaraports.com.au/Home/About-PPA/Annual-Report.
Pillans, B. and Fifield, L. K. 2013. Erosion rates and weathering history of rock surfaces associated with Aboriginal rock art engravings (petroglyphs) on Burrup Peninsula, Western Australia, from cosmogenic nuclide measurements. *Quaternary Science Reviews* 69: 98–106.
Potter, R.M. and Rossman, G.R. 1977. Desert varnish: the importance of clay minerals. *Science* 196:1446-1448.
Vidal, J. 2009. Health risks of shipping pollution have been 'underestimated'. *The Guardian (Environment, Travel and Transport)*, 10 April 2009, viewed 31 January 2016, https://www.theguardian.com/environment/2009/apr/09/shipping-pollution.

Vinnicombe, P. 2002. Petroglyphs of the Dampier Archipelago: background to development and descriptive analysis. *Rock Art Research* **19**, 3e27.
Western Australian Government 2018. L7997-2002-11a Amendment. File number DER 2013/001374. 29 June 2018.

Dr John L Black AM FTSE FAIAST FASAP FNSA Honorary Research Fellow University of Western Australia Research Management Consultant Director John L Black Consulting jblack@pnc.com.au	Stéphane Hoerlé Ingénieur diplômé (M.Sc.Eng.), Ph.D. Materials science Honorary Research Fellow: PACEA (CNRS, University of Bordeaux, Ministry of Culture), France Honorary Research Fellow: Rock Art Research Institute (University of the Witwatersrand), South Africa stephane@rockart.wits.ac.za	Associate Professor, Faculty of Engineering and Mathematical Sciences , School of Engineering, University of Western Australia. Managing Director Environmental Geochemistry Services ron@egservices.com.au