



KEYWORDS: *Petroglyph – Industry emissions – Rock varnish – Acid rain – Murujuga – Scientific integrity*

THE IMPACT OF INDUSTRIAL POLLUTION ON THE ROCK ART OF MURUJUGA, WESTERN AUSTRALIA

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Abstract. MacLeod and Fish have recently suggested that there is no adverse impact on the engraved rock art of Murujuga (the Burrup Peninsula) from industrial pollution. This highly controversial conclusion demands examination because it could influence future government decision-making concerning ongoing applications to expand industrial activity on Murujuga. We, therefore, review the data and arguments underpinning that conclusion. We find the conclusion unsubstantiated, misleading and potentially damaging for the long-term preservation of the Murujuga rock art. Evidence suggests that the petroglyphs are already actively degraded by industrial pollution.

Introduction

Murujuga and its rock art are of exceptional global and national significance. The Dampier Archipelago, incorporating Murujuga, has over a million rock art engravings or petroglyphs said to capture more than 50 000 years of Indigenous knowledge and spiritual beliefs. The Murujuga rock art is among Australia's most extraordinary Aboriginal heritage sites and is of Outstanding Universal Value (Australian Heritage Council 2012; DBCA 2021). The rock art is thought to contain some of the earliest known representations in the world of the 'human face'. It includes some of the world's oldest complex geometric designs, extinct animals including the 'fat-tailed kangaroo' and 'thylacine', as well as recording the evolving fauna of the area through global climate change during and after the last Ice Age (McDonald and Veth 2009; Mulvaney 2011a, 2013). The rock art is enormously significant both to current Aboriginal Custodians and to the global community.

From the 1960s, sections of the Burrup Peninsula have been increasingly industrialised, initially with an iron ore port and salt production facility and, from the late 1970s, with large petrochemical industries, including natural gas plants and others that use the by-products from gas liquefaction. The area is now flagged to become one of 'the largest industrial hubs in the Southern Hemisphere' (Mulvaney 2011b: 17). Aside from the unconscionable direct destruction of petroglyphs during the construction of this industry (Bednarik 2002; González Zarandona 2020), the effects upon the rock art of polluting emissions have been presented and discussed in many reports and publications

(e.g. MacLeod 2000, 2011; Bednarik 2002, 2007a, 2007b, 2009; Lau et al. 2008; Mulvaney 2011b; Moodie 2016; Duffy et al. 2017; Ramanaidou et al. 2017; Parliament of Australia 2018; González Zarandona 2020). Conclusions from governmental reports have been shown to understate the evidence of damage to the rock art from pollution (Bednarik 2007a; Black and Diffey 2016; Black et al. 2017a).

Ian MacLeod and Warren Fish have recently published a conference paper (MacLeod and Fish 2021) in which they claim to provide 'the first definitive answers to the factors controlling the decay mechanisms on engraved rocks in the Pilbara region of Western Australia'. Given the massive volume of published and grey literature on this topic, this is a big statement. The paper concludes that 'the present monitoring data shows that there is presently no adverse impact on the rock engravings from industrial pollution ...'. This is an extraordinary claim that contrasts with findings and expectations of decades of studies (Bednarik 1994, 2002, 2007b, 2009; MacLeod 2005, 2011; Mulvaney 2011b; González Zarandona 2011, 2020; Black and Diffey 2016; Moodie 2016; Black et al. 2017b; Ramanaidou et al. 2017; Data Analysis Australia et al. 2018). The basis of this claim is a set of pH, nitrate, chloride ion and redox measurements on rock surfaces at eight sites across Murujuga, as well as some rock surface colour measurements. We review the current understanding of factors controlling the synthesis and decay of Murujuga rock surfaces to assess whether the extraordinary claim made by MacLeod and Fish (2021) can be considered scientifically sound and credible.



Figure 1. An example of a rock art panel showing part of the Murujuga landscape (photograph: BWS).

The red-brown rocks of Murujuga – the living rocks

The rich red-brown colour that characterises the visible faces of the granophyre and gabbro rocks of Murujuga is not the original natural colour of the rocks, which is blue-grey. Tectonic forces and temperature changes cause rock splitting over time, producing many large flat surfaces ideal for displaying art. The new rock faces degrade extremely slowly (Pillans and Fifield 2013), producing an orange/yellow coloured weathering rind, or leach zone, 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 1979, 2007b; Donaldson 2011; Ramanaidou and Fonteneau 2019). The weathering rind is covered by the hard, red-brown surface outer layer that is only 1 to 200 microns in thickness (Liu and Broecker 2000; Ramanaidou and Fonteneau 2019). It comprises a ferromanganese crust, known as the patina or rock

varnish. The rock art was made by breaking through that patina and into the weathering rind to provide a colour and contour contrast (Fig. 1).

Evidence from studies into the growth of the ferromanganese patina on rocks in similar environments to Murujuga shows that it is formed by biomineralisation processes, where budding bacteria and micro-fungi concentrate manganese and iron compounds and form the hard, cement-like components of the patina (Miller et al. 2012; Dorn 2020; Lingappa et al. 2021). These microbes have evolved in extremely harsh, low moisture, high-temperature rock surface environments and have developed strategies to protect themselves against radiation and oxidative stress.

Dust is the primary source of manganese and iron oxide on rock surfaces (Bednarik 2002; Macholdt et al. 2019). Manganese oxide arriving on the rock surface is reduced to H-Mn^{++} ions by photochemical or biological processes when moisture from dew is present (Lingappa et al. 2021). The H-Mn^{++} ions have been shown to be absorbed by a specific genus of cyanobacteria, *Chroococcidiopsis*, with manganese being concentrated up to 50 times or more from that in the local environment. *Chroococcidiopsis* is the dominant organism living on rock surfaces in extremely dry and harsh desert environments, whether in the Antarctic or hot deserts (Mishra 2020). This bacterium has evolved to tolerate extreme desiccation, ionising radiation and ultraviolet light and can maintain normal metabolic processes following the loss through desiccation of more than 50% of its weight (Kvíděrová et al. 2011).

Lingappa and colleagues (2021) report that the manganese compound in the patina is predominantly in the Mn^{4+} form, but there are specific regions with mixtures of Mn^{4+} and Mn^{3+} . These authors consider that

this mixing of manganese ion types is consistent with the oxidation-reduction recycling process occurring within the patina, where it is part of an ecosystem. Figure 2 shows examples of electron microscope images of budding bacteria in rock varnish and the concentration of manganese and iron within the bacteria. The rock varnish-forming microbes are thought to lie dormant for much of their lives, becoming active only when moisture concentrations are sufficient for active metabolism. When the organisms die, their biomass is oxidised, and the magnesium and iron-

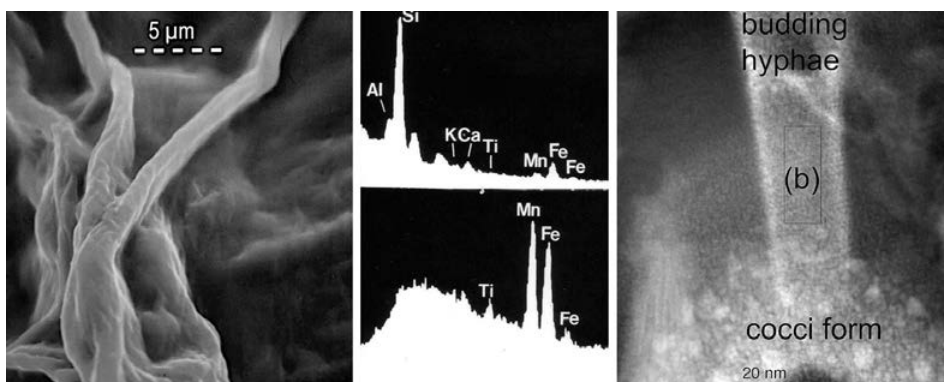


Figure 2. Electron microscope images of rock varnish showing the bacteria sheaths (hyphae) concentrating manganese-iron-rich material in rock patina (left) and a budding hypha is emerging from a cocci bacterial form (right). The centre bottom image is an elemental spectral analysis of the hyphae (left) compared with the adjacent patina (centre top), showing marked concentration of manganese (Mn) and iron (Fe) in the bacteria (right image adapted from Dorn 2020: Fig. 13.3(a); left and centre images from Dorn 2020: Fig. 13.2 originally from Krinsley et al. 2009: Fig. 5(B)). Images with permission from R. I. Dorn – The American Geographical Union grants permission to use figures in academic works).

rich components are incorporated with clays into the rock patina (Dorn 2020; Lingappa et al. 2021). Bacterial remains and fossilised fungi have been observed within the patina of rocks collected from the Pilbara in Western Australia, with Murujuga being part of this region (Flood et al. 2003). Krinsley et al. (2017) suggest that as few as one bacterium every ~400 years may be incorporated into rock varnish under warm desert conditions. Consequently, the rock patina grows at extraordinarily slow rates of 1 to 10 microns per 1000 years (Dorn and Meek 1995; Liu and Broecker 2000; Dorn 2009).

The manganese and iron oxides and hydroxides in the patina are formed only under near-neutral and alkaline conditions (Goldsmith et al. 2014). The ratio of manganese to iron compounds varies with climatic conditions resulting from small differences in local acidity-alkalinity (Dorn 1990; Broecker and Liu 2001). Proportionately more iron compounds form in drier conditions with a more alkaline environment (Dorn 1990). The colour of the patina varies with the proportion of darker manganese compounds relative to the proportion of redder ferrous oxide compounds. When suitable conditions exist, the patina is generally formed in layers, but it can also be largely amorphous and then is known as 'rubbly varnish' as illustrated in Figure 3 (Garvie et al. 2008).

Over periods of 10 000 to 30 000 years, the outer patina can grow over the weathering rind of the original petroglyph to reduce the colour contrast and show primarily a contour or texture contrast (Fig. 4). Critically, the petroglyphs are lost if the outer patina is removed either by being dissolved or detached from the underlying weathering rind (Fig. 4).

The influence of pH on Murujuga rock art decay

Published studies agree that the rich red-brown patina of the Murujuga rocks, as with other forms of rock varnish, is dissolved with increasing acidity (Bednarik 2002, 2007b; MacLeod 2005, 2011; Black et al. 2017b; cf. Dorn 2020). Even a '[s]ubtle change [...] in surface pH of only 0.3' (MacLeod and Fish 2021: 8) can affect the future survival of the rock art.

The impact of increasing acidity on the chemical changes occurring within the patina is most clearly illustrated by

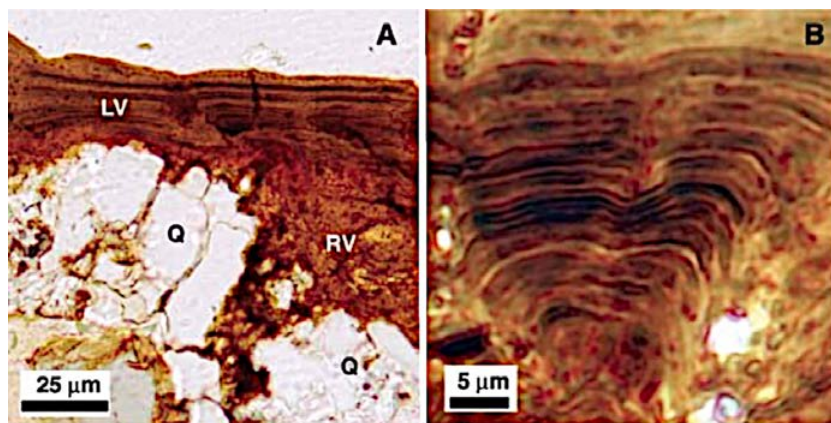


Figure 3. Optical micrographs (A and B) of ultrathin sections of rock varnish showing layering (LV) with different colours and more amorphous 'rubbly varnish' (RV) overlaying a quartz (Q) rock surface (from Garvie et al. 2008, Fig. 1. 'Fair use' permission presumed from The Geological Society of America).

consideration of the Pourbaix diagrams for manganese and iron compounds (Black et al. 2017b). Figure 5 shows the Pourbaix diagram for manganese. The diagram shows the three equations from MacLeod and Fish (2021) for the synthesis of Mn_3O_4 (equation 1, circled 16), MnO_2 (equation 2, circled 20) and $Mn(OH)_2^{2+}$ (equation 3, circled MF3). The range of rock surface pH values reported in MacLeod (2005), Black et al. (2017b), and MacLeod and Fish (2021) are also shown on the diagram, as well as the domain of stability of water where water is thermodynamically stable.

As acidity increases (i.e., pH falls), the manganese



Figure 4. An ancient petroglyph where the patina has grown over the weathering rind to provide only a contour contrast from the background rock (centre-left) and where the patina has detached from the weathering rind (centre-right) and the portion of the petroglyph removed (from Pillans and Fifield 2013; with permission from B. Pillans, and through Elsevier License 5163861131736).

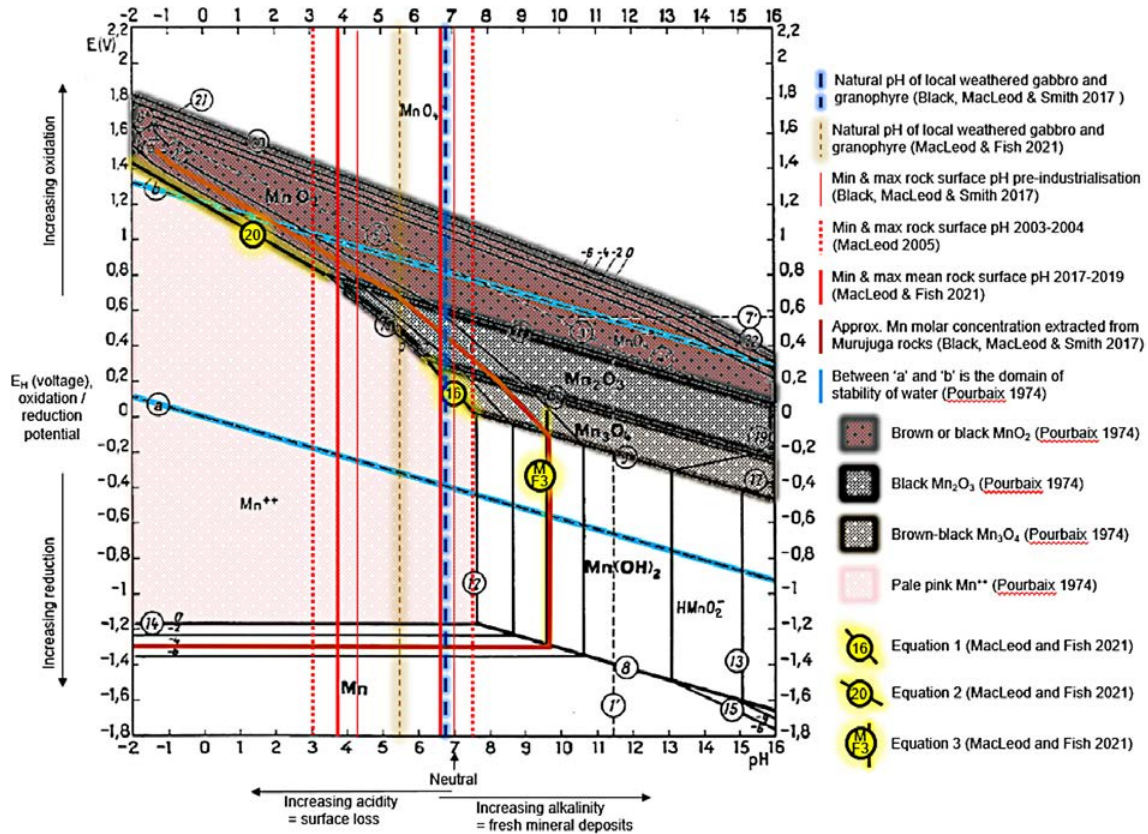


Figure 5. Pourbaix diagram of Mn (manganese) compounds. With increasing acidity, the different Mn oxides progressively become unstable (from Mn_3O_4 to Mn_2O_3 to MnO_2) until only dissolved Mn ions can exist. Any change from the natural pH (blue dashed line) results in surface loss or fresh mineral deposits, which changes the chemical composition of the rock surface and, thus, the appearance of the rock art (MacLeod and Fish 2021: 4). Equation 3 (MacLeod and Fish 2021:5) is at about MF3; however, it does not normally appear on the Pourbaix diagram (Hem 1963). Diagram adapted from Pourbaix (1974) and Black et al. (2017b) with additional data from Black et al. (2017b); and MacLeod and Fish (2021).

compounds in the patina are altered through a series of chemical transformations accompanied by colour changes (brown-black Mn_3O_4 , black Mn_2O_3 , brown or black MnO_2), and finally, they are dissolved (shown as pale pink) to Mn^{++} soluble ions. The soluble manganese ions may then be washed from the rocks in rainfall events.

There is ample evidence that a high concentration of natural organic acids will dissolve the manganese and iron compounds that harden rock patina. The outer patina is completely removed from rock surfaces at Murujuga with natural acid from trees (Bednarik 2009) and bird droppings (Bednarik 1979; Duffy et al. 2017) and also from areas of rock surfaces under lichens (Dorn 1990; Dragovich 1987) and microcolonial fungi (Dragovich 1993) at other desert locations in Australia and southern United States of America (U.S.A.). For this reason, it is not a surprise that acidic industrial emissions have been found to degrade or destroy rock surfaces (Dorn 2020; Giesen et al. 2014).

Industrial NO_x emissions also cause an increase in nitrite and nitrate concentrations on Murujuga rock surfaces. MacLeod (2005) showed that there was a log (10-fold) increase in the growth of bacteria, yeasts, fungi, and lichens for each unit increase in rock surface

nitrate. These organisms release organic acids that reduce the pH of the rock surface. There is a strong relationship between nitrate and pH on Murujuga rock surfaces (MacLeod 2005; MacLeod and Fish 2021). Gleeson and colleagues (2018) speculate that changes to the microenvironment of the rock patina on Murujuga caused by industrial emissions will influence the species and metabolism of the microorganisms on the rock surface. Large numbers of invasive opportunistic microorganisms will have two adverse effects on the rock patina. First, organic acids produced in sufficient quantity will dissolve the manganese and iron compounds in the patina (Dorn 1990). Second, these organisms will outcompete the specialised patina forming *Chroococciopsis* strains, which evolved to survive in extremely low nitrogen rock surface environments by fixing nitrogen from the air for metabolism (Bothe 2019).

Bednarik (2009) states that ferromanganese patina will not occur in areas where the pH of the rain is 5.6 or less, which is consistent with the observation that manganese ions leach from dust or rock varnish when pH falls to 5.7 (Goldsmith et al. 2014; Otter et al. 2020). Osborn and colleagues (1981) measured the pH of rain in the Arizona rangelands, where rock varnish is nota-

bly widespread, to have a mean of 6.8 in places where no polluting industries were operating. Bednarik (2002: 36) states that the pH of natural rain in the Pilbara region of Western Australia was 'in the order of 6.8 prior to industrial development, and reached about pH 7.0 to 7.2 at Murujuga'.

Otter and colleagues (2020) expand on the explanation of how pH changes on rock surfaces following a rain event with a lower pH due to the dissolution of atmospheric carbon dioxide. They propose that rain, even in desert environments, may have a pH sufficiently low to dissolve manganese from dust, but when it lands on rocks, reactions occur that remove protons from the carbonic acid (occurring naturally in rain) to form alkaline minerals. As the sun dries the rocks, the carbon dioxide from the carbonic acid is released, while the alkaline metals remain and further increase pH (i.e., raise alkalinity) with manganese hydroxides from Mn^{2+} to Mn^{4+} continuing to form until pH 8 is reached. Similarly, Goldsmith and colleagues (2014) report that moist dust from the Negev desert in Israel has a pH of about 8 and an E_H of about 0.6 V. Dorn (1990) found a strong correlation between soil pH and the pH of rock varnish at 67 sites across Arizona and California in the U.S.A. The pH of the rock varnish was predominantly in the range 6.7 to 9, with values lower than these being associated with the presence of lichens, organic matter such as leaf litter or microcolonial fungi, all of which produce organic acids.

MacLeod and Fish (2021: 4) assert that 'the natural pH of local weathered gabbro and granophyre is 5.5 ± 0.2 '. This stands in striking contrast to MacLeod's own recordings (Black et al. 2017b) and the known pH of rocks upon which ferromanganese patinas survive in other parts of Australia and the world. Such an allegedly low pre-industrial rock surface pH cannot be reconciled with the observations made by Bednarik (1979), who found that the mean pH was 5.9 across 30 sites on Murujuga where bird droppings had dissolved the rock patina. Bednarik's evidence suggests that, contrary to MacLeod and Fish (2021: 4), rock art will be completely degraded over time on any rock that attains a mean pH as low as 5.5.

With this broader knowledge of the natural formation processes of rock patinas and the deleterious effect of a decrease of pH (greater acidity) considered, we now turn to the specific evidence presented by MacLeod and Fish (2021: 6). From the eight sites that they monitored between 2017 and 2019, all of the rocks show that only one year on from a significant rain event on 6 June 2018, average pH levels had reached an acidity in which manganese ions are known to be leached (all falling to between pH 5.2 and 4.4). Whilst MacLeod and Fish place much emphasis on the impact of rain events in 'resetting the acid clock', the evidence they present shows that rock surface acidity returns to unacceptable levels soon after even a major rain event. The pH of rocks taken from Murujuga to the Western Australian Museum before industrialisation was found

to be 6.8 ± 0.2 (Black et al. 2017b), which corresponds with the range of 6.7 to 9.0 for rock varnish not affected by organic acids in the U.S.A. (Dorn 1990). By contrast, the mean surface pH of the eight rock sites monitored by MacLeod and Fish was 4.71 in 2019. This change in average pH from pre-industrial times is dramatic and, according to the Pourbaix diagram and other evidence (Bednarik 1979; Dorn 2020), is more than sufficient to cause the patina to dissolve.

A rain event does not truly 'reset' the decay clock, as MacLeod and Fish (2021) suggest. It dissolves some of the dry, acidic dust pollution from industry that has been deposited on the rock surfaces. As the dust mixes with water, the resulting solution bathes the surfaces in highly corrosive acids that will dissolve the rock patina in the same way that acid rain eats away at stone buildings and monuments in polluted cities. Very light rains, the most common type at Murujuga, as well as morning dews (which can be heavy during winter months), react with the dry SO_2 and NO_x pollution particles, oxygen and other chemicals to form sulphuric (pKa, or acidity, -3.0) and nitric (pKa -1.37) acid. These acids can reach very low pH and be highly corrosive to ferromanganese patinas. In most years, the amount of water reaching the rock surfaces is insufficient to remove the acidic dust from most surfaces (Clark et al. 2018). It is only during heavy rains, typically cyclonic events, when this acidity is truly washed away. Even this is context-dependent. Smooth granophyre rocks may be washed clean, whilst the rough gabbros may not be sufficiently penetrated to solubilise and carry away the Fe/Mn salts deposited deep in their surface pores. Major cyclonic events have been recorded on average twice a decade over the past forty years at Murujuga (Sudmeyer 2016; Holmes 2021). Whilst this cyclonic removal of acidic particles assists the survival of the rock surface patinas, such events happen too seldom to mitigate the damaging effects of industrial pollution significantly. Heavy rain events also wash away dissolved manganese and iron ions from the pores in the rock surface and diminishes the integrity of the patina (Andreae et al. 2020).

As a result, for the bulk of the time, the rocks at Murujuga are currently subjected to a level of acidity known to be corrosive to ferromanganese patinas. Our own commissioned pH testing in 2017, conducted by MacLeod and reported in MacLeod and Fish (2021), shows that rocks at site 4, adjacent to the Woodside petrochemical plants, have an average pH of below 4. A pH level below 6.5 is sufficient (Goldsmith et al. 2014) to cause loss of iron and manganese particles from the types of patinas that exist at Murujuga and that this damage becomes extreme below a pH of 5.7 (Bednarik 1979, 2009; Goldsmith et al. 2014; Otter et al. 2020). It follows that the average rock surface measurements of pH 5.29 (2017), pH 5.51 (2018), pH 4.71 (2019) reported by MacLeod and Fish (2021), even though these years included a cyclonic event and a massive industrial ammonia leak (alkaline) (MacLeod and Fish 2021: 4),

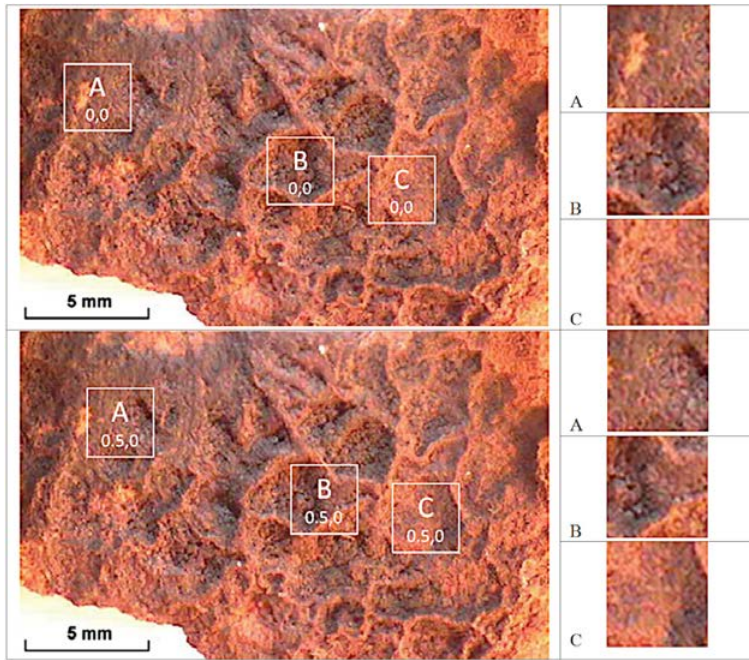


Figure 6. Three square areas (A, B, C) with the same area as a 3 mm diameter aperture positioned on a photograph of the surface patina of a Murujuga rock (Bednarik 2007b: 224, Figure 19) and moved 0.5 mm to the right in the lower panels (reproduced from Black et al. 2017a: Fig. 6).

confirm that acids are actively degrading the Murujuga rock surfaces on the majority of days in the majority of years. As MacLeod and Fish clearly state: 'acidification leads to surface loss' (2021: 4).

Colour changes on the rocks

Colour change should be an important proxy for patina decay, since any leaching of manganese and iron compounds from the rocks will cause the surface to become lighter in colour (Black et al. 2017b). In practice, the measurement of colour change on the rocks of Murujuga has proven to be challenging. CSIRO attempted it as part of a Western Australian government monitoring program at Murujuga from 2004 until 2014. The highly variable results were heavily criticised, both for the method by which they were generated and for how they were analysed and interpreted (Black et al. 2017a; Data Analysis Australia 2016, 2017). There were repeated inconsistencies in results from year to year that arose from changing the colour measuring

equipment and significantly changing conditions under which the readings were taken (Black et al. 2017a). Black and colleagues (2017a) also demonstrated that precise colour change monitoring is almost impossible; they provided the example of a close-up photograph of a Murujuga rock surface and demonstrated that the displacement of the colour instrument measuring head by only 0.5 mm from the previous measurement location could result in a substantial change in measured colour (Fig. 6 and Table 1).

Even with these caveats, Black and Diffey (2016) reanalysed the CSIRO 2004 to 2014 data (Markley et al. 2015) and found that 70% of all spots measured (engraving and background rock) were significantly lighter (L^* increased) and that none were darker over the decade of measurement. CSIRO themselves had claimed that there was no consistent trend in colour change, but these claims were made without statistical analysis of the results. Even with the inherent flaws in the method, the extent of colour degradation of the rock surfaces seems to be significant enough over a decade for it to be evident, even in a colour measuring program that has

been shown to be imprecise.

MacLeod and Fish (2021) confirm that they used one of the colourimeters formerly used by CSIRO and that they measured average colour across the surface, taking multiple different colour measurements on the same rock. Therefore, their work is subject to the same logistic constraints identified for the CSIRO work (Black et al. 2017a). MacLeod and Fish (2021: 7, Fig 8) show colour contrast between background rock and engraved areas for 2019 but present results for only four of the eight sites because they either did not fit the regression (site 7), were claimed to be statistically unreliable (site 6) (p. 7, para. 5) or were omitted, presumably because of a localised wetting event (site 4) or simply omitted without explanation (site 4a). However, Figure 8 does confirm the current understanding that Murujuga rock patina colour is affected directly by the pH of the surface. Indeed, they conclude that '[w]ithout pH monitoring data, it is unwise to base conservation management decisions solely on colour differences

| Square | Position | L^* | | | | a^* | | | | b^* | | | |
|--------|----------|-------|--------|-----|-----|-------|--------|-----|-----|-------|--------|-----|-----|
| | | Avg | Median | Min | Max | Avg | Median | Min | Max | Avg | Median | Min | Max |
| A | 0, 0 | 51 | 51 | 29 | 85 | 26 | 26 | 10 | 44 | 22 | 22 | 6 | 50 |
| B | 0, 0 | 46 | 46 | 17 | 80 | 25 | 25 | 1 | 47 | 19 | 17 | -8 | 47 |
| C | 0, 0 | 59 | 60 | 22 | 79 | 34 | 35 | 16 | 52 | 29 | 29 | 1 | 49 |
| A | 0.5, 0 | 50 | 51 | 14 | 75 | 24 | 24 | 8 | 41 | 19 | 19 | -2 | 46 |
| B | 0.5, 0 | 48 | 48 | 17 | 78 | 25 | 25 | 1 | 49 | 19 | 18 | -8 | 51 |
| C | 0.5, 0 | 55 | 56 | 22 | 76 | 30 | 31 | 8 | 52 | 24 | 26 | 0 | 46 |

Table 1. L^* , a^* and b^* colour space values predicted for each square with the same area as a 3 mm diameter aperture using the Image Color Summarizer (Krzywinski 2017) (reproduced from Black et al. 2017a: Table 6)

between the engraved and background areas of the images.' It is clearly not on an alleged colour change that MacLeod and Fish base their extraordinary conclusion that industrial pollution does not impact the rock art.

Acidic emissions

MacLeod and Fish (2021) assert that 'Woodside Petroleum introduced low NO_x burners between 2005 and 2015, which resulted in greatly reduced nitrate levels', and this seems to be one reason for their optimism that 'the present monitoring data shows that there is presently no adverse impact on the rock engravings from industrial pollution ...'. However, they provide no NO_x emissions data to confirm this alleged reduction. The claim appears to be based on the supposition that rock surface nitrate concentrations are lower on average in 2017–19 than measured by MacLeod (2005) in 2003–04. However, this supposition is invalid because:

- nitrate concentration was measured on different rocks and at different locations in 2003–04 than in 2017–19;
- MacLeod and Fish (2021) chose the highest value of 6.53 ± 5.1 ppm recorded in 2003–04 for comparison;
- MacLeod and Fish (2021) report only a mean value of 0.7 ± 0.5 ppm, when there was a wide range in nitrate concentration sufficient to develop a regression equation relating nitrate concentration to pH; and
- MacLeod and Fish (2021) did not mention that nitrate measured pre-industrialisation was 0.3 ppm (MacLeod 2005).

The emissions data reported by the industry at Murujuga gives less room for optimism. Woodside (2019a) recently reported that they are emitting 8900 tonnes of NO_x annually. On top of the Woodside and ongoing shipping emissions, since 2017, there have also been new and increasing NO_x emissions from Yara Pilbara Nitrates. Yara Pilbara reported recently that their fertiliser plant is emitting 360 tonnes, and their ammonium nitrate plant is emitting up to 135 tonnes of NO_x annually (Yara Pilbara 2019).

Contradictory to statements by MacLeod and Fish (2021), the industry emissions data reported to the National Pollution Inventory (2020) illustrate that NO_x emissions rose steadily from 2000 until 2017 (Fig. 7). Woodside explained the apparent drop in 2014 of Karratha Onshore Gas Plant emissions as a change in the way emissions were calculated rather than a real change in emissions (Woodside 2019b). The reported tenfold drop in Pluto onshore gas treatment emissions from 2018 to 2020 has not been explained. Given that there were no reported major adjustments to any of the main industrial processes or facilities in the year of this ten-fold reduction (National Pollution

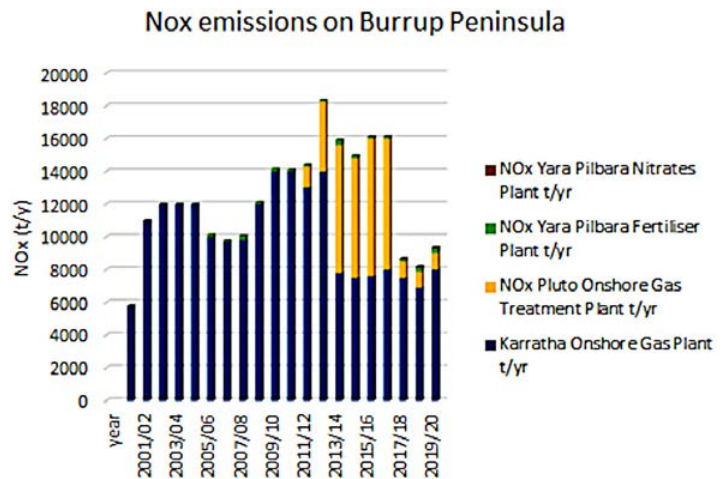


Figure 7. NO_x emissions as reported annually by industry at Murujuga (from National Pollution Inventory 2020).

Inventory 2020), the reduction needs explanation.

Even if the NO_x emissions have declined over the last three years, the emission rate across Murujuga remains high enough to damage the rock art, as seen by the continuing low rock surface pH. A reduction in NO_x concentrations from earlier years is not the criterion for assessing whether the rock art is being damaged. The criterion is the quantities of acidic compounds from industrial emissions deposited on the rock surfaces, which will dissolve the outer rock patina. Clearly, from the discussion above, when rock surface pH falls below 5.9, the long-term survival of the rock art is in jeopardy (Bednarik 1979).

The distribution of atmospheric nitrogen dioxide across Murujuga is clearly illustrated in the data from the Copernicus satellite for a week in 2021 (Fig. 8). Although the highest concentration is located directly over the Woodside facilities and notably in

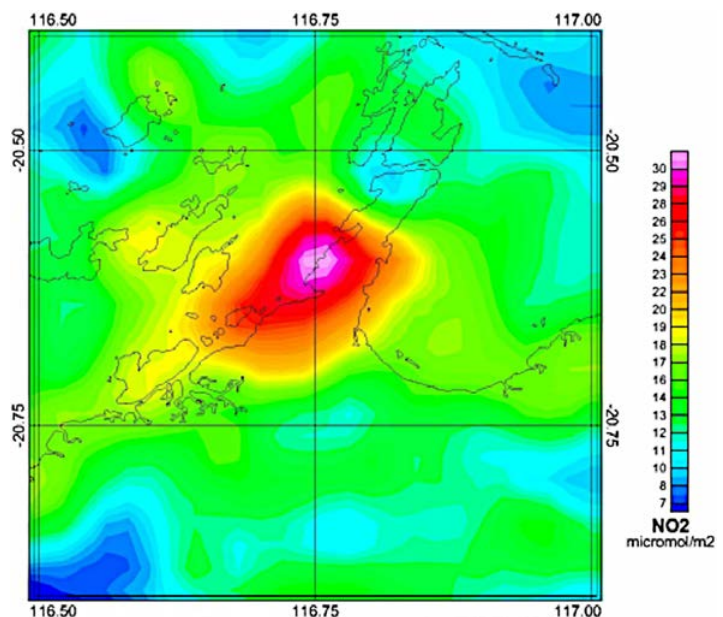


Figure 8. Mean values of NO_2 concentration over seven days (26/4/2021 – 2/5/2021) derived from satellite data (Copernicus data hub 2021). Analysis and map by Christopher Swain.

the immediate vicinity of various sampling sites, the impact is evident across a wide area of Murujuga. A similar distribution of NO_x deposition due to industry across Murujuga and adjacent islands was reported by Parsons et al. (2021) in their study for the Western Australian Government into the impact of cumulative air emissions across Murujuga.

As we have noted above, nitrogen oxides form acid rain when removed from the atmosphere during a rainfall event, and they also undergo dry deposition as dust falling on the rocks at other times. This nitrous-rich dust then forms nitric acid during a period of light rainfall and dew. Results from chemical deposition monitoring in 2012–2014 provided by Woodside show that up to 34% of the emitted nitrogen dioxide was deposited on the rocks (Woodside 2019a, Appendix E – Air Quality, Table 3-8).

We have presented evidence on NO_x emissions, but emissions of SO_x , particularly from shipping, are also extremely high (Black et al. 2017a), and these will be having an equally profound impact on the rock patinas of Murujuga, forming sulphuric acid during periods of light rainfall and dew.

MacLeod and Fish's (2021) claim that these massive and highly acidic industrial emissions are having no impact on Murujuga rock art is, therefore, simply not scientifically credible and not supported by the evidence presented. What then is the basis of the claim? We are genuinely unsure, but it seems to relate to MacLeod and Fish's (2021) term 'precipitation'.

'Precipitation'

There is a suggestion by MacLeod and Fish (2021) that somehow rock patinas, whilst currently etched by acidity during the bulk of the time, are quickly recuperating during the brief interludes (presently only a few weeks a decade) in which the rock surfaces attain a pH level above 6.5. Unlike previous studies, MacLeod and Fish (2021) emphasise that 'alkalisation (from sea salt or ammonia leaks) causes fresh minerals to deposit and thereby change the appearance of the engravings' (p. 4). They report observing from photographs 'an increased amount of the purple-black patina' on the sample rock art from Deep George (Nganjarli) after a massive ammonia leak event from Yara Fertilisers that had turned rock surfaces in this area unusually alkaline. The following year, they found that the reverse side of the rock 'had a deep-purple patina associated with the presence of Mn_3O_4 ' (2021: 5) that was confirmed by redox (voltage) measurements. Unfortunately, no L^* , a^* and b^* data to quantify the colour measurements are presented. They explain the colour changes in terms of the effects of microbial action. By 2019, they reported that this new 'patina' was dissolving (p. 5), presumably as the rock acidity returned to below a pH of 6.5. They describe having seen the same process operating at two other sites among the eight they were monitoring. They conclude that 'dry deposition of ammonia and wind-borne sea salts works to mitigate the release of

iron and manganese minerals from the Murujuga rock engravings' (p. 8). This claim seems to lie at the heart of MacLeod and Fish (2021) assertion that 'there is presently no adverse impact on the rock engravings from industrial pollution ...'.

As we have described in this paper, the ferromanganese rock patinas of Murujuga were formed by biomineralisation processes where microbes concentrate manganese and, to a lesser extent, iron compounds so as to form the hard cement-like components of the patina (Miller et al. 2012; Dorn 2020; Lingappa et al. 2021). They do this only under alkaline conditions, and it happens at extraordinarily slow rates of 1 to 10 microns per 1000 years (Dorn and Meek 1995; Liu and Broecker 2000; Dorn 2009). Dorn and Krinsley (1991) showed clearly that reprecipitation of manganese and ferric compounds following acidic dissolution removes the natural layering of the rock varnish, increasing porosity and redistributing the manganese and ferric deposits along rock wall fractures and not as a new form of varnish. Thus, even if reprecipitation of manganese and iron compounds occurred, it would not be within the hyphae of dead microbes, and the structure and morphology of the patina would be changed with a detrimental impact on the long-term survival of the rock art. We doubt that MacLeod and Fish (2021) have observed examples of this process, and they certainly do not provide evidence of it. Whatever the cause of the colour changes observed by MacLeod and Fish (2021), their data shows it was for a short period, and the re-deposition was already being dissolved by acidity within just a year.

Therefore, the bigger picture is what is important here, namely that the industrial emissions at Murujuga cause acidification of the environment and thereby pose a constant threat to the integrity and survival of the rock art. Occasional industrial ammonia leaks and extreme weather events that temporarily alleviate the overarching acidification of the environment and rock surfaces do little even to slow the degradation and cannot reverse the ongoing deterioration of the rock art. The cause for genuine concern is real and cannot be wished away, particularly as new industrial developments are currently proposed that will result in increased acidic emissions.

Conclusion

A detailed understanding of the rock decay processes at Murujuga has evolved over more than 20 years from painstaking local research, and this has significantly improved our global understanding of the formation processes of ferromanganese patinas in low rainfall environments. The evidence we have presented clearly shows that, with the currently recorded acidity levels, the rock patina and associated art will degrade and disappear over time, as has occurred on rocks with continual bird droppings (Bednarik 1979). This affirmation is also important in the current context because the Western Australian State Government is

considering development applications for a further 50 years of natural gas processing and from two new industries seeking to construct plants at Murujuga. We caution in the strongest possible terms that the 'all is fine' headline of MacLeod and Fish (2021) is not acceptable as an excuse to allow the placement of further polluting industry at Murujuga. The statement is not supported by current science.

On the contrary, current evidence of acidification is of such concern that existing industry should be subjected to far more stringent emission controls to bring Western Australia into line with other global leaders. Excellent technology is available and utilised successfully elsewhere that substantially reduces emissions by industries of the type located at Murujuga. One of the parent companies of Murujuga's own Yara Pilbara is a market leader in manufacturing emissions control technology. The Western Australian Government should heed the warnings of contemporary science and ensure that new industry is placed away from Murujuga, in one of the many identified suitable alternative locations; and that new strict emissions control requirements are enacted to reduce pollution at Murujuga and bring the State in line with global leaders in the fight against industrial pollution and climate change. In direct contrast, the Norwegian Government placed a tax on emissions of NO_x in 2007 (recently 23.48 NOK or AUD 3.40 per kg NO_x emitted (Norway Tax Administration 2021), because of the extremely detrimental effects of NO_x in forming acid rain and damaging human health. A tax of this magnitude would raise approximately \$30 m annually from Woodside operations alone and would undoubtedly change behaviour and help to ensure the long-term preservation and protection of the Indigenous cultural heritage contained in the irreplaceable Murujuga rock art.

Given that the bigger claims of MacLeod and Fish (2021) are at odds with existing science, the onus is on them firstly, to provide more detail about the evidence upon which they base their claims (including their statistical methodology) and secondly, they should make their data publicly available. MacLeod and Fish acknowledge in their paper (2021: 3) that they both work as contractors to the petrochemical industry producing the acidic emissions at Murujuga. The tide is turning against those that seek to play down the impacts of industrial pollution upon the world. Even within the industry, big vested interests are changing tack and, for example, supporting the shift to sustainable energy and net zero-carbon emissions (Murray 2020; Samios and Harris 2021).

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Conflicts of interest

JLB and MAF are members of Friends of Australian Rock Art, an independent non-profit volunteer organisation established in 2006 to protect, preserve and promote Australia's Aboriginal rock art, particularly the ancient petroglyphs of the Dampier Archipelago, including Murujuga. We are all scientists from a range of disciplines, determined to uphold the integrity of the scientific method. All contributions to this paper were voluntary.

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