Surface chemistry of Burrup Rock art at the Yara monitoring sites

Report for Yara Pilbara Nitrates by
W S Fish Consulting

Prepared by Dr Ian D MacLeod
Heritage Conservation Solutions

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Figure 1: View of the TAN plant from site 22

Contents

Executive Summary

- Measurements in November 2017 were conducted on gabbro sites (7, 22 & 23) and granophyre sites (5, 6 & 21) with the sites determined through the CSIRO monitoring program.
- There is a strong correlation of increased colour difference between the engravings and the host rock with increasing rock acidity (recorded using a surface pH electrode).
- The colour differences indicate that the more recently deposited patina over the engravings appears to be dissolving faster than the background minerals.
- In the absence of external impacts, the higher the salt concentration the higher the pH and there is a concomitant lowering of the rate of mineral dissolution.
- Analysis of pH and chloride ion activity indicates that at some locations a major influence on acidity is from chloride obligate bacteria, which leads to increased acidity with increasing salt levels on some sections of the rocks.
- Earlier data showed that FeOOH in the weathered rock surface was dissolving as $Fe(OH)_2^+$ but presently the iron appears to be coming from silicate minerals such as actinolite $\{Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2\}$, augite $\{(Ca, Mg, Fe)_2(Si, Al)_2O_6\}$ and chlorite $\{(Mg, Al, Fe, Li, Mn, Ni)_{4-6}(Si, Al, B, Fe)_4O_{10}(OH, O)_8\}$.
- Earlier data showed that the rock patina was dissolving as Mn^{2+}, but presently the manganese is coming from MnO as $Mn(OH)^+$ due to lowered acidity levels.
- Prolonged dry spells lead to accumulation of wind-borne sea salts which resist acidification.
- Cyclonic downpours between February 2003 and March 2017 have reduced the amount of soluble nitrate and this has brought about a change in deterioration mechanism. However, data from June 2017 away from the Yara sites show increasing rock acidification near the Climbing Man gully and in areas of the former "Museum Compound".
- The nitrate concentration in wash solutions has fallen from 6.3 ppm in 2003, and 4.5 ppm in 2004 down to 0.6 ppm in 2017. Note that the earlier measurements DID NOT include Yara sites so no direct comparative data exists for the six Yara sites.
- The sensitivity of pH to soluble nitrate ion fell with decreasing nitrate ion concentration. The historic data showed that acidity increased with nitrate ion concentration. The Yara sites showed the reverse trend which is likely due to the higher salt buffering and nitrate levels being too low to induce a microbiological response.
- The CSIRO accelerated ageing study showed that chlorite appeared to be one of the first minerals to dissolve with increased acidity. The CSIRO accelerated ageing studies are supported by soluble boron concentration in the washings from 2003 and 2004. Data from the chloride to boron ratios in the Yara sites show that granophyre rocks are eight times more sensitive to chlorite dissolution than gabbro rocks.
- Routine sampling of both gabbro and granophyre rocks near the engraved sites provides opportunities to determine the surface mineralogy (external XRD analyses) for chlorite. This will show if the rock surfaces are dissolving or not and will avoid any sampling of the engraved rock surfaces. Surface pH of the rocks should be recorded in the field prior to sending them to laboratories for analysis.
- Additional sulphate is coming from sources other than the sea for the six Yara sites. The mechanism will be established once the air quality monitoring data has been correlated with the solution and rock surface chemistry data.
- There will be no need for extensive pH, chloride and solution washing monitoring other than for research purposes if chlorite mineralogy is adopted.
- Data from the ASD spectrophotometer readings is yet to be quantified by others.

Background

To comply with the regulations concerning retention of its operating licence, EPBC 2008/4546, Yara Pilbara Nitrates engaged WS Fish Consulting to develop appropriate methodologies to conduct colour monitoring measurements on the six sites surrounding the ammonia and ammonium nitrate plants in the Burrup. The lead consultant (Warren Fish) conducted meetings with the management team from Yara to develop the time table and to engage with key community members of the Murujuga Aboriginal Corporation for permission to come to country in late November 2017 to repeat the colour measurements done in previous years by the CSIRO team. One of the former CSIRO operations members, Bill Carr, was a foundation member of the Burrup Rock Art Monitoring Management Committee (BRAMMAC) team that has monitored the rock art in the region from 2002-2010. The work has been conducted around the Burrup industries and in the outlying island locations since the research program was initiated. Since 2010 Bill Carr has been a member of the reformed group which is now known as the Burrup Rock Art Technical Working Group (BRATWG). Dr. Ian MacLeod was also a foundation member of BRAMMAC owing to his rock art conservation background. Changes in organisational structure in 2005 saw MacLeod replaced on the committee by other Western Australian Museum representatives. MacLeod retired from the Western Australian Museum in 2016 and is now the Principal of Heritage Conservation Solutions. MacLeod has published several peer-reviewed papers on the conservation of Aboriginal rock art and has nearly 40-years' experience in materials conservation (Appendix I).

During the first phase (2003-2004) of research into the condition of the rock surfaces in the Burrup, several engraved rocks in the "Museum Compound" were examined regarding their acidity (as measured with a surface pH electrode), the water-soluble minerals on the rock surfaces and the microbiological activity. Samples of the rock surface were swabbed with sterile culture material and placed into prepared phials. The biological material was stored at zero degrees before being taken to laboratories in Perth (Department of Agriculture) for characterisation. Other reference measurements were conducted on Gidley and Dolphin Islands in the Dampier Archipelago to act as reference points away from industrial activities associated with the Woodside gas plant and iron ore shipping out of Dampier ports.

Analysis of the solution chemistry provided strong indications of the causal link between the amount of nitrate on the rocks and the level of microbiological activity. This in turn indicated that the acidic metabolites from the organisms were significantly contributing to the overall acidification of the rock surfaces and mobilisation of key minerals containing both iron and manganese, as well as copper and nickel. In the light of this background information it was decided to conduct solution sampling on the rock surfaces on the six CSIRO approved sites within the 2 km radius of the Pilbara Nitrates plant. The rock irrigation data was done in conjunction with surface measurements of the pH and chloride ion activity. The wash solutions were analysed for sulphate, sulphite, nitrate and nitrite ions, as well as for oxalate, of which there was none. The electrical conductivity of the wash solutions was also measured as a guide to the overall nature of the soluble minerals and salts that were mobilised during the five minutes of sample collection.

Field work was conducted on the six monitoring stations around the Yara plant in November 2017. A preliminary report on the interpretation of the colour measurements from the Konica Minolta Chromameter has been presented late December 2017. The sites are part of the CSIRO colour and mineralogy monitoring of the Burrup that has been undergoing continuous evaluation for the past 14 years. In addition to conducting the required ASD spectrophotometer readings, used to determine the mineralogy of the rock surfaces and that of the associated engravings, and the chromameter measurements, a series of pH and chloride readings were taken directly on the rocks adjacent to the CSIRO monitoring points. In order to quantify the relationship between the surface chemistry, as measured by the contact with the flat surface pH and chloride electrodes, standard volumes of distilled water were used to temporarily irrigate (wash) the rocks, to collect the water-soluble metal ions and all discernible anions (chloride, nitrate, nitrite, oxalate, and sulphate). The refrigerated samples were stored off site until they were transported by air to the Bentley based laboratories of the ChemCentre for independent NATA accredited chemical analyses.

The Heritage Conservation Services (HCS) initial report indicated that there was a strong correlation between the observed colour differences between the engraving and the parent rock at the six reference sites and the surface pH of the rocks. This report examines in detail the solution chemistry and provides a synthesis on the historical data relating to two sets of solution and surface pH measurements conducted in 12-13 years before the present work was conducted. The referenced sites of interest to Yara included granophyre at the Burrup Road (5), the Water Tanks (6) and Yara West (21) sites, while gabbro rocks were found on sites at Deep Gorge (7), Yara North East (22) and Yara East (23). All these sites lie within a 2 km radius of the present operational sites of the ammonia plant and the Technical Ammonium Nitrate (TAN) site.

Measurement of the rock surface pH and chloride concentration

The pH and chloride ion measurements taken on rocks adjacent to the CSIRO reference engraved sites so that the colour reference rocks would be kept in a "pristine state" as requested by Bill Carr. The pH data was recorded using a flat surface pH electrode which had been calibrated each morning using standard pH buffers at pH 4 and pH 7 before the field measurements commenced. The pH meter was temperature compensated using a thermocouple connected to the Kensington Scientific pH meter (KS-pH-220-BASIC) and the glass electrode was a VWR model no W7567287. Readings of the surface pH were standardised by recording the values after an elapsed interval of one minute. If the surface was more responsive and the pH reading stabilised in 40 seconds, then that value was recorded and keeping the probe in position did not alter the steady value that had been noted. Owing to the porous nature of the rock substrate prolonged equilibration times can result in pH values that are not reflective of the local microenvironment. A small amount of water is needed to keep the bulb wet and the solution in contact with the internal reference electrode. The electrical circuit of the pH electrode is completed through connecting the internal Ag/AgCl reference electrode through two fine wicks which are situated at 180° to each other on either side of the glass membrane and held in place by the soft plastic ring fitting inside the 12-mm external diameter solid epoxy body. The chloride ion activity was measured using a TPS WP-90 ion-pH-mV-°C meter coupled with a 1609-186881 chloride ion specific electrode. The rocks were wetted with two drops (0.08 ml) of a 0.1 molar sodium nitrate solution to provide an electrolyte to stabilise the liquid junction between the sensing head and the rock surface. Stable readings of the chloride activity were obtained within a minute. The electrode was calibrated daily with a 1,000 and a 100-ppm chloride reference solution before any field measurements were made.

Analysis of sea borne salts on the rocks

The amounts of surface chloride detected on the rock surfaces provide direct evidence of the impact of the marine environment and indicate that salt weathering of rocks, with extensive dehydration and rehydration cycles apparently playing a significant role in the local environment. The wash solutions from the rock surfaces showed up a range of ions commonly associated with sea water, namely Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}. Analysis of the way in which the concentrations varied across the Burrup was consistent with known weather patterns of prevailing winds and proximity to the sea. When the wash concentrations of sulphate are plotted as a function of the chloride, most of the data follow a linear relation that reflects the common ratios of the anions that are found in seawater. Data from the most recent irrigation data obtained in November 2017 is shown in Table 1. Significant differences from the normal ratios found in seawater are found on the rock surfaces in the Burrup.

The microenvironment of the rocks was assessed through a combination of surface chloride (TPS combination Cl electrode) and surface pH (WVR flat electrode) measurements on the rock surfaces. The first round of measurements was made using a 0.05 M $NaNO_3$ solution in distilled water electrolyte was used for chloride measurements and the pH was recorded after equilibration with two to three drops (0.04-0.06 ml) of distilled water on the rock surface. The soluble nitrate, nitrite, sulphate, chloride, oxalate concentrations on the rock surfaces were determined by ion chromatography from 15 ml samples of distilled water washings collected from the rock surfaces and standardized to a 200 cm^2 area. Metal ions in the wash solutions were determined by inductively coupled plasma–mass spectrometric (ICP–MS) methods. This study is based on an initial survey in June 2003 (winter) of relocated engraved rocks which was then extended in August 2003 (spring) to include several sites located at a distance from known emission sources was concluded in February 2004 (summer) with repeated measurements on the Burrup. Data obtained for the 2017 measurements for cations measurements were made on 200 ml samples and anions in 100 ml sample bottles collected over an area of approximately 500 cm^2.

Table 1: Ratio of salts in sea water and in the rock washings around the Yara plant

Cation ratios	Seawater	Site 7 Gabbro	Site 22 Gabbro	Site 23 Gabbro	Site 5 Granophyre	Site 6 Granophyre	Site 21 Granophyre
Cl^-/Na^+	1.8	1.2	1.2	0.7	1.3	0.4	0.7
Cl^-/SO_4^{2-}	7.1	0.7	2.2	1.3	1.1	1.3	1.0
Cl^-/Ca^{2+}	47.0	0.6	4.1	1.3	1.6	0.2	1.5
Ca^{2+}/K^+	1.0	8.0	2.5	7.1	2.2	19.2	2.5
Ca^{2+}/Ba^{2+}	8,000	795	200	87	175	1075	258
Mg^{2+}/Ca^{2+}	3.1	0.2	0.0	0.1	0.1	0.1	0.3
Na^+/K^+	27.0	8.0		18.6	4.0	18.0	6.5

It is interesting to note that site 6, the water tanks up on the hill behind the Woodside gas complex, had the highest electrical conductivity at 12.2 mS/m, the highest calcium to barium ratio and the highest Ca^{2+}/K^+ ratio which indicates that there is possible mobilisation of calcium containing minerals on this site. Repeated analysis of the surfaces is likely to provide useful additional data as it must be recalled that this was an extremely dusty site and it had not rained for a long time in this area of the Burrup. Examining the data from the Cl^-/Na^+ ratios there seems to be a natural grouping of sites 7, 22 and site 5 with similar ratios between 1.3-1.2 while sites 21, 23 and 6 have lower ratios ranging from 0.4-0.7, with the site 6 again having the highest sodium content. The much higher calcium content of the gabbro rock crust, 10.9±1.9% CaO, compared with the granophyre crust of 1.4±0.8 % CaO, is not reflected in the relative amounts of calcium in the wash solutions (Ramanaidou and Fonteneau, 2017). There does not appear to be any systematic difference in the cation ratios for salts derived from seawater than can be correlated with the different types of crusts that have typically formed on the two different types of rocks.

There are no systematic differences in the ratios shown in Table 1 that can be correlated with the different rock types. The Cl^-/Na^+ ratio is the same for sites 5, 7 and 22 which is closer to the normal sea water ratio whereas sites 21 and 23 are very similar but with elevated sodium levels and site 6, the water tanks had the highest amount of sodium, compared with chloride ions. The CSIRO analysis of the weathered crusts on granophyre rocks had 3.7 % Na_2O while the gabbro rocks had 1.9%, so some of the elevated sodium levels may be associated with a specific weathering pattern. The mean Cl^-/SO_4^{2-} ratio for all but site 7 at Deep Gorge was 1.4±0.5; the chemistry of the gabbro rocks at site 7 seems to be associated with an elevated sulphate concentration. Comparison of the air quality monitoring data at the nearby site with that of the similar station at site 5 may provide some quantitative reason for the apparent difference in the local surface chemistry. The outlying nature of site 6 is also seen in the Cl^-/Ca^{2+} ratio of a low value of 0.2 which indicates that, apart from elevated sodium levels, the rock surface also has elevated soluble calcium. The similar ratios for Cl^-/Ca^{2+} for sites 5, 21 and 23 may be a reflection that they are exposed to similar air flow coming across the flood plain on which the plant is located. Five of the sites have varying Ca^{2+}/K^+ ratios which are all significantly greater than that found in seawater. This indicates that the potassium is being selectively bound in weathering products such as clays on the rock crusts. Once again, the chemistry of site 6 (water tanks) is quite different to the other sites with a Ca^{2+}/K^+ of 19.2 while the median of the five other sites was 2.5±2.9; the precise nature of the difference is at present uncertain. Access to the air quality monitoring data may shed some light on the mechanisms behind the differences.

The chemical analysis done by CSIRO on the mineralogy of the rock crusts' weathered zones did not show up any significant amounts of barium, so it is considered likely that the presence of varying amounts of this heavy alkaline earth metal came from the sea. The chemistry of the barium minerals was considered a likely candidate to see if there was any systematic change in the rock chemistry from the time of the original measurements made in 2003 and the present round of data collected in 2017.

Because the concentrations of cations in the wash solutions is low, it is more convenient to use a logarithmic value, expressed as pM, in the same format as pH represents the hydrogen ion activity. Higher pM values mean less metal ion activity since pM is equal to the log of the inverse of the metal ion concentration. The most significant difference in the behaviour is that for the February 2004 data there is a change of mechanism of solubilisation of calcium as the slope of the p [Ca] vs pH plots changed from one to two. The most likely mechanism is that for a 1:1 reaction it is the dissolution of calcium carbonate to form a soluble bicarbonate complex,

$$CaCO_3 + H^+ \rightarrow Ca(HCO_3)^+ \qquad (1)$$

This is the reaction that dominates the solution processes for the 2003 and the 2017 conditions. For some reason the mechanism changed to a 1:2 reaction for February 2004 in which the calcium carbonate would have dissolved fully as the disassociated bicarbonate, as shown in Equation 2.,

$$CaCO_3 + 2\,H^+ \rightarrow Ca^{2+} + H_2CO_3 \qquad (2)$$

Table 2: Solution properties of calcium and barium washings on the Burrup rocks

Date	mean pH	mean p[Ca]	mean p[Ba]	slope p[Ca]/pH	slope p[Ba]/pH
August '03	4.97±0.48	3.6 ±0.4	6.6±0.2	1.0±0.1	0.4±0.2
February '04	4.31±0.48	4.1±0.6	7.2±0.4	2.0±0.2	2.0
November '17	5.69±0.51	2.0±0.6	5.2±0.3	1.3±0.3	0.5±0.1

During the same period the mobilisation of barium, which is likely to exist as barium carbonate as part of the sea water evaporite, also changed mechanism. For the solubilization of barium carbonate the reactions are the same as shown in equations 1 and 2, but with barium replacing calcium in the equations. The February 2004 data also showed the lowest free calcium and free barium ion concentrations, compared with the other two sets of measurements and so the likely difference in mechanism is likely to be due to the smaller amounts being mobilised and so the full dissolution reactions shown in equation 2 are more readily facilitated. The mean pH associated with the dissolution reactions in February 2004 was quite low at pH 4.3±0.5 which was nearly five times more acidic than the August 2003 data and more than 20 times more acidic than the measurements made at the six Yara sites. The mechanism of the mobilisation of barium in the August 2003 and November 2017 data show the same mechanism with the stoichiometry being two barium ions being mobilised per proton consumed. It is likely that this data set, which is limited, does not relate to simple evaporites but it reflects minerology associated with co-precipitation of barium with calcium.

Interpretation of the pH effects on iron and manganese mobilisation

Previously published work by MacLeod (2005) and MacLeod et. al. (2017) has shown that at the pH values recorded in 2003 and 2004 (Appendix IV) there was measurable mobilisation of iron and manganese containing minerals. Analysis of the wash solutions from the early data sets has shown up significant concentrations of aluminium, iron, manganese, nickel, copper and some zinc and lead from the parent rock crusts. Because the mineralogy of the highly weathered gabbro and granophyre is characterized by a series of mixed amorphous iron—manganese oxides, in the form of desert varnish, iron(III) oxy-hydroxides and weathered minerals such as smectite, kaolinite, illite and mica (Clark 2004) it is not unexpected to find mobilization of metallic cations under the acidic conditions. It is helpful when undertaking a review of metal ion solubility to understand that the dissolution of the key elements in the rock patina is controlled by the pH or the acidity of the microenvironment. When mineralisation (rock corrosion) products from the weathering of the rock crusts are dissolved it will involve neutralisation of either oxides or hydroxide of metal ions. When metal hydroxides are mobilized by acid dissolution the generic dissolution reaction can be written in the form show in Equation (3),

$$M(OH)_n + n\,H^+ \longrightarrow M^{n+} + n\,H_2O, \qquad (3)$$

In equation 3 the *n* value is the oxidation state of the metal, typically 2 and 3 for iron and mixtures of 2, 3, 4 etc. for manganese. The concentration of the metal ions is derived from the general equilibrium constant for the dissolution of a metal hydroxide into the component elements. Thus $K_{sp} = [OH^-]^n \times [M^{n+}]$, is mathematically the same if we rewrite the expression using the reciprocal values i.e.

$$^1/K_{sp} = \{^1/_{[OH^-]^n}\} \times \{^1/_{[M^{n+}]}.\} \qquad (4)$$

Since the logarithm of $\{^1/_x\}$ is pX, then equation 4 can be expressed by the formula

$$pK_{sp} = n\ p[OH] + pM_{OH}, \qquad (5)$$

By definition, p[OH] = pK_w - pH which can be substituted into equation 5 then rearranged to give equation no 6, remembering that the self-ionisation constant of water, pK_w has a value of 14.

$$pM_{\ hydroxides} = pK_{sp} + n(pH\text{-}14) \qquad (6)$$

For metal oxides of the general formula M_xO_y, the concentration of the metal is given by Equation 7,

$$pM_{oxides} = {}^1/x\ \{pK_{sp} - n\ pK_w) + y\ pH \qquad (7)$$

When the pM values are plotted as a function of pH it is theoretically possible to determine if the dissolution process involves a hydroxide, which has a slope of *n* for the pM vs. pH plot. If the product dissolving is a mixed valency oxide, the slope of the pM vs. pH plot is $^y/_x$, if the soluble ion is an un-complexed free metal ion.

The more acidic surfaces in the 2003 spring and the February 2004 summer measurements were amenable to this form of analysis and plots for iron showed that for both seasons the p[Fe] vs. pH plots have an average slope of +1.98 ± 0.06 pH which confirms the following mechanism:

$$FeOOH + 2H^+ \rightarrow Fe(OH)_2^+ + H_2O. \qquad (8)$$

The Pourbaix diagram for iron in the range of pH observed on the rock surfaces shows that the $Fe(OH)_2^+$ ion is the dominant form of soluble iron(III) under oxidizing conditions (Pourbaix 1974). The pH data is shown in Appendix IV. Similar plots indicate that copper is mobilized by dissolution reactions involving two protons per metal ion as is the case for nickel.

Using washing solution data for the mobilisation of aluminium allows similar plots for the solubility of aluminium with surface pH to be determined. For the Burrup rocks the aluminium mobilisation graphs had an average slope of 1.4±0.2 pH, which is consistent with the dissolution of kaolinite ($Al_2Si_2O_5(OH)_4$) to give the $Al(OH)_2^+$ ion and $AlSi_2O_5^{+,}$ as shown in Equation 9.

$$AlSiO(OH) + 3H^+ \rightarrow Al(OH)_2^+ + AlSiO^+ + 3\,H_2O \qquad (9)$$

Kaolinite has been identified as one of the aluminium containing minerals on the Burrup rocks along with feldspar, chlorite, mica, smectite and some gibbsite (Clark 2004) and it was a major mineral identified in the CSIRO Accelerated Weathering experiments (CSIRO 2016). It is not unexpected for aluminium ions to have been mobilized under the very mild sample collection regime that was used.

The concentration of manganese in the rock irrigation measurements done in November 2017 is plotted as a function of surface pH and shown in Figure 1. It is noted that only half the sites showed a linear response of the pMn vs. pH plots, the detailed explanation for this phenomenon is discussed below.

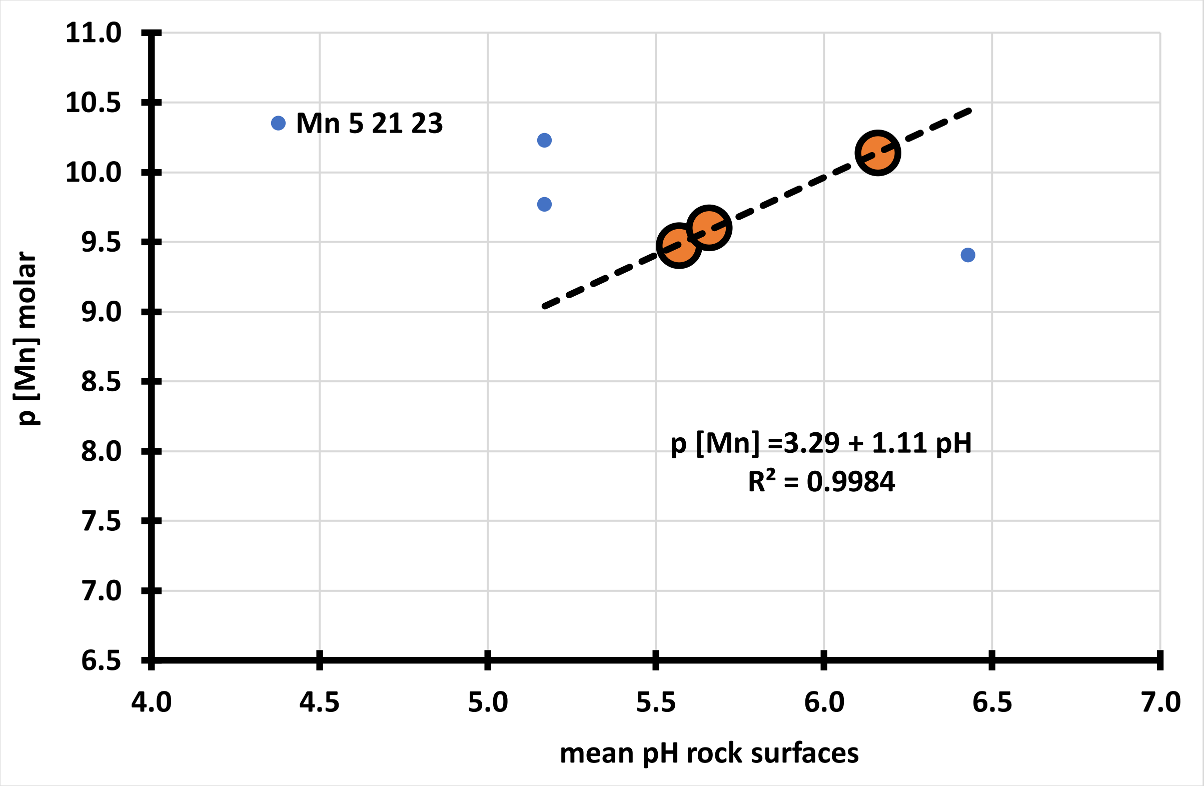

Figure 1: Plot of the Yara sites relationship between solubility of manganese and pH

The corresponding data for iron is shown in Figure 2. The slopes for iron and manganese in the 2017 data indicates that there is an apparent change of dissolution mechanism at the Yara sites compared with the other parts of the Burrup in the earlier seasons. This change is indicated by the relationship that there is a 1:1 slope for the reaction of acidic solutions on the release of manganese. This reaction could simply be the dissolution of manganous oxide since equation 10 would give the observed slope, viz.,

$$MnO + H^{+} \rightarrow Mn(OH)^{+} \qquad (10)$$

The results from the August 2003 and the February 2004 data are shown in Table 2, along with the mean values of the p [Mn] and p [Fe]. It is noted that for manganese there was an apparent change of mechanism controlling the release of manganese from the rock patina in February 2004, with a slope of p Mn vs pH of 2.0 which indicates that the mechanism shown in equation 9 is replaced by the one shown in equation 11,

$$MnO + 2\,H^{+} \rightarrow Mn^{+2} + H_2O \qquad (11)$$

The most likely reason for the change in the mechanism from reaction 10 to 11 is that the mean pH fell from 4.97±0.48 (August 2003) to a value of 4.78±0.27 (February 2004) which was clearly enough to bring about a subtle change in the dissolution mechanism. This result comes from a detailed examination of the 2003 and 2004 washing solution data and a re-working of the manganese data from February 2004. This slope of the p Mn vs. pH plot was previously reported (MacLeod 2005, Black et. al. 2017) as being 0.75 involved a more complex set of acid dissolution combined with a redox reaction, as shown in Equation 12,

$$2\ Mn_2O_3 + 3\ H^+ \rightarrow 2\ Mn(OH)_2^+ + Mn(OH)^+ + Mn^{2+} + 2e^- \qquad (12)$$

The present reinterpretation of the manganese dissolution data presents a simpler decay mechanism. There is a need for additional surface washing data to be obtained, in conjunction with surface pH and chloride readings, before increased reliability on interpretation can be progressed.

The dissolution of manganese species from the solid phase is more complex because the only stable ionic species in the pH range of 4.0-5.5 is the Mn^{2+} ion. Redox processes that are commonly facilitated by fungi that reduce Mn(IV) species to Mn^{2+} ions (Gadd 2004). There is a direct increase in the manganese ions in the wash solution with increasing acidity of the rock surfaces. The solution chemistry of manganese is very complex, with solid phases of Mn^{2+} being MnO and $Mn(OH)_2$, for Mn^{3+} there is Mn_2O_3 and for the mixed valence of Mn_3O_4, which is a mixture. like its iron analogue magnetite, of one Mn^{2+} and two Mn^{3+} ions.

For the 2003-2004 data the slope of the pM vs. pH plots for iron had a slope of 2.0, which is consistent with the dissolution of iron (III) oxyhydroxide, FeOOH viz.,

$$FeO(OH) + 2\ H^+ \rightarrow Fe(OH)^{2+} + H_2O \qquad (13)$$

By way of comparison, the 2017 November data showed that there was a slope of 0.3 pH per pM i.e. there is a completely different dissolution mechanism in the present (2007) rock data around the Yara compound compared with the 2003-2004 measurements. A plot of the data for the gabbro and granophyre rocks measured in November 2017 is shown in Figure 2.

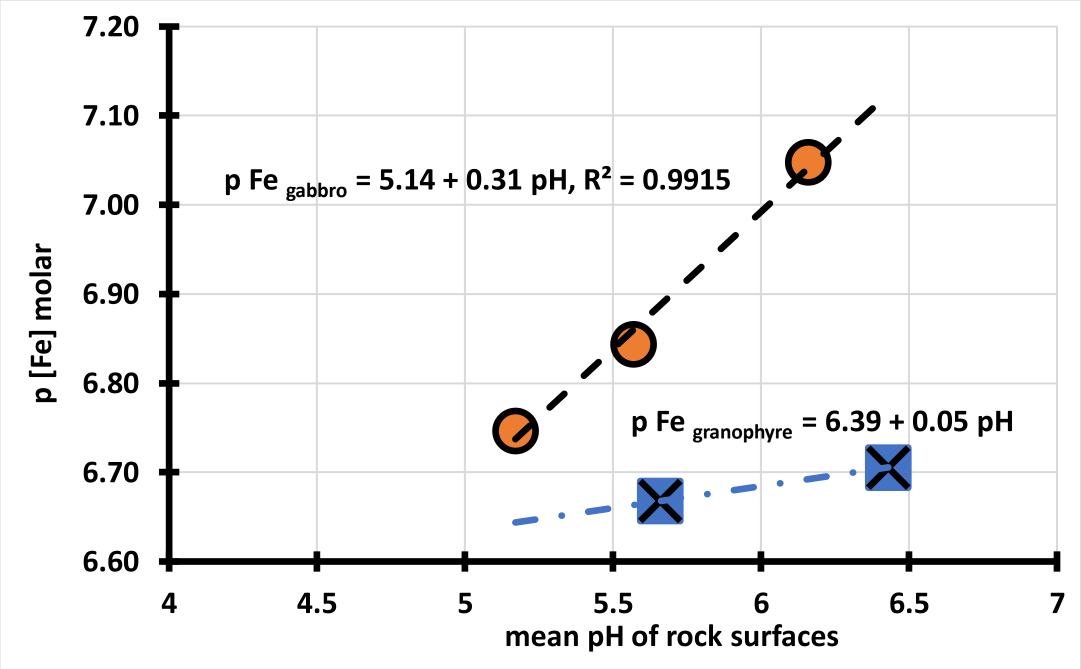

Figure 2: Plot of p [Fe] vs pH for the sites surrounding the Yara plant, November 2017

The present slope (2017) of the p[Fe] vs. pH plot shown in Figure 2 is for a ratio of one proton being consumed per three atoms of iron; but this formulation does not correspond to any known iron-oxy-hydroxides. The detailed examination by CSIRO of the parent and weathered rock surfaces of the gabbro and granophyre rocks in the Burrup has provided an exhaustive list of the minerals that are present in the mineral crusts on the gabbro and granophyre rocks (Ramanaidou et.al. 2017). Iron containing minerals that do not follow simple stoichiometry include actinolite, $Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$, augite, $(Ca, Mg, Fe)_2(Si, Al)_2O_6$ and chlorite $(Mg, Al, Fe, Li, Mn, Ni)_{4-6}(Si, Al, B,$

$Fe)_4O_{10}(OH, O)_8$ which are all found on the Burrup rocks (Ramanaidou et.al. 2017). The accelerated acid ageing study showed that chlorite appeared to be one of the first minerals to dissolve. More detailed studies of pM versus pH should be done with the above-named minerals to see which species is controlling the release of iron from the rocks in the Yara sites.

It may be that the mobilisation of the iron is part of a complex suite of iron-containing species, the nature of which remains to be discerned. Given the complex nature of the rock art patination the apparent stoichiometry can be explained by the iron dissolution reaction being controlled by several steps as the mineral dissolves. Iron in such complex mineralogy (as previously noted) is going to be dissolved along with other minerals such as manganese. The principal point to note is that something had changed the surface chemistry of the six Yara sites, on the assumption that they are representative of the 22 other sites, since the previous round of measurements that were conducted in February 2004.

One of the main factors affecting the rocks appears to be associated with the six massive rainfall events, due to cyclonic activity, in the intervening 13-years. The rainfall events are summarised in Table 3. The main difference between the six Yara sites and their pH values is that since the 2003-2004 measurements is that it appears that there has been a significant alkaline shift from a mean pH of 4.78±0.27 in February 2003 to 5.80±0.50 in November 2017. The shift of just over one pH unit means that the six sites are on average ten times less acidic that the other rocks in the region which were sampled by solution washing.

Table 3: Major cyclonic rainfall (mm) events in the Burrup 2003-2017

02 March 2004	10 January 2006	25 June 2013	31 December 2013	06 May 2014	09 February 2017
190.8	212.4	209.4	112.8	107.4	210.6

The fractional slope for p Fe vs. pH for November 2017 is probably an indication that the dissolution of iron comes from minerals other than the simple oxides and hydroxy-oxides commonly exported by the neighbouring iron-ore industries. It has been previously noted that many of the reference rocks had quite heavy dustings of the local iron-rich soil on their surfaces.

Despite apparent simple changes to the solubility of iron and manganese compounds with pH, the absence of a common dissolution mechanism across the three seasons of measurements makes it difficult to interpret the data. The large standard deviation in the p Fe values (±2.6) for August 2003 measurements makes it impossible to tell if there is any real difference between this data and the material sampled in February 2004.

Table 4: Mean pH and solubility of iron and manganese minerals from rock irrigation

Period	Mean pH	Mean p Fe	mean p Mn	Slope p Fe/pH	slope p Mn/pH
August 2003	4.97 ± 0.48	6.01 ± 2.60	7.17 ± 0.45	2.0 ± 0.1	0.9 ± 0.4
February 2004*	4.78 ± 0.27	6.34 ± 0.44	7.31 ± 0.35	2.0 ± 0.1	2.1 ± 0.1
November ‘17	5.80 ± 0.50	6.80 ± 0.15	9.77 ± 0.35	0.3	1.1 ± 0.1

* the mean pH is determined for the points that were used in the regression analyses.

However, the lower standard deviation of the Feb 2004 and the Nov 2017 data provides an indication that the solubility of the iron minerals decreases with increasing pH, despite the apparent change of mechanism. Although many manganese compounds are more soluble at neutral pH than their iron analogues this is not the case in the rock art washings obtained in the Burrup. The reasons for this are going to lie in the ability of acidic metabolites to complex the cations found in the weathered crusts. It is noteworthy that the mean p Mn values are significantly higher than the mean p Fe values at the same pH, as seen in Table 4. This observation is the reverse of that found 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 can 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, which has hexagonal structured sheets with binding clay minerals $\{(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5H_2O\}$. Lefkowitz et al. (2013) demonstrated that birnessite sheets were disrupted when pH was < 7.0. Under mildly acidic conditions observed in the Burrup the varnish would become thinner and softer with removal of these manganese and iron compounds.

Mobilisation of boron from parent rocks and crusts

The presence of measurable amounts of boron in the wash solutions seemed to vary with the surface pH values recorded in both the 2003 and 2004 measurements. To discriminate between the boron coming from seawater, where it is a minor component at 4.6 ppm compared with chloride at 18,980 it was decided to plot the chloride to boron ratio as a function of the mean surface pH values. The data recorded in the first set of washing solutions from August 2003 showed some interesting patterns. What became clear was that normal Cl/B ratio in seawater of 4,130 was massively lower in the washings from all the Burrup rock art sites, where the maximum value was 143 on rock 938 in the “museum compound”. This supported the view that boron containing minerals were being dissolved leading to much lower chloride to boron ratio from that expected from wind borne sea salts. As the mean rock surface pH fell the ratio also fell, which supports the data from accelerated weathering conducted by CSIRO (Ramanaidou et.al. 2017). This effect is illustrated in Figure 3 and is most dramatic for the mainly granophyre rocks where the Cl/B ratio fell from a maximum of 143 at pH of 4.8 to 16 at a pH of 4.5, which shows that with a pH change of 0.3 (doubling of the acidity) there was a nine-fold increase in the amount of boron in the wash solution. For the gabbro rocks the maximum ratio of 50 at a pH of 5.4 fell to the same minimum of 16 at the same minimum pH values of 4.5 i.e. a three-fold drop in the ratio for an 8-fold increase in acidity.

The mineralogy of the weathered gabbro crusts is different to that of the granophyre as it has an apparently higher buffer capacity. The changes in acidity is mobilising more of the boron containing minerals such as chlorite, $(Mg, Al, Fe, Li, Mn, Ni)_{4\text{-}6}(Si, Al, B, Fe)_4O_{10}(OH, O)_8$. An indication of the relative sensitivity of the two different rock types to increased mobilisation of chlorite is seen in the slopes of the data in Figure 3; where the apparent slope for granophyre rocks for the chloride to boron ratio as a function of pH was 312 ± 56 (19% scatter) and for gabbro rocks the slope was 39 ± 16 (19% scatter). When the data is re-plotted with the ratio of chloride to boron being on the x-axis instead of pH, the following relationships between the pH of the gabbro and granophyre rocks are,

$$pH_{\text{granophyre}} = 4.43 + 0.0032\,\{Cl/B\}$$

$$pH_{\text{gabbro}} = 4.18 + 0.0259\,\{Cl/B\}$$

The much lower slope for the dependence of pH on the ratio of chloride to boron for the granophyre of 0.0032 shows that for this type of rock the pH is relatively insensitive to the boron content. The reverse is true for the gabbro rocks which show an eight-fold greater sensitivity to the chloride to boron ratio. The mean pH of the 20 washed rocks in August 2003 was 4.97 ± 0.45 which was slightly more alkaline that the February 2004 value of 4.82±0.32 that covered a total of 40 sites. It is to be expected that there will be significant differences in the results for the two sets of measurements, since the February 2004 data includes three reference sites each from Gidley and Dolphin Islands.

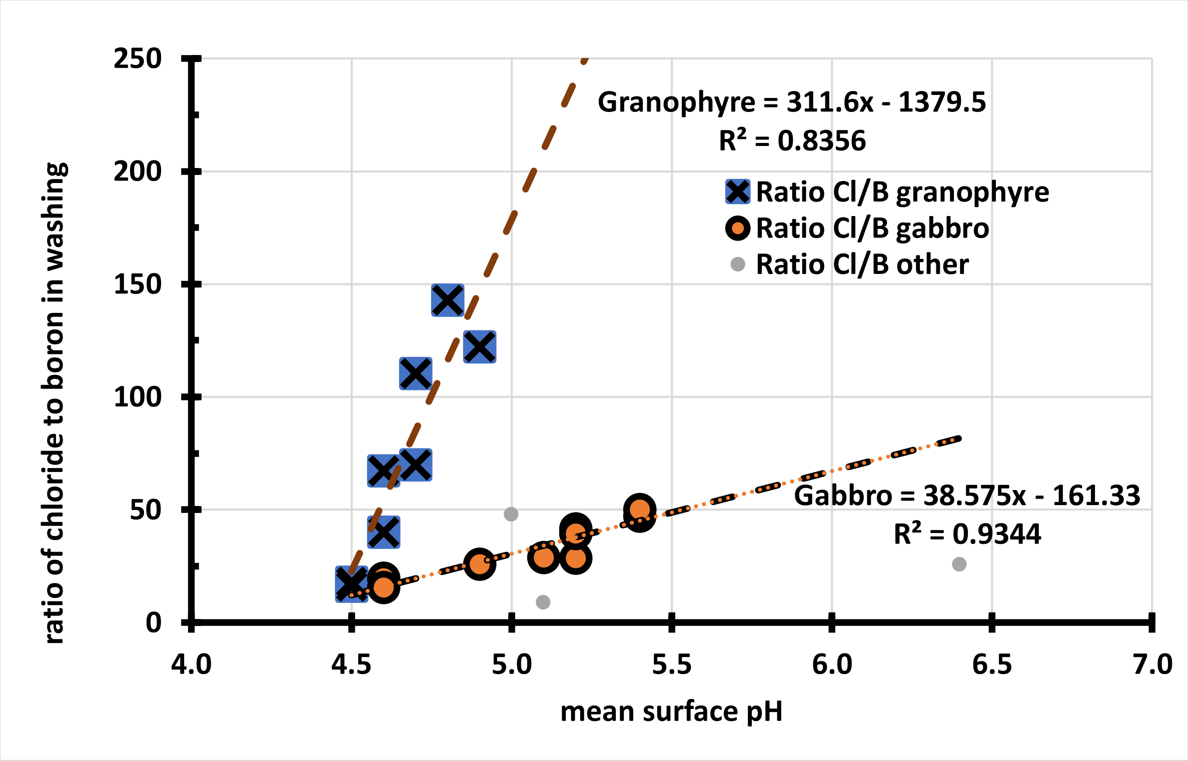

Figure 3: Ratio of chloride to boron vs mean surface pH 2003

Given that the 2003 data indicated that the mobilisation of boron was very pH sensitive, particularly for gabbro rocks it is not unexpected that there would be an increased mobilisation of chlorite i.e. increased boron or lowered chloride to boron ratios in the February 2014 data which had a pH range was from a maximum of 5.4 to a minimum of 4.2 which is one pH unit less (maximum value) than that found in the August 2003 washing. The analysis of the 40 data points from the 2004 washings was more complex than the data from the previous year and a series of linear regressions were obtained, with varying degrees of fit of the data (scatter) and the slopes of the rate at which the chloride to boron ratio changed with pH is listed in Table 5.

The data for the gabbro crusted sites had the same sensitivity in both seasons with the common slope of 39/pH at a mean pH of 5.1 ± 0.2. The least sensitive rock surfaces were seen to be the granophyre rocks which had a sensitivity of 205 ± 26 per pH change. In between the two extreme values were a couple of relationships but when the scatter was considered the two moderate pH slopes are not statistically different from each other.

Table 5: Sensitivity of chloride to boron ratio with changing acidity

Date	mean pH	High{Cl/B} slope per pH	Moderate {Cl/B} slope per pH	Low pH {Cl/B} slope per pH
August 2003	4.97 ± 0.45	312 ± 56		39 ± 16
February 2004	4.82 ± 0.32	205 ± 26	118 ± 22 56 ± 19	39 ± 11
November 2017	5.69 ± 0.51	n.a.	n.a.	n.a.

When the logarithm of the slopes was plotted against the mean pH of the rock surfaces a linear relationship (shown in Equation 14) was found,

$$\log \{Cl/B\} \text{ slope} = 6.85 - 1.035 \text{ pH} \quad (14)$$

For this equation there was a very high R^2 value of 0.9939 which gives confidence that there is a sound physical chemical process controlling the dissolution of chlorite. Rather than having a series of apparently non-related slopes there is a common thread controlling the rates at which the chloride to boron ratio falls as the acidity increases. The most dramatic difference between the data collected in November 2017 and that found in 2003 and 2004 is that only one of the Yara sites, no 6, showed any amount of soluble boron. It will be discussed below in the section on chloride concentrations that there is increasing alkalinity of the sites with increased sea-salt concentration. Thus, the saltier environment of the Yara sites gives a mean pH for site 6 of 5.66 ± 0.22 with a chloride to boron ratio of 330. When this pH is used in the equation from the August 2003 regression line for granophyre rocks the calculated ratio of chloride to boron is 384 which is very close to the observed ratio. For the granophyre equation from the February 2003 data the calculated ratio at the observed pH was 339 i.e. it is the same as was experimentally observed.

It can be concluded that the analysis of the wash solutions provides a unique insight into the chemistry of the reactions taking place on the rock surface. It is also clear that the more acidic the rock surface the more chlorite will dissolve from the crust and the parent rock, which will lead to increased chances of disbondment of the engraving from the substrate. It is likely that a combination of surface pH measurements on reference rocks being analysed for their mineral composition will provide a quantitative method for assessing the dissolution of weathered crusts on Burrup rocks.

Anions in wash solutions

Oxalates:

Analyses from the four field trips showed that only two reference rocks in the collection of the Western Australian Museum had measurable amounts of oxalate ions, $C_2O_4^{2-}$, which were 1.8 mg/l from Enderby Island (B7477) and 0.7 mg/l from Happy Valley (B2494) in the Burrup. These rocks were collected at a time before there was any industrial activity on the Burrup. The washing samples analysed for oxalate were from June and August 2003, February 2004 and November 2017. Oxalates are major biodeterioration of pigments in the Kimberley region where the monsoonal climate has characteristic wet and dry periods. By comparison the arid climate of the Burrup is less amenable to a wide range of bacteria and plants which produce oxalates as their metabolites. Based on this information, oxalate does not appear to have a significant present role in biodeterioration of the rock art in the Burrup.

Chlorides:

The amounts of surface chloride detected on the rock surfaces provide direct evidence of the impact of the marine environment and indicates that salt weathering of rocks, with extensive dehydration and rehydration cycles, play a significant role in the local environment. The wash solutions from the rock surfaces showed up a range of ions commonly associated with sea water, namely Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, B^{3+}, SO_4^{2-} and Cl^-. Analysis of the way in which the concentrations varied across the Burrup was possible as the February 2004 data included several remote sites such as Gidley and Dolphin Islands in the Dampier Archipelago (MacLeod 2005). The deposition of sea salt on the rock surfaces means that the carbonate and bicarbonate ions will tend to act as buffers and minimize any changes in the surface acidity resulting from a combination of microbiological and chemical reactions on the surfaces. The initial monitoring conducted in 2003 and 2004 involved direct measurement of the surface pH and the surface chloride ion concentrations. In addition, the washing of the rock surfaces in August 2003 and February 2004 provided data on the solution concentrations of chloride ions. All the data was then assessed through linear regression analyses and the results are summarised in Table 5, which showed that the pH increased with increasing chloride ion activity. This buffering reaction is demonstrated by the relation between the pH and chloride concentration on the rocks as shown in Equation 15,

$$\mathrm{pH}_{\mathrm{mean}} = a + b\,[\mathrm{Cl}^-] \tag{15}$$

The 2003-2004 linear regression analyses showed that there was a common slope of the pH vs [Cl] plots but they had different intercepts, as shown in Table 6. The intercept values relate to their primary geology of the underlying rocks and the impact of factors such as the amount of nitrate on the rock surfaces, which is discussed in the following section of this report. Cluster analysis of the slopes and intercept data shown in Table 6 showed that there was an apparent sensitivity of the slope to pH, with the data from the 2017 seasons conforming to the relationship shown in Equation 16 viz.,

$$\partial b/\partial \mathrm{pH} = 0.0253 - 0.0001\,[\mathrm{Cl}]_{\mathrm{surface}} \tag{16}$$

In this equation the surface chloride ion concentration is expressed in parts per million. This means that as the sea salts and other buffering agents build-up on the rocks, the response of the rock surfaces to changes in acidity, coming from natural and human sources, diminishes so that the microenvironment develops a chemical resilience to the changes impacting on the rocks. Owing to the differences between the surface chloride measurements relating to a given time interval (one minute) and the limited volume of solution being sampled, it is to be expected that there will be a different set of parameters that relate to the solution values. This data is expressed in Equation 17, viz.,

$$\mathrm{pH} = 4.34 + 0.028\,[\mathrm{Cl}]_{\mathrm{extracted}} \tag{17}$$

It should be noted that this regression analysis, with an R^2 of 0.9339, does not include data from sites 22 and 23, the Yara North East and Yara East sites respectively, which do not fit on this relationship which covers sites 5, 6, 7 and 21 – see Figure 4 for the graphical plot of the data.

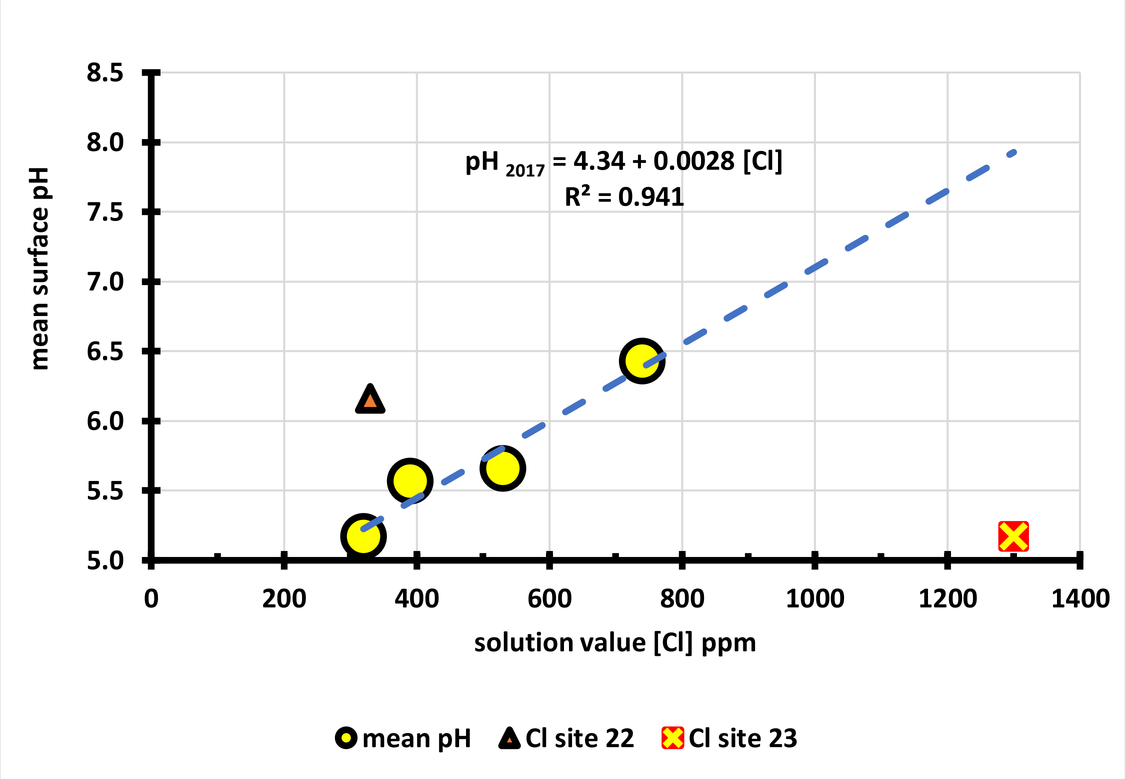

Figure 4: Plot of $[\mathrm{Cl}]_{\mathrm{solution}}$ on the rocks vs. the mean surface pH, 2017 readings

When the data in Table 6 is collected into the times at which the information was collected and the average slope of the pH vs. Cl graphs is also recorded, it became apparent that the build-up of deposits on the rocks does have a real impact on the way in which the rocks respond to changes in the chemical environment, as seen in Figure 6.

Table 6: Analysis of the relationship between chloride and mean pH

Date	mean Cl ppm	Intercept, *a*	Slope, *b*	R^2
June 2003 (winter)		2.95 3.75	0.032 0.027	0.9601 0.9999
August 2003 (spring)	34±31	2.35 3.80 3.87	0.031 0.033 0.036	0.9900 0.9902 0.9569
February 2004 (summer)	21±15	3.25 4.07 4.34 4.72	0.024 0.023 0.022 0.021	0.9914 0.9938 0.9650 0.9890
November 2017				
Wash solution analysis	601±377	4.34	0.0028	0.941
Site 5: Burrup road	32±28	5.56 4.26	0.0082 0.0075	0.9176 0.9922
Site 6: Water tanks	191±97	5.41	0.0014	0.9605
Site 7: Deep Gorge	22±12	5.00	0.026	0.7707
Site 21 Yara west	125±44	5.81	0.0064	0.6393
Site 22: Yara north east	373±24	5.28	0.0085	0.7026
Site 23: Yara east	13±17	5.49	0.021	0.7677

With collation of the different ways in which the slopes of the pH vs. [Cl] graphs varied it was shown that there was a regular trend in the slopes, as shown below in Figure 5. Thus, while the data in Table 6 indicated that there was no direct relationship between the slopes of the pH vs. chloride plots that there was a clear connection between the variables, as shown by Equation 18, viz.,

$$\text{slope } \{{}^{\text{pH}}/_{\text{Cl}}\} = 0.0725 - 0.0121 \text{ pH} \qquad (18)$$

This relationship confirms that all the pH and chloride data are closely linked and that, in the absence of other factors, the ability of the rocks to minimise the response to the development of an acidic microenvironment is largely controlled by the amount of salt deposition. The amount of wind borne salt is outside the range of variables that industry can be expected to manage.

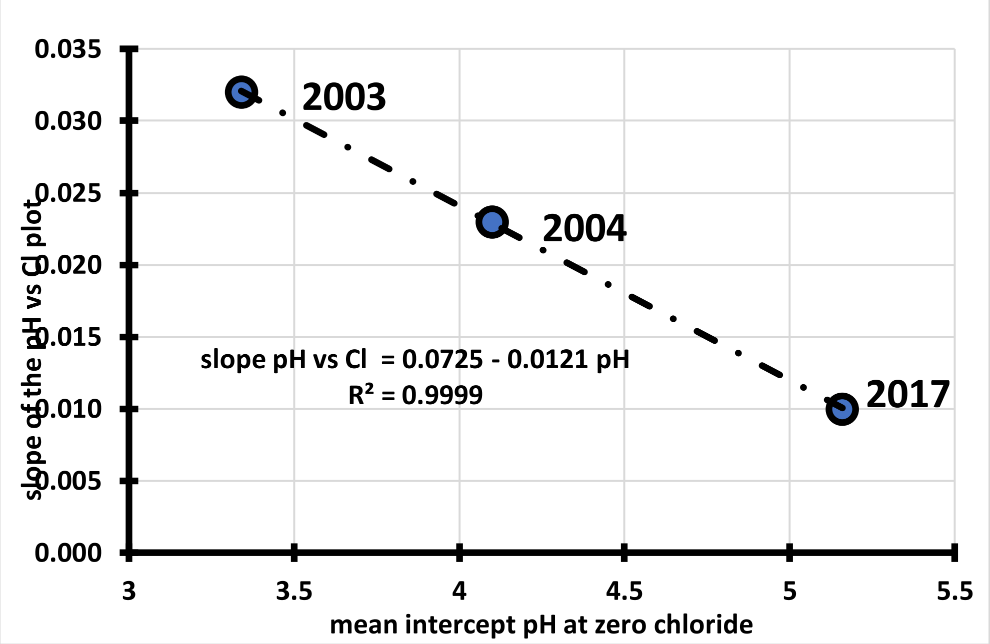

Figure 5: Sensitivity of pH vs [Cl] plots versus the mean pH $_{\text{intercept}}$ at zero chloride

The data for each site recorded in November 2017 is listed in Appendix III in the order in which the measurements were made. Preliminary analysis of the chloride and pH data from site 6 showed that taking a few reference chloride readings did not provide a good comparison with the pH, so at subsequent sites an equal number of pH and chloride readings were taken at the same locations on the specific rocks.

Nitrates:

Previous studies in 2003 and 2004 had focused on the acidity and the concentration of nitrate ions, since there was very strong data supporting the inference that nitrate ions were stimulating the overall microbiological activity on the rocks. Since bacterial and fungal metabolites are often acidic it was decided to check to see if there was a correlation with the number of bacteria and the nitrate levels. Data published in 2005 by MacLeod demonstrated that the logarithm of the number of bacteria was directly related to the decreasing pH, thus the amount of nitrate ions, from both natural and human sources, was likely to be a key determinant in the overall rates of weathering of the rock surfaces in the Burrup. Owing to the contrasting nature of the engraved and background areas there was concern about the long-term impact of such accelerated ageing on the rock surfaces. Surface pH values as low as 3.5 were recorded on rocks near the Climbing Man panels adjacent to the Woodside operational flare tower servicing trains 1-4, as Pluto had not yet been constructed let alone become operational. As part of the February 2004 data collection, samples of rock pH, chloride and nitrate ions were collected on rock engraving sites at Gidley and Dolphin Islands in the Dampier Archipelago, in the belief that these remote sites would be low in nitrates, owing to their distance from apparent point sources on the coastal lands associated with industrial developments. A summary of the relevant data is shown below in Table 6, which lists the mean nitrate for 2003, 2004 and 2007 as well as the range of the maximum to the minimum values that were recorded.

Table 7: Nitrate concentration ranges across Burrup, ppm

Date	Maximum	Minimum	Mean ppm
August 2003	19, Withnell Bay	1.5, at Burrup SW 1–2	6.3 ± 5.1
February 2004	9.2, rock 938	1.3, Deep Gorge	4.5 ± 3.7
November 2017	1.8, site 21	0.1, site 5	0.6 ± 0.7

Although the nitrate concentration was essentially the same in August 2003 and February 2004, the slope of the pH vs $[NO3]_{ppm}$, as seen in Table 8, was significantly diminished by over 40%. This is roughly in line with the 30% reduction in the mean nitrate concentration between the two sets of measurements. The data in Table 8 shows that common intercept pH values, at zero nitrate, at 5.69 for the 2003 and 2004 analyses. The common intercept value shows that the same chemical mechanism is controlling the response of the rocks in those two seasons of measurements. It should be noted that with the R^2 value of 0.97 the 2003 intercept value of 5.33 value is within experimental line fitting error the same as the 5.44 from rocks in the museum compound that was noted in February 2004. Of concern were the lower $pH_{intercept}$ values of 4.95 and 4.66 for sites that included rocks in the museum compound as well as those at the Climbing Man, Deep Gorges and Withnell Bay sites.

In the 13-years since the February 2003 data was collected, there were six cyclonic rain events, as listed in Table 3, which deposited between 107-212 mm of rain in the region in a 24-hour period. These periods of inundation of the rock surfaces is likely to be the underlying reason for the big drop in the nitrate ion concentration found in the rock washings in November 2017. The five-fold fall in nitrate concentration would have been expected to reduce the impact of the biological activity due to the nitrate concentration but other factors appear to have weighed heavily in bringing about a change in acidification. It has been noted that the mean chloride ion concentration on the Yara sites is approximately 30 times saltier than the rocks that were sampled in February 2003.

Table 8: Dependence of pH on the nitrate concentration found in wash solutions

Date	$pH_{\text{zero NO3}}$	Slope pH/[NO3]	R^2
August 2003	5.69, Climbing man, Deep Gorge & Compound 5.33, Burrup SW, King Bay & Compound	-0.14 -0.14	0.92 0.97
February 2004	5.69, Withnell & Compound 5.44, Compound 4.95, Withnell & Compound 4.66, Deep Gorge & Climbing Man	-0.08 -0.08 -0.07 -0.08	0.91 0.99 0.66 0.78
November 2017	6.18, Sites 5,6,7, 21, 22 & 23	+0.94 log [NO3]	0.99

The increase in buffer capacity due to salt accumulation will naturally result in the changes in the surface pH of the rocks being reduced. However, the complete change of direction of the response of the rock pH to the nitrate concentration needs additional clarification. The dependence of pH on the nitrate concentration for the Yara monitoring stations was not as expected, since the mean surface pH at the Yara monitoring sites **increases** with nitrate concentration. The graphed results are shown in Figure 6 where the linear regression analysis shows,

$$^{\text{Yara 2017}}pH_{\text{mean}} = 6.18 + 0.94 \log [NO_3^-] \quad (19)$$

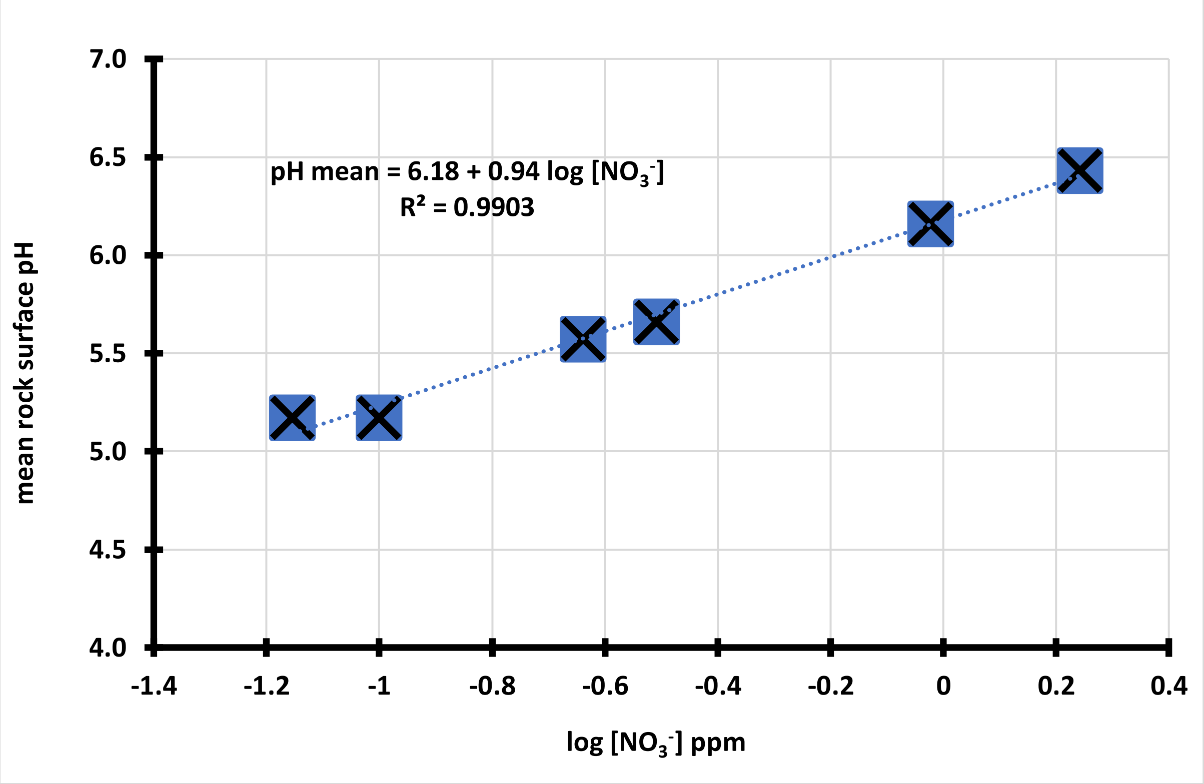

Figure 6: Mean rock surface pH on Yara sites vs. log of nitrate wash concentration

A possible explanation for this behaviour is that to bring about an overall increase in the acidity of the rock surfaces a significantly higher than 1 ppm nitrate needs to be present to provide the bacteria, yeasts moulds and fungi with enough nutrient to overcome the inhibition that the high salt content of the rock surface appears to be providing. Additional monitoring needs to be done on the Yara sites and sites that were previously addressed in the 2003-2004 field work need to be sampled at the same time to see if the Yara sites represent a niche microenvironment or if the overall conditions in the Burrup have changed. It is most unlikely that the latter is the case since independent measurements of many of the previous sites in June 2017 (MacLeod 2017b) has shown increasing acidification of sites near the Climbing Man in the same gully. Rocks from the relocated museum compound were found to have more alkaline pH than in 2003 when they had been thoroughly scrubbed to remove all the paint residues when their "registration numbers" were chemically removed. In an instance when the number had failed to be removed the pH of the rock had fallen i.e. it showed increasing signs of acidification. **It can be therefore concluded that the operations of the TAN plant by Pilbara Fertilisers has had no measurable impact on the acidification of the Burrup rocks, through a distribution of available nitrate ions.**

Sulphate:

The amount of sulphate in the washings also varied from one year to the next, as shown in Table 9, which reports the data from the August 2003 and February 2004 rinses, along with the most recent data on the Yara sites from November 2017.

Table 9: Range of sulphate ions in the wash solutions on Burrup and Yara sites

Date	Maximum	Minimum	Mean ± SD
August 2003	66.7 Rock 938	1.2 Burrup SW2	9.8 ± 14.2
February 2004	26.1 Rock 938	0.8, Deep Gorge	4.9 ± 5.5
November 2017	9.8, Site 23	1.5, Yara NE, 22	5.2 ± 3.0

It is apparent that there is a two-fold drop in the mean sulphate concentration in the wash solutions between August 2003 and February 2004. The data shows that there has been essentially no change in the amount of sulphate present in the 2017 compared with the 2004 readings, other than the maximum value for 2004 was nearly three times that observed in 2017 at the Yara sites. The highest values reported were found on rock 938 in the "museum compound" which lay inland from the Climbing Man gully and was located behind the hills from the Woodside gas production facility. Unfortunately, there is no corresponding wash solution data from the relocated rock 938 in the June 2017 report. In August 2003 the pH was 4.82±0.41 and in February 2004 it was 4.94±0.61 which makes them statistically the same i.e. there was no correlation between the wash solution sulphate concentration and the underlying acidity. It has been previously noted that the pH of the rock surfaces is significantly affected by the chloride levels, coming from the sea salts, so it is instructive to see how the $^{Cl}/_{SO4}$ ratios vary across the Burrup in the different periods of measurement.

Table 10: Ratios of chloride to sulphate ions in the wash solutions from Burrup rocks.

Date	**$Cl^-:SO_4^{2-}$**	**$Cl^-:SO_4^{2-}$ high**	**$Cl^-:SO_4^{2-}$ low**	**$Cl^-:SO_4^{2-}$ sea**
August 2003	5.7 ± 5.4	6 sites @ 11.8 ± 6.6 Climbing Man, off museum site rock 162,	14 sites @ 3.1 ± 1.2 Dampier, King Bay, Deep Gorge	7.1
February 2004	21 ± 15	14 sites @ 9.9 ± 5.1 Climbing Man, off museum site, Rock 3	27 sites @ 4.3 ± 1.2 Gidley Island, Dampier, Dolphin Island, Rocks 86, 162, 938,	7.1
November 2017	1.1 ± 0.3	n.a.	n.a.	7.1

Despite the large standard deviations of the mean values for 2003 and 2004 data the high ratios of $Cl^-:SO_4^{2-}$ do reflect the expected amount of sulphate present in the individual rock washings when compared with the chloride ratios found in seawater. From the numbers of sites sampled, roughly one-third of the rocks had the expected chloride to sulphate ratio. For the ratios that are significantly lower than those found in normal seawater, this implies that there is additional sulphate present in the rock surface washings i.e. sulphate is not coming from the sea. For the Yara sites there is a further significant reduction in the $Cl^-:SO_4^{2-}$ ratio which means that additional sulphate is coming from sources other than the sea and it is a much higher contribution than observed on the other rocks. It is likely that deposition of SO_x is affecting 60% of the Burrup rock art sites and that this impact is felt even on remote sites such as Gidley and Dolphin Islands.

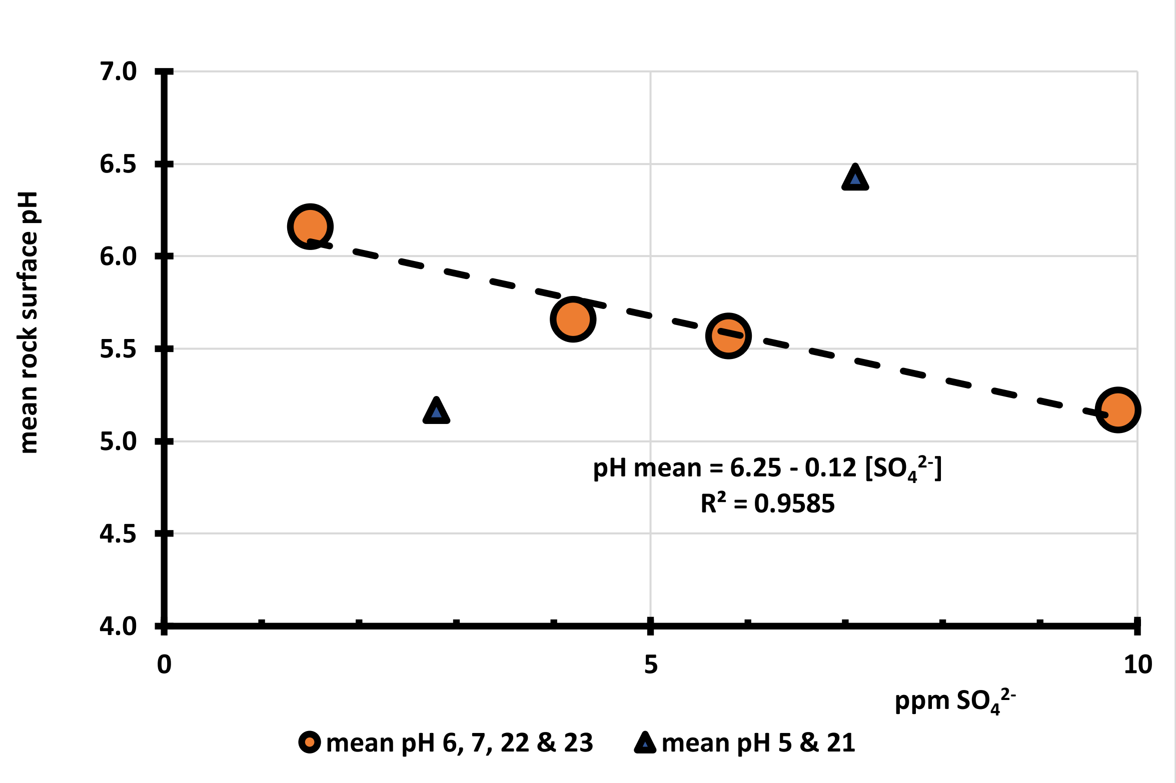

Figure 7: Plot of the mean rock surface pH for the Yara sites vs. wash SO_4^{2-}.

The data in Figure 7 indicates that there is an increase in acidity with increasing sulphate on the six Yara sites, with the outliers being sites 5 and 21. Site 5 had a pH below the line predicted by equation 20,

$$^{\text{Yara sites}}\text{pH}_{\text{mean}} = 6.25 - 0.12\,[SO_4^{2-}] \qquad (20)$$

In this equation the concentration of the sulphate ions is in the same units as in the ChemCentre analysis sheet i.e. in mg/litre. With an R^2 of 0.9585 there is a very good correlation for this linear regression. When the pH scale was changed to the pH intercept values, calculated from the linear regression analyses of how pH responded to chloride ion concentration at the particular sites, the intercept pH value increased from 6.25 to 6.39 and the slope of the equation increased from 0.12 to 0.20, which indicates that the sensitivity of pH to the sulphate levels, with the effect of the chloride "eliminated" through use of the $\text{pH}_{\text{intercept}}$ values, is higher due to the effective removal of the buffering capacity of the chloride bearing sea salts. The site with a more alkaline mean pH than the rest of the sites in and around the Yara plants was site 21. This site is in a very open location on the flat ground in between the two ranges of hills in which the industrial estate has been established. It is subject strong airflow patterns from Hearson's Cove and this may be a contributing factor to the more alkaline surface. This site has the highest chloride ion content reported in the wash solutions and so the increased alkalinity is understandable, without having to invoke unusual chemistry. This site also had the lowest chloride to sulphate ratio and the highest amount of nitrate, which is directly downstream from the production plants.

Conclusion

The analysis of the relationship between the pH and the amount of metal ions reporting to the wash solutions enabled the mechanism controlling the release of key iron and manganese containing minerals to the wash solutions to be determined. Unlike previous measurements in 2003 and 2004, which showed that FeOOH was dissolving to produce the di-hydroxy ferrate ion, $Fe(OH)_2^+$ the dissolution of iron on the Yara sites in 2017 did not correspond to any known simple iron (III) oxides, hydroxides or oxy-hydroxides but is consistent with mobilisation of iron-containing minerals such as actinolite, augite and chlorite. In comparison the data supported the dissolution of MnO to produce a partially hydrolysed manganous ion $\{Mn(OH)^+\}$ in solution. In the more acidic microenvironment found in 2003 and 2004 data the free Mn^{2+} ion reported to solution. The re-examination of the data obtained from the previous studies indicates that this apparent change of mechanism controlling the release of manganese ions into the wash appears to be subtly controlled by the alkalinity associated with increased salt deposits. The Elders noted that prior to the 2017 November measurements there had been a long dry spell.

Analysis of the relationships between the surface pH and the ions associated with wind borne sea salts has shown that it is most likely that calcium is reporting to solution through the formation of a mixture of calcium carbonate dissolving to produce either free Ca^{2+} ions or the soluble calcium bicarbonate. Increasing chloride ion concentration is an indicator of increasing deposition of sea salts on the rock surfaces. One major effect of the increased salts is that it produces a buffering effect and appears to be inhibiting the activity of micro-organisms associated with the metabolism of nitrogen (nitrate) containing species found on the rock surfaces. The impact of seven major cyclonic downpours between February 2003 and March 2017 has significantly reduced the amount of soluble nitrate that is available to the sites and this has brought about a change in deterioration mechanism for the more alkaline Yara sites. Measurements at other locations in June 2017 provide clear evidence of continuing acidification of rocks near the Climbing Man gully.

For the six sites examined in and around the Yara facility there is an increased amount of sulphate ions than cannot be explained by the increased presence of sea salts. The increased sulphate concentration supports the view that a different source of sulphate is contributing to the concentration of sulphate around the plant. The SO_x derived from nearby offshore ship-loading operations appears to be falling on the Yara sites needs to be reviewed along with the Yara data collected from its air quality monitoring stations. Through the combination of the rock surface pH and chloride measurements and the ChemCentre analytical data from the irrigation of the rock surfaces and the Air Quality Monitoring (AQM) data it should be possible to determine the mechanism of adsorption of gases and transfer of potential nutrients to the rocks. Once the transfer and activity ratios have been determined it should be possible to develop future reports based on the AQM data, with only periodic checking of the rock surface pH and solution chemistry as by exception when the AQM data indicates that a significant excursion from the norm has occurred. The present analysis strongly supports the view that the operations of the TAN plant by Pilbara Fertilisers has had no measurable impact on the acidification of the Burrup rocks, through a changed distribution of available nitrate ions.

A future monitoring regime should involve recovery of reference rocks adjacent to the monitoring points and have the surface pH recorded along with the mineralogy of the rock surfaces. The samples of rock can be sent to Perth to standard x-ray diffraction laboratories to quantify the amount of chlorite, and other minerals, present on the rock surface. The combined data on surface pH and chlorite concentration will provide a clear indication as to what impact industrial activities are having on the long-term preservation of the rock art.

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APPENDIX I: MacLeod publications on rock art conservation

Refereed journal articles

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MacLeod, I.D., Haydock, P & Charton, E., (1992) "The effects of avian guano on the preservation at *Walga Rock*". Report to the Australian Institute of Aboriginal and Torres Strait Islanders Studies, Canberra, pp 1-45.

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Ford, B., Officer, K. and MacLeod, I.D., (1999) *A study of lichen invasion of Nursery Swamp II, Aboriginal Rock Art Site, Namadji National Park, Australian Capital Territory, Final Report May 1999*, Australian Capital Territory National Parks Association, Canberra 1999, pp. 1-28.

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APPENDIX II: Chemical analysis of the wash solutions from the CSIRO monitoring sites.

Concentrations are in mg/L other than electrical conductivity which is in mS/m
Report dated 7 December 2017

ChemCentre Id	Method Code	Limits of Reporting	17S2175-002	17S2175-001	17S2175-004	17S2175-005	17S2175-006	17S2175-003	17S2175-007
Client Id			Site 5	Site 6	Site 7	Site 21	Site 22	Site 23	Blank
Sampled			21/11/2017	20/11/2017	22/11/2017	22/11/2017	23/11/2017	21/11/2017	24/11/2017
Al	iMET1WCICP	0.005	<0.005	0.016	0.007	0.009	0.006	0.019	<0.005
As	iMET1WCMS	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
B	iMET1WCMS	0.005	<0.005	0.008	<0.005	<0.005	<0.005	<0.005	<0.005
Ba	iMET1WCMS	0.0001	0.0061	0.011	0.0043	0.0097	0.0024	0.0064	0.0004
Ca	iMET1WCICP	0.1	1.1	11.5	3.2	2.5	0.5	5	0.1
Cd	iMET1WCMS	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cl	iANIO1WAIC	0.5	3.2	5.3	3.9	7.4	3.3	13	<0.5
Co	iMET1WCMS	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cr	iMET1WCMS	0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cu	iMET1WCMS	0.0001	0.0066	0.0016	0.0007	0.017	0.001	0.0021	0.0023
E Cond	iEC1WZSE	0.2	1.6	12.2	3.1	5.2	0.8	7.6	<0.2
Fe	iMET1WCICP	0.005	<0.005	0.012	0.008	0.011	0.005	0.01	<0.005
K	iMET1WCICP	0.1	0.5	0.6	0.4	1	0.2	0.7	0.2
Mg	iMET1WCICP	0.1	0.1	0.7	0.5	0.7	<0.1	0.6	<0.1
Mn	iMET1WCMS	0.0001	0.0026	0.0038	0.0051	0.006	0.0011	0.0009	0.0003
NO2	iNTR1WFIA	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NO3	iNTA1WFIA	0.05	0.25	0.46	0.38	1.9	1.1	0.22	0.15
Na	iMET1WCICP	0.1	1.2	7.2	1.6	5.2	1.4	9.3	0.3
Ni	iMET1WCMS	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Oxalate	iANIO1WAIC	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
Pb	iMET1WCMS	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
S	iMET1WCICP	0.1	1	2.6	2	2.5	0.3	3.2	<0.1
SO4	iANIO1WAIC	0.1	2.8	4.2	5.8	7.1	1.5	9.8	<0.1
V	iMET1WCMS	0.0001	0.0003	0.0006	0.0004	0.0004	0.0002	0.0006	<0.0001
Zn	iMET1WCMS	0.001	0.008	0.009	0.003	0.01	0.004	0.004	0.004

Sample volumes for the metal ion analyses were 200 ml and for the anions the volume was 100 ml
Samples were collected on the same rocks and stored in different containers which were kept cool with ice-bricks

APPENDIX III: Acidity and chlorinity measurements adjacent to the CSIRO monitoring sites

Site 6: Water Tanks **20-Nov-17**

Location	pH	Cl ppm
1	5.61	134
2	5.72	195
3	5.83	
4	5.33	
5	5.85	
6	5.54	108
7	5.85	326
8	5.81	
9	5.28	
10	5.80	
mean	**5.66**	**191**
stdev	**0.22**	**97**

RH	49.9%
T air	31.4
T surface	45.9
T dew point	19.6

Date **21/11/2017**

Site 5: Location off Burrup road

location	pH	Cl ppm
1	6.04	55
2	5.79	28
3	5.7	12
4	5.75	30
5	5.17	24
6	5.19	22
7	5.06	106
8	4.37	10
9	4.36	18
10	4.82	4.2
11	4.57	40
mean	**5.17**	**32**
stdev	**0.60**	**28**

Latitude	-20.62109
Longitude	116.76925

Time	07:15	08:45
RH	77%	42%
T air	23.7	34
T surface	25.7	32
T dew	19.2	
Ts-Td	8.4	

Location	**pH**	**Cl ppm**
1	5.68	4.5
2	5.75	6.2
3	5.62	15
4	4.45	55
5	5.49	8
6	6.39	42
7	4.42	26
8	5.47	6
9	5.76	6
10	5.93	16
mean pH	**5.50**	**18**
stdev pH	**0.62**	**17**

Site 23
Yara East
21/11/2017

Latitude	-20.6229
Longitude	116.797
Time	09:30
RH	37.3
T air	34.9
T surface	34.2
T dew	17.3
Ts-Td	17.6

Site 7 Deep Gorge

location	**pH**	**Cl ppm**
1	6.21	35
2	5.16	
3	5.53	32
4	5.93	30
5	4.92	
6	5.29	7.2
7	5.43	30
8	5.57	
9	5.3	12
10	5.9	34
11	5.32	
12	5.58	9
13	5.9	18
14	6.41	
15	5.09	8.2
mean pH	**5.57**	**22**
stdev pH	**0.42**	**12**

Date	**22-Nov-17**
Latitude	-20.63722
Longitude	116.78831
Time started	06:30
Time finished	08:30
Relative humidity	40.40%
Temperature air	31.4
Temperature surface	37.8
Temperature dew pt.	17
Ts-Td	21.3

Location no Site 21 Yara West

Date of measurements 22-Nov-17

Location	**pH**	**Cl ppm**
1	7.29	214
2	6.91	132
3	6.35	140
4	6.52	90
5	6.39	88
6	6.56	140
7	6.49	214
8	5.78	165
9	5.98	125
10	5.98	120
mean	**6.43**	**143**
stdev	**0.45**	**44**

Time of initiation	09:45
T air	38.6
T rock	38.8
T dew	11.3
Ts -Td	26

Site 22

Date 23/11/2017

Location	**pH**	**Cl ppm**
1	**6.58**	**26.5**
2	**6.42**	**14.5**
3	**6.42**	**27.6**
4	**6.16**	**97**
5	**6.49**	**21**
6	**5.43**	**46**
7	**6.59**	**36**
8	**5.34**	**14.6**
9	**6.42**	**24**
10	**5.74**	**26**
mean	**6.16**	**33**
stdev	**0.48**	**24**

Latitude	-20.6176
Longitude	116.7996

	Begin	End
Relative humidity	86.80%	15.20%
Temperature air	26.5	43.7
Temperature rock	30.8	33
T dew point	24.4	
Ts-Td	5.2	

APPENDIX IV: Surface pH measurements 2003-2004 in the Burrup

	17-Jun-03	28-Aug-03	23-Feb-04	
Location		pH	pH	
Dampier W1		5.03	4.90	
Dampier W1		4.85	4.82	
Dampier W1		5.14	4.77	
Dampier W1		5.13	5.18	
Dampier W1		4.61	4.47	
Dampier W1		4.95	4.59	
Dampier W1		4.37	4.80	
Dampier W1		4.10	4.88	
Dampier W1		4.49	4.76	
Dampier W1			4.71	
Dampier W1			4.64	
Dampier W1 mean		**4.74**	**4.77**	
Dampier W1 st. dev.		**0.37**	**0.19**	
Dampier W2		4.30	4.41	
Dampier W2		4.34	4.32	
Dampier W2		4.96	4.61	
Dampier W2		4.80	4.63	
Dampier W2		4.86	4.40	
Dampier W2		4.72	4.27	
Dampier W2		4.78	4.16	
Dampier W2		4.94	4.78	
Dampier W2		4.82	4.50	
Dampier W2		4.33	4.68	
Dampier W2 mean		**4.7**	**4.5**	
Dampier W2 st. dev.		**0.3**	**0.2**	
				27-Feb-04
Burrup SW1		4.70	4.43	4.63
Burrup SW1		4.69	5.33	4.76
Burrup SW1		4.94	4.52	4.97
Burrup SW1		4.49	4.89	4.79
Burrup SW1		4.96	4.68	4.78
Burrup SW1		4.16	4.60	4.92
Burrup SW1		4.42	4.92	3.89
Burrup SW1		4.66	4.98	4.94
Burrup SW1			5.01	4.94
Burrup SW1			4.65	5.02
Burrup SW1 mean		**4.63**	**4.80**	**4.76**
Burrup SW1 st. dev.		**0.27**	**0.27**	**0.33**

Burrup SW2		5.39	4.88	4.87
Burrup SW2		5.32	4.49	4.68
Burrup SW2		4.64	4.82	4.83
Burrup SW2		4.44	4.83	5.16
Burrup SW2		4.60	4.72	4.83
Burrup SW2		5.43	4.69	4.80
Burrup SW2		5.00	4.65	4.98
Burrup SW2		5.40	4.72	5.00
Burrup SW2		5.38	4.63	5.19
Burrup SW2			4.59	5.24
Burrup SW2 mean		**5.07**	**4.70**	**4.96**
Burrup SW2 st. dev.		**0.40**	**0.12**	**0.19**

27-Feb-04

King Bay 1		4.89	4.61	4.91
King Bay 1		4.37	5.34	4.73
King Bay 1		5.27	5.15	4.46
King Bay 1		4.98	4.69	4.79
King Bay 1		5.41	4.39	4.64
King Bay 1		5.30	4.70	4.98
King Bay 1		4.85	5.02	4.80
King Bay 1		4.94	5.00	4.87
King Bay 1		6.04	5.12	4.93
King Bay 1		5.33	4.93	4.88
King Bay 1		5.36		4.91
King Bay 1		5.17		
King Bay 1 mean		**5.16**	**4.90**	**4.81**
King Bay 1 st. dev.		**0.41**	**0.29**	**0.15**

27-Feb-04

King Bay 2		5.27	4.85	4.61
King Bay 2		5.24	4.89	4.75
King Bay 2		5.27	4.89	4.80
King Bay 2		5.41	4.74	4.95
King Bay 2		5.31	5.29	4.86
King Bay 2		4.59	4.77	5.30
King Bay 2		4.88	5.22	4.78
King Bay 2		3.82	5.41	4.76
King Bay 2		5.05	4.93	5.02
King Bay 2		4.91	5.17	3.54
King Bay 2		5.48		5.02
King Bay 2		5.44		4.78
King Bay 2 mean		**5.06**	**5.02**	**4.76**
King Bay 2 st. dev.		**0.5**	**0.2**	**0.42**

Withnell Bay		5.15	5.02
Withnell Bay		4.95	5.01

Withnell Bay		5.18	5.27
Withnell Bay		4.95	4.97
Withnell Bay		4.98	4.73
Withnell Bay		4.79	5.19
Withnell Bay		4.47	4.82
Withnell Bay		4.70	5.50
Withnell Bay		4.85	5.04
Withnell Bay		4.46	4.55
Withnell Bay		4.91	5.01
Withnell Bay mean		**4.85**	**5.01**
Withnell Bay st. dev.		**0.24**	**0.26**

Withnell Bay 2		4.92	5.76
Withnell Bay 2		4.73	5.28
Withnell Bay 2		4.26	5.52
Withnell Bay 2		4.45	5.52
Withnell Bay 2		4.89	5.24
Withnell Bay 2		4.97	5.26
Withnell Bay 2		4.78	5.44
Withnell Bay 2		4.83	5.26
Withnell Bay 2		4.93	5.50
Withnell Bay 2		4.66	5.68
Withnell Bay 2 mean		**4.74**	**5.45**
Withnell Bay 2 st. dev.		**0.23**	**0.18**

North Withnell Bay 1		4.48	4.66
North Withnell Bay 1		4.59	4.80
North Withnell Bay 1		4.17	4.85
North Withnell Bay 1		4.86	4.62
North Withnell Bay 1		4.37	4.66
North Withnell Bay 1		4.54	4.75
North Withnell Bay 1		4.29	4.76
North Withnell Bay 1		4.51	5.03
North Withnell Bay 1			5.16
North Withnell Bay 1			4.89
North Withnell Bay 1			
North Withnell Bay 1			
North Withnell Bay 1			
North Withnell Bay 1 mean		**4.48**	**4.82**
North Withnell Bay 1 st. dev.		**0.21**	**0.17**

North Withnell Bay 2		4.77	4.65
North Withnell Bay 2		4.74	3.45 soil area

North Withnell Bay 2		4.66	4.87
North Withnell Bay 2		4.31	4.79
North Withnell Bay 2		4.83	5.09
North Withnell Bay 2		4.65	4.76
North Withnell Bay 2		4.58	4.88
North Withnell Bay 2		4.50	5.13
North Withnell Bay 2		4.63	5.05
North Withnell Bay 2			4.73
North Withnell Bay 2			5.03
North Withnell Bay 2 mean, no soil		4.63	4.90
North Withnell Bay 2 st. dev. no soil		0.15	0.17
North Withnell Bay 2 mean			**4.9**
North Withnell Bay 2 st. dev.			**0.2**

Deep Gorge 1		4.91	4.71
Deep Gorge 1		4.54	5.06
Deep Gorge 1		4.87	4.74
Deep Gorge 1		4.72	4.87
Deep Gorge 1		4.89	4.90
Deep Gorge 1		4.10	5.14
Deep Gorge 1		4.32	4.98
Deep Gorge 1		4.06	4.80
Deep Gorge 1		5.19	4.80
Deep Gorge 1		4.17	5.07
Deep Gorge 1		4.14	
Deep Gorge 1 mean		**4.54**	**4.91**
Deep Gorge 1 st. dev.		**0.40**	**0.15**

Deep Gorge 2		4.59	4.69
Deep Gorge 2		4.93	4.97
Deep Gorge 2		4.46	5.45
Deep Gorge 2		4.63	5.31
Deep Gorge 2		4.57	5.20
Deep Gorge 2		4.79	5.04
Deep Gorge 2		4.71	5.16
Deep Gorge 2		4.36	5.12
Deep Gorge 2		4.70	5.31
Deep Gorge 2			3.85
Deep Gorge 2			
Deep Gorge 2 mean		**4.64**	**5.01**
Deep Gorge 2 st. dev.		**0.17**	**0.46**

Deep Gorge 3			5.19
Deep Gorge 3			4.91
Deep Gorge 3			5.06
Deep Gorge 3			4.73
Deep Gorge 3			4.78
Deep Gorge 3			4.91
Deep Gorge 3			5.39
Deep Gorge 3			5.27
Deep Gorge 3			5.23
Deep Gorge 3			5.10
Deep Gorge 3 mean			**5.06**
Deep Gorge 3 st. dev.			**0.22**

Climbing Man Gully 1		5.37	4.96
Climbing Man Gully 1		5.53	4.80
Climbing Man Gully 1		5.39	5.03
Climbing Man Gully 1		4.84	4.78
Climbing Man Gully 1		5.41	4.97
Climbing Man Gully 1		4.83	4.63
Climbing Man Gully 1		4.81	4.93
Climbing Man Gully 1		5.70	5.03
Climbing Man Gully 1		3.04	5.37
Climbing Man Gully 1		5.55	4.22
Climbing Man Gully 1		5.42	5.53
Climbing Man Gully 1		4.62	4.26
Climbing Man Gully 1			4.58
Climbing Man Gully 1 mean		**5.0**	**4.9**
Climbing Man Gully 1 st. dev.		**0.7**	**0.4**
Climbing Man Gully 1 mean (-acid spot)		5.22	
Climbing Man Gully 1 st. dev. (-acid spot)		0.37	

Climbing Man Gully 1-1		5.05	4.92
Climbing Man Gully 1-1		4.85	5.00
Climbing Man Gully 1-1		5.03	3.95
Climbing Man Gully 1-1		5.97	4.45
Climbing Man Gully 1-1		5.78	3.94
Climbing Man Gully 1-1		5.46	3.83
Climbing Man Gully 1-1		5.79	3.97
Climbing Man Gully 1-1		5.45	3.68
Climbing Man Gully 1-1		5.23	4.94
Climbing Man Gully 1-1		5.31	3.85
Climbing Man Gully 1-1 mean		**5.39**	**4.25**
Climbing Man Gully 1-1 st. dev.		**0.37**	**0.52**

June 03 Adjacent to Climbing Man	3.74		4.86

Feb 04 Climbing Man itself	4.31		4.85
Feb 04 Climbing Man itself	4.54		3.91
Feb 04 Climbing Man itself	4.19		3.61
Feb 04 Climbing Man itself	4.1		4.87
Feb 04 Climbing Man itself	4.27		3.75
Feb 04 Climbing Man itself	4.78		4.86
Feb 04 Climbing Man itself	4.55		4.82
Feb 04 Climbing Man itself	3.58		4.68
Feb 04 Climbing Man itself			5.13
Feb 04 Climbing Man itself			4.68
Feb 04 Climbing Man itself mean	**4.23**		**4.55**
Feb 04 Climbing Man itself st. dev.	**0.39**		**0.53**

Climbing Man gully 2B			5.19
Climbing Man gully 2B			5.04
Climbing Man gully 2B			5.23
Climbing Man gully 2B			5.28
Climbing Man gully 2B			5.21
Climbing Man gully 2B			5.06
Climbing Man gully 2B			5.35
Climbing Man gully 2B			5.43
Climbing Man gully 2B			5.29
Climbing Man gully 2B			5.53
Climbing Man gully 2B mean			**5.26**
Climbing Man gully 2B st. dev.			**0.15**

Compound, off site up hill		4.88	3.81
Compound, off site up hill		4.49	5.06
Compound, off site up hill		4.76	4.94
Compound, off site up hill		4.33	4.76
Compound, off site up hill		5.17	5.67
Compound, off site up hill		4.17	4.65
Compound, off site up hill		4.16	3.88
Compound, off site up hill		4.73	3.86
Compound, off site up hill		4.61	4.59
Compound, off site up hill		4.67	4.40
Compound, off site up hill		4.64	
Compound, off site, uphill, mean		**4.60**	**4.56**
Compound, off site, uphill st. dev.		**0.30**	**0.60**

Compound off site, 2			3.85
Compound off site, 2			4.62
Compound off site, 2			3.82
Compound off site, 2			4.66
Compound off site, 2			4.58
Compound off site, 2			4.91
Compound off site, 2			4.51
Compound off site, 2			4.52
Compound off site, 2			4.83
Compound off site, 2			3.94
Compound off site, 2 mean			**4.42**
Compound off site, 2 st. dev.			**0.40**

Rock 3	4.67		4.46
Rock 3	4.76		4.79
Rock 3			4.63
Rock 3			5.03
Rock 3			4.40
Rock 3			4.16
Rock 3			4.71
Rock 3			4.69
Rock 3			4.82
Rock 3			4.54
Rock 3 mean	**4.72**		**4.62**
Rock 3 st. dev.	**0.06**		**0.25**

Rock 86	4.56	4.71	4.98
Rock 86	4.67	4.72	4.95
Rock 86	4.46	4.62	5.09
Rock 86	4.63	5.04	5.08
Rock 86	5.57	4.89	4.86
Rock 86	5.3	4.96	5.10
Rock 86	5.12	5.22	4.90
Rock 86		4.99	4.92
Rock 86		4.96	4.64
Rock 86		5.05	5.21
Rock 86			5.05
Rock 86 mean	**4.90**	**4.92**	**4.98**
Rock 86 st. dev.	**0.43**	**0.18**	**0.15**

Rock 97	5.21		4.87
Rock 97	5.26		5.30
Rock 97	5.74		5.11
Rock 97			5.03
Rock 97			6.06
Rock 97			5.68
Rock 97			5.34
Rock 97			5.41
Rock 97			5.67
Rock 97			5.00
Rock 97 mean	**5.40**		**5.35**
Rock 97 st. dev.	**0.29**		**0.37**

Rock 162	4.92	4.72	4.88
Rock 162	5.87	4.63	4.82
Rock 162	5.29	4.86	4.81
Rock 162		4.73	4.88
Rock 162		4.68	5.21
Rock 162		4.50	5.41
Rock 162		4.54	5.12
Rock 162		4.68	5.14
Rock 162		4.71	5.21
Rock 162			5.06
Rock 162 mean	**5.36**	**4.67**	**5.05**
Rock 162 st. dev.	**0.48**	**0.11**	**0.20**

Rock 938		3.97	5.83
Rock 938		4.38	5.12
Rock 938		4.75	5.06
Rock 938		5.15	4.83
Rock 938		4.87	5.45
Rock 938		4.57	4.56
Rock 938		4.64	5.75
Rock 938		5.20	4.35
Rock 938		4.50	4.47
Rock 938		4.80	3.98
Rock 938		5.00	
Rock 938		4.85	
Rock 938		5.63	
Rock 938		**4.7**	
Rock 938		**5.4**	
Rock 938 mean		**4.82**	**4.94**
Rock 938 st. dev.		**0.41**	**0.61**

Rock 1681	5.63	4.57	4.14
Rock 1681	5.36	4.43	5.18
Rock 1681	5.53	4.38	4.93
Rock 1681	5.59	4.17	4.40
Rock 1681	5.28	4.29	4.88
Rock 1681	5.45	4.43	4.8
Rock 1681	5.40	4.21	4.93
Rock 1681	4.86	4.76	4.73
Rock 1681	5.34	4.32	4.85
Rock 1681	4.90	4.10	4.63
Rock 1681	5.64	4.15	
Rock 1681	5.67	3.92	
Rock 1681	4.74	3.86	
Rock 1681	5.81	3.85	
Rock 1681 mean	**5.37**	**4.25**	**4.75**
Rock 1681 st. dev.	**0.33**	**0.26**	**0.30**

Gidley Island 1			25-Feb-04
Gidley Island 1			10:00
Gidley Island 1			4.45
Gidley Island 1			4.81
Gidley Island 1			5.09
Gidley Island 1			4.96
Gidley Island 1			5.06
Gidley Island 1			4.93
Gidley Island 1			4.86
Gidley Island 1			5.08
Gidley Island 1			4.63
Gidley Island 1 mean			**4.17**
Gidley Island 1 st. dev.			**1.67**

Gidley Island 2			25-Feb-04
Gidley Island 2			10:30
Gidley Island 2			4.73
Gidley Island 2			4.52
Gidley Island 2			4.68
Gidley Island 2			4.67
Gidley Island 2			5.24
Gidley Island 2			4.94
Gidley Island 2			4.65
Gidley Island 2			4.78
Gidley Island 2			4.76
Gidley Island 2			5.00
Gidley Island 2			4.57
Gidley Island 2 mean			**4.78**
Gidley Island 2 st. dev.			**0.21**

Gidley Island 3			25-Feb-04
Gidley Island 3			11:00
Gidley Island 3			4.61
Gidley Island 3			5.54
Gidley Island 3			4.70
Gidley Island 3			5.10
Gidley Island 3			4.50
Gidley Island 3			4.92
Gidley Island 3			5.25
Gidley Island 3			5.26
Gidley Island 3			5.50
Gidley Island 3			4.21
Gidley Island 3 mean			**4.96**
Gidley Island 3 st. dev.			**0.45**

Dolphin Island 1			25-Feb-04
Dolphin Island 1			12:10
Dolphin Island 1			4.93
Dolphin Island 1			4.85
Dolphin Island 1			4.72
Dolphin Island 1			4.63
Dolphin Island 1			4.61
Dolphin Island 1			5.05
Dolphin Island 1			4.86
Dolphin Island 1			4.71
Dolphin Island 1			5.08
Dolphin Island 1			4.95
Dolphin Island 1			4.52
Dolphin Island 1 mean			**4.81**
Dolphin Island 1 st. dev.			**0.19**

Dolphin Island 2			25-Feb-04
Dolphin Island 2			12:35
Dolphin Island 2			5.14
Dolphin Island 2			4.91
Dolphin Island 2			4.89
Dolphin Island 2			3.68
Dolphin Island 2			3.74
Dolphin Island 2			5.04
Dolphin Island 2			4.85
Dolphin Island 2			5.07
Dolphin Island 2			4.79
Dolphin Island 2			5.04
Dolphin Island 2			4.72
Dolphin Island 2			0.54
Dolphin Island 2			
Dolphin Island 2 mean			**4.97**
Dolphin Island 2 st. dev.			**0.12**

Dolphin Island 3			25-Feb-04
Dolphin Island 3			12:55
Dolphin Island 3			5.22
Dolphin Island 3			5.32
Dolphin Island 3			5.15
Dolphin Island 3			5.66
Dolphin Island 3			5.07
Dolphin Island 3			4.65
Dolphin Island 3			3.87
Dolphin Island 3			4.81
Dolphin Island 3			5.25
Dolphin Island 3			5.07
Dolphin Island 3			5.22
Dolphin Island 3 mean			**5.03**
Dolphin Island 3 st. dev.			**0.46**