

AVIAN GUANO AND ITS EFFECTS ON THE PRESERVATION OF ROCK PAINTINGS

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Summary

A study of the interactions of water-borne materials from avian guano at *Walga Rock* has enabled the characterisation of the nature of the changes that occur when the pigments interact with the guano. The major effect is the *preservation* of fugitive white pigments. Measurements on the excreta confirmed that some proteinaceous materials have survived the desiccating environment and that significant amounts of phosphate remain in the guano. Room temperature simulation experiments indicate that proteins may be involved in the *preservation* processes that transforms kaolinite to a stable iron hydroxy silicate, greenalite [$\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$] and also results in the formation of the calcium hydroxide silicate, rustumite [$\text{Ca}_4\text{Si}_2\text{O}_7(\text{OH})_2$]. The presence of mixed magnesium/calcium minerals in the modified pigments indicates that dissolution and redeposition reactions, in conjunction with anion/cation exchange reactions, are occurring on the site. Calcareous pigments have undergone phosphate substitution and the presence of calcium fluoro-phosphate is indicative of an aged deposit. The proposed reaction scheme is consistent with the in-situ surface pH measurements and colourimetric studies on the rock surface in the areas of interest.

Introduction

It has been noted in numerous rock painting sites around Australia, that the presence of avian guano appears to assist with the preservation of white pigments (North & Clarke, 1986; Haydock, 1992). Previous studies of the paintings at *Walga Rock* (Haydock, 1986) concluded that fog inception and driving rain, rather than dew, were the most likely ways by which water comes into contact with the rock face. Inspection of the site had shown that in areas located vertically beneath avian guano deposits, at higher levels of the rock face, the white pigment was comparatively well preserved. The aim of the research was to characterise the precise nature of the interaction of avian guano with the white rock art pigments. The principle method of characterisation of the *guano affected* or *altered pigments* was based on x-ray diffraction (XRD) as well as using conventional wet chemical analyses. Our analyses of the painted surfaces dispelled the original assumption that all or most of the white pigments were based on kaolinitic minerals; significant amounts of original pigments appear to be calcitic. The interactions of calcitic and kaolinitic minerals with urea, proteinaceous materials and phosphorus-containing compounds has been studied to gain an insight into the complex and interactive processes that apparently occur on sites such as *Walga Rock*. Some proteins have been shown to survive prolonged exposure to desiccation and high levels of ultra-violet radiation. Detailed discussion and experimental details can be found in the full report (MacLeod, 1992).

Experimental

Surface pH measurements were made using an Activon BJ 431 flat-surface combined glass electrode connected to a Watson Victor 5003 digital pH meter. X-ray Diffraction (XRD) data was collected using a Phillips automatic diffractometer, and the Scanning Electron Microscopy (SEM) examinations were performed using a Jeol JSM-2 or a Geosem instrument equipped with a Robinson detector (Robinson, 1979). The use of the low vacuum back-scattered secondary electron mode of operation on the SEM provides an image of good atomic number contrast, and reveals the micromorphology of the sample and eliminated problems associated with coating. Semi-quantitative elemental analyses were obtained from Energy Dispersive X-ray Analysis (EDAX) - the sensitivity of the detectors means that it is easier to identify calcium containing species rather than magnesium species. Fourier Transform Infrared (FTIR) spectroscopy was carried out using an FTS 40 Biorad Digilab instrument at the Chemistry Centre of WA. The signals were recorded using a mercury cadmium tellurium detector. The total phosphate and acidity concentrations were determined using standard analytical procedures with either direct or

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WALGA ROCK

Walga Rock is located 45 km south west of Cue in the Murchison district of Western Australia. The painting site is located at the south western side of the rock itself, which is a granite monolith some 1.5 km long and up to 0.5 km wide. A more detailed description of the site is found in earlier reports (Haydock, 1986; MacLeod, 1992). The site is in a semi-arid region and the nearby town of Cue has an average annual rainfall 224 mm which is highly variable, but with an annual average of 42 rain days, with most rainfall recorded in the autumn and winter months. There is some thunderstorm activity in the summer months due to tropical "heat-lows" settling over the Murchison and Gascoyne districts. There are also occasional remnants of tropical cyclones through the area. Autumn and winter rains are associated with north west cloudbanks interacting with cold fronts that sweep across the South West of Australia. The average maxima varies from 38°C in January to 18.4°C in June with the average minima of 23.3°C in January to 7.0°C in June (Bureau, 1991).

Results and Discussion

pH Measurements: On-site measurements were made over two days and nights in March 1991 with the three major areas affected by the avian guano noted as areas "A", "B" and "C", as seen in figure 1 with a detail of area "C" shown in figure 2. This area represents the main focus of the study. The outside vertical flow lines from the guano above the paintings marks the area of preservation of the white pigment. The results of the surface acidity measurements are illustrated in figure 3. All the pH readings were acidic with the granite surface ranging from pH 5.3 to 5.9 and the avian guano flow lines varied from 4.9 to 5.1. The surface acidity is higher in the areas closest to the avian guano and becomes more alkaline closer to the ground.



Figure 1: View of rock paintings and the guano from inside the site at *Walga Rock*.

Although there is some variability in the gradient, all the profiles obtained over various areas under the guano all indicate that the guano is the primary source of the acidity. The pH of areas outside the avian guano showed less variability with height. Small samples of the substrate were sampled after the pH measurements had been made. The mean pH of fresh swallow, kestrel and owl guano was 6.4 ± 0.1 while the dried material had a mean pH of 5.83 ± 0.31 which is not as acidic as the pH of 5.4 for the material collected at *Walga Rock*. Since site conditions more closely equated with an extractive pH a sample of the guano was mixed with 1:1 volume of water and the pH was monitored for a period of four hours. In the first fifteen minutes the pH fell from an initial value of 5.41

to a low of 3.9 before climbing to a steady value of 4.55 ± 0.07 .

The variation in the extractive pH is probably due to rapid extraction of acidic species being followed by a slower buffering reaction with the guano residues. The pH of the water soluble materials from the old guano provides good evidence that guano is a significant source of acidity. The lower acidity of the zoo guano is probably due to its freshness and to differences in the diet of the *free-range* and the captive birds.



Figure 2: Close-up of the white pigments preserved by the

Analysis of Avian Guano

Since proteins have very good binding properties for friable pigments (Mora et al, 1984) it was necessary to establish if they might have been involved in the preservation process. The aged guano from *Walga Rock* contained 0.02% protein or about 10% of the amount in fresh material from the zoo. This is clear evidence of proteins surviving in the guano and therefore being potentially available to interact with the pigments. The presence of proteins and uric acid in the aged avian guano deposits is also seen in the FTIR spectrum with a strong band in the $1700\text{-}1725\text{ cm}^{-1}$ region, which is characteristic of the amide carbonyl linkage in amino acids (i.e. the $\text{-NHC(O)CH}_2\text{-}$ unit) and in uric acid. The changes in composition that occur with ageing of the guano deposits are complex but some of the differences are of specific relevance to the interaction of the pigments with the water-borne species. Fresh kestrel guano contained three major phosphate minerals, namely $\text{FeH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ while the aged material contained the calcium pyrophosphate $\text{CaH}_2\text{P}_2\text{O}_7$ along with the more acidic hydrated pyrophosphate $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot \text{H}_2\text{O}$. The iron hydrogen phosphate had disappeared and the ammonium ion, present in the fresh guano as ammonium sulphate (mascagnite, $(\text{NH}_4)_2\text{SO}_4$), reappears as an ammonium pyrophosphate $(\text{NH}_4)_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$. The presence of several pyrophosphates in the aged material is consistent with dehydration and cation exchange reactions under the hot and acidic surface conditions on the rock. Calcium carbonate was found as aragonite in the fresh material and was found as vaterite (CaCO_3) and as whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, in the aged guano. The latter mineral is a typical alteration product associated with the weathering of calcareous materials (MacLeod et al, 1991, Ford et al, 1994). The general trend to desiccation and dehydration of mineral phases is also seen in the transition of the hydrated iron formate, $\text{Fe}(\text{CHO}_2)_3 \cdot \text{H}_2\text{O}$, to the anhydrous form in the aged guano.

Analysis of "unaltered" pigment

The material collected from the painted areas away from the guano flow lines was principally calcite with some whewellite. The absence of kaolinite in the sample (GSWA 46769) does not preclude its presence in some of the other white pigments from different sections of the site. Since the weathered granite had an inherently acidic surface, with $5.9 < \text{pH} > 5.3$, any calcitic pigment would tend to have poor adhesion since the acidic surface would tend to dissolve the pigment. This problem would be further compounded by acidic rain associated with thunderstorms. The whewellite in the sample is probably a biproduct of calcite reacting with some oxalate derived from a plant or microbial metabolite. Despite the inherent instability of calcite as a pigment we believe that it is pre-contact and therefore at least 100 years old. There is clear evidence in the sequence of the paintings that overpainting was practised extensively at the site. Analysis of minerals recovered from maritime archaeological sites has shown that mineral conversion reactions readily occur at temperatures in the range 18-28 °C (MacLeod, 1991). It is therefore possible that changes at *Walga Rock* have occurred in a relatively short time span. Similar observations have been made by Clarke, Dangas and Perigord at Nourlagie (Clarke, 1989).

Analysis of "altered" pigments

Pigments samples were taken from area "A" (denoted by the presence of the painted ship) and from area "C" in the large central painting that has been offered the greatest level of natural protection. Owing to small sample size, the pigment from the painting in the ship area was only characterised by EDAX analysis and SEM examination which showed that the deposit was coarse with well developed grains that were consistent with materials where there had been some dissolution/precipitation reactions. The main elements were calcium with a lesser amount of phosphorus with minor amounts of sodium, sulphur, chloride and potassium. The latter species are probably indicative of salt weathering of the host rock. The phosphorus contamination of the pigment may have come from the avian guano deposits in the vicinity as the sample area is less than half a metre from the guano flow line.

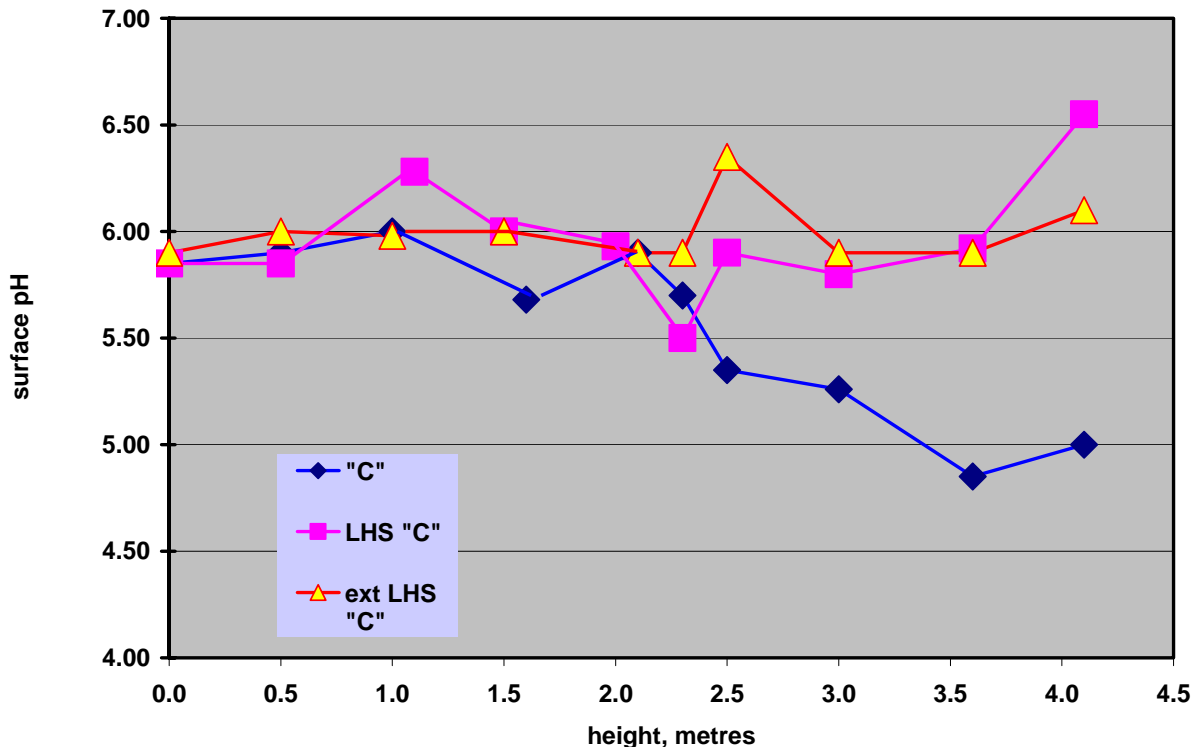


Figure 3: Vertical pH gradients beneath and adjacent to the avian guano in area "C".

The samples of pigments from area "C" under the more direct influence of the avian guano deposit were examined by XRD. Not surprisingly a large number of the phases identified are most likely associated with the weathered rock and its interaction with the guano. Our principal interest is in the alteration products of the

pigments. Given that an abundant source of calcium exists in the guano deposit, it is not unreasonable to deduce that the rustumite, $\text{Ca}_4\text{Si}_2\text{O}_7(\text{OH})_2$, may be the end product of a reaction between kaolinitic minerals of the form $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and calcium ions. Although this mineral may be due to the interaction of the guano with the weathering products from the granite, we believe them to be derived from kaolinitic pigments interacting with the guano. However it is likely that the aluminium hydroxy silicate pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), a non expanding dioctahedral layered silicate (Deer,1971) is probably due to contamination of the pigment with clay minerals derived from the weathered rock surface.

Apart from the silicate minerals, all the other species are dominated by phosphate which has most probably come from the old guano which contained 4.20 wt% phosphorus. A total of six calcium-containing phosphate minerals were found in area "C". The calcium phosphate fluoride $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ has a fluoroapatite structure; the end product of isomorphous replacement of the hydroxide by the similarly sized fluoride ion. The adsorption of fluoride by such minerals has been used as a method for dating archaeological deposits (Coote,1982) since the incorporation of fluoride is a well defined exchange process. No attempt has been made to use this, or the other fluoro-phosphate CaMgPO_4F , for dating since the amount present in the pigments was only very small (<8% of the pigment samples). The identification of three mixed calcium phosphates amongst the pigments in the form of $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$, CaMgP_2O_7 and $\text{Ca}_3\text{Mg}_3(\text{PO}_4)_4$ is a strong indication that the pigments have been subjected to a whole range of ion-exchange processes during the interaction of the pigments with the water-borne materials from the avian guano. The fact that none of the phosphate minerals present in the fresh and in the aged avian guano deposits are found in the same form in the aged pigment areas further supports the hypothesis that a series of chemical changes have taken place that have fundamentally altered the nature of the pigments.

The insoluble iron phosphate $\text{Fe}_3(\text{PO}_4)_2$ and the sodium iron hydrogen phosphate, $\text{NaFeH}_2(\text{PO}_4)_2$, are probably derived from the reaction between the iron formates and the hydrated sulphate bilinite ($\text{Fe}_3(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$) and the phosphate ions. The presence of the magnesium hydroxy bicarbonate nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$) is probably due to reactions between dissolved carbonates and magnesium leached from the granite or the guano. The magnesium sulphates such as leonite ($\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) and magnesium sulphate probably results from exchange reactions between cations associated with the weathering rock and from the sulphates present in fresh guano as ammonium sulphate and the hydrated iron sulphate bilinite. Given the high solubility of many ammonium salts it is not surprising to find that no ammonium compounds were identified in the altered pigment samples.

Reaction of kaolinite with avian guano

In order to determine the nature of the interactions of the water soluble materials with kaolinitic pigments on *Walga Rock*, a series of room temperature experiments were performed with pigment from nearby Mt Magnet. The iron hydroxy silicate greenalite, $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$, was formed due to substitution of the Al^{3+} ions in the parent kaolinite with Fe^{3+} ions which were present in the fresh guano. Several other iron compounds were found in the reaction mixture but the products were largely due to a series of oxidation and hydrolysis reactions that did not involve any silicate minerals. The hydrated copper phosphate $[\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}]$ was found in the reaction mixture; it is likely that this compound is the form of the copper found as a trace impurity in the pigments at *Walga Rock*. There were no new silicate minerals formed when the kaolinite was reacted with the aged guano. Frequency shifts in the absorption spectra of the amide linkage indicate that residual proteins in the aged guano are interacting with the kaolinite.

Colour measurement of rock surfaces and images

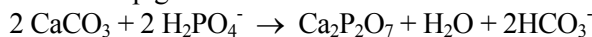
Since the description of the colours of rock art images is fraught with difficulty, a chromameter was used to obtain quantitative colour data. Differences in colours relate to the differences in three dimensional (Euclidean) space which is determined by the lightness (L) and the a (red-green) and b (yellow-blue). The colour difference is defined by δE^*_{ab} , the straight line distance between coordinates of the two samples,

$$\delta E^*_{ab} = \{(\delta L^*)^2 + (\delta a^*)^2 + (\delta b^*)^2\}^{1/2}$$

The white pigment seems to be generally lighter (higher L^* values), less red (lower a^* values) and less yellow (lower b^* value) under the influence of the avian guano with a colour difference $\delta E^*_{ab} = 12.6$ between the two areas of white pigments. Removing dust from some red pigmented areas showed that the dust lowers the lightness (L^*) value and it increases the redness (a^*) values but has no effect on the yellow (b^*) values.

Interpretation of results

The site at *Walga Rock* is very complex with multiple episodes of apparent repainting and what appears to be the use of at least two different types of pigments. With rock surface pH ranging from 4.9-6.1, the dominant form of phosphate is the H_2PO_4^- ion represents more than 90% of the soluble form of phosphate. A possible reaction scheme for the stabilisation of the calcitic pigments involves a substitution and a "dehydration" step,



In the surface pH range observed on the site the bicarbonate ion would either wash away or precipitate out other cations. The identification of the fluoride-substituted phosphates and the range of pyrophosphates/phosphates containing mixtures of alkaline earth cations (Mg^{2+} , Ca^{2+} , Ba^{2+}) in the areas of the interaction of the guano flow with the pigments is clear evidence of a series of complex reactions involving not only the water-borne phosphates reacting with the pigments but also with the weathered rock surfaces. The major mechanism for transport of the phosphates from the guano is most likely to be associated with rain or some other situation where there is a real surface "wetness".

Since the whole of the *Walga Rock* surface is underpainted with layers of red pigment, the movement and reactions of phosphates will also be dependent on their reactions with iron. Any free Fe(III) ions will be readily complexed by the phosphate. This is demonstrated by the presence of compounds such as iron phosphate, $\text{Fe}_3(\text{PO}_4)_2$, and sodium iron hydrogen phosphate, $\text{NaFeH}_2(\text{PO}_4)_2$, in the guano-affected pigment, and manganese iron hydroxide phosphate, $\text{MnFe}_4(\text{PO}_4)_3(\text{OH})_5$, on a section of altered rock. The low frequency of rain or fog suggests that the conversion of calcite with apatite-like phosphate minerals would be a very slow process. Positive indicators that conversion processes involving kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, occurring in the guano-affected painted areas of the site are found in the presence of the hydroxy silicates rustumite, $\text{Ca}_4\text{Si}_2\text{O}_7(\text{OH})_2$ and pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. The formation of greenalite, $[\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4]$, as a reaction product of *Mt Magnet kaolinite* with the fresh avian guano is an example of the ion exchange reactions of kaolinitic minerals with ferric ions that can occur under laboratory conditions at $24 \pm 2^\circ\text{C}$. These types of interaction may be part of the reason that the kaolinitic pigments in the flow lines have withstood the weathering processes. The changing nature of the cations in the silicate sheet layer lattices will also alter the fundamental hydration properties of the pigments. This will render the inherently unstable kaolinitic materials less subject to the stresses of alternating cycles of rehydration and dehydration (Deer et al, 1971). The modifying influence of organic compounds such as proteins and uric acid on the surface properties of the kaolinitic minerals has not been determined. However, the surface chemistry of such minerals is characterised by a range of adsorption and absorption reactions so it is possible that some initial reaction with soluble muco-protein modified the surface properties of the pigment and facilitated cation exchange reactions that resulted in the stabilisation of the pigment.

Conclusion

Our studies have clearly demonstrated that the interaction of rock art pigments with avian guano is a very involved process. From a combination of XRD of the pigments and their interaction products and the use of SEM and FTIR spectroscopy, the results show that a wide variety of mineral and chemical compounds are formed. The availability of phosphorus-containing species has a major effect on the weathering processes observed on the rock surfaces and also on the pigments themselves. The chemical transformation of calcium carbonate pigments into more stable calcium phosphates appears to be one of the ways in which the avian guano has stabilised the pigment. Intermediate compounds derived from the by-products of guano metabolism may be involved in intricate reactions which form a series of carbonates, phosphates and fluoro-phosphates. Kaolinitic pigments appear to be converted into stable iron and calcium hydroxy silicates as a result of the interaction with the water borne materials from the guano. It is very clear that it is dangerous to assume that the presence of avian guano on rock paintings is always deleterious.

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