

Rock Art Pigments from Kimberley region of Western Australia: identification of the minerals and conversion mechanisms.

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SUMMARY

Pigment samples from Aboriginal rock art sites, situated mainly in the Napier Ranges of Western Australia, were characterised by microscopic examination, wet chemical and X-ray analysis. In the white to grey and black range of colours the majority of pigments were found to consist of huntite, dolomite, calcite or whewellite (a hydrated calcium oxalate). Colour modifying additives to the basic white pigments are also described.

The widespread occurrence of pigment layers composed largely of whewellite is discussed in terms of possible origins -either as a mineral deposit utilised by the Aboriginal artists as a source of pigment, or as the result of an *in-situ* chemical alteration of huntite and/or calcite by acidic solutions containing oxalate ions. It is also postulated that calcite in pigment layers may have formed *via* the chemical alteration of huntite. Laboratory experiments have confirmed that acid dissolution of huntite in the presence/absence of oxalate and sulphate ions reproduces the same species as observed on material collected on the rock art sites.

1. Introduction

In 1988 the Western Australian Museum's Department of Materials Conservation received funding from the Western Australian Heritage Committee to conduct research into the conservation of rock art in the Kimberley region of Western Australia (W.A.). The Australian National Gallery also provided funds for the participation of Bruce Ford. The major emphasis of the research, which was carried out in the dry season of June and July 1990,

was on microclimatic conditions within shelters, however mineralogical, biological and management issues were also covered since they impinge on the overall site stability. A knowledge of the nature of the pigments and how they interact with the microenvironment at the sites forms an essential part of the programme of determining appropriate conservation management strategies for the custodians of the sites. Following the success of the initial dry season work a subsequent grant was obtained to repeat all the assessments during the wet season in 1992. Detailed reports on the way in which the local environment changes with the wet and dry seasons will be the subject of another paper. At this stage it is sufficient to state that significant differences in surface acidity and microbiological activity for the two seasons were noted. The principal cause for the differences appears to be the availability of moisture.

The study area in the North-West of Western Australia is well known for its large number of rock paintings, many of which are predominantly composed of either white or off-white pigments. Some of the images are also executed over a white background applied to the rock or underlying paintings. In a previous study in the area, Clarke¹ found that the white mineral huntite [$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$] had been widely used and that its physical properties and method of application predisposed it towards serious deterioration, particularly under the damp or humid conditions which are regularly experienced during the wet season in the tropical north of Australia. During the initial dry-season field work, it became apparent that a variety of minerals were represented in the white, cream and grey pigment layers, and that the condition of the paintings containing them would be influenced by specific interactions between pigment and rock surfaces and successive pigment layers, and by the behaviour of those pigments in different microclimates. Since the white pigments are the most inherently unstable materials on the sites, a relatively large number of samples, in the white to grey spectrum, along with other material were taken in order to establish their chemical and mineralogical properties. Other samples taken included a number of botryoidal accretions which are prevalent throughout rock shelters in the Kimberley region. These samples were taken for comparative studies.

2 Location and cultural context

Thirty seven of the forty samples subjected to detailed examination and analysis were taken from four sites within

30 km of each other at the base of the Napier Range near Fitzroy Crossing, Western Australia in the south western Kimberley region. The range is an exposed Devonian limestone reef, at or near the base of which occur shelters within which the art was made. A map of the area and a typical sectioned view of a site are shown in figures 1 and 2. All four sites within this range fall under the Aboriginal custodianship of the Bunuba people. The cultural uniformity between the four sites with respect to materials and techniques cannot be assumed, although it is likely that there is a degree of similarity because of a shared geological setting and cultural context. Three samples of white pigments from two sites located in the Mitchell Plateau (northern Kimberley) region of Western Australia were also analysed. In this case the shelters were located in siliceous sandstone strata. The relevant Aboriginal owners have requested that more precise locations for the sites be withheld from publication.

3 Analytical Results and Examination Methods

3.1 Sampling

Pigments were scraped from the rock face directly into glass vials using a small scalpel or needle. They were usually taken from places which had suffered previous damage, and where possible from flakes about to exfoliate. Multilayered samples for cross-sectional examination were only taken from loose flakes and the edges of exfoliated areas. For this reason, sampling tended to be opportunistic rather than systematic. A photographic record was made of each of the sample areas but because of the cultural sensitivity of the sites these photographs are not for publication. Some samples of rock surfaces within shelters adjacent to art motifs were taken in order to determine the nature of brown and black surface layers. Aboriginal custodians, or their representatives, were present at all times for those aspects of the project which involved a physical presence or intervention within sites, and pigment and other mineral samples were taken under their direct supervision. The authors felt that retention of site integrity outweighed considerations of more statistically valid sampling methodology.

3.2 Visible light microscopy

Loose pigment samples were first examined on a glass microscope slide under visible and ultraviolet light at 100-300 magnification using dark field incident illumination. A portion of the sample was lightly crushed to break up aggregates in order to estimate particle sizes and reveal particles hidden within clumps. A small portion of some

samples was dispersed in a drop of methanol in order to separate the pigment particles from each other and to examine them for the presence of organic binding material. The observation that no evidence of binding materials was found is consistent with traditional accounts painting techniques which include brushing of a water-based dispersion and spraying from the mouth. Multilayered samples were embedded in a polyester resin, polished and examined under dark field incident illumination at the above magnifications. All samples were photographed at magnifications which yielded useful information.

3.3 Electron microscopy and energy dispersive X-ray analysis

A Jeol SM6400 and a Cambridge S360 electron microscope fitted with energy dispersive x-ray analysers (EDAX) were used to examine pigment samples. Samples were prepared for combined electron microscopy and EDAX analysis by mounting them on aluminium stubs with double sided sticky tape and coating with carbon. Higher quality images were obtained in some cases by using a gold coating once EDAX analysis was complete.

3.4 X-ray diffraction

Because of the small sample sizes, they were prepared as unoriented mounts on a low background silicon holder. Copper K α radiation was used at 35kV and 30mA tube power, scanning at 1 $^\circ$ /minute from 3 $^\circ$ -70 $^\circ$. Minor phases (<10%) may not have been detected in some samples, again owing to small sample sizes. X-ray diffraction (XRD) on some of the tiny pigment samples was performed using standard techniques for Debye-Scherrer cameras, with the crystals mounted on the end of silica sticks with vaseline.

4 Results and Discussion

4.1 Mineralogical classification of pigments and rock surface layers.

The major mineralogical components of forty samples of white, cream, red, yellow, grey and black pigments were determined on the basis of XRD and the results are shown in Table 1.

Table 1. Mineralogical analysis of rock art pigments

Mineral	Formula	Chemical name	Occurrence as a significant component*	JCPDS no.
Huntite	$Mg_3Ca(CO_3)_4$	magnesium calcium carbonate	11	14-409
Whewellite	$CaC_2O_4 \cdot H_2O$	calcium oxalate hydrate	15	20-231
Weddellite	$CaC_2O_4 \cdot 2H_2O$	calcium oxalate dihydrate	2	17-541
Dolomite	$MgCa(CO_3)_2$	magnesium calcium carbonate	5	11-78
Calcite	$CaCO_3$	calcium carbonate	9	24-27
Antigorite	$Mg_3Si_2O_5(OH)_4$	serpentine mineral	1	7-417
Illite	$(K,H_{30})Al_2Si_3AlO_{10}(OH)_2$	silicate mineral	1	26-911
Hematite	Fe_2O_3	iron oxide	1	24-72
Goethite	$FeO \cdot OH$	iron oxy - hydroxide	1	17-536

* The occurrence of a mineral component was deemed to be significant when the compound was present in an amount greater than 30 %. The total numbers of minerals present as a significant component (46) is therefore greater than the number of samples (40).

All seven samples of dark brown and black rock surface deposits were identified as whewellite, with minor amounts of ankerite $[(Ca,Mg,Fe)CO_3]$, calcite, and in one case, jarosite $[KFe_3(SO_4)_2(OH)_6]$ and pyrite $[FeS_2]$.

Whewellite occurred as a minor constituent in four samples of calcite and two samples of huntite pigments. It was only present as the major (>90%) or minor (<10%) constituent in samples from the Napier Range (limestone).

Where whewellite was identified as the major component the samples were

large enough to include one or more complete paint layers. Only two samples of the dihydrate of calcium oxalate, weddellite, were found. The material came from the ceiling of a shelter in the Mitchell Plateau. The dolomite samples were found both in the presence and absence of whewellite. Goethite and hematite were found to be components in samples of red pigment that also included kaolin and mica which probably formed a background prior to the application of the red pigment. The aluminium phosphate mineral taranakite, $K_3Al_5H_6(PO_4)_8 \cdot 18H_2O$, was a major component in a layer deposited on the surface of a weathered sandstone site at one of the sites in the Mitchell plateau. Other minerals associated with this deposit were quartz and minor amounts of kaolinite and calcite. Although this deposit overlay one section of the paintings it is not believed to have been a pigment. The presence of this phosphate mineral is unexpected and its significance in any deterioration process is not known. The material overlaying some of the images adjacent to the source of the taranakite consisted mainly of amorphous silica and some whewellite.

Carbonate minerals have previously been identified as rock art pigments in the tropical north of Australia, including huntite in the Kimberley¹ and Kakadu², and both calcite and dolomite [$MgCa(CO_3)_2$] in Kakadu². Apart from the presence of the major minerals listed above, clay minerals appear to be common minor constituents of the pigments^{2,3}. Antigorite and whewellite have not previously been reported as pigments. Other components identified in the samples included adventitious minerals such as mica, quartz, feldspar and kaolin.

Calcite, huntite and whewellite pigment layers were represented at all of the Napier Range sites, both in different motifs and in different layers of the same motif in some cases. The antigorite sample was from the Mitchell Plateau, and another pigment from that region, which was not subjected to XRD, had an EDAX spectrum consistent with a clay mineral. The only pigment positively identified as a clay mineral was illite which came from the Napier Range. This particular pigment also contained a trace of ankerite [$Ca(Mg_{0.67}Fe_{0.33})(CO_3)_2$]. Gypsum [$CaSO_4 \cdot 2H_2O$] was detected in several pigment samples as a minor component. The element sulphur was ubiquitous in all of the pigments and occurred at higher levels in the whewellite samples in the form of gypsum. The gypsum present in the mineral samples is probably due to contamination of the material with varying amounts of weathered rock substrate. Quartz was almost invariably found where sample sizes were large enough to

determine minor constituents.

Elemental analysis using EDAX revealed that nearly all of the samples contained minor (1-10%) amounts of Mg, Al, Si, S, P, and several contained K, Cl, Ti and Fe. The presence of these minor elements is not unexpected for samples of pigment collected from rock surfaces. North and Clarke² also found unusually high levels of titanium and sulphur in many of the pigment samples from many sites in the Kakadu National Park. A typical EDAX spectrum for a sample of a huntite [$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$] pigment is shown in figure 3 where the impurities of iron, phosphorus, silicon, chlorine, titanium and sulphur are shown along with the major elements of magnesium and calcium. It should be noted that the EDAX is relatively insensitive to magnesium when compared with calcium.

4.2 Macroscopic and microscopic appearance of pigments

The antiquity of some sites in the Napier Range is indicated by the number of layers revealed in cross sections, in which many different coloured pigment strata are interspersed with what appear to be mineral accretions - most likely either calcite, gypsum or oxalates. A typical section is shown in figure 4. Many of these layers contain quite extensive deposits of charcoal, which occur both as a result of the deliberate use of charcoal either alone or in admixtures with other pigments. Deposition on exposed surfaces during bush fires must also occur as charcoal can be found embedded in non-pigment mineral accretions and rock skins not associated with art. Also revealed in cross-section are black layers which do not appear to be charcoal. They may be composed of calcium oxalates or gypsum, both of which have been previously described as black deposits on rock surfaces in tropical and other environments⁴, or they may be organic deposits of some kind. North and Clarke² have noted that finely divided minerals associated with dissolution/precipitation phenomena will often trap incident light and so appear to be much darker than the massive forms of the same mineral.

The huntite pigments are of a characteristic vivid white appearance, and under microscopic examination form uniform and compact paint masses. The samples scrutinised in this study were all reasonably pure, containing only small quantities of quartz, charcoal, and yellow to red-brown particles which were identified by XRD as the mineral muskoxite, [$\text{Mg}_3\text{Fe}_4\text{O}_{13}\cdot 10\text{H}_2\text{O}$]. Another iron and magnesium containing impurity found in a sample of

huntite from a "quarry" in the West Kimberley was the mineral amakinite $\text{Fe}_{.73}\text{Mg}_{.22}\text{Mn}_{.05}(\text{OH})_2$, (15-125). EDAX identification of the minor elements and the morphology of the samples suggest the presence of iron and aluminium containing minerals. Where sample sizes were large enough, the subsequent XRD analyses confirmed the presence of goethite, hematite, mica, kaolin and feldspar. North and Clarke² have identified materials such as laterite, iron oxides, gypsum and potassium chloride amongst the minerals present on sites in Kakadu National Park in the Northern Territory. None of the huntite samples in this case appeared to have been mixed with other pigments in quantities sufficient to produce coloured paints such as described by Clarke¹. Electron microscopy reveals very characteristic rhombohedral platelike huntite crystals of a uniform 1-2 micron particle size.

The calcite pigments were all from paints described in the field as grey, except for one which was cream. Microscopically they are open, porous masses, in which smaller pigment particles (1-5 μm) clump together in 10-30 μm aggregates. Their grey colour is a result of the admixture of charcoal of highly variable particle size (typically 10-500 μm). Without charcoal, the paint is cream in colour and easily distinguishable from the brilliant huntite whites.

All of the calcite pigment layers contained significant amounts of light red-brown particles ranging up to 100 μm , which were initially assumed to be iron oxides or laterite, however EDAX reveals little Fe, and neither does XRD identify common red-brown iron minerals. Since the red-brown materials were not soluble in either dilute or concentrated hydrochloric acid and it was thought that they might be an organic resinous material. The particles are not carbonised when heated to high temperature over a flame, nor do they fluoresce under ultraviolet light with the characteristic blue-green of resins. These characteristics tend to rule out an organic nature. Since quartz was detected in all of the calcite samples, it is probable that the particles are iron stained ortho-quartzites.

Some of the samples which were identified as mainly whewellite appeared to be morphologically very similar to the calcite pigments under the light microscope, with clumping of smaller (1-10 μm) particles into much larger (20-50 μm) aggregates. Included in this category was a black pigment, in which the colour arose from a heavy loading of charcoal. The micromorphology of the carbon was more consistent with test samples of carbonised spinifex (a

local grass) rather than being derived from wood. Another whewellite sample took the form of a hard multilayer exfoliated crust or flake, in which predominantly white layers were interspersed with black and red strata. A transverse section of the flake, that included all the layers, was crushed and analysed by XRD. Since whewellite was the only mineral identified, the multiple layers must be primarily the same mineral with other phases being absent or having poorly defined crystallinity. A similar portion of the same sample tested strongly for phosphorus across all of the layers (using EDAX), however no phosphate minerals were identified in the XRD. The lack of positive identification of any phosphate mineral in the sample may be due to the presence of inorganic species of poorly defined crystallinity. Further work is required to determine the nature of the phosphorus containing materials. It is commonly observed that many phosphates arising from substitution reactions have poorly defined mineralogy and often give XRD's that are essentially distortions of the standard spectra⁵.

In addition to the twelve samples which were mainly composed of whewellite, the mineral was also detected in the XRD spectra of a further ten samples as a minor component. Six of those samples had calcite as a major component. One of the samples identified as whewellite came from the same motif, and possibly the same paint layer, as a sample which was identified as mainly calcite. An older paint layer from the same figure was composed of huntite. The pigment identified as illite was a muddy grey colour in the field, and microscopically appeared to be from a porous 'sugary' pigment layer similar in appearance to the calcite pigments. The grey colour was due to charcoal, and there were also red and red-brown mineral inclusions which contained iron.

The pigment sample containing mainly antigorite (from the Mitchell Plateau) exhibited a more compact nature than that typical of calcite pigments, but it was more sugary and porous in appearance than huntite. The particle size of the antigorite ranged from 0.5-3 μm , the majority being about 1 μm and of a flattened cubic shape. The paint flake represented two layers from the same painting; one layer being white and the other grey. Both layers were composed of antigorite; the grey side contained a comparatively larger proportion of charcoal of particle size from 2-40 μm but most commonly about 10 μm . Quartz, calcite and feldspar were also identified in this sample along with unidentified red and red-brown inclusions.

4.3 The origin of whewellite pigment layers

One of the most surprising findings is that a substantial proportion of the pigments are either wholly or partly composed of whewellite. There are two possible explanations for this finding; either whewellite has been used as a pigment, or it has formed *in situ* by the chemical alteration of other pigments.

The occurrences and possible origins of oxalate crusts associated with rock art sites in Australia have been summarised by Watchman⁴, where instances of the formation of oxalates as rock patinae, and films overlying or underneath pigment layers, are cited. There is, however, no report of the use of oxalates as pigments in their own right, or of the major alteration of other pigments to whewellite. Minor alteration of carbonate based pigments such as calcite and huntite to oxalates and sulphates, has been noted² in Australia's tropics.

If whewellite were to have been used as a pigment, substantial deposits of the mineral in a reasonably pure white form would have to be available as a raw material (some of the motifs in which the mineral was found cover a square metre or more). Oxalate minerals occur as natural deposits in cavities and fractures within calcareous rocks, coal seams, uranium deposits and clay beds^{6,7}. In geological formations whewellite is more common than weddellite (the dihydrate of calcium oxalate) owing to its greater thermodynamic stability⁷. No major deposits of whewellite are known to occur in the Kimberley region⁸. On this basis, there is no reason why the native mineral could not have been used as a pigment but the lack of a nearby local source of the mineral would naturally be a major impediment to its use in the original paintings.

It is understood that whewellite may form as a result of the alteration of the original calcareous pigments by oxalic acid. Our hypothesis is that this is the predominant mechanism of formation for the sites in the West Kimberley. The formation of calcium oxalates in nature can occur via the production of oxalic acid by epilithic and endolithic cyanobacteria⁹ and lichens¹⁰ as well as by anthropogenic air pollution¹¹. Organic acids in rainwater resulting from the emission of hydrocarbons by plants and the decomposition and burning of vegetation, particularly in the tropical environment⁴ are another source. Indirect evidence for the rainwater-source of oxalate is the identification

of substantial levels of sulphuric, formic, acetic and propionic acids in rainwater and clouds from Australia's tropical north¹², although oxalic acid itself was not specifically determined. Clarke¹³ has found circumstantial evidence for the atmospheric origin of some oxalate deposits in Kakadu, where accretions built up on land that sloped gently on the windward side and steeply on the lee side.

Apart from air-borne origins of oxalate, the principal sources are derived from biological sources as a metabolite from microbial activity and plant material. At the time of the initial field work, at the height of the dry season, there was little obvious local growth of fungi or algae within the shelters or evidence of past activity. However, samples of rock and dust taken under sterile conditions were cultured and found to be harbouring various bacteria, yeasts and moulds. The aerobic bacteria were identified using standard plates and cultures and some samples had counts as high as 850,000 bacteria per gram of substrate¹⁴. The counts for yeasts and mould were also high at greater than 3,000¹⁴. While these values may not be typical they do indicate a significant level of biological activity under appropriate conditions. Measurements on the same site in the 1992 wet season yielded counts of greater than 1.92 million bacteria per gram for an active drip line on a calcite straw-like stalactite¹⁴ hanging from the roof of the shelter. Whilst direct comparisons of microbiological activity are not possible, the increased counts in the wet season are consistent with all the other observations based on biological activity. There is no evidence that the occurrence of oxalate pigment layers are correlated with specific microclimates. Recent work at *Walga Rock*, which is in a semi-arid environment, found whewellite on aged avian guano and on pigments affected by the "flow lines" underneath the guano deposits. Calcite, huntite and oxalate pigment layers were all found in close proximity and in apparently identical environments at all of the Napier Range sites.

The formation of whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) through displacement reactions on the surface of gypsum crystals has been investigated by del Monte and Sabotini¹⁰. It was found that whewellite was preferentially formed from oxalic acid and alkali oxalate solutions at temperatures slightly above room temperature while weddellite crystallises predominantly at lower temperatures. Recent analyses by the authors of material recovered from the inside of the roof of a shelter, in the sandstone country in the Mitchell Plateau, confirmed the presence of weddellite. This form of a calcium oxalate was only found in the coolest parts of the site. The sample

also contained major amounts of whewellite and gypsum with smaller amounts of quartz and kaolinite. Applying these data to the warm tropical environment with calcite as the source of calcium ions, rather than gypsum, whewellite would generally be expected to form. The presence of small amounts of whewellite and gypsum in most of the calcite pigment samples and the identification of each of the six rock surface samples as whewellite by the authors, is a strong indication that conversion of calcite to calcium oxalate is taking place. The formation of gypsum from calcite would necessarily involve a source of sulphate, such as from rainwater. Unfortunately not enough non-art rock surface samples were taken from shelters to determine the extent of conversion of the native rock to whewellite or its correlation with microclimates.

4.4 *The conversion mechanism*

Given the ability of calcareous pigments, such as huntite, to be changed into calcium oxalates, there is an interest in the conversion mechanism. A series of experiments involving huntite and mildly acidic solutions was carried out at room temperature ($22\pm 2^\circ\text{C}$) both in the presence and absence of sodium oxalate. The reaction mixtures were buffered with potassium hydrogen phthalate solutions which had initial pH's in the range 5.5 - 5.9 which corresponded to the range in surface pH observed on rock surfaces in the dry season in the Kimberley. A slurry of huntite and the solutions were placed in a sintered glass filter funnel (porosity 4) for periods of between three weeks (no oxalate) and ten days. The filtrate was analysed by atomic absorption spectrophotometry (AAS) for magnesium and calcium. In the absence of oxalate, the molar ratio of Mg/Ca in the filtrate was 3.25, only slightly higher than a value of 3.0 expected for the parent mineral. This indicates that the huntite simply dissolved in weakly acidic solutions. The presence of oxalate (0.084 M) changed the molar ratio of Mg/Ca in the filtrate from 3.25 to 48.3 - this is clear evidence for selective solubilisation of magnesium i.e. calcium had been retained as a solid substance when the huntite dissolved. Plots of the pH of the filtrate versus the volume of hydrochloric acid showed inflection points which confirmed that the filtrate contained bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and oxalate ($\text{C}_2\text{O}_4^{2-}$) ions.

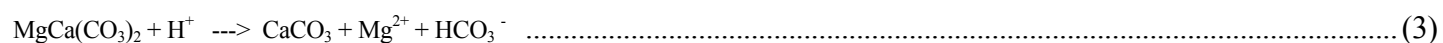
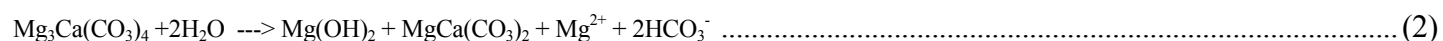
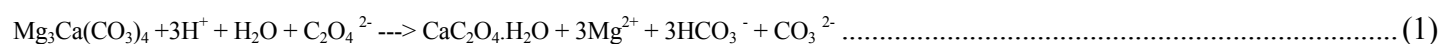
The solid matter from the reaction of huntite with oxalate ions was analysed by XRD in order to identify any reaction products. The additional phases are listed below in Table 2.

Table 2: Minerals identified in huntite conversion process

Mineral name	Chemical formula	JCPDS no.
Whewellite	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	20-231
Brucite syn.	$\text{Mg}(\text{OH})_2$	7-239
Vaterite syn.	CaCO_3	25-127
Dolomite	$\text{MgCa}(\text{CO}_3)_2$	11-78

The identification of materials such as dolomite indicates that the dissolution of huntite, in the presence of oxalate in a mildly acidic microenvironment, may go by a stepwise mechanism. Calcium carbonate, in the mineral form of vaterite, was found in association with the same hydrated calcium oxalate species as on the rock art sites. This is a very strong indicator that the whewellite and calcite, found on so many of the Kimberley sites, may have come from the interaction of the original huntite with the mildly acidic oxalate solutions. It should be noted that our reactions were carried out at $22 \pm 2^\circ\text{C}$ whereas the temperatures on the rock surfaces is often $32 \pm 10^\circ\text{C}$ and this may account for the relatively low abundance of dolomite in our samples of pigments. Measurements of the ratio of the stable carbon isotopes $^{13}\text{C}/^{12}\text{C}$ would be needed to determine whether or not the oxalate ions in the minerals originated from the microbial decay of organic materials or from precipitation. If the minerals have formed as a result of biological activity the isotope ratios will be very different to those found for inorganic origins, such as the result of lightning storms. A research program to measure the stable carbon isotopes in the whewellite samples from the rock art sites is progressing.

It is possible to write equations for the conversion of huntite into whewellite and a variety of other species. These equations formally describe the mineral changes that took place in our experiment.



Equation 1 refers to the conversion of huntite into whewellite, the second equation is for the conversion of huntite into brucite and dolomite, while the third is for the formation of vaterite. Since most of the magnesium reports to solution as the soluble bicarbonate species, it is not surprising that only calcium salts were found on the rock art samples that were analysed.

The fact that whewellite was only found either as the major or a minor component of a pigment layer - never in between - may simply be a reflection of the proximity of the pigments to sources of oxalate ions. It may also be due to the possibility that there are at least two routes for the conversion of huntite into "magnesium free" minerals. One route would involve acid dissolution in the absence of oxalate with subsequent interaction of the calcium ions with another source of oxalate and the other, dissolution in the presence of the oxalate ions. The alternative reaction schemes for the formation of whewellite are illustrated in figure 5.

In our discussion we are assuming that the dolomite is present as a result of the dissolution of huntite and not present as a pigment. Support for this assumption is gained from analysis of our huntite sample which was present at greater than 95% of the material in the sample analysed by XRD. If the image painters had used a similar source of huntite pigment then the dolomite had probably come from the thermodynamically favoured route for the dissolution of huntite to produce dolomite and magnesite (MgCO_3)¹⁶. The presence of the "intermediate" conversion mineral of dolomite in the pigments identified in Table 1 is good evidence that the conversion process is the most probable cause of this "partly leached" form of huntite being observed as a pigment on the rock art on sites in the Napier Range. It is possible that some of the calcite observed as a pigment may have been derived from dissolution of dolomite into calcite and magnesite or some other form of magnesium. The previously reported presence of dolomite and calcite as pigments in the Kakadu sites in the Northern Territory² may be a reflection of the original huntite pigments having been partially and totally converted into the calcium-rich forms by reacting with an acidic rainwater that is free of oxalate and sulphate.

It may be that our samples are naturally biased to reflect pigment conversion phenomena since the interactions of huntite with non-oxalate containing acidic solutions may have resulted in the loss of large areas of pigment. In

one particular motif, an apparently single paint layer was sampled in two places about a meter apart, with almost pure oxalate in one place and calcite in another. Assuming the same provenance and repainting sequence for these two samples, the reason may lie in the differences in the microenvironment on the site. The presence of drip-lines and other sources of biological feed stocks can have major differences in microbial and fungal activity. This is supported by our observation that the total bacterial counts on the same site can differ by more than two orders of magnitude¹⁴ within the distance of a few metres.

In the light of our experimental observations it is possible that some of the calcite that has been found as a "pigment" may have been derived from huntite as an end product from the acid dissolution of the original pigment in the absence of any oxalate ions. However this scheme is not necessarily in agreement with the data of Königsberger and Gamsjäger¹⁶ which reports the dissolution of huntite into the parent ions of Mg^{2+} , Ca^{2+} and CO_3^{2-} . It should be remembered that their laboratory conditions of 50°C and constant ionic strength are very different to the conditions experienced at the sites! Both magnesium and calcium form a range of oxalates and hydrated oxalates, but the calcium oxalate is almost fifty times less soluble than the corresponding magnesium entity¹⁵ which would explain why we only observe the hydrate calcium oxalate in the pigments.

Huntite has a very high surface area of 13.5 square metres per gram and has been shown to absorb multilayers of water after the initial monolayer has been adsorbed¹⁷. The adsorption of water by huntite increases markedly at relative humidities above 60% and so during the "wet season" the pigment will rapidly respond to water bearing acidic solutions of nitrate, sulphate and oxalate ions. These reactions would result in the formation of calcite, gypsum (calcium sulphate dihydrate) and whewellite. One possible source of sulphate in the rain water is via oxidation of H_2S which is a by-product of anaerobic degradation of plant materials. Due to the fact that magnesium sulphate is 575 times more soluble than calcium sulphate, it is not surprising that only the calcium mineral results from the acid dissolution of huntite in the presence of sulphate ions.

Wet season measurements on 1987 repainted areas showed already some areas of significant conversion of huntite into dolomite. This indicates that the conversion processes may be more rapid than had previously been imagined.

Field trials involving huntite under different microclimate conditions would provide useful information regarding the influences of microflora and local environment on the rates of the conversion processes.

The calcite and oxalate pigment films are difficult to differentiate under the light microscope, and this strong structural similarity, with inclusions of similar appearance could point to a common origin. The EDAX elemental analyses for the two groups of pigments are very similar within their individual variations, except that the whewellite samples have a consistently higher concentration of sulphur. The reason for the association of sulphur with whewellite is not known. Watchman⁴ has previously commented on the association of gypsum and whewellite in rock surface deposits. Whewellite occurs on rock surfaces as a brown or black deposit in the Northern Territory and in the West Kimberley, whereas the whewellite pigments in question range from white through yellow to black. This may be a reflection of the different levels of impurities incorporated during the mineralisation process. Differences in colour can also be due to the size and porosity of the minerals.

4.5 Stability of pigment layers

That some paintings have superimposed layers of different pigments, whether by application or alteration, has important ramifications for their stability. A recently repainted figure (1987) which is visibly undergoing rapid deterioration, is composed largely of a new layer of huntite applied directly to a previous version of the painting, the upper layer of which was identified as being composed of calcite in one part and whewellite in another. The new and old paint layers have very different structures, the older layer being porous and aggregated in appearance, as described for the calcite and whewellite pigments, whereas the new huntite layer is characteristically compact. Such changes in morphology are consistent with the proposed dissolution mechanisms outlined above.

Since huntite absorbs water very readily (see section 4-4), when the relative humidity is in excess of 60%¹⁴, it will undergo changes in volume as the successive layers of water are adsorbed. Not only will this affect the intra-plate bonding but the increased volume and the different response to stress and shear forces of the extensively hydrated pigment will cause the bonding to other layers and to the parent rock to change. This type of behaviour is different to the response of calcite and whewellite to variations in the relative humidity and temperature variations. It is

differences in the way the various minerals respond to humidity and temperature that often underlies the breakdown of the painted images. The part of the repainted motif, mentioned above, that was deteriorating most rapidly also received direct sunlight. This indicates that specific environmental factors contributed to the effect. Other motifs repainted at the same time which were also composed of huntite over calcite or whewellite, and which received less or no direct sunlight, have a less dramatic stability problem. The other areas showed significant "cupping" of the surface where the centre of a pigment flake remains flat and the edges lift up to form a cup-shaped semi-detached flake.

A further sample of the repainted site was taken during the 1992 wet season and the analysis of the pigment identified dolomite but no whewellite. This type of degradation is consistent with the reaction scheme outlined in equation 2, where the huntite has been subjected to acid dissolution from rain that contained no sulphate or oxalate.

Another panel painted on a nearby site showed that the huntite had completely converted into calcite, as outlined in equation 3, which is also probably due to a similar acid dissolution process since the sample contained no traces of whewellite or gypsum. Analysis of the paintings at an old site (no repainting in the past generation) some ten kilometres from the sites mentioned above, showed that all the accretions overlying areas of red and muddy yellow pigments were composed solely of whewellite and gypsum. Regardless of whether whewellite in pigment layers has occurred as a result of alteration processes involving local biological activity or atmospheric oxalates, the resulting changes appear to preserve the art in terms of the retention of the shape and style of the images. This depends on the relative effects of simple dehydration/rehydration cycles in unaltered huntite and the effects of the conversion processes on huntite. The overall effect of all these phenomena depends on whether the process itself disrupts or consolidates the pigment mass.

4.6 Dating

Many of the pigments contained charcoal, either alone or admixed with white minerals for the production of greys and blacks. They also occur as a result of contamination during pigment preparation and deposition from bush fires. There is considerable potential for the use of small-sample radiocarbon dating techniques such as accelerator mass spectroscopy (AMS) dating to determine their age. The factors of contamination, sample types and other

issues regarding the use of these samples to determine an apparent age have been documented^{18,19}. For the oxalate pigment layers that are a result of alteration processes, involving organic acids from biological sources metabolising only 'new' carbon, the potential exists for establishing an upper limit for their age. It should be remembered that in such work it is often difficult to obtain samples free of contamination. Readers wishing to investigate this aspect of the work should consult the relevant papers by Watchman^{4,20,21}. Specific approval of the traditional custodians would be needed before any of the samples of pigments were subjected to dating measurements.

Conclusions

The white pigments in rock art motifs in the study areas are composed of several different minerals, more than one of which may be represented at the same site and in different layers of the same motif. This indicates that it is wrong to assume that there is necessarily a traditional single source of pigment at all periods for particular sites or motifs. The presence of whewellite in pigment layers apparently comes from either reaction of oxalate ions with huntite or from interactions originating in oxalate ions in contact with the calcite substrate. The source of the oxalate is either from electrical storms and/or from the metabolites of bacteria, fungi and plants. Carbon isotope measurements on the whewellite samples collected in the two seasons are in hand. The mechanism should be clarified once the results of these measurements are known since the $^{13}\text{C}/^{12}\text{C}$ ratios are very sensitive to fractionation by microorganisms. The presence of dolomite in the paintings that were repainted with huntite in 1987, strongly supports the theory that whewellite has been produced in-situ.

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References

1. CLARKE, J. 'Two Aboriginal rock art pigments from Western Australia: their properties, use and durability' *Studies in Conservation*, **21** (1976) 134-142.

2. NORTH, N.A., and CLARKE, J. 'Conservation of post-estuarine period rock art in Kakadu National Park: pigment identification'. *Unpublished report*, Australian National Parks and Wildlife Service.(1988)
3. WATCHMAN, A. Pers communication 1990.
4. WATCHMAN, A. 'A summary of occurrences of oxalate-rich crusts in Australia' *Rock Art Research* 7(1) (1990) 44-50
5. JUST, J. Personal Communication, 1991.
6. WIEDMANN, H.G and BAYER, G. 'Formation of whewellite and weddellite by displacement reactions' *The oxalate films: origin and significance in the conservation of works of art*. Proceedings, Milano, 25-26 October, 1989, Centro Congressi Cariplo.127-131
7. QUELLMALZ, W. 'The calcium oxalate whewellite - mineralogy and natural occurrences' *The oxalate films: origin and significance in the conservation of works of art*. Proceedings, Milano 25-26 October 1989, Centro Congressi Cariplo. 103-110
8. PLAYFORD, P., Personal Communication, 1992
9. del MONTE, M and SABBIONI, C. 'Weddellite on limestone in the Venice environment' *Environmental Science and Technology* 17 (1983) 518-522
10. del MONTE, M and SABOTINI, C. 'A study of the patina called 'scialbatura' on Imperial Roman Marbles.' *Studies in Conservation* 32 (1987) 114-121
11. SAIZ-JIMENEZ, C. 'Biogenic vs anthropogenic oxalic acid in the environment' *The oxalate films: origin and significance in the conservation of works of art*. Proceedings, Milano 25-26 October, 1989, Centro Congressi Cariplo, 207-214
12. NOLLER, B.N., CURREY, N., AYERS, G., GILLETT, R., HARRISON, A., and RASMUSSEN, R.A. 'Chemistry of rain-water acidity, nutrient and heavy metal characteristics. Alligator Rivers Region Research Institute Annual Report Summary for 1985-1986 Australian Government Publishing Service, Canberra. 53-55
13. CLARKE, J. Personal communication (February 1991)
14. MACLEOD, I.D., HAYDOCK, P. & FORD, B., 'Conservation research into the preservation of rock paintings in the West Kimberley region of Western Australia' Report to the Western Australian Heritage Committee, 1991, pp 1-89.
15. Stability Constants of Metal-Ion Complexes Supplement 1. Part 1 Inorganic Ligands, Special Publication number 25., The Chemical Society, London 1971.
16. KÖNIGSBERGER, E & GAMSJÄGER, H., Solid-Solute Phase Equilibria in Aqueous Solution. I. Solubility Constant and Free Enthalpy of Formation of Huntite. *Ber. Bunsenges. Phys. Chem.* 91, 1987, 785-790.

17. MACLEOD, I.D., HAYDOCK, P & FORD, B "The water absorption properties of huntite and talc-the effects of surface areas and relative humidity on pigment stability".-in preparation
18. McDONALD, J. OFFICER, K., JULL, T., DONAHUE, D., HEAD, J., & FORD, B. 'Investigating ¹⁴C AMS: Dating prehistoric rock art in the Sydney Sandstone Basin, Australia' *Rock Art Research* **7**(2) (1990) 83-92.
19. RUSS, J. HYMAN, M., SHAEFER, H.J., ROWE, M.W. 'Radiocarbon dating of prehistoric rock paintings by selective oxidation of organic carbon'. *Nature* **348** (1990), 710-711
20. WATCHMAN, A.L. 'Preliminary determinations of the age and composition of mineral salts on rock art surfaces in the Kakadu National Park'. *Archaeometry: further Australasian studies*, (1987) 36-42 W.R. Ambrose and J.M. Mummery (Eds), Research School of Pacific Studies, Department of Prehistory, Australian National University.
21. FORD, B.L. and WATCHMAN, A.L. 'Art on the rocks' *New Scientist* **7** July, 1990. 33-37

FIGURE CAPTIONS.

Figure 1: Map of Western Australia's Kimberley region showing location of rock art sites in the Napier Range () & the Mitchell Plateau () regions.

Figure 2: Cross section of a typical rock shelter and the location of the images on the site, with approximate human scale.

Figure 3: An EDAX spectrum of a huntite pigment sample from a Napier range site showing the major peaks due to magnesium and calcium as well as typical impurities of Fe, Cl, Ti, S, Al and P.

Figure 4: A typical cross section of the pigment layers showing at least twelve repainting episodes. The width of the image is 1.5 mm.

Figure 5: Schematic diagram showing the routes for the transformation of huntite.