



KEYWORDS: *Pigment characterisation – Sydney Basin – SEM-EDXA – XRD – PIXIE/PIGE*

## CHARACTERISTICS OF A PIGMENT ART SEQUENCE: WORONORA PLATEAU, NEW SOUTH WALES

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**Abstract.** This paper presents the results and interpretations of a pilot study of pigment characterisations conducted between 2002 and 2006 on the rock art assemblage of the south Woronora Plateau located immediately west of Wollongong, New South Wales. Eighteen samples from ten sites are described. Analyses of the geochemistry, mineralogy and micro-morphology of samples was undertaken using a combination of scanning electron microscopy including energy dispersive x-ray analysis, x-ray diffraction, particle induced x-ray emission and particle induced gamma-ray emission techniques. With one exception the analyses show that composite clay-based paints were used to produce both iconic and non-iconic rock art on the Woronora Plateau and adjacent Mittagong Tablelands. We discuss differences in the processing of paints used for iconographic and stencil art, and consider the possible chronological and behavioural implications of paint chemistry and morphology. The results of the study, while indicative, provide an exciting example of the type of archaeometric work which can be undertaken successfully in the taphonomically complex Hawkesbury Sandstone rockshelters of the Sydney Basin.

### Introduction

Archaeological investigations of raw materials in the Sydney region have concentrated on lithics despite the surface finds of ochre with 'use wear' and ochre specimens from stratified archaeological deposits (Attenbrow 2002: 122–3). The impetus for the pilot study presented here was to examine the potential of redressing this imbalance through an investigation designed to test the viability of pigment characterisations and the potential of pigment provenancing studies in the rock art of the Sydney Basin. The term 'provenance' is used here to define the systematic observation of the chemical composition of an artefact (usually at the resolution of trace element content in parts per million) and that characteristic composition's relationship to the chemical composition of the raw material(s) from which it has been manufactured. This may be distinct from the 'provenience' (find spot) — though the two may not be mutually exclusive (Pollard et al. 2007).

The importance of characterisation investigations as a means for acquiring knowledge about inter-group contact, past trade routes and exchange systems has been demonstrated by a number of Australasian studies conducted on a variety of diverse materials such as lithics — particularly stone axes and obsidian, pearl shell, pituri and pigments (McCarthy

1961a; Akerman and Stanton 1994; McBryde 1987; Mulvaney 1976; Mulvaney and Kamminga 1999; Binns and McBryde 1972; Ambrose 1975; Torrence and Swadling 2008; Phillips and Speakman 2009; Smith et al. 1998; Lemonnier 1993; Summerhayes et al. 1998). Figure 1 shows the location of previous pigment characterisation studies conducted in Australia. These studies have been conducted with several motivations, including:

- The provenancing of specimens from stratified archaeological deposits (Smith and Fankhauser 2009; O'Connor and Fankhauser 2001; Smith et al. 1998), ethnographically known pigment sources (Haydock 1989; Smith et al. 2002; Mawk et al. 1996; Ridges 1998; David et al. 1993; Crawford and Clarke 1976) and rock art (Goodall and David 2001; Goodall et al. 1996; Goodall and David 1998; Thomas 1998; Grave et al. 1999; Clarke and North 1991a; Watchman et al. 1993a).
- To authenticate Aboriginal rock art and to investigate the Aboriginal use of European materials (Sale and Watchman 1993; McConnell 1987; Sale and Baker 1991; Cole and Watchman 1993).
- To investigate instances of retouch/repainting (McDonald et al. 1991; Thomas 1998).
- To inform conservation practices and site management (Clarke 1976; Sale 1989; Clarke and North



Figure 1. Bibliographic references and locations of previous pigment characterisation studies conducted in Australia.

1991b; Watchman 1997c; Walston and Dolanski 1976; Hogue 1990; Ford et al. 1994; Charton et al. 1992; Cook et al. 1990; Clarke and North 1989).

- To investigate the potential of direct dating (McDonald et al. 1990; McDonald 1991; McDonald and Veth 2008; Cole and Watchman 1992; Watchman 1997a; Watchman 1997b; Watchman 1997c; Watchman and Cole 1993; Watchman et al. 1997).
- To inform palaeoenvironmental reconstructions which have in turn been used as a proxy for dating (Goodall et al. 2009; Campbell and Mardaga-Campbell 1993; Mardaga-Campbell et al. 2001; Watchman et al. 2000).

- The microscopic and spectrographic analysis of rock art and mineral accretions/coatings has revealed the application of pigment where no visible evidence was extant (Ward et al. 2001; Watchman et al. 2001; Watchman et al. 2000; Campbell and Mardaga-Campbell 1993; Mardaga-Campbell et al. 2001; Ford 2006).

The study area for the pilot pigment investigation presented here is located on the southern half of the Woronora Plateau (refer to Fig. 2) east of the Cumberland Plain and north-east of the Moss Vale Tableland (Hazelton and Tille 1990). The Illawarra Escarpment marks the eastern barrier of the Plateau and drops steeply to the Wollongong Plain below. The 76 822 hectares study area, known as the 'Metropolitan Special Area', is jointly managed by the Sydney Catchment Authority and NSW Department of Environment, Climate Change and Water. The Metropolitan Special Area is a remnant ecosystem of mostly unmodified terrain under predominantly indigenous vegetation,

which has been preserved to a large extent through its incorporation into the water catchment for the large metropolitan population of Sydney from the late nineteenth century (Nanson and Young 1983). It includes the upper catchment of the Nepean River, the Avon, Nepean, Cataract and Cordeaux Dams (shown in Fig. 2) and contains 663 archaeological sites registered on the NSW Department of Environment, Climate Change and Water's Aboriginal Heritage Information Management System. In addition to pigment samples from the Woronora Plateau, two extra-local pigment specimens were included in the study from a site located on the adjacent Moss Vale Tableland (refer to Fig. 2).

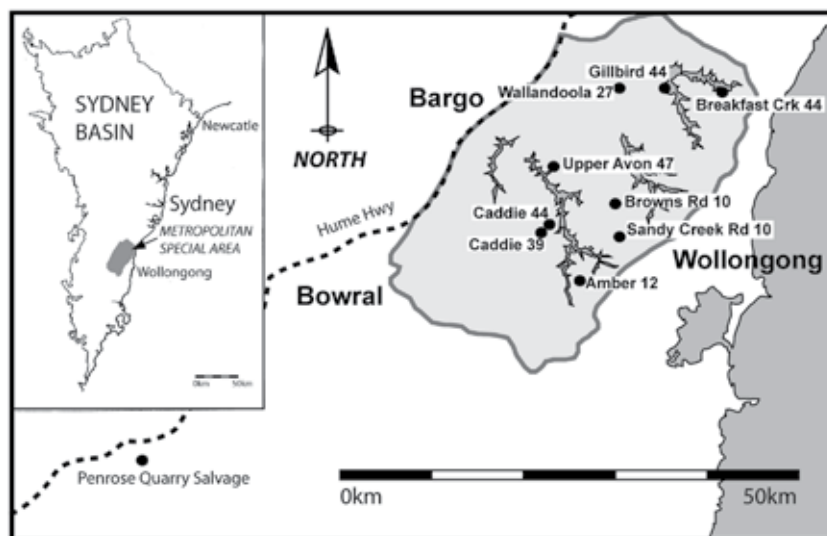


Figure 2. Location of the study area showing sites from which pigments were harvested. Note the Sydney catchment dams within the study area (from left to right the Nepean, Avon, Cordeaux and Cataract).

Fig. 2).

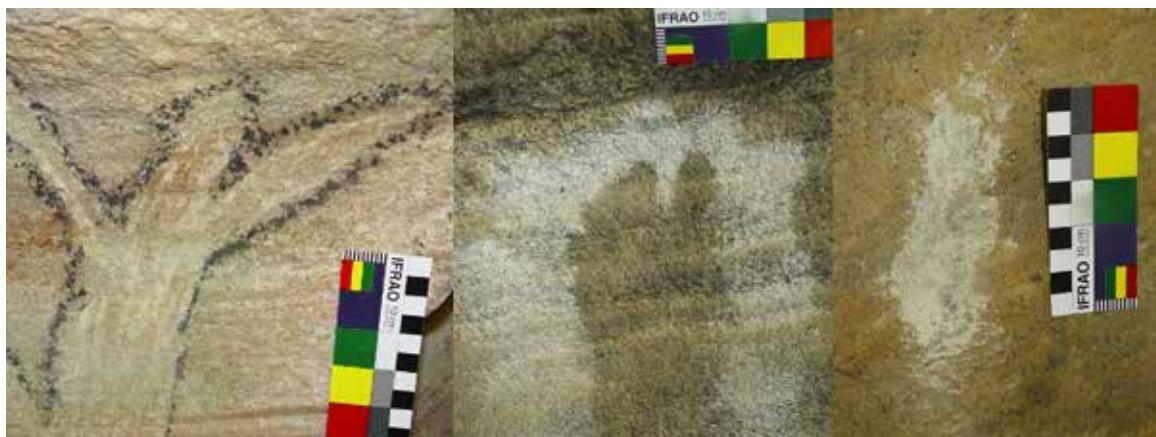
The dominant geology of the Woronora Plateau is Hawkesbury Sandstone, a middle Triassic even-sized, medium grained, quartzose sandstone with thin, spatially constricted shale lenses, which is composed almost entirely of quartz grains bonded by carbonate and clay-rich cement making the sandstone very susceptible to weathering processes (Hazelton and Tille 1990; Twidale and Campbell 1993; Twidale 1968; Vinnicombe 1980). It was observed by McDonald that the geological homogeneity of the Hawkesbury Sandstone country is significant because it provides a consistent canvas for the production of rock art (McDonald 2008). While it is true that Hawkesbury Sandstone geology provides a relatively consistent

Sample identification	Sample colour	Initial weight (mg)	Motif type	SEM-EDXA results	XRD results	PIXE/PIGE results
A121	White	62	Graphic (zoomorph)	Si, Al (K)	Not analysed by XRD	Not analysed by PIXE/PIGE
BC451	Black	67.4	Stencil (hand)	C, Si, Al (K, C, Mn)	Not analysed by XRD	V, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Pb
BR292	Yellow (black)	55	Graphic (anthropomorph)	Si, Al, S (S, K, Cl)	Quartz, muscovite, (Kaolinite)	V, Cr, Co, Cu, Zn, Ga, Se, Br, Rb, Sr, Zr, Pb
BR295	White (black)	52.6	Graphic (anthropomorph)	Al, Si, (Cl, S, K, Ti, V, Cl, Ga)	Quartz, kaolinite, (muscovite)	Not analysed by PIXE/PIGE
C391	White	71	Stencil (foot)	Si, Al (K, C)	Not analysed by XRD	V, Cr, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Pb
C392	White	88.1	Amorphous application of paint	Si, Al (K, C, S)	Quartz, kaolinite, (Muscovite)	Not analysed by PIXE/PIGE
C393	White	69.5	Stencil (hand)	Si, Al (K)	Quartz, muscovite, (kaolinite)	V, Cr, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Pb
C442	White	70.2	Stencil (hand)	Si, Al (K, S, C)	Quartz, kaolinite	Cr, Ni, Cu, Zn, Ga, R, Sr, Zr
C443	White	79.4	Amorphous application of paint	Si, Al (P, Ti, C)	Quartz, kaolinite	Cr, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Pb
G441	White	79	Graphic (zoomorph)	Si, Al (K, S)	Quartz, muscovite	V, Ni, Cu, Zn, Ga, Ge, As, Br, Rb, Sr, Y, Zr, Pb
PQ1	Red	Na	Graphic (anthropomorph)	Not analysed by SEM	Quartz, kaolinite, haematite	Not analysed by PIXE/PIGE
PQ2	Black	Na	Graphic (residual pigment – form unknown)	C (Si, Al, Ti, Fe)	Not analysed by XRD	Not analysed by PIXE/PIGE
SCR101	White	65.9	Graphic (anthropomorph)	Si, Al (C, Ga)	Not analysed by XRD	Not analysed by PIXE/PIGE
SCR102	White	64.8	Amorphous application of paint	C (Si, Ai)	Quartz, kaolinite	Not analysed by PIXE/PIGE
SCR103	Red	70.5	Graphic (anthropomorph)	Si, Al, Fe (K, C, S)	Quartz, muscovite, haematite	V, Cr, Cu, Zn, Ga, Ge, Se, Br, Sr, Zr, Pb
SCR104	Black (white)	64.8	Graphic (anthropomorph)	C, Si, Al (S, C)	Analysis produced only noise due to small sample size	Not analysed by PIXE/PIGE
UA471	Orange	111.6	Graphic (zoomorph)	C, Si, Al (K, Fe)	Quartz, kaolinite, (muscovite, haematite)	V, Zn, Ga, Ge, Br, Rb, Sr, Y, Zr, Pb
W271	White	63.8	Stencil (hand)	Si, Al (K, C)	Quartz, kaolinite	Not analysed by PIXE/PIGE

**Table 1.** Description of samples and summary of results. Note elements and minerals which are bracketed are moderate to minor components. The colours which are bracketed are the second, unsampled pigments present in bichrome motifs.

environmental context for the archaeology of the Woronora, the chemical and physical weathering processes which have created and continue to shape the shelters included in this study represent complex taphonomic histories. A keen understanding and recognition of the taphonomic processes present within each of the rock art panels sampled has provided the fundamental context for sample selection, sample harvesting and interpretation of the analyses undertaken in this study.

It has been argued by Smith and Fankhauser (2009) that unlike grindstones and stone axes, ochres and clays have an advantage as the subject of characterisation and sourcing studies because they are frequently found in stratified and potentially dateable contexts (they refer specifically to archaeological deposits). The pigments included in this study (refer to Table 1) have been relatively temporally constrained within the Upper Nepean rock art sequence described by Dibden (2003a, 2003b and 2003c) and the broader Sydney Basin art



**Figure 3.** Sample locations SCR104 (graphic motif), C391 (stencil) and C392 (amorphous pigment application/smear).

sequence described by McDonald (2008). Samples A121, BC451, BR292, BR295, C391, C392, C393, C442, C443, G441, SCR101, SCR102, SCR104, W271 and UA471 from the Woronora Plateau (refer to Fig. 1) correspond to the third phase of Dibden's proposed sequence and are hypothesised as being a maximum of 1600 years or in age, but may be as recent as the period of contact between Europeans and the indigenous population of the area. PQ2 from the Mittagong Tablelands corresponds to the third phase of McDonald's proposed sequence and is similarly hypothesised to be a maximum of 1600 years in age, but may have been produced as recently as the contact period. Finally, SCR103 and PQ1 correspond to the second phase of Dibden and McDonald's relative sequences respectively and are hypothesised as being produced between 4000 and 1600 years ago.

### Sampling

A total of 16 samples from nine sites on the Woronora Plateau, and two samples from a site on the adjacent Moss Vale Tableland were analysed as part of this pilot study. Samples from rock art included iconographic motifs, stencils and amorphous pigment smears (details of samples are summarised in Table 1). The term amorphous smear is used to describe heterogeneously shaped, non-iconic pigment applications, which appear to have been sprayed onto the rock matrix via the mouth of the artist, but are not stencils (refer to Fig. 3). Amorphous smears do, however, conform to a category of rock markings described by Rosenfeld (1999) as gestural marks and include stencils and other types of non-iconic marks (Dibden 2003a, 2003b, 2003c).

The sampling strategy employed for the Woronora Plateau was totally opportunistic. Due to time constraints, site locations were preferentially selected for their relative ease of access. Decisions about the conditions under which samples would be harvested were not only made in light of the archaeological questions being asked of the art, but as part of serious ethical considerations. The responsibility of essentially destroying in part the motifs, stencils and

amorphous smears selected for research was not taken lightly (Bednarik 1992; Clottes 1992; Watchman 1992). The rock art selected for the study was judged to have enough extant surface pigment to support samples being harvested without adverse visual impact to the motifs. Samples were harvested from throughout locations selected with the aim that there would be no visual impact. Detailed photographs were taken before and after samples were harvested (refer to Fig. 4). Paint was removed using dental probes with samples scraped directly into 25 ml Eppendorf tubes (each tube containing the cumulative sample from throughout each sample location). In order to assist with the interpretation of analyses detailed field observations of the taphonomic conditions present at each site and sample location were recorded during field reconnaissance and sample collection.

The two extra-local samples analysed were prepared in the laboratory from small sections of rock matrix which had been removed from a shelter on the Moss Vale Tablelands. No detailed photographic record or weights were recorded for these samples as they had already been removed from the rockshelter and there was no restriction to the impact of sampling.

### Analysis

Scanning electron microscopy, including energy dispersive x-ray analysis (SEM, SEM-EDAX), x-ray diffraction (XRD) and particle induced x-ray emission/particle induced gamma-ray emission (PIXE/PIGE) analyses were used to characterise the pigments sampled. A desire to examine micro-morphological features limited the application of multiple analytic techniques to some samples; however, SEM-EDAX, XRD and PIXE/PIGE were able to be applied successfully to samples as small as 55 milligrams in initial weight (for example BR292).

SEM was undertaken using a JEOL JSM6400 (SEM 1990) fitted with an Oxford ISIS EDXA. All samples were impregnated in epoxy-resin. For the sample PQ2 which was still bonded to the rock matrix air was subsequently evacuated from the resin; however,



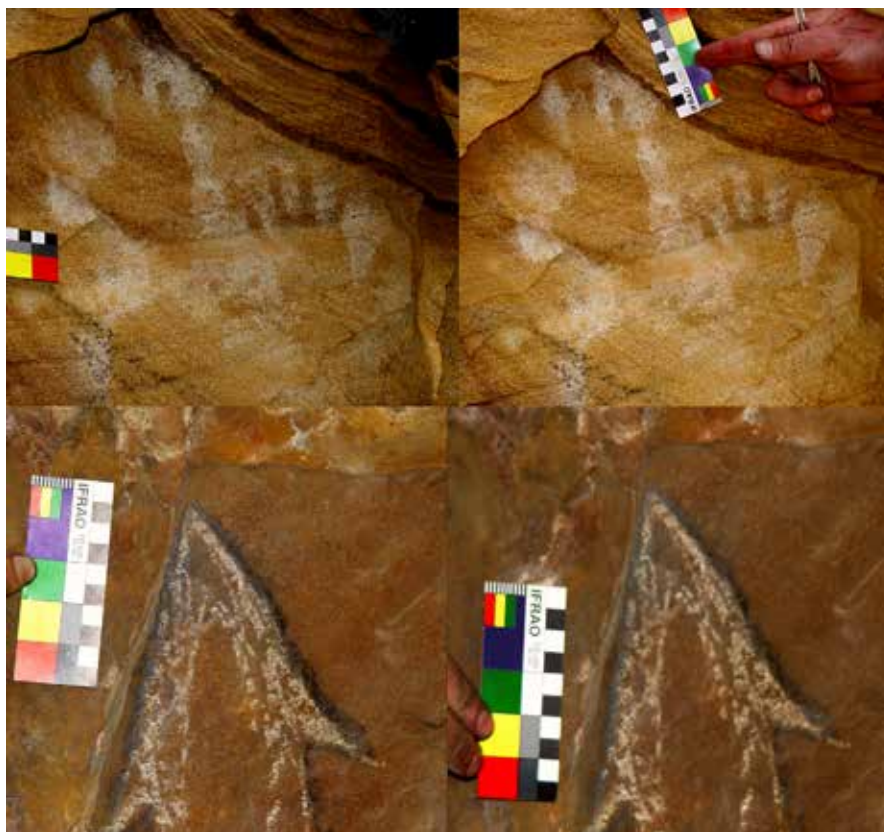
air was not removed from the remaining specimens as this would risk lifting the powder pigment from the surface of the disks making it very difficult to expose the samples. The resin disks were air dried, polished using diamond paste to expose the sample and then carbon coated.

XRD analyses were conducted using two diffractometers, a SIEMENS D5005 Bragg-Brentano and a SIEMENS D501 Bragg-Brentano. Both were equipped with a graphite monochromator and scintillation detector, using CoK radiation. The scan range for the SIEMENS D5005 was 4 to 80° 2-theta, at a step width of 0.02°, and a scan speed of 2 seconds per step. The SIEMENS D501 scan range was 2 to 70° 2-theta, at a step width of 0.02°, and a scan speed of 1° per minute. The results of both diffractometers were interpreted using the SIEMENS software package *Diffracplus Eva* (2000). Samples were ground in an agate mortar and pestle, suspended in acetone and transferred by a pipette to a quartz single-crystal low-background holder for analysis.

PIXE/PIGE was selected for trace element analysis at the behest of the Aboriginal stakeholders who expressed wishes during consultation for the study that any samples taken were retained for future analysis. The pigment samples prepared for PIXE/PIGE were manually mixed with pure graphite ('F'-rated carbon powder) and pressed into 5 mm diameter pellets with a hydraulic press using pressures above 2500 psi. This sample preparation was chosen as some of the small sample sizes were problematic for more conventional preparations such as a filter paper. The same preparation method was used for all samples for consistency and to ensure the results were comparable and replicable. While this sample preparation has altered the state of the pigment, the pellets have been retained and can be made available for future analyses if required. PIXE/PIGE analyses were run simultaneously using the iron beam facilities at Australian Nuclear Science and Technology Organisation.

## Results

Observation of samples macroscopically in the field and microscopically under SEM indicated that, with the exception of PQ2, all the pigments analysed in this study are paints — composite mixtures of minerals



**Figure 4.** Sample location W271 prior to (top left) and after (top right) sample harvesting. Sample location A121 prior to (bottom left) and after (bottom right) sample harvesting.

applied as liquid (wet) to the rock matrix (Maynard 1977). The results of SEM-EDXA and XRD analyses showed that all the paints analysed are clay based. For the purposes of this study, the term clay is used to group layered silicate minerals or other minerals which impart plasticity and which harden upon drying or firing. This includes micas, which are aluminium silicate minerals whose sheet structure is flexible and plastic when hydrated. The major mineralogical distinction found by XRD was between paint samples (i.e. all samples excluding PQ2) with either dominant kaolinite (clay) or muscovite (mica) patterns. The majority (73%) of the 11 samples examined by XRD were dominated by kaolinite with the remaining samples dominantly muscovite and 45% of samples contained both minerals. Clay mineralogy was confirmed by SEM-EDXA which returned spectra typical of clay in all samples analysed (major Si, Al and minor K elemental peaks), with the exception of PQ2.

Orange, red, yellow and black paints are composite paints, shown by SEM-EDAX and XRD analysis to be mixtures of colorants dispersed within a clay base. Orange sample UA471 and red samples PQ2 and SCR103 have haematite mineralogy in addition to clay (confirmed by major Fe peaks in SCR103 and moderate Fe peaks in UA471 under SEM-EDXA). Yellow paint BR292's mineralogy was specifically analysed against haematite and goethite patterns to test the assumption

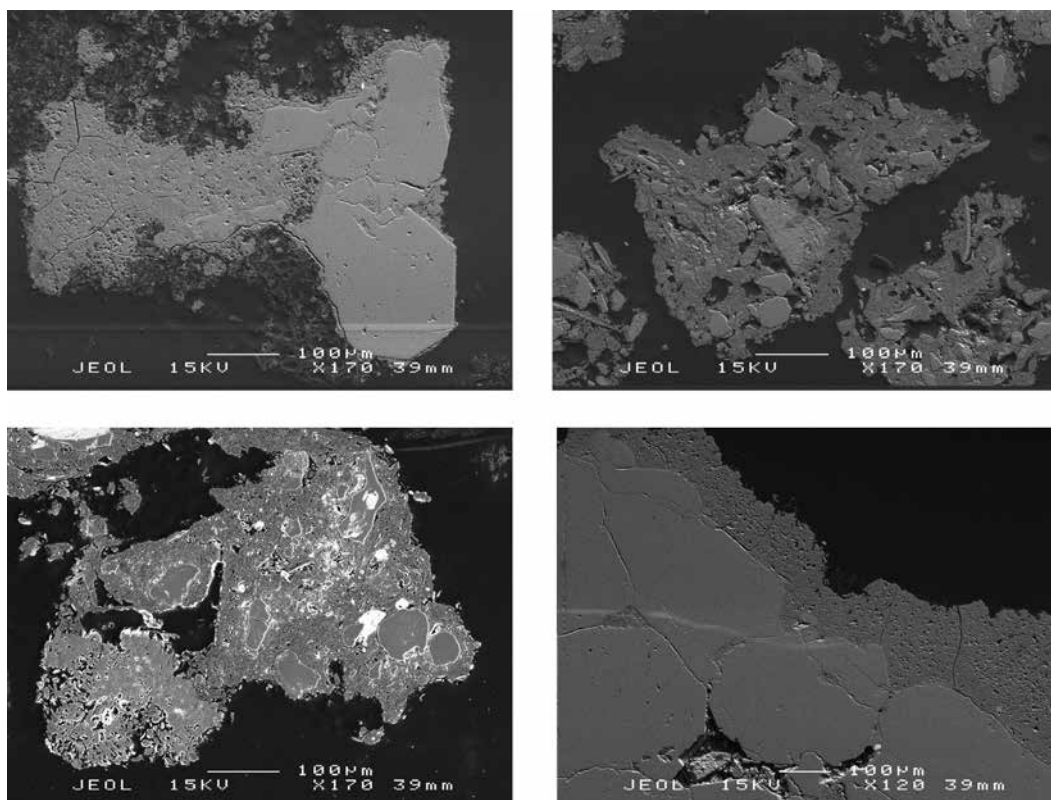


Figure 5. SCR104 graphic paint (secondary electron image top left), W271 stencil paint (secondary electron image top right), C443 amorphous paint application (back scattered electron image bottom left) and PQ2 profile of sandstone matrix (secondary electron image bottom right). Note scale is 100  $\mu\text{m}$ .

that iron-oxide was responsible for the yellow colour. Neither iron-oxide pattern matched BR292's XRD spectrum and only clay minerals were identified. Major and minor S and moderate Cl peaks were observed under SEM-EDXA in BR292 indicating a possible sulphate mineral. Black paints BC451 and SCR104 are C rich with major, moderate and minor peaks observed under SEM-EDXA in addition to elements characteristic

of clays and probably contain pulverised charcoal.

In addition to variability in mineral composition, a morphological distinction between paints used to produce iconographic and 'gestural marks' (stencils and amorphous smears) was found during SEM analysis. The clays of iconographic paints are more tightly compressed while the paint from stencils and amorphous smears tends to have more dispersed constituents. Differences are also evident between the quartz grains of the iconographic and stencil/amorphous smears. The size of the quartz grains in iconographic paints is generally larger than those in stencils/amorphous smears and the smaller quartz grains of the latter are more angular and more dispersed within the paints (refer to Fig. 5). The smaller quartz grains are distributed throughout stencil and smear paints while the larger quartz grains of iconographic motif pigments are most often found at the outer edge of clay constituents.

Elevated carbon (C) peaks were found in samples SCR102, SCR103, UA471 and PQ2 under SEM-EDXA. An investigation of the micromorphology of SCR102 revealed one discernible charcoal grain that was identified against known reference collections as a hardwood, species *Eucalyptus* (Dadswell 1972) (Fig. 6). No micromorphological features such

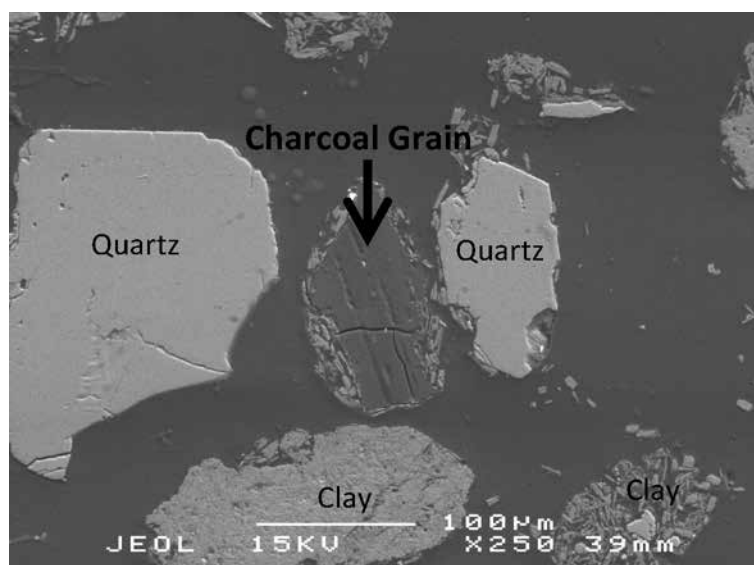


Figure 6. Secondary electron image of charcoal grain, SCR102.

as charcoal grains were observed in SCR103 or UA471. Consistent moderate and minor C peaks are present in SCR103 and major as well as moderate and minor C are present in UA471. Carbon was the major component of PQ2. Spectra typical of clay, observed for all other pigments analysed are absent from EDAX analysis of PQ2. Some minor K was observed in the rock matrix to which PQ2 is adhered; however, none was observed in the black pigment itself. Moderate and minor Al, Si and Ti as well as minor Fe peaks were noted in PQ2 under SEM-EDXA.

Consistent C peaks were observed in all of the paints derived from stencils and amorphous smears from the Woronora Plateau. Excluding the black paint from stencil BC451, major, moderate and minor C are consistently observed in white stencil and smear paints C391, C392, C393, SCR102 and W271. C peaks are present in stencil and smear paints C442 and C443; however, these are minor concentrations.

Three of the pellets analysed at ANSTO via PIXE/PIGE (samples SCR101, SCR 102 and W271) did not achieve a homogeneous mixture and resulted in measurements which described carbon powder. The remaining nine pellets resulted in trace element concentration (parts per million) measurement of 16 elements from V through to Pb (refer to Table 1). Basic multivariate statistical analysis of PIXE/PIGE data (corrected for minimum detection limits and error terms) showed a lot of variability in the trace element concentrations, though grouping of geochemical data is visible in relation to C442 and C443 (refer to Fig. 7).

### Discussion and interpretation

As the results outlined above show all of the paints analysed (i.e. all pigments analysed excluding PQ2) are clay based, including orange, red, yellow

and black. The colour of orange and red samples is derived from iron-oxide (haematite); however, this is not the case for yellow paint (BR292). The major S peak consistently noted in BR292 under SEM-EDAX suggests that a S-rich substance dispersed into a clay base has been used to create the yellow paint. Decomposed Hawkesbury Sandstone matrix weathering via chemical processes in situ in the rockshelters from which samples were harvested could have been utilised as a source of yellow colorant and would be consistent with the major S and moderate Cl peaks observed in BR292.

The consistent C present in black paints BC451 and SCR104 and black pigment PQ2 indicates that a carbon bearing substance, likely charcoal, is responsible for the black colour. While Mn was observed as a minor component of BC451 this was isolated to a few spot analyses and is not present in sufficient quantity to account for the black colour of the sample. As stated above, the spectra typical of clay observed for all paints analysed are absent from EDAX analysis of PQ2. The moderate and minor Al, Si and Ti as well as minor Fe peaks noted in the sample are more typical of the rock matrix analyses and differ from the consistent Al, Si and K peaks observed in paints. While some minor K was observed in the rock matrix to which PQ2 is adhered, none was observed in the black pigment itself. The significant difference in element concentrations between PQ2 and the black paints analysed (SCR104 and BC451) as well as the absence of spectra typical of clays indicate that this sample is not a composite paint and may be derived of nothing more than charcoal mixed with water (Clarke and North 1991a), or dry charcoal pigment applied to the sandstone matrix.

Major C was also observed in orange sample UA471. As no carbonate minerals (such as siderite) were

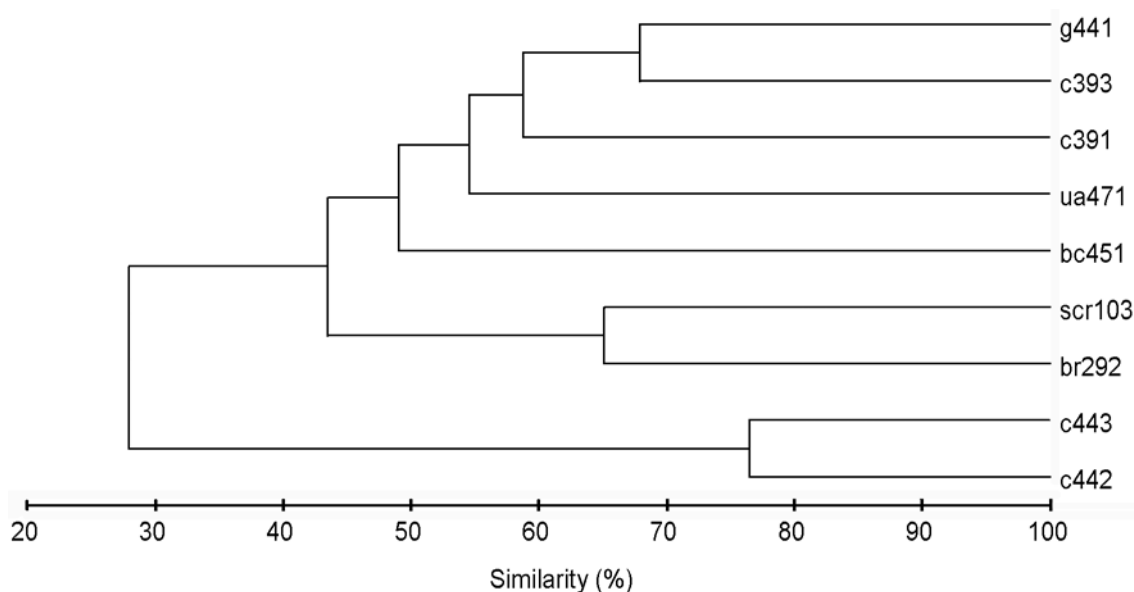


Figure 7. Cluster analysis of trace element composition of the nine samples analysed by PIXE/PIGE.

observed under XRD this C fraction is interpreted as being derived from ubiquitous spider webs observed throughout the zoomorphic motif when it was sampled (Ford 2006). The carbon identified in red sample SCR103 is likely to be contamination from black pigment which once overlay the red rather than being attributable to an organic compound used in the paint recipe. The superimposition sequence of the art panel from which SCR103 was harvested suggests that while no macroscopic evidence of superimposition was observed during sample collection, it is probable that there was once a less stable black pigment on top of the sample location. This hypothesis is strengthened by a previous recording made by McCarthy (1961) which shows he observed more consistent black pigment infill in the zoomorphic motif superimposed over the location from which SCR103 was subsequently harvested. The *Eucalyptus* charcoal grain found in white paint SC102 does not account for the consistent presence of carbon throughout the spot analyses conducted. As stated in the results above, carbon was consistently found in all of the paint samples from stencils and amorphous smears.

The micromorphological distinction on the Woronora Plateau observed between paints from iconographic motifs and stencil/amorphous smears is consistent with the findings of Cole and Watchman (1996) in their study of pigments from white stencils in the Laura region of Cape York, far north Queensland. Cole and Watchman found that the quartz grains from stencil paints were smaller than those of iconographic motif paints, though the particle size of pigment was approximately the same. They interpret this morphological distinction as representing the possibility that stencil paints are more highly processed than iconographic paints in the Laura region, and/or that the mica pigment of stencils was especially selected from source location(s) due to its particulate fineness (Cole and Watchman 1996).

While it is possible that discrete procurement locations were targeted for their particulate fineness in relation to the production of stencils (including amorphous smears) on the Woronora Plateau, the morphology and chemistry of these paints seems to suggest complementary evidence of pigment processing and application. The presence of major, moderate and minor C peaks in C391, C392, C393, SCR102 and W271 and minor carbon peaks in C442 and C443 may be the result of pigment processing and application as these paints would have been sprayed onto the rock via the mouth of the artist(s), carbon representing the residual chemical signature of the saliva used to bind the paint. This interpretation is further supported by the micromorphological distinction of quartz grains from iconographic and stencil/smear paints observed under SEM (again refer to Fig. 5). The smaller, more angular and more dispersed quartz grains observed in stencil and smear paints indicates that they were more highly processed than the paints used to create iconographic motifs. As with the consistent presence of carbon, the

differential quartz grain morphology observed under SEM may be similarly explained by further processing of the paint in the mouth of the artist — for instance if the clays were chewed prior to being applied to the rock matrix.

It is interesting to note that the stencil C442 and amorphous smear C443, which have consistent minor carbon peaks, are the only samples taken from a discrete site known as Caddies 44. The quartz grains in C442 and C443 are consistent with the smaller, more angular and more dispersed morphology outlined. The absence of major and moderate C concentrations could reflect the fact that the original C fraction in these samples was not as large as in stencil and smear paints derived from other site locations, for example if the C442 and C443 paint was extended with water prior to being applied to the rock matrix. Or it may be that difference in C fractions between sites represents a temporal distinction, with the stencilling occurring at the sites at different times — the relative dearth of carbon at Caddie 44 possibly indicating that the stencils are older than those at other sites. Assuming that the consistent presence of carbon within the paints derived from stencil and amorphous smears on the Woronora Plateau is due to saliva, this indicates that these paints are quite recent and probably a maximum of a few hundred years in age as the fragile carbon signature created by saliva is unlikely to survive any longer. This is supported by the observations of other researchers that the lack of organic binders in the majority of pigment samples from rock art contexts is due to the fragility of organic specimens (Clarke and North 1991a, 1991b).

While no quantitative analyses were conducted, the SEM spot analysis (EDXA) of C391, C392, C393, SCR102 and W271 indicates that these paints may contain enough C to generate AMS <sup>14</sup>C targets. However the EDAX analyses also demonstrated significant variations of carbon concentrations within discrete sample locations (motifs) with major, moderate and minor carbon peaks observed. In essence, the problems experienced by previous researchers in directly dating Sydney Basin rock art (McDonald 1991) could easily be replicated if careful consideration is not given to the composition of pigments. The results of this study have demonstrated that rock art of the Woronora Plateau and adjacent Moss Vale Tablelands is subject to the complexities posed by dealing with processed pigments — in this case composite paints — which are likely to have altered chemical compositions due to their location in actively weathering geological environments (Smith and Fankhauser 2009, 1996). As further testing of the chronological sequences of the Woronora Plateau and Sydney Basin rock art assemblages is desirable, future chronometric research should focus on samples whose microstratigraphic, compositional and taphonomic contexts are well understood (Watchman 1990, 1997d). If dateable targets are generated directly from painted motifs, it is recommended, based on the results of the paint characterisations presented here, that multiple



discrete locations are tested from throughout a single painted event in order that several age estimates can be compared to ensure the chronological information obtained is reliable.

It has been a common convention of many archaeological accounts of contact between indigenous populations and colonisers, including rock art studies, to focus on the identification of motifs and materials of non-Indigenous appearance or origin (Frederick 1999; McConnell 1987; Cole and Watchman 1993). In Australia archaeological descriptions of contact have largely concentrated on the presence or absence of European materials (McNiven and Russell 2002; Wolski 2000). The geochemical signatures of European paints generally contain Pb, Ba and Co (Sale and Watchman 1993; Sale and Baker 1991). No evidence of 'European' materials was observed in any of the paints analysed in this study. While the carbon content of white stencil and smear paints from the Woronora Plateau suggests a maximum antiquity of hundreds of years for these motifs, no direct evidence of 'contact' between Aboriginal people and Europeans was found in the paint characterisations.

There was no observed discrepancy between the paint recipes used to produce rock art in the second and third phases of the Woronora or Sydney Basin art sequences described by Dibden and McDonald. Paints sampled from the second phase of the Woronora and Sydney Basin art sequences displayed the same mineralogical and geochemical characteristics as those samples derived from the third and final phase of both relative sequences. Nor was there any discrepancy between characteristics of paints used to create rock art on the Woronora Plateau or adjacent Moss Vale Tablelands observed in the study. While the very small sample size of paints characterised is acknowledged as a limitation to the robustness of this conclusion, based on the results of this study motifs from both phases of the relative rock art sequences located in both the local and extra-local area were found to be almost exclusively composite clay-based pigments with colouring agents dispersed throughout the clay base to create red, yellow, orange and black paints.

The lack of difference observed between the paint recipes used by Aboriginal people on the Woronora Plateau and adjacent Moss Vale Tableland through time could be significant regarding the context of rock art production. Changes in the sources of pigments used by people to create rock art have been inferred as reflecting changes in territoriality, for instance if colonial forces affected access to resources (Frederick 1999). This may be reflected in the geochemical and mineralogical signatures of paints used to create rock art, should access to pigment sources or discrete procurement locations become unavailable. Changes in paint recipes may also reflect changes in cultural convention, as choices regarding every aspect of rock art production, from pigment procurement to paint preparation, placement, application, and motif form

are culturally mediated choices.

It is recognised that the small batch size and wholly opportunistic sampling strategy employed for this study have resulted in a non-random sample which is neither statistically significant, nor robust. Statistical analyses were therefore undertaken in order to provide indices that the provenance (source of the paints) and/or discrete source locations (provenience) were visible in the trace element proportions and to explore the possible relationship between trace element proportions and rock art categories such as motif (stencil, iconographic, smear) and colour. As previously stated basic multivariate analysis of PIXE/PIGE data showed a lot of variability in the trace element concentrations, though some grouping of geochemical data is visible in relation to C442 and C443 (refer to Fig. 7). The grouping of samples C442 and C443 indicates that a discrete source location (find spot or provenience) may be geochemically visible. No correlation between the categories motif and/or colour were observed in the results for the statistical analyses undertaken. This may indicate that clays from specific procurement locations were used to produce both stencil/smear and iconographic motifs, again supporting the interpretation that the differences in quartz grain morphology between iconographic and stencil/smear paints represents differential processing rather than provenience.

Records from the Minerals Council of NSW showed that kaolinite clays, referred to in most historic records as fireclays, were commercially exploited in the Illawarra as early as 1940s with stoneware pipes, tiles and bricks manufactured from the local shale beds associated with the coal measures (Coleman 1961; Jones 1946; Mullholland 1945). The XRD and SEM analyses of this study are consistent with the mineralogical and chemical characterisations of commercially exploited clays and potential clay resources of the Illawarra region investigated as part of mineral exploration and extraction in the 1960s and 1970s (Burg 1963; Coleman 1961; Langley 1974; Slansky 1973). Both show a lot of variability within the results obtained. This indicates that the clay paints of the Woronora rock art were likely sourced locally from the shales of the Wianamatta group and Camden sub-group shales of the Illawarra Coal Measures which would be expected to exhibit within-source geochemical and mineralogical variability (Burg 1963; Coleman 1961; Langley 1974; Slansky 1973). While it was not possible in the scope of this study to test local clay sources against the paint characterisations obtained, records of potential and commercial clay extraction locations held by the Minerals Council of NSW represent exciting possibilities for future research.

## Conclusion

This pilot pigment investigation has demonstrated that successful pigment characterisation studies are possible within the taphonomically complex

rockshelters of the Sydney Basin. Furthermore, that a variety of information relating to pigment sources, pigment application, chronology and taphonomy are gained through these types of archaeometric investigations of rock art.

The results of this study have revealed that with one possible exception the samples analysed are paints, liquid pigments applied wet to the rock matrix. The possible exception to this is PQ2 whose chemical composition suggests that either charcoal was applied to the rock matrix as dry pigment, or that water was used as the binding agent for this pigment (which has left no chemical trace). The micromorphology of quartz grains and clay constituents combined with the residual carbon observed in stencil and smear paints from the Woronora Plateau indicate that these paints were processed in, and applied to the rock matrix via, the mouth of the artist(s). The analysis of red, orange, yellow and black paints (excluding PQ2) indicates they are composite mixtures with colouring agents such as iron-oxide, charcoal and chemically weathered Hawkesbury Sandstone dispersed into a clay (kaolinite and/or muscovite) base. These results demonstrate that compositional analyses of pigments can provide information not only relating to physical properties of rock art – what the pigments are, but also the behavioural aspects of rock art production – how pigment might have been prepared and applied.

The results also suggest the significant potential for compositional analysis of pigments to contribute to defining the age of rock art, either in the absence of, or within a direct radiometric dating program. The carbon fraction present in stencil and amorphous smear paints on the Woronora indicates a recent age of not more than a few centuries, with the possible exception of paints from site Caddie 44 which may be older. However the same analyses show that direct  $^{14}\text{C}$  dating of these paints is expected to be problematic, given the significant variation of carbon concentrations within discrete motifs observed via SEM-EDXA. While the results indicate a recent age of some imagery, with the implication that some of this art may have been produced during the contact period, there is no evidence of paints of European origin within the pigments analysed. The absence of European materials does not deny a recent age for the art, but rather confirms that contact art, as revealed elsewhere (Frederick 1999), was produced with indigenous as well as introduced materials.

The lack of discrepancy between paint compositions from the second and third phases of the relative chronological rock art sequences of the Upper Nepean and Sydney Basin, or between the composite paints derived from the Woronora Plateau and adjacent Moss Vale Tablelands are interesting phenomena which require further investigation. The structural analyses of the rock art assemblages of the Upper Nepean and Sydney Basin undertaken by Dibden and McDonald provide a base for constructing archaeometrically testable hypotheses which can be addressed via further

pigment characterisation research. For instance, changes in the geochemical and mineralogical signatures of paints used to create rock art could reflect restriction of access to pigment sources or discrete procurement locations, and/or changes in cultural conventions through time or between different territorial groups.

In addition to temporal information, the SEM-EDAX analysis of paints has shown that if sufficient diagnostic features survive, microfossil charcoal, as small as  $100\ \mu\text{m}$  by  $60\ \mu\text{m}$  in size, can be successfully identified to genus. These types of results may be used to inform palaeoenvironmental reconstructions as well as providing further evidence of the behaviour of artists regarding the selection and preparation of materials for the production of rock art.

Trace element resolution analysis of pigments in the Sydney Basin may provide sufficient resolution for the provenance and provenience of rock art and other material culture to be established, even in relation to pigment sources with a large amount of within-source geochemical variability. The expected within-source variability of the clays and micas of the Illawarra coal measures is as yet unquantified; however, the information generated by previous mineral exploration represents exciting possibilities for future research. The results of the trace element analysis undertaken on the Woronora indicated that while large geochemical variability is present, the grouping of some clays (samples C442 and C443) does occur, indicating that the identification of discrete procurement locations may be possible.

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