LOOKING UP AND LOOKING DOWN:
PIGMENT CHEMISTRY AS A CHRONOLOGICAL MARKER IN THE SYDNEY BASIN ROCK ART ASSEMBLAGE, AUSTRALIA

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Abstract. One of the most fundamental problems facing rock art researchers is understanding the age of their subject. In the absence of numeric age determinations, rock art chronologies have often been inferred by extrapolating the ages associated with subsurface ochres. Here I have used portable x-ray fluorescence spectrometry (pXRF) to assess if the association between rock art and buried ochres proposed by researchers at two sites in the Sydney Basin — Dingo and Horned Anthropomorph and Yengo 1 — can be demonstrated. I found that pXRF can determine if there is no relationship between archaeological pigments. Where geochemical similarities are found, pXRF does not have the analytic precision to unequivocally link archaeological ochres, but it does provide a robust and readily accessible step in the right direction. The method outlined here therefore provides an inexpensive means of generating complementary chronological (and behavioural) information within rock art studies.

Introduction

Researchers continue to infer the possible antiquity of pigment motif production based on the similarity of colour between pictograms and ochres from excavated sediments (cf. David 2002; David et al. 2011: 75; David et al. 2013: 7). Here, I have used portable x-ray fluorescence (pXRF) spectrometry to examine if there is geochemical evidence to support these types of assertions. I have characterised rock art and the stratified pigments recovered from archaeological deposits at two sites in the Sydney Basin, New South Wales (Fig. 1). Ochres from archaeological deposits at Dingo and Horned Anthropomorph and Yengo 1 rockshelters (now housed in museum collections) have been argued to be contemporaneous with the production of pigment art on the shelter walls and ceiling. In the first attempt to assign a numeric age to rock art in Australia, Macintosh (1965: 85) argued at Dingo and Horned Anthropomorph rockshelter, the stratified pigment sequence was evidence of chronologically successive, distinct rock art panel compositions. At Yengo 1, McDonald (2008) presented a broader argument. She proposed that pigment art was produced in association with the period of most intensive shelter occupation, represented by the largest numbers of artefacts in the deposit, including not only pigment, but also knapped stone, edge ground stone implements and hearths.

Some points of definition are pertinent here. What these researcher are arguing is comparable are natural pigments or ochres, unprepared nodules from shelter deposits and crushed ochres used as paints to create

rock art. Most definitions of ochre restrict the term to iron-oxides minerals (Popelka-Filcoff et al. 2007; Bonneau et al. 2012; MacDonald et al. 2012). Here, I adopt a more inclusive definition of ochres as natural earth pigments, recognising that Aboriginal Australians include numerous natural earth pigments (clay and calcite materials) in their use of the term ochre (Clarke 1976; Clarke and North 1991; Crawford and Clarke
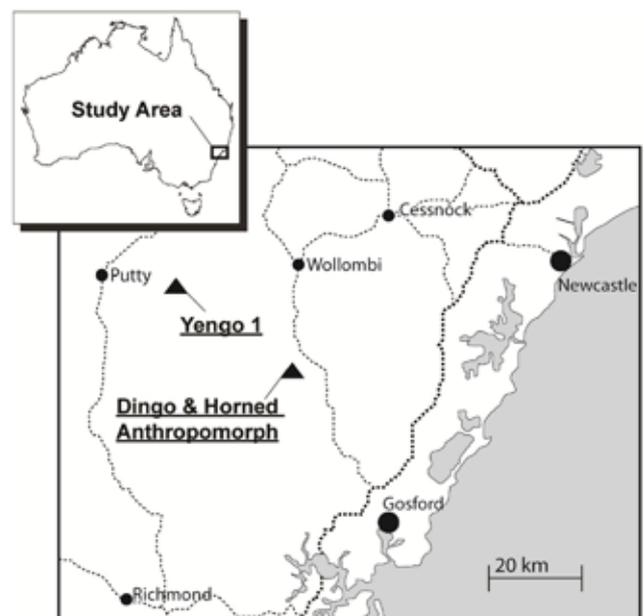
Figure 1. Location of Dingo and Horned Anthropomorph and Yengo 1 showing major towns, roads and the coastline.

Figure 2. *Montage of archaeological pigments examined. Clockwise top left to bottom right: Macintosh's motif 6, Dingo and Horned Anthropomorph; desiccated sandstone from the lower strata of the southern overhang Dingo and Horned Anthropomorph (Jar 1 Table 1); red ochre from square 4A spit 7 Yengo 1; white hand stencil Yengo 1; pXRF on red stencil Yengo 1; pXRF on 'pink wash' Yengo 1; ochreous sediments and charcoal lower strata southern overhang Dingo and Horned Anthropomorph (Jar 1 Table 1); high-quality faceted ochre nodule southern shelter Dingo and Horned Anthropomorph.*

1976; Attenbrow 2002). The pigments examined in this study comprise:

- 'Prepared' white, pink, orange, yellow and red rock art pigments extant on shelter walls and ceilings;
- Different textured nodules of red, purple and white ochres from subsurface contexts;
- And stratified bright to deeper red iron-stained sandy sediments (detrital sandstones) from Dingo and Horned Anthropomorph site that were referred to as 'ochres' by Macintosh (see below, Fig. 2).

Dingo and Horned Anthropomorph

Dingo and Horned Anthropomorph (D&HA) is a Hawkesbury Sandstone shelter located near Mt Manning in the Mangrove Creek catchment of the central coast hinterland of New South Wales (Macintosh 1965; Attenbrow 2004: 86). The shelter is made up of two overhangs where spatially distinct floor deposits are separated by a protrusion of bedrock in the centre of the scalloped tafoni. Macintosh referred to these as the southern and northern shelters. pXRF analyses were

undertaken on a red horned anthropomorphous figure in the southern overhang (motif 6, Macintosh 1965: Pl. 1) and a red 'eel' motif in the northern overhang (motif 31, Macintosh 1965: Pl.1). These motifs represent a sample of the relative temporal sequence described as:

> Six dark red ochre paintings in the southern shelter comprise a male and female anthroporph each with cephalic cornua, a male and female dingo, a male and female echidna. This ritual group is deduced, from radiocarbon analysis of charcoal associated with matching ochre in the floor deposit, to have been painted approximately A.D. 1400.
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> In the Northern Shelter, successive series of paintings in light red ochre, charcoal and white, depicting mainly the local fauna and some hand stencils, are similarly deduced to have been painted between A.D. 1750 and A.D. 1830 (Macintosh 1965: 85).

When in situ analyses were conducted in 2011, the yellow and white chalk outlines applied between 1930 and 1961, and the white 'pipe-clay' eyes Macintosh recorded on the horned anthropomorph (1965: 87, 89) were not visible. It is probable that analysis of

Figure 3. Southern overhang excavation, Dingo and Horned Anthropomorph. Slide of photograph by N. W. G Macintosh, 1961, reproduced with the permission of the Shellshear Museum, University of Sydney. The excavation is reported as 1 m².
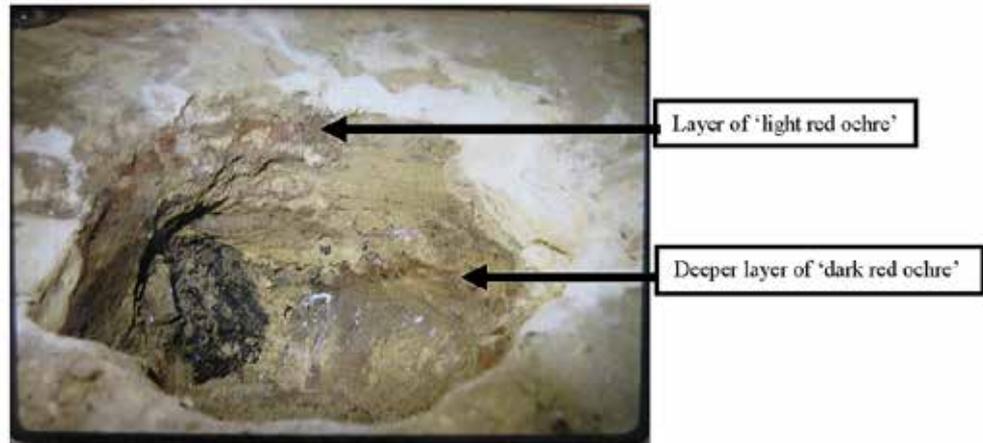
the horned anthropomorph included the location at which a 'solitary red ochre nodule' recovered from the excavated stratum was '… applied … for rubbing directly onto an area of 10 sq. cms. …' in order to check for a colour match between the motif and excavated pigment (Macintosh 1965: 94). Further, analytes on the red 'eel' from the northern overhang are likely to have included dispersed superimposed 'charcoal' and white pigment described by Macintosh (1965: 90). These surficial pigments were partially visible during in situ pXRF analyses, however, the white right hand stencil recorded on the head of the motif was not (ibid.).

Provenance of the excavated 'pigments' from D&HA was ultimately determined to relate to the strata reported in Table 1. Figure 3 reproduces a profile of the excavation in the southern overhang, illustrating the morphology of 'ochre layers' described by Macintosh as:

> 'Excavation of 30.0 cms depth of undisturbed floor deposit. Note the patchy distribution of surficial layer of light red ochre at levels of 4.0 to 6.75 cms below the surface; and deeper layer of dark red ochre at 24.0 to 27 cms … Radio-carbon age of charcoal immediately above the upper layer of ochre is 1806 A.D., 1830 A.D.; and charcoal immediately below the lower ochre layer is 1396 A.D. (Macintosh 1965: 92).

Yengo 1

Yengo 1 (Y1) is a Hawkesbury Sandstone shelter in the Howes Valley, New South Wales, approximately four kilometres northeast of Mt Yengo. The shelter is on an east-facing slope of the valley floor, ~250 metres above a semi-permanent creek (McDonald 2008:

pXRF analyte	Description	Excavation provenance
Jar 1	Labelled on jar: 'Deep layer, darkened ochre under kangaroo'	Presumed to be associated with extensive investigations of the northern overhang deposit which was sieved in its entirety and determined to have no stratigraphic integrity (Macintosh 1965: 94–95).
Jar 2	Labelled on jar: 'Upper layer brighter red under kangaroo'.	Presumed to be associated with extensive investigations of the northern overhang deposit which was sieved in its entirety and determined to have no stratigraphic integrity (Macintosh 1965: 94–95).
Jar 3	Labelled on jar – 'Pale red layer northern cave under eel'.	Presumed to be derived from the '… undisturbed patch of light red ochre' near the margin of the back wall in the northern overhang deposit which was subsequently determined to have no stratigraphic integrity (Macintosh 1965: 94).
Sand 1	Labelled 'top' red on vile.	Presumed to be associated with Macintosh's upper red strata in the southern overhang and dated to AD 1750–1830 (layer 1, Fig. 3).
Sand 2	Labelled 'deep' red on vile.	Presumed to be associated with Macintosh's lower red strata in the southern overhang dated by radiocarbon of associated charcoal to AD 1400 (layer 2, Fig. 3).
Ochre	Large high-quality (lustrous) ochre nodule with extensive use-wear (striations and polish).	An ochre nodule that has 'rub-polish …' on three of its eight surfaces, recovered from within a layer of dark-red ochre 24.0 to 27 cm below the surface of the southern overhang, dated by radiocarbon of associated charcoal to AD 1400 (Macintosh 1965: 92) (layer 2, Fig. 3).

Table 1. Provenance of excavated pigments from Dingo and Horned Anthropomorph, housed in the Shellshear Museum, University of Sydney.

Ochre colour	Spit recorded/stratum reported	Chronological association/depth below surface (cm)
Red	2/I	No age estimate
	III	1530 ± 110 BP (ANU-6216)/30.5
Red/white	7/IV	1950 ± 400 BP (ANU-6054)/52 (one age determination was produced for this stratum)
Red	8/IV	
Red/purple	9/IV	
	V	4590 ± 300 BP (ANU-6055)/54.5
	VI	5980 ± 290 BP (ANU-6059)/93.5

Table 2. *Summary of subsurface ochres from Yengo 1, square 4A included in this study (after McDonald 2008: 98).*

69–70). Stencils are the dominant motifs comprising 82.9% of the recorded assemblage. Hand stencils, axes, boomerangs, clubs, straight sticks and several unidentified objects have been recorded, with white the most common colour, followed by yellow, black and red (ibid.: 71–72). Y1 is the only known site in the Sydney Basin where paint 'washes' have been reported, presumably applied to either cover existing art or to 'prepare' the panel surfaces. These 'washes' occur at four locations in the shelter executed in pink, tan and white pigment (ibid.: 74). Stencils and the paint 'washes' were targeted for pXRF analysis because they are the thickest applications of pigment.

Curatorial issues with excavated materials from Y1 resulted in difficulties locating ochre specimens and discrepancies between the archaeological provenance reported (McDonald 2008: 125, 129) and that recorded on the materials accessed. The red ochres recovered from the basal layers (squares 1B, 2A and 6) could not be relocated, nor could the single yellow ochre specimen recovered from the excavation (ibid.: 125). Where discrepancies occurred, the label on the specimens at the Australian Museum was reconciled against the reported stratigraphy (see Table 2) (ibid.: 98). All ochres analysed in this study derived from square 4A, the deepest excavation unit that produced the most age determinations (ibid.: 97–98, 132). Based on the amount of cultural material in the deposit, McDonald concluded that initial occupation of Y1 dated to 5980±290 BP (uncalibrated). A second phase of occupation ended around 2840±240 BP, after which the most intensive occupation of the shelter commenced from 1950±400 BP, site use continuing until <540±180 BP (2008: 131). McDonald further argued that pigment art was produced during the most intensive period of site occupation and that the function of the site became less ritualised over time. She proposed the shelter was '… used and decorated by the entire group as a base camp' at the time of peak occupation/art production ~1500 years ago (ibid.: 136, 140).

Other relevant background
It is important to understand what is being measured. This section will therefore discuss aspects of the physics and mechanics of pXRF, and the material properties of the archaeological pigments and rockshelter environments studied. Recognising the surficial nature of pXRF is critically important to

this study (Williams-Thorpe 2008: 179). XRF is a bulk analytic technique where chemical characterisations are averaged from analyte[1] volume (Shackley 2011: 10). pXRF therefore estimates bulk composition, from a surface measurement (Potts 2008: 10). The technique works by using primary/incident x-rays to bombard the surface of a sample, creating inner electron shell atom vacancies that de-excite and produce secondary/ fluorescent x-rays with energies diagnostic of the sample's chemistry (Pollard et al. 2007: 101). Analyte volume increases with the atomic weight of the element measured (see Jenkins 1999 for a discussion of the principles of XRF and Liangquan et al. 2005: 80 for an equation to calculate critical depth penetration in natural minerals). Studies on aluminosilicate materials such as the pigments analysed here have shown maximum critical depth penetration of light z elements such as Ca to be ~30 μm, and Fe down to ~170 μm (Potts et al. 1997: 33). Critical penetration depth for heavier z element such as Rb and Zr has been estimated to ~1500 μm and ~2750 μm respectively (Grave et al. 2012: 1676, their Fig. 2). However, *half* of the bulk chemical composition is derived from the surface because the analyte is tear drop shaped. Therefore, the majority of the chemical profiles discussed here were generated from the first half a millimetre (500 μm) of the pigment surface. A surface forms the boundary between the pigment and its environment, consequently the site of mineral segregation — the compositional difference between the exterior of an artefact and its bulk composition (Malainey 2011: 171). The following section discusses the geological weathering products whose chemical expression is likely to have been captured within the pXRF analysis.

Rock art pigments have the potential to directly impact their own weathering, acting as a surface modifier changing albedo, light transmissivity, and the thermal and moisture properties of the underlying rock (Sumner et al. 2009: 242). The morphology and aspect of the rockshelters in this study would ameliorate these effects. D&HA and Y1 are well protected from sun having north-easterly and easterly aspects, the art panels are only exposed to direct sunlight in the early morning, completely shaded during the hottest midday and early afternoon periods. The low entrance heights

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1 In chemistry an *analyte* is the spatial area of the sample measured. In the case of XRF, the area irradiated to produce the elemental profile is the analyte.

of scalloped overhangs at both sites protect the extant art from direct rain and most wind. However, the rock art pigments are likely to be porous due to high clay content (Huntley 2012; Huntley et al. 2011) and therefore susceptible to altered chemical composition via the incorporation of geological weathering products, particularly precipitous silicates and iron-oxides (Young and Young 1992: 74; Prikryl et al. 2007: 419).

Silica rich accretions, commonly known as amorphous silica skins (hydrated amorphous silicon dioxide, $SiO_2.nH_2O$; Watchman 1996: ii), are a well-known geological weathering product to rock art researchers due to their potential to contribute numerical age determinations from radioisotope components either encased by, or deposited within, the rock coating (Watchman 1993; Watchman et al. 1997; Watchman et al. 2001; Watchman et al. 2005). Small ~50 mm diameter opaque, dull white precipitate accretions were noted in sections of unpainted shelter ceiling at Y1. The circular shape and location of these accretions indicates they are derived from percolation through the sandstone massif, rather than by water running across the surface as is a common characteristic of amorphous silica (Watchman 1996: 122). This, in conjunction with their dull texture, contrasting the opal lustre associated with amorphous silica (Lovering 1952), suggests a different major mineralogy, perhaps from the calcium fraction of the sandstone matrix. Similar spherical, dull opaque white accretions, ~10 mm in diameter were observed on the bottom of the art panel in the southern overhang at D&HA. A larger 250 mm by 150 mm square patch of the accretion was recorded immediately adjacent to the southern leg of the horned anthropomorphous motif analysed.

Case-hardened surfaces were observed throughout the rock art panels at both D&HA and Y1. Precipitation of secondary minerals deposited at, or near, the substrate surface forms this less permeable, structurally harder, mineralised layer (Young and Young 1992: 74; Prikryl et al. 2007: 419). Case-hardening can be catalysed by microflora as it alters the rock chemistry, extracting iron and minor associated elements, concentrating them immediately at or below the substrate surface (Machill et al. 1997; Twidale 1968: 144; Nanson and Young 1983; Lovering 1958). No microflora was present on panel surfaces during in situ pXRF analyses, though microflora was noted on the external shelter walls.

Soluble salts catalyse and accelerate cavernous weathering in Hawkesbury Sandstone (Lambert 1980; Young 1987; Young and Young 1992) as well as case-hardening by enhancing dissolution of precipitous minerals, particularly iron, clay and calcite phases (Mol and Viles 2011: 302; Prikryl et al. 2007: 409; Young and Young 1992: 74). Percolation of salts through the rock matrix and their deposition at and on the surface weakens the rock, making it susceptible to processes such as honeycomb weathering and granular disintegration — both observed at D&HA and Y1 (Twidale and Campbell 1993: 497). Salts can also cause

a chemical reaction in rock art pigments, resulting ionic exchange ultimately causing 'failure'/exfoliation, particularly in clay-based paints (Clarke and North 1991: 92).

In terms of the subsurface taphonomy, Hawkesbury Sandstone rockshelter deposits are expected to be lightly acidic, pH increasing with depth in archaeological sediments devoid of alkaline materials such as shell (McDonald 2008: 189). McDonald argued the acidity of deposits was evident in the inconsistent survival rates of 'pipeclay' at Y1, where white ochres were only recovered from the upper strata (II and III) (McDonald 2008: 125, 137, 189). Further evidence of subsurface acidity has been observed in the Mangrove Creek catchment in close proximity to D&HA, where the cortex of chert artefacts experiences colour change commensurate with increasing excavation depth (Attenbrow 2007: 51–52). The acidity of subsurface sediments is likely to result in leaching of ochre matrix minerals (Huntley and Freeman in press).

Iron-oxides (haematite, maghemite and goethite) are present throughout Hawkesbury Sandstone matrix cement with concentrations between 5.7% and 20.4% reported (Hunt et al. 1977: 114–5). Chemical weathering of the sandstone can result in iron-enriched, horizontally bedded strata that range in colour from brown to red, yellow and less commonly, white. Similar to the acidity of iron in ochres (Leondorf and Leondorf 2013: 146–7 cite Popelka-Fillicoff 2006: 171), iron in sandstones may act as a 'soft acid' facilitating chemical substitutions/mineral transitions. At D&HA, Macintosh (1965: 86) recorded sandstone strata including shales and lateritic capping — pisolitic, limonitic and ferric profiles resulting from 'advanced leaching' — noting that low-grade iron deposits were locally widespread and common in the cracks and joints of the bedrock. No geochemical analysis was undertaken on the pigmentaceous sediments excavated from the southern overhang that Macintosh argues are associated with rock art production (Fig. 3). However, microscopic examination concluded the pigmented sediments in the shelter deposit

> … consisted of silica sand and silt and a little clay; … the sand fraction in turn is of two types — sharp edge grains and well rounded grains and all grains have a thin coat (some incomplete) of red clay; the red colour is doubtless due to iron-oxide. Material from the deeper stratum differs from that of the superficial stratum only in demonstrating coarser sand and more iron-oxide (Macintosh 1965: 94).

Methodology

The pXRF analyses described here were undertaken in the initial stages of a larger project designed to explore the archaeological utility of pXRF for rock art applications (Huntley 2014). To develop a rubust protocal for in situ rock art applications (ibid.: Appendix A) it was necessary to conduct the rigorous field program that forms the basis for this paper. Further, it was important to field test pXRF for rock art

semi-quantitative, Net Peak Areas (NPAs) — element abundances through standardless fundamental parameters. NPA calculations for light z-element analytes were between 0.6– 0.5 KeV and for heavy z-elements between 3–21 KeV, each using nine correction cycles for escape and background peaks. Elements selected for NPA calculation were based on the evaluation of untreated spectra in S1PXRF, following a review of relevant geomorphic literature. For pigment characterisation, NPA data is comparable to highly precise, accurate geochemical methods as each are only able to evaluate trends in compositional groups (Popelka-Filcoff et al. 2012; MacDonald et al. 2012). NPA data was sufficient therefore to answer the research question posed, namely whether there is geochemical evidence to support the contemporaneity of rock art and excavated pigment at D&HA and Y1?

Figure 4. Unweathered block of Hawkesbury Sandstone showing the location of spatial transects. (Data from experimentally applied motifs were excluded from this study.) Blue grid squares are 1.5 cm. White dashed line represents light element profiles. Black dashed line represents heavy element profiles. Yellow ovoid shows the location and scale of pXRF aperture.

applications prior to remote area fieldwork (Huntley et al. 2015) (to manage practical instrument mechanics such as battery life, performance of aperture windows for vacuum assays, resilience of instrument/vacuum leads and fitting etc.).

Instrument parameters

All analytes were collected over a 300 second live-time count at FWHM between 150 and 185 using the same Bruker Tracer III-V pXRF equipped with a Peltier-cooled Si-PIN detector, rhodium tube and a 1024 channel analyser at a resolution of approximately 170eV FHWM at the manganese Kα peak (5.9 keV at 1000 counts per second). Light z-element parameters were 12 keV, 20 μA, initially without, and subsequently using a 25 μm titanium filter in the x-ray path, under vacuum (supplementary online material: SOM Table 1). This configuration optimised K-Shell excitation from Al to Zn (from 1.3 to 9.5 KeV), the titanium filter used to reduce incident rhodium L-Shell x-rays as measurement of fluorescent Cl and S K-Shell x-rays was desirable. Parameters for heavy z-element analytes were 40 keV, 13 μA, using a 76 μm copper/30.5 μm aluminium/6 μm titanium filter in the x-ray path to optimise K-Shell excitation of from K to Zr (from 3.2 to 20.4 KeV), including potential instrumental artefacts such as Rh in the Bremsstrahlung radiation (SOM Table 2).

Spectral processing used Bruker-supplied software — X-rayOps to adjust tube, operating voltage and current settings and S1pXRF to monitor count rate, signal acquisition and evaluate live data. Spectra 7.2.1.1 was used during post-possessing to calculate

Data collection protocol

Care was taken to minimise matrix and instrumental effects (potential sources of error in the chemical dataset). Analyses were conducted in dry conditions, following periods of several weeks of fine weather to minimising moisture content/differences in sandstone matrix density (Liangquan et al. 2005: 28). The thickest applied pigments were targeted to maximise pigment volume in analytes (Huntley 2012: 79). Care was taken to ensure 'best contact' between pXRF aperture and the sample, minimising attenuation from air and angles of incidence (De Boer 1989; Forster et al. 2011; Jenkins et al. 1999: 39; Mantler and Klikovits 2000: 20–30; Potts et al. 1997; Williams-Thorpe 2008). Mechanical degradation (L-drift, Johnson 2012) is not considered a factor in this study because analyses were completed over less than 18 months using the same instrument.

Two controls were included to assess 'matrix effects' (Markowicz 2008; Shackley 2011) and instrumental drift (Johnson 2012). Ohio Red Clay is a standard reference material in archaeometric pigment investigations (Glascock 1992; Kuleff and Djingova 1998; McDonald et al. 2008; Popelka-Filcoff et al. 2008: 735) and fired ceramic solid was used as an internal standard during this study (see SOM). A block of Hawkesbury Sandstone devoid of case-hardening (Fig. 4) was sampled using spatial transects to explore chemical variation, the resulting data used as a proxy for the unweathered shelter substrate (see SOM). These transects included

areas of (presumably iron-oxide rich) yellow, red and tan natural staining, but deliberately excluded experimentally applied pigment (again see Fig. 4).

Data analysis and chemometrics

Chemical data is routinely interrogated using mathematical and statistical methods (chemometrics), and the history of such analyses in archaeometry is extensive, having been practiced for over sixty-five years (Baxter 2008: 698). In this study, composite element profiles were interrogated using chemometric methods routinely deployed on compositional data from archaeological artefacts (Baxter 2003; Neff 2002). Principle components analysis (PCA) using a correlation matrix and (Ward's) hierarchical cluster analysis was undertaken using JMP 11 (statistical analysis and data visualisation software) to observe trends in chemical characterisations and explore compositional groupings (Baxter and Jackson 2001: 131; Glascock et al. 2004). As is standard for ochre chemistry, all heavy element profiles were initially calculated as ratios to Fe (Popelka-Filcoff et al. 2007; Popelka-Filcoff et al. 2008; Eiselt et al. 2011; MacDonald et al. 2011; MacDonald et al. 2012). This use of iron normalisation was, however, novel as not all pigments examined are red. Fe was persistent in all heavy element analytes, variance having the potential to dilute or amplify elements 'diagnostic' of particular ochre sources (MacDonald et al. 2012: 6). Significance tests and loading of multivariate vectors helped determine relationships between Fe/other components. Significance tests, in conjunction with Fe ratios, were used to explore if geochemical profiles represented depleted, increasingly variable or enriched taphonomic derivation in respect of the diagenetic environment of the sandstone/ochres (Ogburn et al. 2013; Popelka-Filcoff et al. 2007: 22) and to identify post-depositional alterations from shelter environs (Huntley 2012). Scatter plots of the first three principal components and dendrograms were used to visualise correlations between analytes.

Results and interpretations

There were indeed patterns present in the pXRF data collected, and the chemometric tests and treatments applied here were used to examine that patterning. This section outlines the patterns observed in light and heavy element profiles in turn, discussing specific chemical expressions of environmental and cultural processes. PCA of light element profiles collected with no filter were statistically significant for the first six components (chi squares), accounting for 98.5% of variability. The first three components accounted for 79.6% of variability (eigenvalues 4.5, 2.8 and 1.5 respectively) and their relationship in multivariate space is illustrated in the top left scatter plot of Figure 5. Light element profiles collected with a Ti filter were statistically significant for the first nine components accounting for 99.7% of variability. The first three components accounted for 69.9% of variability (eigenvalues 3.3, 2.6 and 1.8

respectively) and their relationship in multivariate space is illustrated in the bottom left scatter plot of Figure 5. Loading plots of the non-filtered light element profiles revealed a strong correlation between S and Ca, and Ti and Mn across the first three components and a correlation between Ca, S and Cl in the first component. PCA loading plots of the Ti filter profiles revealed a strong correlation between K and Ti across the first three components and a correlation between Ca, S and to a lesser extent Cl; while Si was separated from other constituents in the third component.

The light element profiles show a strong trend to high Si abundances in the spectra collected at the rockshelters compared to those from the museum-housed ochre specimens. This, combined with the separation of Si in the vector loadings for PCA, suggests mobilisation and enrichment of Si at the sandstone matrix surface. Low Fe abundances for the in situ rock art analytes compared to the control block (Fig. 4) confirm that Si is present at the shelter surfaces, lowering fluorescent yields for heavier elements (Huntley 2012). Si enrichment in the in situ data is not as prevalent at Y1 as it is at D&HA (SOM Table 1).

Elevated Fe abundances in excavated sandstone slabs from D&HA shelter show enrichment occurs in subsurface contexts and they are consistent with Macintosh's observation that the excavated layers of granular 'pigment' were in situ weathered sandstone. Higher Fe abundances in the natural orange hued surface of the shelter matrix at Y1 compared to the applied orange hand stencils also indicates Fe is a significant precipitate in the formation of case-hardened surfaces (SOM Table 1). Fe abundances for the red 'eel' motif in the northern overhang of D&HA are roughly equivalent to those of the shelter matrices without applied pigment, consistent with the surficial, dispersed nature of pigment observed.

Evidence for salt-catalysed chemical processes, such as honeycomb and cavernous weathering, is largely absent from light element rock art profiles. Two analytes did produce high S and Cl — the cream child's hand stencil and the pink 'wash' from Y1. These analytes containing thickest paint/largest pigment volume per spectra within this study (the open pink and black diamonds in scatter plots/spectra 31 and 38 in the dendrogram, Fig. 5). Both analytes also have a very high abundance of Ca, complemented by low abundance of clay elements (Al, K and Ti, see SOM Table 1). These results are diagnostic of calcium rather than clay matrix ochres. The high salt component and the strong correlations between Ca, S and Cl in the vector loading of the PCA are considered a reflection of the diagenetic environment of the ochre source(s), rather than shelter taphonomy (post depositional weathering). This is supported by the dearth of S and Cl observed in the rockshelter environment at Y1 via the in situ sandstone blanks and other rock art analytes.

Consistently high Ca complemented by low abundances in clay elements were also observed in
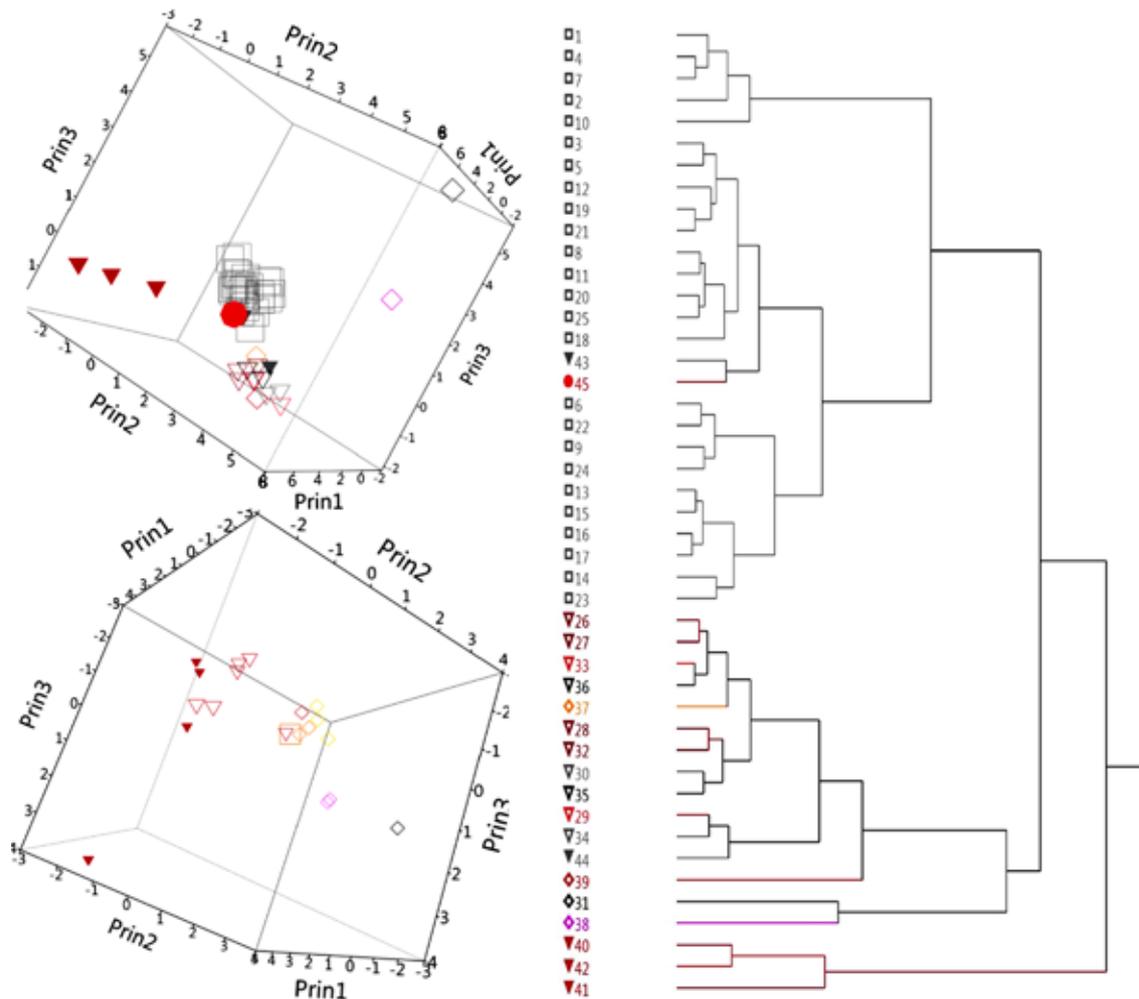
Figure 5. *Top left (a): three-dimensional scatter plot of the first three components of PCA light element profiles (no filter), untransformed NPAs (SOM Table 1). Bottom left (b): three-dimensional scatter plot of the first three components of PCA Ti filter light element profiles, untransformed NPAs (SOM Table 1). Right: hierarchical cluster of Ti filter light element profiles, untransformed NPAs. Dendrogram scaled by distance.*
Key: sandstone control block transects = hollow squares, Yengo 1 = diamonds; Dingo and Horned Anthropomorph = triangles; Ohio Red Clay Standard = solid circles; solid symbols = subsurface artefacts; open symbols = in situ rockshelter surface; symbols are coloured according to pigment hue; grey is used for sandstone, black outline for white pigment.

the element profiles of the ground/faceted red ochre recovered from the deposit in the southern overhang at D&HA (bottom centre, Fig. 5.2). This suggests a calcium matrix mineralogy for this 'high-quality' red pigment source (solid red triangles of the scatter plots/analytes 40–42 in the dendrogram, Fig. 5.5). The yellow and white 'presumably chalk' outlines noted by Macintosh on rock art at D&HA between 1938 and 1961 may have altered the chemistry at the edges of motifs. In the twentieth century, commercially produced chalks were made from 'pure' limestone, $CaCO_3$ (Montagner et al. 2013: 410; Macintosh 1965: 87). Unsurprisingly there was no detected chemical trace of the chalk applied over half a century ago in the light element profiles. The Fe normalised heavy element profiles that cluster together (Fig. 5.6b) show a relationship between one of the six analytes from the high-quality excavated ochre and one of three analytes from the horned anthropomorph (motif 6) — but this is not

evident in the light element profiles. Rather than being chemical residue from chalk or evidence the ochre was used to produce rock art, this is probably from 'testing' of the ochre at the time of excavation, where, after noting that the colour of the subsurface ochre nodule and the horned anthropomorph 'matched precisely' Macintosh describes that his application of the ochre '… brushed off again relatively easily' (Macintosh 1965: 94). Conversely, elevated K in one of the spectra collected on red 'eel' located in the northern overhang is consistent with the incorporation of superimposed white clay pigment (rather than calcite).

The panel surface without rock art at D&HA showed elevated Ca abundances compared to the subsurface sandstone slab recovered from the deposit and the average concentrations of Ca in the sandstone control block (Fig. 4). There is insufficient evidence to identify the composition of the opaque white skins observed on the rock art panels at both sites as they were not
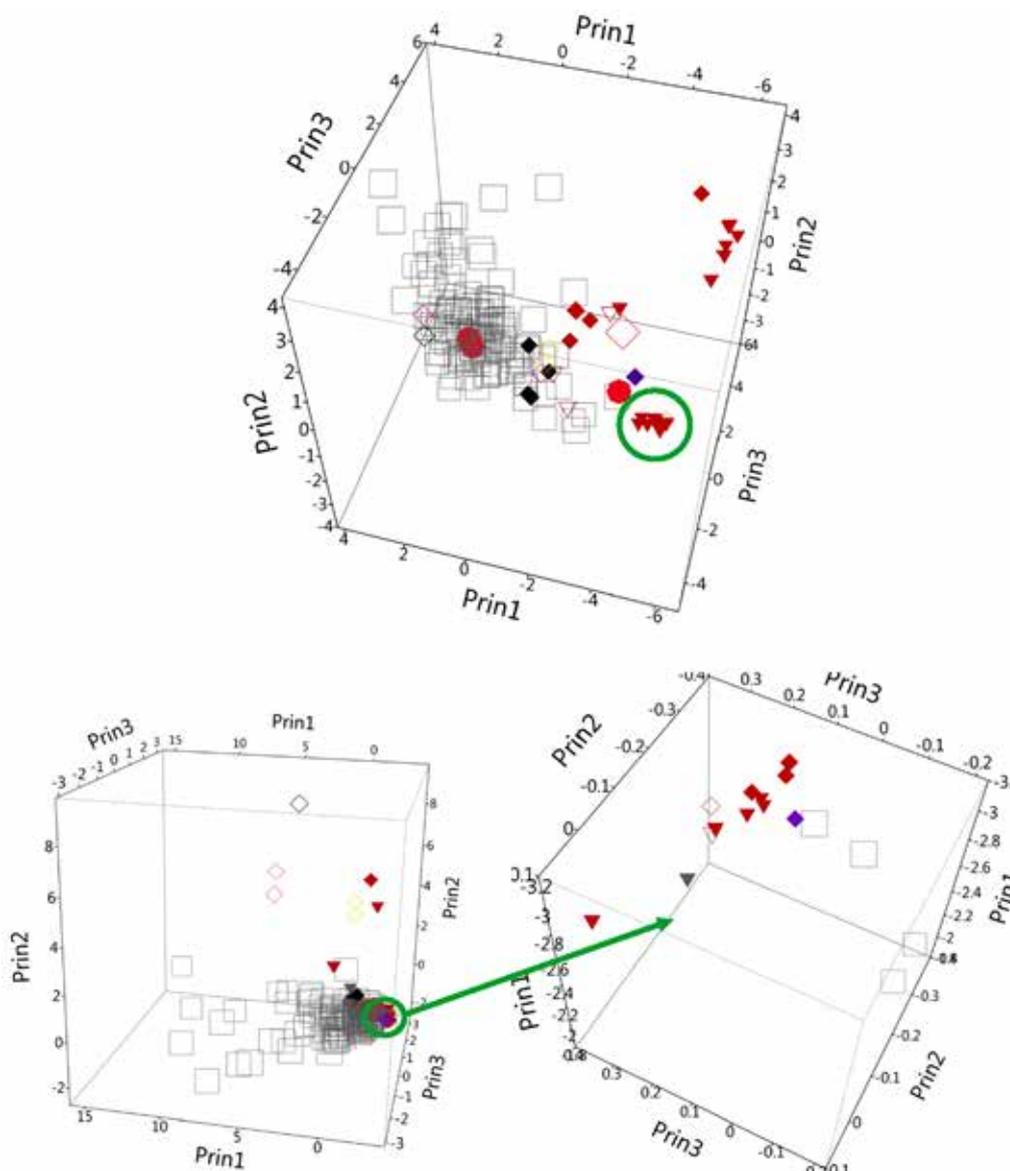
Figure 6. *Top (a): three-dimensional scatter plot of the first three components of PCA of heavy element profiles (SOLM Table 2). Bottom right (b): three-dimensional scatter plot of the first three components of PCA of Fe normalised (radioed) heavy element profiles (SOLM Table 2). Bottom left: detail of clustered red hue pigments shown in (b). Key: sandstone control block transects = hollow squares, Yengo 1 = diamonds; Dingo and Horned Anthropomorph = triangles; Ohio Red Clay Standard = solid circles; solid symbols = subsurface artefacts; open symbols = in situ rockshelter surface; symbols are coloured according to pigment hue; grey is used for sandstone, black outline for white pigment.*

directly analysed. However, elevated Ca in the shelter matrix in consort with the dull, opaque white colour of the skins and their spherical morphology, suggests calcium accretion mineralogy precipitated from within the sandstone massif. In contrast, the elevated Ca abundances in the yellow hand stencil at Y1 are interpreted as deriving from composite spectra that incorporate the underlying white/cream stencil of a club (SOM Table 1).

Trends are also evident in the heavy element datasets. The untreated heavy element profiles of the sieved sediments from the northern overhang at D&HA (Jar 1, Table 1) and 'ochrous sediments' in the southern overhang (Jar 2, Table 1), mostly cluster with the orange hand stencil from Y1 (Fig. 6a). This is

consistent with previous Australian and international pigment studies that have concluded ochre sources in sandstone environments incorporate detrital lenses from the local geology (Macintosh 1965: 86; Zoppi et al. 2002; Huntley et al. 2011; Bonneau et al. 2012; Huntley 2012). The scatter plots of heavy element profiles (Fig. 6a and b) show similar patterning to those from the light element analyses in regards to the pink 'wash' and white stencil at Y1 — these separate from other white hue pigments in multivariate space. The white stencil (black outlined diamond) and white pigment from the excavation (black solid diamonds) appear unrelated and, as with the light element data (Fig. 6a), this is interpreted as a fundamental difference in mineralogy, the white hand stencil deriving from calcium while the

excavated ochre is a clay (SOM Table 2 reports Ca and K concentrations).

Analysis of paired means for the untreated, that is not ratioed to Fe, heavy element profiles relative to Fe showed statistically significant relationships for all elements using t-tests (p = ≤0.0001, NPA values are given in SOM Table 2). Mn and Cr positively correlated with Fe, though the correlation for Cr was weak (correlation coefficient = 0.295). The remaining elements all negatively correlated to Fe. Strong correlations were observed between Fe and As, V, Y, Zn and Zr (≤-0.05); weak correlations between Fe and K, Ti, Cu and Rb (≤-0.2); and very weak correlations were observed between Fe and Ni/Sr (-0.545 and -0.286). This significance testing independently validates the use of iron normalisation on the entire heavy element dataset, including non-red pigment and unpainted sandstones.

The clustering of red-hued pigments from excavated and rock art contexts was further explored in multivariate space, both through a detailed scatter plot (Fig. 6c) and hierarchical clustering (not illustrated here due to the size of the dendrogram). Both methods returned the same patterning. Grouping of red archaeological ochres indicates that the same types of pigments, in terms of mineral constituents and therefore likely procurement contexts (ochre extraction locations), were being used to execute red rock art classed as secular at Y1 (MacDonald 2008: 139–140) and ritualised in social context at D&HA (Macintosh 1965: 85).

Solid red triangles in the detailed scatter plot (Fig. 6c) represent the 'high-quality', faceted red ochre from the excavation of the southern overhang at D&HA (illustrated in Fig. 3). The darker red ochre from the outline of the northern leg of the horned anthropomorph (left hand side of photograph, Fig. 3) is represented by the open red triangle in this scatter plot. Their proximity in multivariate space suggests a correlation in their chemistry not evident in the light element profiles. In this specific instance, the rock art analyte is likely to have incorporated the location from which the ochre nodule was 'rubbed' directly onto the motif by Macintosh (1965: 94). Further support for this interpretation is seen in this single correlation from the possible six analytes collected on different surfaces of the ochre nodule, and three possible analytes from different locations within the anthropomorphous motif.

The proximity of analytes from red pigment in spits 7, 8 and 9 of the fourth stratum of excavation unit 4A at Y1 is illustrated in Figure 6. This clustering indicates that the majority of pigment at the time of peak site use ~1500 years ago, whether purple or red, came from similar ochre sources. The exception is a porous red ochre specimen from spit 7 that has a high Sr ratio, which indicates a Ca matrix pigment. Sr is often used as a surrogate for Ca in chemical composition as these elements readily substitute in mineral lattices (Koenig et al. 2014).

Discussion

A number of recent studies have shown that pXRF analysis produces insights into the production of rock art from purely qualitative and semi-quantitative data (Huntley 2012; Wesley et al. 2014; Koenig et al. 2014; Huntley et al. 2015). Acknowledging the analytic precision of pXRF does not negate the research potential and utility of the technique. Recent work has concluded that pXRF datasets from a range of applications produce element profiles that pattern in the same way as those from high-precision laboratory techniques such as desktop energy dispersive XRF and neutron activation analysis, but pXRF produces concentrations that differ from these independent measurements (Johnson 2012: 2 cites Craig et al. 2007; Goodale et al. 2012; Nazaroff et al. 2009). Though pXRF cannot readily exceed a semi-quantitative resolution for unprepared aluminosilicates (Potts et al. 1997; Cesareo et al. 2008; Huntley 2012; Koenig et al. 2014), profiles generated are equivalent to laboratory techniques in terms of the number of measured elements (SOM Table 2). Here I measured eight transition mentals compared to the six with laboratory-based energy dispersive XRF and instrument neutron activation during recent archaeological ochre studies (Popelka-Filcoff 2007: 22).

Taphonomic implications

Understanding the chemical expression of taphonomic processes facilitates (as far as possible) the separation of environmental from cultural chemical signatures — a prerequisite for comparing rock art and excavated pigments. Under or overlying mineral accretions, superimposed pigments and the (mineralogically segregated) rockshelter substrate are all captured in pXRF analysis of rock art. Research must therefore include the comprehensive observation of site taphonomy to reliably interpret chemistry for rock art applications, a caveat demonstrated repeatedly during previous direct radiometric dating investigations (McDonald et al. 1990; Watchman 1990; Watchman et al. 1997; McDonald 2000; Watchman et al. 2000; Watchman et al. 2001). The idea of simply 'subtracting' the chemical signature of the background rock matrix (Olivares et al. 2013) in mineralogical heterogeneous sandstone, which has the same chemical constituents as the rock art pigments overlying it, is not feasible. Indeed, it is undesirable to exclude the chemical indices of geological weathering/rockshelter taphonomy as these have important conservation and management implications (Huntley 2012; Huntley and Freeman in press).

More broadly, the taphonomic environments of ochre can be classified as diagenetic and/or post-depositional. The chemical signature of diagenetic processes comes primarily from substitution, where elements with similarly sized atoms and charges replace each other in the crystal structure of a mineral as a result of geological conditions specific to the formation and subsequent weathering of pigment sources (Pollard et

al. 2007: 213; MacDonald et al. 2012: 6, 11). Diagenetic chemical expression is primarily observed in transition metal and rare earth elements such as V, Cr, Co and Zn that readily substitute for Fe in haematite (and other iron-oxide minerals) (MacDonald et al. 2012: 12), though critically for this study, the same elements will substitute for Al in muscovite (clay) (Jercher et al. 1998: 397).

The results of research at D&HA and Y1 illustrate that rock art pigment chemistry reflects both post-depositional processes and ochre diagenesis. For example, the positive correlation of transition metals Mn and Cr with Fe in heavy element profiles is interpreted as evidence of rockshelter taphonomy. These elements are mobilised together in the rock substrate as precipitates resulting in the case-hardened surfaces at D&HA and Y1. Whereas V, Zn and Zr negatively correlate with Fe in heavy element profiles, interpreted as evidence of ochre diagenesis. K and Ti (also transition metals) also negatively correlate with Fe but are highly mobile ochre matrix minerals and I therefore consider them unreliable diagenetic correlates.

This study bears out the results of previous research, finding that the greatest opportunity to observe not just ochre matrices, but also the effects of chemical weathering in aluminosilicates, is in highly mobile light elements such as Si, Ca and K (Ogburn et al. 2013: 1825), including the leaching of Ca through its surrogate Sr (Williams-Thorpe et al. 1999; Lundblad et al. 2011). However, this study also contributes important new taphonomic data. The chemical visibility of Ca in the ~1500-year-old red ochre at Y1 (through its surrogate Sr) suggests that despite the acidity of the deposits, calcite ochres can survive in the order of thousands, not hundreds of years as previously thought (McDonald 2008: 98). This finding has implications for previous interpretations of the subsurface ochre assemblage from Y1 that concluded the inconsistent survival rates white ochres (only recovered from the upper strata) was purely taphonomic, rather than representative of cultural patterns (ibid.: 125, 137, 189).

Chronological implications

I conclude that it is possible to compare rock art with other archaeological samples using pXRF (unlike Velliky 2013). In relation to the comparison of pigments in the Sydney Basin, McDonald has observed that 'Unless both the occupation evidence and the art have been dated, the association between the two … is not easily proved' (McDonald 2008: 220). Lack of a possible association between pigments can be demonstrated using purely qualitative chemical composition. The research presented here has shown that multivariate analysis of element abundances produced with pXRF can discern compositional groupings. Though establishing an association between rock art and stratified ochres from excavated contexts using pXRF is far from conclusive, the methods outlined in this study can be applied as a screening tool to add value

to further high-sensitivity archaeometric analysis by targeting pigments known to be similar. Chronological markers are evident in both light and heavy element datasets. Preferences for different mineral pigments may vary over time, and so might pigment sources with the same mineralogy. In establishing a relationship (or otherwise) between archaeological pigments it is therefore critical to characterise the major chemistry of ochres (matrix constituents) using light element optimisation to understand which minerals are being selected; as well as variation in the minor and trace elements of ochres, especially transition metals, using heavy element optimisation to understand the variation in ochre sources.

Behavioural implications

The red sediments that Macintosh observed in the deposit of D&HA are likely the result of cultural activities. Fe enrichment of the buried sandstone slab and microscopic observation of advanced weathering that increases commensurate with subsurface depth for the in situ (detrital sandstone) pigment sediments is inconsistent with the preservation of Ca ochre matrix in the lower strata at D&HA (Macintosh 1965: 95). Rather than representing rapid post-depositional alteration for detrital sandstones, the ~AD 1400 age determination below very weathered pigment sediments that also contained the high-quality calcite ochre nodule indicates detrital sandstone was anthropogenically incorporated into the shelter deposit (Macintosh 1965: 92). This is consistent with the findings of previous rock art analyses in the Sydney Basin that have concluded weathered sandstone lenses were used as pigment (Huntley et al. 2011; Huntley 2012). In addition, clustering of analytes from both D&HA and Y1 in multivariate space indicates that detrital sandstones from the local geology were used as a staple pigment source, through time.

Previous research has classified archaeologically known ochre sources as dominantly calcite or clay minerals (O'Connor and Fankhauser 2001). The importance of this approach is reinforced by my finding of calcite mineralogy for the 600-year-old 'high-quality' ochre nodule from D&HA, and a recent hand stencil, ochre 'wash' and ~1500-year-old red ochre nodule from Y1. To my knowledge this is the first time calcite matrix ochre has been reported in Sydney Basin archaeological assemblages. The Wianamatta Group shales that overlay the Hawkesbury Sandstone, and the shales and kaolin within the coal measures that underlay it, are thought to be primary sources for clay ochres in the Sydney Basin (Baker and Uren 1982; Hughes and Sullivan 1983; Hazelton and Tille 1990; Attenbrow 2002: 43; Haworth 2003; Ford 2006; Huntley et al. 2011; Huntley 2012). Identification of calcite mineral pigments, particularly the association of S and Cl abundance in the rock art at Y1 that appears diagenetic in origin, is new evidence for ochre sources with distinct chemical signatures, likely to have been gathered at geographically restricted

procurement locations (ochre quarries). As well as providing exciting possibilities for future research, this result cautions against previous methodologies that have excluded common ochre matrix elements in their analyses, describing them as 'coarse-grained inclusions' prone to post-depositional processes such as leaching (Jercher et al. 1998: 397; Smith et al 1998; Smith and Fankhauser 2009: 41).

Conclusions

pXRF has become a staple analytic tool in museums, academic departments and other organisations engaged in anthropological research. The methods presented here therefore provide a readily accessible and inexpensive means to continue to test the assumed relationship between archaeological ochres and to generate complementary taphonomic, chronological and behavioural information in regional rock art studies. Though I found no geochemical evidence to support contemporaneity of rock art and excavated pigment at D&HA or Y1 rockshelters, there is evidence of an association between one surface of the faceted, 'high-quality' red ochre nodule recovered from the archaeological deposit and the red horned anthropomorph, both located in the southern overhang at D&HA. This is likely the location where Macintosh rubbed the ochre nodule directly onto the pictograph at the time of excavation to check for a colour match. None the less, this finding demonstrates that ochre sources associated with rock art can indeed be identified, at least preliminarily, using non-invasive techniques. Further, the association between the excavated and rock art pigments at D&HA attests to the importance of targeting characterisation to chemistry indicative of both the diagenetic environment, primarily evident in heavy element profiles, and post-depositional environment, primarily evident in light element profiles.

The first scientific description of calcium ochres in the Sydney Basin archaeological assemblage represents exciting possibilities for future provenance research due to the restricted geological environments in which calcite ochres can be found locally, in the Hawkesbury Sandstone and surrounds. Ochres from the archaeological deposits at Y1 show that calcium pigment sources were used from the mid-Holocene, with increasing archaeological visibility of calcium pigments in the late Holocene at both Y1 and D&HA hinting at increasing exploitation of these sources in the most recent period of site use, consistent with calcium ochres in the most recent art phases of Y1. The coeval use of clay matrix red pigments, seen throughout the rock art and subsurface archaeological sequences at both sites, suggests local clay sources, including detrital lenses of local sandstone, continued to be exploited through time.

Supplementary material

The two data sets (relative abundances for light and heavy element optimised spectra) are provided as Supplementary Online Materials (at *http://www.ifrao.com/auranet-library/*). The locations of rock art spectral acquisition are illustrated in a detailed project report lodged with the Australian Institute of Aboriginal and Torres Striate Islander Study in Canberra, Australia.

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