

Pigment geochemistry as chronological marker:

The case of lead pigment in rock art in the Urrmarning 'Red Lily Lagoon' rock art precinct, western Arnhem Land

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Abstract

This paper presents selected results of an experimental study using portable x-ray fluorescence (pXRF) for the non-destructive analysis of rock art pigments in northern Australia. During two weeks of fieldwork in the dry season of 2011 at the Red Lily Lagoon area in western Arnhem Land, 32 rock art motifs in four rockshelter sites were analysed. A total of 640 analyses were undertaken, including of white, red, black, yellow and blue pigments from both early and contact art motifs. This paper discusses the geochemical analysis of one particular motif painted with black pigment. It was determined that processed metal lead was the most likely pigment base. Contrary to previous stylistic analysis that suggested the motif had an old age, our analysis suggests that the motif was painted within the last 200–300 years.

Introduction

Direct dating of most rock art is often unresolved because pigments are inorganic and not suitable for radiocarbon dating and/or because the geology, such as the Kombolgie Sandstone Formation in western Arnhem Land, does not facilitate the use of other direct dating techniques (see Aubert et al. 2007). Establishing age determinations can assist with dating sequences of Aboriginal rock art. Rock art age determinations in Arnhem Land have traditionally been assisted by methods such as superimposition, typology or the archaeological context of inhabited sites.

The earliest evidence for rock art in northern Australia, dated to 28,000 cal. BP, was established through radiometric dating of stratigraphic layers that contained a painted fragment of sandstone from an excavated deposit on the Arnhem Land plateau (David et al. 2012). The current chronology and sequence of rock art in Arnhem Land, however, has been proposed mainly without the aid of direct dating techniques (Brandl 1970; Chaloupka 1984, 1993:89; Chippindale and Taçon 1998:107; Jelinek 1978, 1989; Lewis 1988).

The Red Lily Lagoon area (Urrmarning) in western Arnhem Land of the Northern Territory (NT), has long been recognised as one of the most significant complexes of rock art in the Gunbalanya region (Edwards 1974:136, 1979:51) (Figure 1). Red Lily Lagoon lies on the edge of the extensive freshwater wetlands and plains to the east of the East Alligator River and falls within the Gagudju/Erre/Mangereridji language group zone. Taçon (1993:116) found that Freshwater Period motifs in this zone consisted of an extensive selection of fish (most commonly painted in x-ray and solid/stroke infill), painted hand or hand-and-arm stencils, beeswax compositions, stick figures and energetic style stick figures. This complex of rock art motifs

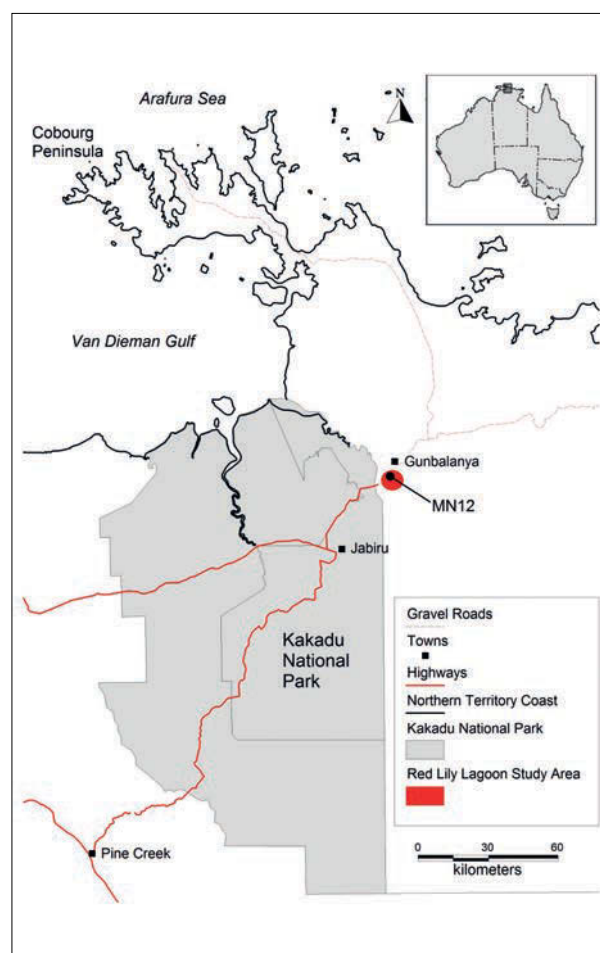


Figure 1 Location of Minjnyimirdawabu (MN12) within the context of Kakadu National Park and Arnhem Land.

as described by Taçon (1993) was found in abundance in the Urrmarning rock art precinct.

Despite documentation of rock art in the Urrmarning precinct, no geochemical studies of rock art pigments in this study area had previously been conducted (Chaloupka 1993; Gunn 1992; Jelinek 1989; Mountford 1956). Geochemical studies of rock art pigments in general are only infrequently conducted, as they involve controlled destruction of small parts of motifs that are then subject to laboratory analyses (Huntley et al. 2011; Jercher et al. 1998). The application of the non-destructive portable x-ray fluorescence (pXRF) technique in the field remedies this situation, although this approach has significant constraints on precision and accuracy of the geochemical results (Huntley 2012).

In this paper we present data from an experimental pXRF study of the pigments comprising one particular motif, and discuss how low resolution geochemical data can be used to infer meaningful archaeological interpretation if the pigment raw material indicates a non-Indigenous provenance (cf. Cole and Watchman 1993). Our study is part of an ongoing project to develop practical conservation strategies to assist Indigenous rangers and traditional owners in monitoring disturbances to places of cultural significance. The results cast some doubt on previous age determinations by stylistic typology and give evidence for the potential of pXRF to provide important data for the understanding of the chronological sequence of rock art in western Arnhem Land.

Minjnyimirndawabu Rockshelter

Our particular focus is the Minjnyimirndawabu rockshelter (MN12, previously recorded by Gunn [1992] as MN15), located approximately 40 m above the sandy plain on the edge of the sandstone escarpment which is part of the Kombolgie Formation (Plumb and Roberts 1992) (Figure 2). This site is notable for the presence of a 'contact' painting of a sailing ship and several decorative infill hand and forearm paintings, along with a diverse array of painted and beeswax motifs. This particular panel of the sailing ship and painted hand is amongst the most widely publicised examples of this style of rock art.

These paintings have particularly high social significance to the Manilkarr traditional owners owing to personal connection with the painter of these motifs. According

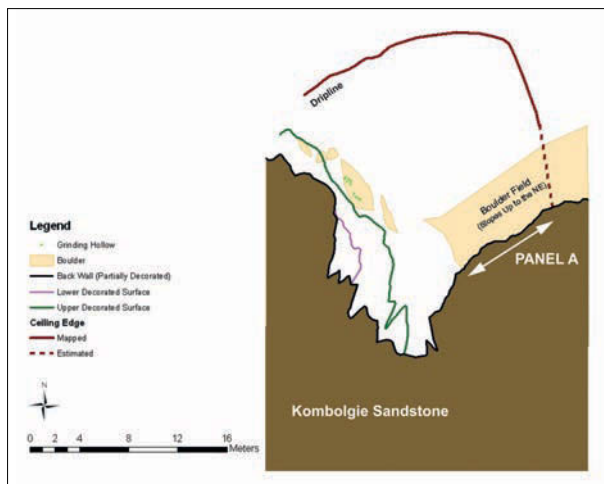


Figure 2 Plan view of Minjnyimirndawabu (MN12) rockshelter indicating the location of Panel A.

to senior traditional owner, Jacob Nayinggul (dec.) (pers. comm. 2011), the ship and a decorative hand painting to its right were of recent antiquity, having being painted by his adopted father in the early twentieth century. A substantial silty, charcoal rich, cultural deposit with numerous stone artefacts and faunal remains is present on the shelter floor, while grinding hollows and ground surfaces attest to the likely processing of local seeds, plants, fibres and ochre (Jones and Johnson 1985; Meehan et al. 1985).

Panel A in MN12 is on a vertical sandstone face orientated to the northeast and measures approximately 40 m². It consists of 30 clearly identifiable motifs, with evidence for many others obscured by weathering (Figure 3). The subject matter of motifs includes anthropomorphic figures, weapons, x-ray fish, solid infill fish and macropods executed in red, yellow, white and black pigments. Mountford (1956:153) described the anthropomorphic figures as 'supposed to be self-portraits of the Mimi people'.

A sample of these figures was selected for pXRF analysis based on motif pigment colour, thickness and colour diversity, including:

- Motif 1 – a large red male anthropomorphic figure (Figure 3.1);
- Motif 2 – a scene of four or five red anthropomorphic figures (Figure 3.2); and,
- Motif 3 – a large black female anthropomorphic figure (Figure 3.3).

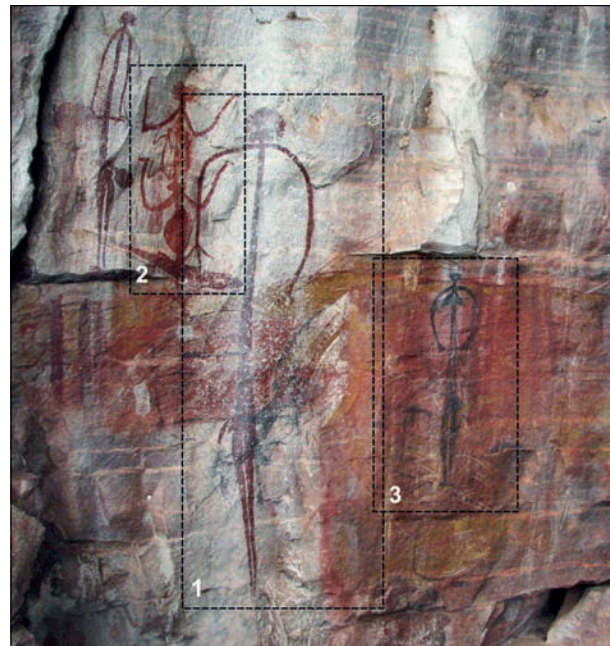


Figure 3 MN12 Panel A with Motifs 1, 2 and 3. Motif 3 is shown in more detail in Figure 4 (Jelinek 1989:173; Mountford 1956:154, Figure 41).

Motif 1 is a vertical figurative depiction of a male individual (displaying genitalia) painted with red pigment in an outline and solid infill method in frontal view. It is depicted with short spears with large rounded ends, a spear thrower and possible 'goose spears' (Chaloupka 1993:148). The motif is uncommonly large, measuring 190 by 120 cm.

Motif 2 consists of a scene composed of line and solid infill human figures. The scene is centred on two human figures that are joined vertically, with another shown upside down.

The figures are painted in a characteristic manner common to human figures: static and frontal with outstretched bent arms and legs. The uppermost figure appears to have two smaller human figures around, or attached to, the torso area. All figures are painted in red pigment and have been executed over faded indistinguishable motifs. The motif measures 90 by 40 cm.

Motif 3 is a large anthropomorphic female human figure rendered in a black pigment in a line and solid infill form. Figure 4 reveals further details showing the complexity of painted elements of Motif 3 revealed through D-Stretch filter YBK. This motif is surrounded by other black pigment motifs, however it cannot be ascertained whether these constitute a scene with this motif. This motif is an atypical depiction of a female because there are at least three types of spears painted across the figure from right to left, with one spear painted across the figure from left to right giving the impression the female figure is being 'speared'. This is atypical within the general corpus of Arnhem Land rock art, as male figures have a higher representation of such depictions of 'spearing'. The uppermost spear appears to be a composite 'shovel-nosed' type, with a solid stone or flat wooden point (Chaloupka 1993). That painted across the figure's torso is typical of a uniserial barbed spear (Chaloupka 1984; Lewis 1988). A further three lines are painted diagonally across the torso that resemble a composite three pronged spear, or are perhaps three separate simple spears. A fourth spear is painted diagonally from left to right across the thigh portions of the figure. An oval shape with small lines protruding from the outer edge of the shape is painted over the right thigh. Unlike Jelinek (1989:173), Mountford (1956:153–154) did not make any reference to the multiple spears that seem to be associated with this figure, nor that it was painted in a black pigment.

Antiquity of Motifs According to Taphonomic Indicators and Stylistic Analysis

Classification of anthropomorphic motifs according to form, or 'style', is exceedingly problematic, mainly owing to the appearance of such figures throughout the entire painting sequence (Bednarik 2002:1214). Motifs with non-diagnostic features, such as those lacking individualising forms, methods or stylistic conventions, depicted without material culture, are difficult to allocate to a temporal phase. It is only through mobilising multiple lines of evidence—'cabling', as discussed by Chippindale and Taçon (1998:93)—that assumptions about the antiquity of motifs can be made. Most researchers continue to utilise the revised chronological stylistic sequence for western Arnhem Land presented by Chippindale and Taçon (1998:107), with the basis of art styles originating from Chaloupka (1993). Yet major issues with the chronology remain. Research undertaken in the early 1990s to test the stylistic sequence, for example, recorded the superimposition of all motifs within the Kungurr and Brockman sites in Kakadu National Park (Chippindale and Taçon 1993). The results illustrated that the majority of art within the sample could not be allocated to a Chaloupka style. Other researchers, such as Lewis (1988) and Haskovec (1992), have suggested major changes are required to the sequence owing to major disagreements over particular stylistic sequences.

Mountford (1956) argued that the motifs at Minjnyimrindawabu could be assumed to have considerable age owing to the use of the term 'Mimi'. This term was used by Indigenous informants to denote art work which

was produced by earlier peoples (Chippindale and Taçon 1998:94), though they also painted Mimi figures themselves. Jelinek (1989:173, Figures 188a and 190a) recorded similar motifs within his Gallery 1 at Inanagurduwil I–III, describing them, 'whether white or red, [as belonging] to the same (Late Archaic) style and probably [coming] from the same period' (see also Jelinek 1989:179). Although he did not specifically refer to black pigment, Jelinek (1989) included these motifs within his general assessment of the panel and it is highly likely he attributed the black pigment motifs to this period as well. Under his chronology, the Late Archaic style was attributed to a period spanning from the Pleistocene to 5000 BP (Jelinek 1989:479–480).

Yet there are several indicators suggesting that the motifs may be much younger. Motif 3 is amongst the last painting events in the sequence of superimposition on the panel. Motif 3 superimposes a number of now significantly weathered motifs, with the weathered non-distinct imagery being polychromatic (yellow, red and white). White and orange pigments are known to have the least permanency, as they do not bond to the rock substrate like pure red pigment and thus are highly susceptible to weathering (Chippindale and Taçon 1998:103). As such, paintings containing white, orange and yellow pigments have been generally assumed by archaeologists to be of a younger age, especially in poor preservation contexts such as MN12.

Motif 1 is a static, full bodied simple figure and, as such, could be diagnostic of numerous styles from the Intermediate (10–6 K) or New Phase (6 K to present), as depictions of large human figures are found throughout these phases (Chippindale and Taçon 1998; Taçon and Chippindale 1994). Assessing the material culture associated with the motif in this case assists in chronological identification (after Lewis 1988). The spears depicted in Motif 1 are typical of ethnographic examples of goose hunting spears (Spencer 1914). This type of technology is commonly associated with the 'Freshwater Period', when magpie geese colonies flourished in the expansive freshwater wetlands (Finlayson et al. 1998; Whitehead et al. 1990).

The non-distinct classification of human motifs also impacts on the stylistic classification of Motifs 2 and 3. The depiction of upwards bent arms and legs in a static and frontal position, as depicted in Motif 2, can be commonly found in anthropomorphic motifs throughout the entire sequence of Arnhem Land art, though it is most common in the late Holocene period (Chaloupka 1993). The material culture in Motif 3 indicates that the motif might be of a younger age. While simple, uniserial and pronged spear types are known to have been utilised throughout the Holocene, shovel-nosed spears or leilira blades are known only to occur in the late Holocene or contact period (Allen 1989; Taçon 1991). It is presumed that the production of shovel-nosed spears was bounded in different social circumstances than the more common smaller projectile points, and indeed, ethnographically, shovel-nosed spears were recorded as part of tribal ritual exchange around Gunbalanya in the 1940s (Allen 1989; Berndt and Berndt 1988).

Methods

The rock art motifs selected were analysed by pXRF in three stages for a wide variety of chemical elements in situ in the field. For pXRF analyses a Bruker Tracer III-V pXRF was employed, equipped with a rhodium tube, peltier-cooled

Si-PIN detector at a resolution of approximately 170 eV (electron Volt) FWHM at the Mn K peak (5.9 keV [kilo electron Volt] at 1000 counts per second) and a 1024 channel configuration multichannel analyser. Initially, instrument parameters for this case study were 40 keV, 15 μ A, using 0.1524 mm Cu [copper], 0.0254 mm Ti [titanium] and 0.3048 mm Al [aluminium] filters in the x-ray path, and a 100 second live-time count at 185 FWHM setting. This is the manufacturer recommended setting for higher Z elements (>Fe [iron]) for silicate rocks. Additional analyses were conducted for light elements (Si [silicate], S [sulphur], P [phosphorus], K [potassium], Ca [calcium], Ti, Mn [manganese]) with 15 keV, 15 μ A without filter for 100 seconds in a vacuum and finally in 'lab-rat mode' with 40 keV, 1.1 μ A for 180 seconds, also in a vacuum. Interferences from air were minimised by placing the instrument as close as possible to a flat surface of the sample. Net values of the samples were calculated with the Bruker ARTAX Spectra 7.1 package. Nine correction cycles were run for background stripping and peak deconvolution. Presence of elements in the pigment were assessed by subtracting mean net values of three bedrock analyses in close vicinity of the motif¹ and mean net values of four red pigment analyses of underlying rock art motifs. For this study, we refrained from calibrating the net values to actual elemental composition, as the argument is based on qualitative presence/absence of important signature elements for common lead ores in Australia (S [sulphur], Zn [zinc], Ag [silver]).

The difficulties of in situ analysis of rock art pigments have recently been discussed by Forster et al. (2011) and Huntley (2012). The main methodological obstacle is the surface structure of the analysis spot and the critical penetration depth of the x-ray beam² (Potts et al. 1997a, 1997b). As the penetration depth of the beam is an equation of the density of the penetrated surface, the energy input for analysed

elements and the mass attenuation coefficient, it is assumed here that for heavier elements only a maximum of ~50% of the count rate is related to the pigment itself (Markowicz 2011). On the other hand, light element geochemistry is particularly difficult to assess in non-laboratory conditions, as the penetration depth of the beam is only a few hundred microns, making it exceedingly susceptible to surface morphology (Forster et al. 2011; Liangquan et al. 1998; Potts et al. 1997a, 1997b). Considering these limitations, it is necessary to analyse not only the pigment itself, but also the underlying bedrock and, in the case of superimposition, the geochemical composition of underlying earlier paintings.

Results

As shown in Table 1, we report analysis of selected light and heavy elements (Si, P, S, K, Ca, Ti, Mn, Fe, Ni [nickel], Cu, Zn, As [arsenic], Sr [strontium], Zr [zircon], Ag, Sn [tin], Sb [antimony] and Pb [lead]).

Bedrock

The bedrock of the area is described as quartz sandstones, conglomerates and dolostones intersected with hematitic and brown ferruginous sandstones of the Katherine River Group in the Kombolgie Formation (Ahmad and Scrimgeour 2006; Mitchell et al. 1983; Plumb and Roberts 1992; Smart et al. 1980). As such, it consists mainly of quartz (SiO₂), dolomites, (CaMg[CO₃]₂), feldspars ([K,Na,Ca]AlSi₃O₈) and iron-oxides (Fe₂O₃). The pXRF analysis detected Si, K, P, S, Ca and Ti in significant amounts in the bedrock. Bearing in mind the limitations of geochemical analysis in non-laboratory conditions, it is suggested that all analyses of elements lighter than Fe, such as Si, P, S, K and Ca (Forster et al. 2011), are quantitatively unreliable. In reference to the possible natural origin of the pigment, Cu, Zn and Ag were detected in the bedrock.

1 Analysis spots were selected after assessment of the area with D-Stretch (Harman 2010).

2 Equation to calculate penetration depth of x-ray beam: $t = -\ln(I/I_0) / ((\mu/p)*p)$ [$-\ln(I/I_0) = 4.61$], where p equals the density of the analysed compound.

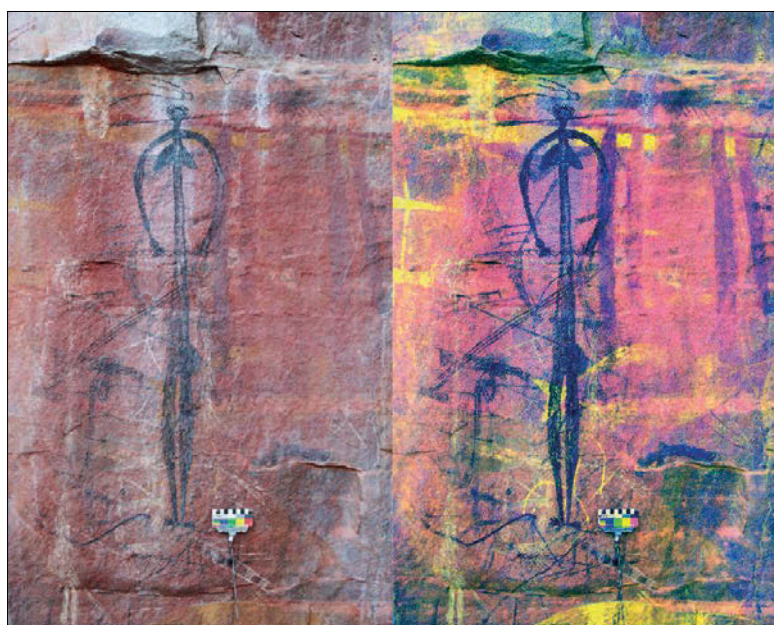


Figure 4 MN12 Motif 3 shown with D-Stretch filter YBK for black pigment enhancement.



Figure 5 MN12 Motif 3 illustrating the locations sampled for pXRF.

Motif 3

The art panel studied contains multiple painting episodes, with the black Motif 3 underlain by red pigment motifs. Figure 5 illustrates the locations from which pXRF samples were taken on Motif 3. The geochemical composition and its colour suggest that iron-oxide (e.g. hematite) is the main constituent of the underlying red pigment. Comparatively high counts of iron and sulphur were detected in Motif 3. Some amount of lead was also identified in the analysis (Table 1); however, it is unclear whether this originates from weathering of the black pigment.

Initially, it was assumed that the black pigment consisted of charcoal or a manganese-oxide, as these materials have been previously reported for western Arnhem Land rock art and elsewhere (Chaloupka 1993; Huntley et al. 2011). Manganese, however, was not detected in amounts exceeding the background readings. Elements identified with significant higher counts than underlying bedrock or red pigment are Si, As³ and Pb (Table 1). As discussed before, net values of Si are dismissed as either machine-induced or as a weathering product of the underlying sandstone. The main constituent of the black pigment is Pb, although without significant amounts of S and Zn, elements commonly associated in Australian natural lead mineralisation, suggesting processed metal lead as the most likely source of the raw material (Geoscience Australia 2004). The identification of

lead in the pigment is supported by analysis of several spots with less black pigment cover (Figures 6A and 6B), reducing significantly the amount of lead detected (Table 1).

Discussion

Naturally Occurring Lead Sources

Natural occurring near-surface lead deposits have been reported across Australia. The most common lead mineral with a dark grey streak is galena (PbS). In Australia, surface deposits of galena are usually metamorphic formations, though galena can occur in limestones, sandstones and calc-silicate rocks. Weathering of galena results in carbonated lead minerals, such as cerussites (PbCO₃), or lead sulphites, such as anglesites (PbSO₄); however, these minerals can be excluded as a possible source of the pigment, as their streak is white (Deer et al. 1992). In the NT, particularly in the 'Top End', lead ores are usually associated with uranium deposits, the closest to MN12 being the Cahill Formation in the Pine Creek Inlier, which is now mined at the Ranger Uranium Mine (approximately 30 km southwest of Urrmarning) where small amounts of lead-zinc ores are

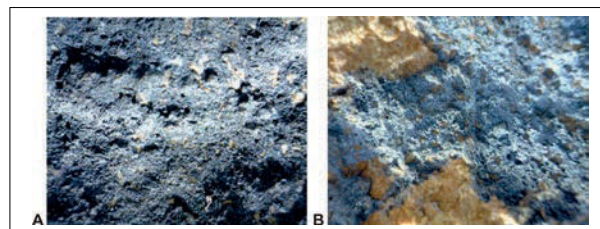


Figure 6 Microphotograph of black pigment showing (A) thick and (B) thin cover.

3 The detection of As in the presence of high Pb with pXRF has been problematic in the past, as the K α peak of As at 10.5 keV and the L α peak of Pb at 10.6 keV overlap to produce a strong interference and result in a significant increase of the detection limits for arsenic.

	Bedrock		Underlying Red Pigment		White Erosion Crust		Black Pigment (Thin)		Black Pigment (Thick)	
	Average (n=4)	SD	Average (n=4)	SD	Average (n=4)	SD	Average (n=3)	SD	Average (n=3)	SD
Si K12	4517	672	3763	495	16,843	8836	6588	2682	20,415	2635
P K12	7768	5440	2245	2509	---	---	122	155	2	1
S K12	1676	1290	5050	1182	949	28	4147	1780	2175	391
K K12	5867	4018	5744	176	2538	49	5569	1324	3017	93
Ca K12	1662	1517	1955	749	615	172	1114	528	2318	211
Ti K12	1122	654	2170	484	269	85	1563	267	1198	850
Mn K12	879	431	880	165	578	154	462	132	770	114
Fe K12	18,883	9714	81,916	13,351	3271	1954	64,046	9737	61,873	26,413
Ni K12	245	30	116	18	133	4	133	8	239	36
Cu K12	110	7	55	8	59	14	63	26	77	15
Zn K12	255	100	103	4	112	5	111	28	318	23
As K12	42	4	55	4	9	2	70	28	452	136
Sr K12	3797	3224	626	74	1589	403	760	70	4281	355
Zr K12	2834	124	411	90	499	318	368	80	1682	265
Ag K12	1715	66	335	34	396	139	439	80	2145	371
Sn K12	694	130	495	95	447	165	555	53	608	259
Sb K12	892	27	537	168	27	21	687	109	760	204
Pb L1	129	64	666	104	19	6	991	192	10,122	2768

Table 1 Summary statistics of net values of MN12 pXRF analysis of bedrock, white erosion crust, hematite and lead pigment; the thicker the black pigment the higher lead counts, indicating that the black pigment indeed is metal lead. The white erosion crust was also measured to assess possible contamination through leaching of lead from the bedrock; no lead was found in the erosion crust.

associated with uranium-oxide mineralisation (Needham 1988). Galena, as well as other common lead mineralisations, can be excluded as potential sources for the pigment, as the pXRF analysis only showed traces of Zn and S comparable with the background amounts, indicating they were associated with the underlying bedrock rather than the pigment.

Processed Metal Lead

The lack of elements usually associated with natural lead mineralisation indicates that the lead used for painting motifs is more likely to derive from processed metal. It is suggested that procurement of lead pigment most likely resulted from interaction and/or exchange with Macassan, Dutch or other European settlers. Initial contact between Aboriginal groups and Macassans and Dutch explorers is known to have occurred from the 1700s (Allen 2008; Clark and May 2013; Hiscock 2008). Settlement of the Arnhem Land region by British colonists is documented as beginning ca 1839. Indigenous and British interactions in the area intensified with the development of the buffalo hunting industry in the 1890s and is known to have involved the bartering and exchange of high value items, such as metals and tobacco (Powell 1996). Lead was a very common multipurpose metal in colonial times, used variously for minting coins, water pipes, lead-based paints, sheeting, sheathing for hulls, anchor stocks, seals, stamps, tablets, musket balls and shot cartridges (Tripathi et al. 2003; van Duivenvoorde et al. 2013). The largest amounts of lead transported, however, were most likely ship ballast.

It has been well established that there was pre-European evidence of trading with Macassan fishermen and that metals were part of the items exchanged (Clarke 1994; Hiscock 2008; Lamilami 1974; MacKnight 1969, 1986; Mitchell 1994, 1996). MacKnight (1969:223) reported finding a lead ball (possibly a musket ball) at the Anuru Bay Macassan trepang processing site on the northwest Arnhem Land coast. Fredericksen (2003) reported miscellaneous finds of lead musket balls from the colonial Fort Dundas (occupied from 1824–1828) on Melville Island. Evidence of metal in general, mostly tin and iron, has been recovered from excavations and observed on the surfaces of many rockshelters in western Arnhem Land (Chaloupka 1993; Clarke 1994; Guse 1998; Guse and Woolfe 2006; Mitchell 1994; Schrire 1982). Although there have been no reports of lead in these studies, Macassan contact with European traders in the Indonesian archipelago reaches back into the sixteenth century (Knapp and Sutherland 2004).

Apart from minor exploratory incursions, the Red Lily Lagoon area experienced regular European settlement only after 1891. The large Asian water buffalo herds of the East Alligator River were a potentially lucrative enterprise for European settlers in the NT and in 1891 Paddy Cahill became one of the first shooters to move into the area. Aboriginal labour was soon incorporated into buffalo enterprises, and Indigenous people were attracted to Cahill's settlement, where tobacco and meat could be readily obtained (Forrest 1985:87). The incorporation of Aboriginal labour into the buffalo industry starts to be widely reported in the local newspapers during the 1890s (*Northern Territory Times and Gazette*) (Figure 7). By 1897, rifles, shotguns and lead ammunition started to enter into Indigenous ownership in Arnhem Land in large quantities (Wesley 2013). Aboriginal men were typically armed with less expensive, older Martini Henry rifles and shotguns to assist the horse-mounted white shooters to follow up and dispatch the wounded buffalo (Wesley 2013).

We cannot be certain of the exact source of the pigment used in Motif 3 in MN12. We can infer, however, that the lead in the pigment most likely derived from pulverised shotgun ammunition. In Australia and abroad, evidence of trading in shotgun bullets between Indigenous groups and European settlers is scarce. Lead bullets from Martini Henry rifles occasionally occur in archaeological sites, including Leija on the Barkly Tablelands (Ken Mulvaney pers. comm. 2013) and in the Urkuk Village sites in the Duke of York islands (Ian Lilley and Sally Brockwell pers. comm. 2013). Surface artefact assemblages elsewhere at Red Lily Lagoon include flaked glass implements, iron wire, clay pipes, beads and wooden implements worked by metal, all of which demonstrate that European materials were purposely adapted for local use. Excavations on the wider Arnhem Plateau, such as at Malarrak rockshelter in the Wellington Range, recovered large amounts of tin, iron and glass. Roberts and Parker (2003:26) documented a cache of material culture at 'Artefact Cave' near Mt Borradaile (Awunbarna), some 40 km to the northeast of Urrmarning, including a Bell and Black matchbox tin (1870), a Macassan adze, a domino piece, a tobacco pipe, a bag of shot (Figure 8), and hand-forged nails and screws.

This research has illustrated the difficulty of placing rock art motifs within a chronological framework regardless of the style in which the motif has been painted. The importance of applying pXRF to this study has allowed us to identify the introduction of a foreign raw material into the material culture of Indigenous society in Arnhem Land, which can be considered as an important chronological 'event marker'. Event markers, along with proliferation events, are significant in the identification of the introduction of new cultural materials (see Hiscock 2008). The growing body of research on Arnhem Land culture contact points to seventeenth century origins for foreign materials entering Arnhem Land (Clarke 1994; MacKnight 1969; Mitchell 1994; Taçon et al. 2010; Theden-Ringl et al. 2010). The use of an introduced material to paint motifs that are irrefutably Indigenous subjects rather than introduced imagery (i.e. ships, guns, Europeans) attests to the difficulty in assigning chronology based solely on style. Without knowledge of the use of lead in the pigment, and based on current assumptions on the introduction of Arnhem Land rock art styles, the age of the black motif could be grossly over-estimated. Estimating motif age is arguably one of the most difficult areas of rock art research in general. Given the evidence presented above, the most likely period for painting Motif 3 coincides with the escalation of English settlement in Arnhem Land from the mid- to late nineteenth century, owing to the introduction of much larger quantities of foreign materials into Indigenous society.

Conclusion

The application of pXRF to the study of rock art is a relatively recent development in Australian archaeology and is still in its experimental phase (Huntley 2012). However, this study has demonstrated that the use of pXRF can make a meaningful contribution to the study and conservation of rock art. The application of pXRF analysis to one such motif has demonstrated that it, at least, comprises lead rather than some other black substance, such as charcoal or manganese. This discovery has expanded our knowledge of pigment diversity and contributed significantly to a greater chronological understanding of the rock art sequence at Minjnyimirnjdawabu, and indicated that at least some of



Figure 7 Buffalo shooters (NT Library; Kathryn Brown Collection. Photo Number PH0413/0041).



Figure 8 Cache of contact materials at a rockshelter near Awunbarna to the north of the study area containing a 'bag of lead shot' (photo sourced from <<http://www.flickr.com/photos/winam/3734029464/>>).

these motifs, previously assessed as being of substantial antiquity, are clearly younger than a seventeenth century origin. Importantly, it demonstrates that assumptions about chronology based on style alone may be seriously flawed and direct dating is required for the Arnhem Land artistic sequence.

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