Distinctive mulberry paintings found in northern Australia, particularly those of the Kimberley region, have been argued to represent some of the oldest surviving rock art on the continent. Significant research efforts continue to focus on resolving the age of these motifs, but comparatively little attention has been given to understanding their physical composition and potential source(s). In a pilot investigation, we conclude that (at least) two mineralogically distinct mulberry pigments occur in Gwion motifs and demonstrate that their major components can be indicatively chemically differentiated, non-invasively. Characterization of a ‘quarried’ mulberry ochre source demonstrates that these pigments occur locally as natural minerals.

KEYWORDS: MINERAL PIGMENTS, MULBERRY, OCHRE, GWION, ROCK ART, NORTH-WEST KIMBERLEY, AUSTRALIA, pXRF, SEM–EDXA, POWDER DIFFRACTION

INTRODUCTION

The presence of a distinctive mulberry hue of rock art paint has been noted in the older sections of the relative sequences described throughout the rock art provinces of the top end of Australia (from east to west):

- bichrome zoomorphic motifs in Cape York Peninsula (Trezise 1977; Cole and Watchman 1995) including Chasm Island (McCarthy 1967);
- human–snake composites in the Riversleigh World Heritage Area (Taçon 2008);
- large naturalistic animal motifs and Dynamic Figures of Arnhem Land (Chaloupka 1993; Lewis 1997; David et al. 2011, 75; Welch 2012b);
- anthropomorphic figures with headdresses and tassels in the Wadeye–Fitzmaurice region (Taçon et al. 2003; Watchman et al. 2010);
- object prints, hand stencils, animal and anthropomorphic (Karlinga) figures of Keep River (Taçon et al. 2003);
- stencils (hand and material culture), Irregular Animal Infill and Gwion figures of the Kimberley (Walsh 1988, 1994, 2000; Welch 1993b,c); and
- there are also indications that mulberry pigments are present in the oldest sections of rock art sequences in the broader South-East Asian region (Plagnes et al. 2003; Fage 2012).
Although the mulberry hue appears to be strongly associated with the older section of rock art sequences described (cf., Welch 1993c), it is not confined to them. Mulberry pigments are reasonably common in the Kimberley motifs of the Painted Hand2 and Wanjina3 periods (Welch 1993b,c; 2003, 5; Walsh 2000). Nonetheless, arguments have been made for an association between (particularly monochrome) mulberry pigments and the speculative antiquity of motifs (Welch 1993a; Walsh 2000).

Both relative stylistic sequences proposed for the rock art of the Kimberley rely on image superimposition and interpretations of ‘differential weathering’ for chronological control (Welch 1993a,c; Walsh 1994). Both sequences can be broadly surmised from earliest to most recent periods as follows: Pecked Cupule (petroglyphs); Irregular Infill Animal; Mambi Gwion; Yowna Gwion; Wararrajai Gwion; Painted Hand; and Wanjina (Welch 1993a; Walsh 1994). Much attention has been paid to trying to resolve the age of rock art styles executed in mulberry pigments in Australia (Watchman et al. 2010), particularly the Gwion motifs of the Kimberley (cf., Morwood et al. 1994; Roberts et al. 1997; Watchman et al. 1997; Aubert 2012), while comparatively little effort has been expended on understanding the composition of this distinct paint hue. Routine pigment characterizations have been incorporated into comprehensive numerical dating investigations (Watchman et al. 2010), again particularly in the Kimberley (Watchman 1990, 1997a; Watchman et al. 1997; Ward et al. 2001), but few archaeological or conservation-based studies have reported mulberry4 pigment characterizations outside of these (cf., Clarke and North 1989). There is therefore little data from northern Australia that can be used to examine if the distinctive mulberry paint observed across the top end of the continent is derived from a distinctive mineralogical ochre source or sources; as part of a composite paint recipe (Welch, 1993a, 15; Morwood et al. 1994, 83); or if the mulberry hue is attributable to site taphonomy. As part of an ongoing research programme in the north-west Kimberley, we have chemically and mineralogically characterized mulberry rock art pigment to begin to address these broader questions.

The Kimberley study area

The Lower Mitchell Falls area was intensively surveyed by our project team in June 2010, with a total of 32 archaeological sites recorded at ‘Reindeer Rock’ (Wilson 2006; Welch 2012a) and a further 25 in the Malauwarra7 site complex approximately four kilometres to the south (Fig. 1). These sites were predominantly rock shelters containing pigment art and other surface finds such as ochre and knapped stone. Mulberry pigment samples (MM20 and RRS) were collected in the Reindeer Rock complex, with a third legacy specimen (K1) from the Drysdale River National Park being re-examined (Roberts et al. 1997; Watchman 1997a; Watchman et al. 1997; Fig. 2). A fourth mineral accretion sample from the Malauwarra complex (KSMA) is described to contextualize pigment characterizations.

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2The name convention of the Wunambal Traditional Owners—previously ‘Clawed Hand’ (Welsh 1994, 2000).
3The spelling currently used by the Wunambal Traditional Owners. Wandjina has historically been the dominant spelling (e.g., Crawford 1968, 1997; Morwood et al. 1994, 2010; Ward et al. 2001).
4The Wunambal name for this motif style—previously ‘Sash’ figures (Welsh 1994, 2000).
5Wunambal nomenclature—previously ‘Clothes Peg Figures’ (Welsh 1994, 2000; Watchman et al. 1997; Ward et al. 2001) and bichrome art period, straight part figures (Welch 1993a,c).
6This denotes a distinctive purple hue of paint equivalent to the Pantone Matching System (PMS, C = solid coat) 4965C to 519PC. ‘Mulberry’ is the term used historically to describe this distinctive hue in Kimberley rock art (Walsh, 1988, 1994, 2000; Welsh 1993a,c). Researchers working in other regions of northern Australia have sometimes used the term ‘purple’ to describe the same distinct colour (e.g., Taçon et al. 2003). For the purposes of the discussion herein, we consider these terms interchangeable.
7The Wunambal name, given to the area by the Traditional Owners.
Inevitably, an overlap exists between the geochemical signatures of rock art production and products of geological weathering: (1) because rock art pigments are mixtures of natural minerals (often termed ‘ochres’), themselves products of geological weathering (Watchman 1990; Rowe 2001); and (2) because the complex taphonomy of rock shelter environments is far from static, especially in monsoonal (palaeo)climates (Ford et al. 1994; Bowler et al. 2001; MacLeod and Haydock 2008; Wyrwoll et al. 2012). The geology of the north-west Kimberley is a Proterozoic craton, bounded at its southern extent by orogenic belts (Li 2000). Our field observations of the geology in the Lower Mitchell Falls are consistent with descriptions of pale purple and white, to pale pink quartzarenite successions of King Leopold Sandstones by Williams to the south-east (2005, 114, table 1). The King Leopold succession is unmetamorphosed and essentially undeformed (Schmidt and Williams 2008), an important distinction, as the harder strata are not quartzite—rather, they are highly silicified sandstone (Watchman 1997b, 23) or quartzarenite. The quartzarenite strata we observed were characteristically texturally ‘mature’ regardless of colour (Williams 2005, 118). The harder quartzarenite expressed a distinctive block-form in response to geological weathering processes as opposed to the underlying poorly consolidated, ‘true’ coarse-grained sandstones, which display scalloped, cavernous weathering, often resulting in columns or piers (Twidale 1968). The substrate from Drysdale River National Park (K1) is darker purple and grey banded medium-grained quartzarenite, with unidentified mulberry grain inclusions. Pigmentaceous geological units occur locally as minor intervals of siltstone and (rarer) conglomerate in the King Leopold Sandstone (Griffin and Grey 1990; Dowens et al. 2012).
Figure 2  A detail of Mambi Gwion (top left), with the MM20 conjoin highlighted in black outline (top right): scale 10 cm. K1 prior to sampling (bottom) (photograph by Grahame Walsh, 1989). Mambi Gwions centre of the panel, ~65 cm tall; Yowna Gwions bottom of the panel, ~20 cm.
2007). In the centre of the study area, a basalt dyke of Carson Volcanic (the Mitchell Plateau) includes pigmentaceous strata as interbedded micaceous siltstones with minor pyroclastic rocks and feldspathic sandstones (Williams 2005, 111; Dowens et al. 2007, 87).

**Previous mulberry pigment characterization in the Kimberley**

Previous characterizations of Kimberley rock art have summarized mulberry paints as being dominantly composed of an inorganic jarosite mineralogy, and red paints hematite (Table 1) (Watchman et al. 1997, 39; Ward et al. 2001, 17). Watchman et al. analysed five partial motifs to draw this conclusion, including the K1 Mambi Gwion⁸ (Ward et al. 2001, 18). Previous investigations specifically examined the use of blood and/or other organic constituents as a binding/colouring media (Loy et al. 1990; Watchman 1997a, 45), as contemporary reports had attributed the distinctive mulberry hue from Irregular Infill Animal and Gwion motifs to an organic base, possibly tree sap (Mosby 1993, 120–1; Welch 1993c, 15; Morwood et al. 1994, 83; Crawford 2001, 93–4; Ward et al. 2001, 17). No carbon-bearing binders were observed via scanning

### Table 1  Compounds of minerals discussed in the text

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jarosite</td>
<td>KFe⁺⁺⁺⁺(OH)₆(SO₄)₂⁻⁻⁻⁻</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₄Si₂O₅(OH)₄</td>
</tr>
<tr>
<td>Illite</td>
<td>(K,H)₂O(Al,Mg,Fe)₆Si₄O₁₀[(OH)₂,(H₂O)]</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₃Si₄AlO₁₂(OH,F)₂</td>
</tr>
<tr>
<td>Halloysite</td>
<td>Al₄Si₄O₅(OH)₄</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Aluminium phosphates</td>
<td>AlPO₄</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl₂Si₂O₈</td>
</tr>
<tr>
<td>‘Chinese Purple’</td>
<td>BaCuSi₃O₉</td>
</tr>
<tr>
<td>Calcium fluoride</td>
<td>CaF₂</td>
</tr>
<tr>
<td>Amorphous silica</td>
<td>SiO₂·nH₂O</td>
</tr>
<tr>
<td>Taranakite</td>
<td>K₆Al₆(HPO₄)₆·(PO₄)₂·18(H₂O)</td>
</tr>
<tr>
<td>Whewellite</td>
<td>Ca(C₂O₄)·(H₂O)</td>
</tr>
<tr>
<td>Weddelite</td>
<td>Ca(C₂O₄)·2(H₂O)</td>
</tr>
<tr>
<td>Mica (phlogopite)</td>
<td>KMg₂Al₃Si₂O₄F(OH)</td>
</tr>
<tr>
<td>Scawtite</td>
<td>Ca₄(Si₆O₁₈)CO₂·2H₂O</td>
</tr>
<tr>
<td>Syngenite</td>
<td>K₃Ca₃(SO₄)·2H₂O</td>
</tr>
<tr>
<td>Loweite</td>
<td>Na₁₂Mg₆(SO₄)₁₃·15(H₂O)</td>
</tr>
<tr>
<td>Bassanite</td>
<td>2(Ca)₂(SO₄)·(H₂O)</td>
</tr>
<tr>
<td>Dawsonite</td>
<td>NaAl(CO₃)·(OH)</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>(Na,Ca)₂⁰⁺⁺⁺⁺(Al,Mg)₆Si₂O₁₀(OH)₂·n(H₂O)</td>
</tr>
<tr>
<td>Magnesium copper sulphide (similar to alpersite)</td>
<td>MgCu(SO₄)·7H₂O</td>
</tr>
<tr>
<td>Rostitie</td>
<td>Ca₃(Co,Mg)(AsO₄)₃·(H₂O)</td>
</tr>
</tbody>
</table>

electron microscopy (SEM) (Watchman 1997b, 39; Ward et al. 2001). Rather, consistently present minor-phase alumina silicate matrix minerals such as quartz, kaolinite, illite, muscovite and less common halloysite were interpreted as a binding/extending medium (Ward et al. 2001, 18–19). There was no suggestion that these were deliberately added as part of a paint recipe; rather, they were present as pigment matrices. Alumina silicates, calcium sulphates (gypsum/anhydrite) and aluminium phosphates were also persistent as minor phases, suggesting a complex and actively weathering geological environment for rock art (Ford et al. 1994; Ward et al. 2001, 18–19).

Jarosite is a secondary mineral requiring water (typically dilute sulphuric acid in ground water) to form (Klingelhofer et al. 2004; Bell et al. 2010). In terrestrial environments, jarosite compounds form via the oxidation of iron sulphides such as pyrite, and are likely to be present as low-grade mineralized veins within metamorphic and igneous rocks (Watchman 1997b, 53; Dutrizac 2004, 11). Jarosite has been reported in geological weathering products of humid, subtropical climates internationally (Tuttle and Breit 2009, 1550) and explicitly in the tropical climates of the Kimberley region, Australia (Ford et al. 1994; MacLeod and Haydock 2008).

Watchman used the term ‘jarosite’, as do we, to describe the alunite–jarosite series of sulphate minerals including natroalunite, natrojarosite, plumbojarasite and schlossmacherite, all of which may occur together and have been found in mulberry rock art pigments in the north-west Kimberley with other sulphate minerals including anhydrite and/or gypsum (Watchman 1997b, 45–6; Ward et al. 2001, 17). Jarosite has also been identified in \((n = 1)\) yellow and \((n = 1)\) red Kimberley rock painting, and with pyrite as a phase in dark brown to black shelter surface deposits (but it is not clear if these surface crust were within our study area or the Napier Range) (Ford et al. 1994, 59; Watchman 1997b, 47).

SEM (including energy-dispersive X-ray analysis, or SEM–EDXA) was routinely used by Watchman for pigment characterization, particularly where insufficient sample was available for conventional powder X-ray diffractometry (XRD), or to decipher or confirm crystallography (Watchman 1997b; Watchman et al. 1997, 2010; Mardaga-Campbell et al. 2001; Ward et al. 2001). Hematite was distinguished from jarosite via SEM–EDXA by the presence of Fe and the absence of K and S (Watchman 1997b, 47). Phosphate, concluded to be aluminium phosphate, was found to occur in \((n = 2)\) mulberry, \((n = 1)\) red–mulberry and \((n = 2)\) red rock art paints in the Kimberley via SEM–EDXA (Watchman 1997b, 50–1).

**Other mulberry pigment characterizations**

In the Wadeye–Fitzmaurice region east of the Kimberley, characterization of a single mulberry anthropomorphic figure is reported. Described stylistically as akin to the Gwion motifs of the Kimberley and the Karlinga figures of the Keep River region, rather than the Dynamic Figures of Arnhem Land (Taçon et al. 2003, 2), its mineralogy was determined to be quartz, gypsum, hematite and anorthite (feldspar), and the colourant ‘presumably hematite’ (Watchman et al. 2010, 224). In the Laura region of Queensland, jarosite was identified as a minor phase in both \((n = 1)\) white and \((n = 2)\) red rock art (Watchman et al. 1993, 143; Ward et al. 2001, 18). The consistent minor contribution of jarosite was concluded probably to be a ‘contaminant’ from weathering of local iron-rich minerals (Watchman et al. 1993, 143). Because of this potential for ‘contamination’, minor jarosite phases within red motifs were described as ‘uncertainly anthropogenic’ (Ward et al. 2001, 20). In the Chillagoe region of northern Queensland, Watchman, again using elemental analysis (SEM), identified jarosite as the major constituent of red and yellow pigments in lamina rock shelter surface crusts (Mardaga-Campbell et al. 2001, 203).
South Australia, natrojarosite has been observed as the colour-producing constituent in yellow ochres, a minor phase in red ochre quarries (Jercher et al. 1998, 385, 390).

A variety of mulberry archaeological pigments have been reported internationally, most produced via technologically complex processes. For instance, the ‘Chinese Purple’ used to decorate the famous Terracotta Warriors and Han dynasty pottery was created using a lead flux during firing at temperatures between 900°C and 1100°C (Liu et al. 2007, 1878–9). ‘Tyrian’, or royal purple, was obtained from shellfish glands and its earliest documented uses are associated with highly ritualized burial practices (Colombini et al. 2004; Devièse et al. 2011). Of particular relevance, naturally occurring mulberry hematite (death’s head—caput mortuum, also referred to as usta, ostrum and usta purpurissimum) and purple calcium fluoride (called murra, murrha, murrina and myrrhina) were reportedly used by fresco artists, including a process of synthesizing a ‘violet’ hue from red ochre by heating it with vinegar (ostrum) (Richter et al. 2001, 1–2; de Oliveira et al. 2002, 536).

Previous mineral accretion characterization in the Kimberley

As with the work presented here, previous mineral accretion investigations were undertaken to help untangle the chemical and structural signatures of environmental and cultural processes. Watchman’s work in the north-west Kimberley concluded that ‘... accretions are generally composed of amorphous silica which has been precipitated from seepage water. Thin oxalate-rich deposits are also formed in some rock shelters and ceilings’ (1997c, 39). Ford et al. (1994, 60) identified tatanakite, an uncommon aluminium phosphate mineral, as the major accretion component in a sandstone shelter on the Mitchell Plateau (cf., MacLeod et al. 1997, 68–9). A finding consistent with the observation of aluminium phosphates in both red and mulberry Gwion motifs, white rock art pigments and an orange mineral accretion in the Drysdale River National Park (Watchman 1997b, 21; Ward et al. 2001, 51, 88).

Salts (including phosphate salts) and clays are reported in all amorphous silica accretions in the north-west Kimberley (Watchman 1997a). All mulberry Gwion motifs analysed by XRD contained gypsum, and the majority also contained anhydrite (Ward et al. 2001, 88). Oxalates, most commonly whewellite, were identified in the younger Wanjina motifs (Ford et al. 1994; Watchman 1997b, 47; Ward et al. 2001, 18–19). In situ chemical alterations of lamina calcite pigment (conversion of calcite to calcium oxalate) in Wanjina motifs has been posited in the western Kimberley (Ford et al. 1994), as have calcite pigment conversions in the white rock art pigment of the Kakadu National Park, located west of the Kimberley (Clarke and North 1991). Weddellite, whewellite and gypsum with minor quartz and clay (kaolinite) were identified in the coolest parts of the roof of a sandstone shelter on the Mitchell Plateau (Ford et al. 1994, 64). Oxalates have been used to produce numerical age determination for rock art within the study area (Morwood et al. 2010, 5), as have the organic fractions laminated within amorphous silica skins (Watchman et al. 1997).

Calcium oxalate minerals in other rock art regions

Whewellite has been reported as a constituent in rock art pigments in the United States, South Africa and Argentina (Edwards et al. 1998; Wainright et al. 2002, as cited in Arocena et al. 2008, 301; Escott et al. 2006). Like Ford et al. (1994), most attribute its occurrence to biofilms (Wainright et al. 2002; Arocena et al. 2008). However, recent studies in South Africa and Mexico have proposed, on the basis of the presence and uniform distribution of globular habit crystal
morphology, that whewellite (from plant sap such as aloe vera) has been purposely added to paint as a binder, extender and/or whitener (Arocena et al. 2008; Watchman pers. comm.).

The archaeology of mulberry pigments in northern Australia

Mulberry pigments are noted in Irregular Infill Animal, Gwion and Painted Hand sections of the relative Kimberley rock art sequence (Welch 1993a,c; Morwood et al. 1994; Walsh 1994, 2000). However, the distinctive mulberry hue has been noted as most prevalent within the Yowna or ‘Bent Knee’ Gwion phase (Welch 1993a, 27; Walsh 1994, 2000). This patterning is of archaeological interest given the ethnographically observed spiritual significance of particular ochre sources in the region (cf., Mowaljarlai and Vinicombe 1995, 44). It has been suggested that various cultural motivations could have influenced the preparation and use of mulberry pigment. There is some ethnohistorical suggestion from Arnhem Land (to the east) that ‘highly prized’ ochre traded throughout the region was specifically selected for its mulberry colour and associated physical properties, described as having ‘... the effect of providing a rich sheen to the painted surface’ (Morphy 1989, 30–1). In the Kimberley, mulberry pigments have been attributed to an unidentified (organic) paint constituent (Welch 1993c, 15, 27; Morwood et al. 1994, 83; Ward et al. 2001); a desire for anthropomorphic figures to ‘stand out’ in high colour contrast to the rock face (Welch 1993a, 27); and the portrayal of specific subject attributes (such as very dark skin: Welch 1993a, 27). Minimum numerical age determinations produced by $^{14}$C AMS for mulberry Gwion and Irregular Infill Animal motifs of the north-west Kimberley (3880 ± 110 BP and 3140 ± 350 BP: Watchman et al. 1997, 25) and anthropomorphs in the adjoining Wadeye–Fitzmaurice and Keep River regions (4870 ± 50 BP and 4060 ± 210 BP respectively: Watchman et al. 2010, 226) are broadly contemporaneous, providing some indication that if taphonomy were to be responsible for the distinct mulberry hue, these processes would be likely to be incremental, requiring thousands of years to affect rock art. Speculative assertions of this sort can only begin to be turned into hypotheses and addressed through the collection of large (statistically significant), spatially and temporally meaningful data sets. Below, we present a methodology for the in situ indicative differentiation of major mineral phases in mulberry rock art via portable X-ray fluorescence spectrometry (pXRF), contextualize and interpret our findings with complementary laboratory techniques, and argue that this represents an exciting tool with which to collect such data.

ANALYTICAL METHODS

Sampling was opportunistic. A naturally weathered (spall) flake containing rock art motif (MM20) and small pieces of ochre from the ‘quarry’ (RRS in Fig. 3) were collected as surface finds. Both the legacy and mineral accretion samples (K1 and KSMA in Fig. 4) were semi-detached natural spall flakes removed from shelter panels (Watchman 1997b, 4; and see Table 2).

pXRF
Elemental analysis of all (unprepared) samples was undertaken via pXRF using a Bruker Tracer III-V with a rhodium tube, a Peltier-cooled Si-PIN detector, a 1024 multichannel analyser (resolution ~170 eV FWHM, manganese K$_\alpha$ peak/5.9 keV, 1000 counts per second). Parameters were 12 keV, 20 μA, a 300 s live-time count, and 185 FWHM under vacuum with a 25 μm titanium filter (Huntley 2012, 83). To reduce attenuation or fluorescence intensity loss from
Figure 3  A plan of Reindeer Rock, showing the location of RRS and other archaeological features. Mulberry shale slabs with striations and grinding (inset) and sediments containing ochreous material are mapped.
angles of incidence and detection (de Boer 1989; Jenkins 1999, 39), the instrument was placed against the surface, parallel to the area of interest, minimizing gaps created by irregular surface morphology. The thickest areas of paint were selected to maximize paint volume, as rock art is infinitely thin for XRF (Cesareo et al. 2008, 209; Shackley 2011, 10; Huntley 2012, 79). Spectra were processed using Bruker X-RayOps, S1PXRF and Spectra 7.1 software. Calculation of net peak areas (NPAs) used nine correction cycles for escape and background peaks from 0.6 to 10.5 keV (cf., Heginbotham et al. 2011 for a discussion of standardless fundamental parameters).

**SEM–EDXA**

SEM analysis of K1 and KSMA was undertaken in cross-section using a Zeiss EVO 50 SEM fitted with a LaB$_6$ filament. Chemical analyses were carried out using an iXRF EDS energy-dispersive X-ray spectroscopy (EDS) system, equipped with a 10 mm$^2$ Si(Li) detector (2006). SEM–EDXA analysis of RRS and element mapping of K1 and KSMA was undertaken using a Philips XL30 SEM with Oxford ISIS EDS (1997) and a Gatan Mini Cathodoluminescence Detector (2011).

**Powder diffraction**

Conventional powder XRD of RRS and KSMA was undertaken using a Philips PW1710 Diffractometer (1983) with Cu–K$_\alpha$ radiation and a graphite monochromator. Scanning was conducted at 0.04°/10 s from 5° to 70° 2θ. Mineral identification was undertaken using Panalytical HighScore software (2006) and *The International Centre for Diffraction Data*.
Table 2  A summary of the samples analysed

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Internal project reference</th>
<th>Site complex/Location</th>
<th>Description</th>
<th>PMS* colour</th>
<th>Analytical technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM20</td>
<td>MM20 RS-888-1</td>
<td>Reindeer Cave / Lower Mitchell Falls</td>
<td>Spall flake—partial <em>Mambi Gwion</em> (headdress)</td>
<td>491C</td>
<td>pXRF; Synchrotron PD</td>
</tr>
<tr>
<td>RRS</td>
<td>LMRO1a ochre source</td>
<td>Reindeer Cave / Lower Mitchell Falls</td>
<td>Anthropogenically exploited seam of pigment (silstone)</td>
<td>5135C</td>
<td>pXRF; Powder XRD</td>
</tr>
<tr>
<td>K1</td>
<td>K1 legacy sample, c.1994</td>
<td>Legacy Sample / Drysdale River National Park</td>
<td>Spall flake—partial <em>Yowna Gwion</em> (headdress)</td>
<td>497C</td>
<td>pXRF; SEM–EDXA</td>
</tr>
<tr>
<td>KSMA</td>
<td>LMR02c mineral accretion (off art)</td>
<td><em>Malawarra</em> – Kangaroo Shelter / Lower Mitchell Falls</td>
<td>Mineral accretion from a vertical rock art panel, including <em>Gwion</em>, Painted Hand and zoomorphic motifs</td>
<td>White (NA) and pink 5005C to 5025C</td>
<td>Powder XRD: SEM–EDXA</td>
</tr>
</tbody>
</table>

*(Pantone Matching System (C = solid coat).)*
database (2002). Mulberry pigment from MM20 was analysed at the Australian Synchrotron Powder Diffraction (Synchrotron PD) beamline. The pigment was mounted in a 0.3 mm diameter borosilicate capillary and data sets collected at a wavelength of 0.953 Å, from 5 to 85° 2θ, using a Mythen microstrip detector at a step size of 0.002° and a collection time of 10 min (5 min per detector position). Phase identification was again undertaken using Panalytical Highscore. An unsuccessful attempt was made to harvest enough pigment from K1 for Synchrotron PD.

RESULTS

pXRF

All samples were analysed using pXRF to determine major chemical components and investigate whether the distinction between iron oxide (hematite) and iron sulphide (jarosite) pigments reported via SEM (Watchman 1997b; Ward et al. 2001) was observable in Gwion motifs using this non-invasive method. Figure 5 presents a spectral overlay of the two partial headdress motifs: MM20, a *Mambi Gwion*; and K1, an ‘unrecognizable’ stylistic type (Watchman 1997b, 4) (no normalization is applied due to the close agreement of bremsstrahlung scattering). Consistent with the distinction between hematite and jarosite reported using SEM–EDXA (Watchman 1997b, 47), there is a relative dearth of P, S and K within MM20 (indicating a major hematite mineralogy) and much larger K and Fe peaks in the K1 sample (indicating a major jarosite mineralogy). This demonstrates that the geochemical differentiation of the two minerals on the basis of major elemental composition reported in prior SEM studies is observed *in situ* via pXRF (Table 3).

Figure 5  The pXRF spectral overlay for K1 (top flake, solid line) and MM20 (bottom flake, dashed line). Large K–Kα and Fe–Kα have been cropped to view detail of less abundant/lighter elements. The unlabelled peak is Fe–Kβ.
Table 3  Net peak area pXRF data (semi-quantitative): elements indicatively diagnostic of jarosite/hematite differentiation are presented in bold italics; relative abundances <20 NPA are considered below the detection limits of the instrument for this application

<table>
<thead>
<tr>
<th>Spectra</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Kα</td>
<td>195</td>
</tr>
<tr>
<td>Si-Kα</td>
<td>344</td>
</tr>
<tr>
<td>P-Kα</td>
<td>61</td>
</tr>
<tr>
<td>K-Kα</td>
<td>59</td>
</tr>
<tr>
<td>Cl-Kα</td>
<td>52</td>
</tr>
</tbody>
</table>

K1, pigment

K1, pigment, second loci

K1, substrate, case-hardened

K1, substrate, case-hardened, second loci

K1, substrate, case-hardened/mineral accretion

K1, substrate, fresh

K1, substrate, fresh, loci 2

MM20, pigment

MM20, pigment, second loci

MM20, substrate, case-hardened

MM20, substrate, case-hardened, second loci

MM20, substrate, fresh

MM20, substrate, fresh, loci 2

RSS, laboratory

RSS, laboratory, second loci

RSS, laboratory, third loci

RSS, field

RSS, field, second loci

RSS, field, third loci

RSS, field, fourth loci

RSS, field, fifth loci

RSS, field, sixth loci

Ohio Red Clay Standard (fired solid), field

Ohio Red Clay Standard (fired solid), laboratory

Ohio Red Clay Standard (fired solid), field

Ohio Red Clay Standard (fired solid), laboratory

Ohio Red Clay Standard (fired solid), field

Ohio Red Clay Standard (fired solid), laboratory
SEM–EDXA

The morphologies of the ochre source RRS and rock art K1 were compared via SEM. RRS has distinctive clusters of disc-shaped Fe structures, typical of hematite (Sepulveda et al. 2012, 98), which occur as compact bands in a clay matrix. The distinctive disc aggregation was retained in the ochre after it was ground (Fig. 6, top right). By contrast, the rock art paint (K1) has large-layered, Fe sheet structures as well as a mixture of large to much smaller Fe grains dispersed throughout the P-rich matrix. EDXA of the sheets, grains and matrix in K1 revealed that the Fe was a consistent component, whereas Fe in RRS was largely absent from the clay matrix, confined to the aggregated iron oxide discs. Another morphological feature of note within RRS are the atypical zircons (Fig. 7). While these crystals are to be expected in the shale’s ochreous matrix, the form of the zircons is exceptional. They are consistently found to have the remains of a coating determined by SEM–EDXA to be almost pure Y (minor amounts of Al considered to have derived from the clay matrix being incorporated into the spectra due to spot size).

Element maps (Fig. 8) were used to examine the occurrence and morphology of mulberry pigment constituents, Fe and clay (K, Si and Ti) previously reported as indicative of hematite mineralogy, and P, S, K and Fe identified as indicative of jarosite. Geological weathering products

Figure 6  SEM secondary electron images: cross-sections K1 (left) and RRS (top right, after grinding; bottom right, unprepared).
Figure 7. SEM secondary electron images of RRS zircons, showing the persistent remains of the Y coating; scale 10 μm (bottom left).

Figure 8. Element maps: KI motif and rock shelter substrate (left) and KSMA (right).
such as salts, commonly associated with cavernous weathering (Na, S and Cl), and chemical indices of precipitates such as calcium oxalate and magnesium calcium carbonate minerals reported in Kimberley rock shelter environments (P and Ca, and Mg, Al and Ca) were also mapped. The results show that P occurs throughout the Gwion paint (K1) and in the surface of the underlying shelter substrate. Conversely, P is only present on the surface of the mineral accretion (KSMA), and is not associated with Ca, as would be expected for oxalate mineralogy (Fig. 8). C was also mapped in relation to the potential for organic paint constituents in the K1 sample, as indicated by previous archaeological and ethnographic studies in the Kimberley (Welch 1993c, 15; Morwood et al. 1994, 83; Crawford 2001, 93–4; Ward et al. 2001, 17). C is not illustrated, as it was absent from the rock art, rock substrate (K1) and mineral accretion in both samples (KSMA), with the exception of two isolated grains, >10 μm in diameter, located on the immediate surface of the rock art (K1).

**DISCUSSION**

While the results that we have outlined in this pilot are drawn from a small number of samples, the indicative differentiation of mineral pigments via major chemistry, *in situ*, with pXRF represents a significant finding for rock art research applications. For the mulberry rock art pigments described across northern Australia, the qualitative discrimination of jarosite (Fe with elevated K and S) and hematite (Fe with much lower K and lower to absent S) via a non-invasive, field-portable technique affords greater opportunities to begin to address the types of research questions outlined in the introduction. That is, are the mulberry rock art pigment hues derived from a specific mineralogical source, from a paint recipe or due to taphonomy? We acknowledge that pXRF should be viewed as an addition to the physical analyses available for pigment characterization due to the inherent complexities of the technique for rock art applications, especially in respect of the infinitely thin nature of most rock art (Cesareo et al. 2008, 209; Lirtzis and Zacharias 2011, 127). The variation of paint thickness that we observed in the K1 via SEM (~25 to ~350 μm); the mineralogical segregation of both the rock shelter substrate and the mineral pigments (rock art) (Potts 2008, 10; see data in Table 3 regarding case-hardened versus fresh substrate surfaces); and the irregular surfaces encountered in field sampling (Potts et al. 2005) mean that pXRF cannot readily exceed a semi-quantitative resolution for rock art applications (cf., Huntley 2012 for further discussion). Despite these inherent complexities, our results demonstrate that qualitative chemical analysis of mulberry pigments with pXRF is indicatively mineralogically diagnostic, considerably alleviating ethical considerations associated with sampling rock art (Bendarik 1992; Clottes 1992; Watchman 1992). Field-based pXRF provides opportunities to collect numerically large, statistically robust data sets (Williams-Thorpe 2008) that can be targeted at a spatial resolution appropriate to archaeological research (Huntley 2012).
The occurrence of P differs markedly within the rock art pigment (K1) and mineral accretion (KSMA) observed via SEM (Fig. 8). In relation to aluminium phosphate and calcium oxalate minerals previously reported in rock shelter environs in the Kimberley, P and Al are predominantly present in the surface of the accretion in two strata (the top has slightly higher P, the second strata slightly higher Al). P occurs independently of Ca in the mineral accretion, while Ca is present in minor, disparate grains in the K1 rock art paint. Conversely, P is present in consistent relative abundance throughout the Gwion motif and at the surface of the underlying shelter substrate in K1. These different occurrences of P are interpreted as reflecting different contexts of deposition; one predominantly cultural (the K1 paint layer) and the other natural/environmental (KSMA and the surface of the rock substrate in K1). The pXRF data show consistently high relative abundances of P in the rock art paints, whereas P is largely absent from the unprocessed mulberry ochre RRS and unpainted rock substrates of K1 and MM20 (Table 3), indicating a cultural attribution such as a constituent of a paint recipe. On the basis of the morphology of P on the surface of the rock shelter, the substrate of sample K1 (Fig. 8) is thought to derive from a similar environmental context as the upper strata of the mineral accretion—KSMA, probably a precipitated aluminium phosphate. Similarly, the aluminium phosphate and quartz mineralogy identified in Mambi Gwion pigment MM20 by Synchrotron PD are interpreted as deriving from the surface of the rock shelter substrate, incorporated into the sample when the well-bonded paint was removed from the flake. These findings are consistent with the elevated P noted at the base of a Mambi Gwion paint layer by Watchman et al. (1997, 21; their identification number KF1), concluded as resulting from an aluminium phosphate mineral such as taranakite being present in a vermiciform silica skin on the surface of the rock shelter substrate at the time the painting was executed. Watchman’s conclusions that phosphate salts and alumina phosphate silica are present in the mineral accretions of the northern Kimberley were based on the analysis of amorphous silica accretions (Watchman 1997a). Our results indicate that similar environmental processes result in the incorporation of phosphate salts and/or alumina phosphate within predominantly gypsum mineral accretions (KSMA).

Major scawtite and minor loweite and dawsonite mineral phases within the KSMA mineral accretion indicate that dolomite may be present within the immediate geological environment of the Malauwarra site complex, although this is likely to be a discrete and/or minor occurrence on the basis of field observations. Restricted dolomite outcrops are noted in the study area (Tille 2006, 110), although only Hart Dolerite is mapped within the King Leopold succession, the nearest occurrence being some 5 km to the north of Reindeer Cave (Griffin and Grey 1990). Dolerite minerals are consistent with the low relative abundance of Na and Mg and the high relative abundance of S and Ca throughout the KSMA accretion, whereas the clearly banded, stratified morphology of alumina phosphate and clay minerals is characteristic of rapid precipitation, probably due to the monsoonal climate (Fig. 8). As further complimentary evidence of rock shelter geology, both samples contain large discrete Si (quartz) grains; however, Si is clearly more abundant and more consistent within the matrix of the rock shelter substrate K1 (again Fig. 8). This is seen as evidence of the silicification of the King Leopold succession forming the quartzarenite geology previously described (Williams 2005; Schmidt and Williams 2008).

Consistent with observed chemical and mineralogical differences, the morphology of the hematite ochre source and jarosite rock art (Fig. 6) suggests different geomorphic settings for the minerals. The mulberry ochre source has a shale macrostructure and occurs as a siltstone seam, slabs of which have been anthropogenically exploited to harvest pigment (Fig. 3 insets). There is
a proliferation of small pieces of desiccated ochre scattered atop (and probably throughout) the sediment surrounding the siltstone seam (Fig. 3). Watchman (1997b, 53) proposed a northern Kimberley source for jarosite series minerals on the basis that jarosite pigments were not previously identified in rock art characterization studies in the south and west of the region (Clarke and North 1976; Ford et al. 1994). Other research in the north-west Kimberley has reported the lateritic gravels of the Mitchell Plateau Bauxite deposit as likely ochre sources (Randolph and Clarke 1987; Veitch 1996). While the basalt country of the Mitchell Plateau provides a suitable geological environment for jarosite series minerals, this is not confined to the bauxites. It is probable that ochreous seams of hematite and/or jarosite occur throughout the study area within the interbedded micaceous siltstones, minor pyroclastic rocks and/or feldspathic sandstones present as low-grade mineralized veins (Watchman 1997b, 53; Dutrizac 2004, 11; Williams 2005, 111; Dowens et al. 2007, 87). We therefore suggest that both hematite and jarosite pigmentaceous minerals are likely to have a local provenance, with several geomorphic expressions such as the lateritic gravels and seams/veins within the geological stratum.

As the first archaeologically described, unequivocally anthropogenically exploited, mulberry ochre source in the Kimberley region, RRS provides an opportunity to investigate and comprehensively document within-source geochemical variability in relation to pigment provenance (preliminarily described in Table 2). Provenance continues to be a theme in Australian ochre research (Smith et al. 1998; Smith and Fankhauser 2009; Popelka-Filcoff et al. 2012) and a focus of recent international pigment studies (Popelka-Filcoff et al. 2008; Eiselt et al. 2011; Bu et al. 2013; MacDonald et al. 2013). Investigation of ochre chemistry via laser ablation–inductively coupled plasma–mass spectrometry (Green and Watling 2007) has most recently included a proposal that concentrates on zircon crystal ablation (Zipkin 2012). The exceptional zircons identified within the RRS (again Fig. 7) therefore represent future possibilities regarding geochemical ‘fingerprinting’ due to the unique remnant Y coating, which will probably exhibit characteristic chemistry.

CONCLUSIONS AND FURTHER WORK

At least two mineralogically distinct mulberry pigments, jarosite and hematite, were used to produce the mulberry *Gwion* motifs of the Kimberley. We have presented a methodology for *in situ* indicative differentiation of these mineral phases on the basis of their (qualitative) chemistry with pXRF. This methodology has significant implications for pigment characterization investigations, providing an additional, non-invasive tool to investigate the cultural context of rock art production. Iron oxides and iron sulphides will occur in the same geological environment, but critically for archaeological investigations, each will occur in a different geomorphic context/separate procurement location. The ability to non-invasively differentiate major mineral phases in mulberry rock art therefore presents an unprecedented chance to gain information regarding the choices made by artists. We have also presented the first published description of an anthropogenically exploited mulberry ochre source in northern Australia, demonstrating that these pigments occur locally as natural minerals. The identification of exceptional micromorphological features in the quarried ochre (zircons with remnant Y coating) represents unique possibilities for further provenance investigations.

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