1.0 Introduction

_in the early 1980s Rhys Jones considered archaeometry a partnership between the “...practitioner of the scientific techniques in question and the ... archaeologists whose material is being examined” (Jones 1982: 23). Nowadays, more often than not, that practitioner is an archaeologist._

Archaeometric studies of ochre have been fundamentally constrained by the expense of large scale scientific analytic programs and the sampling requirements of destructive and/or composition altering techniques. Recent instrumental advances such as non-destructive direct sample mounting for Particle Induced X-ray/Gamma-ray Emission Spectroscopy, minimally destructive Laser Ablation Inductively Coupled Plasma Mass Spectrometry and local access to high powered sources such as the Australian Synchrotron have vastly reduced sample size requirements, opening possibilities for a range of archaeological enquiries. These analyses still necessitate a sample to be taken back to a laboratory. The advent of field portable scientific devices around four decades ago alleviated some sampling limitations; however, the recent commercial production of hand held spectrographic instruments has spurred their widespread take up in anthropology related disciplines. These small, relatively inexpensive devices have had a revolutionary impact in archaeometry because of their accessibility and because they can be non-invasively applied in the field/museum as well as the laboratory. The ubiquity of recent studies using field portable spectrometry (portable X-ray Fluorescence, portable Raman and portable Fourier Transform Infrared spectrometers) reflects the accessibility of these techniques and aggressive marketing to the anthropology sector by some manufacturers. The availability of portable analysers has seen their rapid take up in archaeological enquires. As a result, there is a range of scientific expertise held by the researchers applying portable spectrometry in anthropology related disciplines. This range extends from qualified material scientists to researchers with no scientific training or experience. Consequently, the literature to date has focused on evaluating instrumentation and methods.
By volume of published investigations, the most prevalent portable technique is X-ray Fluorescence. Yet only a handful of archaeological pigment studies using this instrumentation have been reported (see Section 1.3.1 below). The dearth of portable X-Ray Fluorescence (pXRF) investigations of ochres, and specifically rock art pigment, in the decade since the first published study (Newman and Leondorf 2005), despite the accessibility and ubiquity of hand held analysers, can be attributed to an absence of critical scrutiny, explanation and specific methodologies for this application. This thesis redresses the gap via a series of research papers, which explain, evaluate and provide innovative methods for field based analysis of rock art using pXRF, and for comparing rock art with ochres from excavated contexts. The methods presented are a means by which large scale studies of the elemental character of rock art and other archaeological ochres can now be undertaken. The success of the archaeological interpretations presented, rely on understanding the complex taphonomy of ochres and rock art and the ways these processes are expressed chemically, something that has not been adequately considered or addressed previously. The research documented herein demonstrates that prudent pigment characterisation can contribute an alternate perspective to regional studies, the narration of the cultural context of rock art and may offer a fresh perspective in the archaeology of cultural landscapes.

Anthropogenically modified pigments are held to be some of the earliest, most unambiguous and persistent evidence for behavioural modernity and human capacity for symbolic thought. Historically, the mere presence or absence of anthropogenic pigment within Pleistocene contexts was used as archaeological evidence of modern cognition; some researchers going further to argue pigments represent symbolic activity. In both instances little, if any, analysis of the ochres has been undertaken beyond the observation of grinding and/or incising. Recently, increases in the sophistication of analytic techniques applied to pigments, and the theoretical frameworks for interpreting these, have renewed archaeological interest in ochre. This is reflected in a spike in actualistic studies (Henshilwood et al. 2011; Hodgskiss 2013; Marean et al. 2007; Rifkin 2011, 2012; Rosso et al. 2014; Wadley 2005, 2009; Wadley et al. 2003; Watts 2009, 2010; Zipkin et al. 2014) investigations of ochre geochemistry (Eiselt et al. 2011; MacDonald et al. 2012; MacDonald et al. 2008; Popelka-Filcoff 2012; Popelka-Filcoff et al. 2007a, 2007b, 2008:201; Zipkin et al. in press) and pigment morphology (Jacobson et al. 2013).

In the last ten years, developments in theoretical frameworks underpinning archaeological ochre investigations and actualistic studies have retained a bias toward Pleistocene assemblages, which is reasonable given that the cognitive and symbolic connotation of pigment use becomes less archaeologically important, in and of itself, as we move away from the debate around the emergence of human modernity. Australian assemblages occupy a unique and important place in these debates as Sahul (Greater Australia) was only ever colonised by behaviourally modern humans. The resulting material record therefore may reflect behavioural innovation and adaptation, but does not reflect development of modern cognition. Ochres too occupy a unique place in these debates, frequently argued to represent symbolic activities, despite their function
being unknown. Indeed the sorts of theorising and actualistic studies undertaken around ochres are driven by a desire to establish intentionality. My research takes a different tack, targeting Holocene archaeological ochres, focusing on pigments with at least one known, indisputably symbolic function—the production of rock art.

Archaeometric studies of pigment assemblages have overwhelmingly relied on, and continue to deploy, ‘The Provenance Postulate’—the staple theoretical underpinning of chemical characterisation for a variety of archaeomaterials from ceramics to lithic technologies. Rock art provides a unique perspective to archaeological ochre and provenance studies because it is fixed to place, at once a physical and metaphorical part of the cultural landscape. In this thesis, I revisit the ‘The Provenance Postulate’ and find that, as a conceptual framework for ochre studies, the diffusionist focus it implies can limit how we conceive and interpret the archaeological information gained via geochemical characterisation of pigment. In ochre research this is exacerbated by aspects of the theories underpinning the archaeology of trade and exchange, which emphasise the ‘exotic’ as imbued with elevated social significance, accentuating diffusion as a social process. These conceptual limitations are reinforced by the heavy technical focus of archaeometric studies that measure the success of instruments and methods not only by their ability to assign ochre to a source of raw material, but the resolution at which this is achieved. Such conceptual boundaries can have significant consequences for understanding archaeological ochres, particularly those of unknown function. Expressly separating characterisation from the assignment of provenance, rock art pigments and other archaeological ochres are described and interpreted from the perspective of the information they can contribute to regional prehistories; signposting the potential of this research to contribute a fresh perspective to the archaeology of cultural landscapes.

The elemental character of pigments is explored to elucidate the cultural context of art production, reporting ancillary data relevant to rock art conservation and management where appropriate. I demonstrate the archaeological utility of qualitative/semi-quantitative geochemical pigment characterisation using Holocene assemblages from the Sydney Basin, New South Wales and northwest Kimberley, Western Australia. The central material focus of this thesis is unequivocally symbolically utilised pigments; those from distinct rock art: graphic motifs, stencils and prepared panel surfaces or ‘washes’. Resultant geochemical profiles are interpreted and evaluated by studying the context of rock art panels more broadly; including shelter geomorphology, local geology, surface finds of ochre, an ochre quarry, and pigments from excavated strata. Similarly, a number of other archaeometric techniques are used to interpret and evaluate hand held pXRF, including conventional laboratory and Synchrotron X-ray Diffraction (XRD), Micro Computed Tomography (μCT), Scanning Electron Microscopy (SEM), portable Optically Stimulated Luminescence (pOSL), conventional Risø luminescence readers and benchtop XRF1. While intrinsically technical in focus, four of the five papers included address questions arising from the regional prehistories of case

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1 An unsuccessful attempt was made to identify pigment on sandstone substrate flakes with extant rock art using Fourier Transform Infrared Spectroscopy (FTIR) and portable FTIR, see the Preface to Chapter Six: 144.
studies, contributing complementary chronological and structural information, lifting this work beyond merely the advancement of a scientific procedure. pXRF analysers are commonly owned by archaeology and conservation science departments and are available for hire most everywhere in the Western world. The methods described here can therefore provide archaeologists, archaeometrists and rock art researchers in particular, with a means of generating additional lines of evidence and thereby an alternative perspective in regional studies.

This thesis has been completed ‘by papers’ whereby the substantive chapters contained within are in the format of journal articles/book chapter contributions for peer reviewed academic publications. This introductory chapter provides substantial background information to contextualise the five internal chapters, fleshing out the overarching concerns that have informed the overall project, in effect providing the glue holding the five papers together. This introductory chapter is therefore a blend of the first chapters of a traditional monograph format thesis and incorporates Literature Review, Regional Environment/Archaeology, Theory and Research Design elements. Also, in a departure from the monograph format there is no separate Methodology chapter in this document. The self contained published outputs from this research that follow required detailed method sections. As is to be expected in a project of this type, the methods employed evolved during the course of research, the aim of which was to provide methodologies for the analysis of rock art pigment and other archaeological ochres, via pXRF. Due to the diversity of archaeological questions that can be examined or augmented by the methods developed, the final summary chapter of this thesis outlines considerations for in situ rock art analysis by pXRF as an outcome of research. These considerations are discussed in general terms, rather than outlining a prescriptive protocol for a specific model of pXRF instrument (though see Appendix A).

1.1 Archaeological Investigations of Ochre

Most archaeological definitions of ochre restrict the term to iron-oxide minerals (Popelka-Filcoff et al. 2007a; Bonneau et al. 2012; MacDonald et al. 2012; Watts 2010) including a proportion of matrix materials, general clays and other crystals such as quartz and feldspar (Ambers 2004:770; Rosso 2014:86). Restricting the definition of ochre to iron-oxides limits the colour pallet to red hues including mulberry, orange and yellow, occasionally incorporating black and brown (Ford et al. 1994; Hodgskiss 2013; Jercher et al. 1998). Most research concerning the analysis of paintings refers to ‘earth’ pigments, coarsely describing these by their physical structure as ochres and/or clays (Hradil and Hradilová 2012:86). Aboriginal Australians make no such distinctions and include a variety of iron-oxide, manganese oxide, clay and calcite minerals in their application of the term ochre, incorporating hues from red, to black/brown, grey, blue and white (Attenbrow 2002; Clarke and North 1976; Cole and Watchman 1993; Crawford and Clarke 1976; Clive Freeman, Boodeeree Aboriginal Community pers. com. 2012; Mosby 1993). Consequently, a broader definition of ochre is adopted in this thesis, referring to the naturally occurring geological minerals deliberately procured by Aboriginal people as pigments. Because this research uses pigments with a known
function, the production of rock art, as a starting point, the intentional collection of ochres for use as pigment is certain. This research is thereby set apart from previous analyses of (generally Pleistocene) archaeological ochre assemblages that have inferred the function of pigments based on archaeological and archaeometric analysis.

The earliest evidence of anthropogenic pigment use appears restricted to red hued iron-oxides (Marean et al. 2007; McBrearty and Brooks 2000; Watts 2009, 2010). Mineralogy for these is generally inferred from their colour, rather than substantiated by petrography, or established by diffraction or chemical analyses (with few exceptions such as Barham 2002; Henshilwood et al. 2011). The dominance of red pigment in Pleistocene archaeological contexts is likely to be a result of taphonomic processes. Iron is more chemically inert than clay and calcite matrix minerals (see Chapter Three), resulting in more red hued pigment being preserved than whites/creams. There is also some suggestion that post-depositional processes such as heating and oxidation have led to an over representation of red ochre in the archaeological record due to mineral phase transitions (Cook et al. 1990; Wadley 2009). Around eighteen archaeological sites across Africa now report anthropogenically modified pigment assemblages from the middle Pleistocene (Watts 2010:393). Red ochres certainly dominate African Middle Stone Age assemblages but, "yellow limonite, specular haematite, green and grey shales, black manganese, white kaolinite and brown goethite are also reported" (Barham 2002; Henshilwood et al. 2009; Wadley 2009 cited by F. Rifkin 2011:133).

Pigmentaceous material has been found in association with the fossil record throughout human history. Unmodified pigment was recovered from archaeological deposits containing hominin remains dating back 1–1.5 million years ago at Gadeb and Olduvai Gorge in Africa. Similarly, unmodified pigments occur in archaeological contexts dated to 736 000 BP in Isernia la Pineta, Italy and 500 000 BP in Garba I, Melka Kunture, Ethiopia (Chavaillon and Berthelet 2004; Desmond Clark and Kurashina 1979; Leakey 1958; Rosso et al. 2014). Lithic technologies with pigment residues found alongside ochre fragments in Acheulean levels of Tuff K4, in the Kaphurin Formation of Kenya, Africa, are dated to >275 000 BP and are widely cited as the earliest known, securely dated evidence of hominin pigment use (Deino and McBrearty 2002; McBrearty and Brooks 2000; Marean et al. 2007:905; Rosso et al. 2014:86; Watts 2010:393). This is roughly contemporaneous with arguments for the earliest evidence of anthropogenic ochre use in the Lower Palaeolithic ~250–300 000 BP from sites in France (Terra Amata and Achenheim), India (Hunsgi) and Spain (Ambrona) (Bednarik 1990; de Lumley 1969; Howell 1966; Salomon, 2009; Thévenin 1976 as cited in Rosso et al. 2014:86). These broadly correspond with evidence for ochre use by Neandertals found in the Netherlands (Maastricht-Belvedere) in subsurface contexts dated to >200 000–250 000 BP (Roebroeks et al. 2012).

By 120 000 BP systematic anthropogenic pigment use seems established in Africa (Marean et al. 2007). Earlier modified pigments are common in sites such as the Twin Rivers, Zambia (Barham
2002) and Sai Island, Sudan (Van Peer et al. 2003) where ground and striated ochre fragments were found in strata dated between 141–400 000 BP, and 180 000 BP respectively. However, a growing body of evidence shows widespread, recurrent grinding, scraping, incising and notching of ochres, as well as pigmentaceous staining on lithic technologies, shell and personal ornaments in Pleistocene sites by 120 000 BP (Marean et al. 2007).

Although systematic use of pigment is common in African Middle Stone Age sites, there is a sampling bias in studied assemblages, with most restricted to Southern Africa (d’Errico et al. 2012; Hodgskiss 2012; Rosso et al. 2014:86; Watts 2010). The most well reported are Apollo 11 (Wendt 1974; Vogelsang et al., 2010), Blombos (Henshilwood et al. 2004, 2009, 2011), Border (Villa et al. 2012), and Sibudu Caves (Hodgskiss 2012, 2014), as well as Diepkloof (Dayet 2012, 2013), Hollow (Högberg and Larsson 2011), Klasies River Mouth (Wurz 2000; d’Errico et al., 2012) and Pinnacle Point Rockshelters (Marean et al. 2007; Watts 2010). A recent noteworthy find was two ochre processing ‘kits’ at Blombos Cave, South Africa dated to 300 000 BP (Henshilwood et al. 2011). These show that composite pigment processing, including the curration of associated paraphernalia, was occurring from the Pleistocene. The manufacturing of ochre compounds necessarily requiring complex cognition, multi-tasking and thinking in abstract terms about the qualities and necessary quantities of manipulated ingredients (Wadley 2013).

Outside of Africa, materials indicating systematic ochre use emerge at roughly the same time. Evidence for ochre exploitation is common in the Middle East from ~100 000 BP (Bar-Yosef Mayer et al. 2009; d’Errico et al. 2009; Hovers et al. 2003) and a modern human presence India as early as 74 000 BP is marked by coeval ochre and lithic technologies (Petraglia et al. 2007). These independent, geographically dispersed, early ochre finds strengthen the argument that the habitual collection and use of pigment is evidence of cognitive development, and may be considered a one of the material hallmarks of modern human behaviour. Used in this context, the presence of ochres alongside other evidence such as blade technologies, can serve as a proxy for establishing the timing behavioural modernity (Henshilwood et al. 2002), unhindered if the function of pigments remains unknown.

There is no doubt the habitual collection and transport of non-local pigments required long range thinking and thus complex cognition, but demonstrating this archaeologically is fraught. Definitively incised or ground ochres make up a small proportion of Pleistocene pigment assemblages, generally <5% (Bar-Yosef Mayer et al. 2009; Henshilwood et al. 2001; Hodgskiss, 2013; Marean et al., 2007; Wadley 2005a, 2013; Watts, 2010). Accordingly, much energy has been expended in actualistic studies to try and infer function from replicative experiments that correlate ethnographically known ochre uses to use-wear patterns observed archaeologically (Hodgskiss 2010, 2013; Rifkin, 2011, 2012; Wadley, 2005a, 2009; Wadley, 2009; Wadley et al. 2003). However well argued, function inferred from actualistic studies is restricted to some degree of speculation as a multitude of diverse possible functions for ochre powders are historically known.
These include:

- To prepare and preserve animal hides (Rifkin 2011; though see Watts 2002; Watts, 2009);
- Medical uses such as a styptic or antiseptic treatment for wounds and the eradication of internal or external parasites (Audouin 1982; Hodgskiss 2005; McBrearty and Brooks 2000:524; Mphuthi 2013; Plomley 1966; Velo 1984)
- In adhesives used for hafting tools (Hodgskiss 2005; Lombard 2007; Wadley 2010, 2013; Wadley et al. 2003; though see Zipkin et al. 2014);
- As a barrier to protect people against the sun, cold and insects (Figure 1.1)(Backhouse 1843; Brian 1979; Davies 1846; Hodgskiss 2005:6; Plomley 1966; Sagona 1994:23).

![Figure 1.1. Top left: Watercolour painting by Thomas Bock, 1837 ‘Manalargenna – A chief of the eastern coast of Van Dieman’s Land’ – housed at the Tasmanian Museum and Gallery, reproduced from Sagona 1994. Top right: close up of the Toolburnner ochre quarry Tasmanian facing north, 2012. Bottom: Overview of the Gog Range Tasmanian, the location of the Toolburnner ochre quarry, facing north, 2012.](image)

Parallel to the spike in actualisitic studies has been a renewed interest in archaeometric pigment investigations. Successful sourcing projects have been able to differentiate local from exotic pigments and provide a spatial dimension to the extent of archaeological ochre procurement (Eiselt et al. 2011; MacDonald et al. 2008; Scaddling et al. in press; Smith et al. 1998). Recent geochemical ochre investigations have been conducted predominantly in North America (Eiselt et
al. 2011; MacDonald et al. 2008, 2011, 2012; Popelka-Filcof et al. 2007a, 2007b, 2008) although South American (Popelka-Filcof et al. 2007b), South African (Bonneau et al. 2012; Zipkin et al. in press), European (Montalto et al. 2012) and Australian pigments are beginning to receive attention (Popelka-Filcof et al. 2012a, 2012b). These geochemical studies, like previous work, have tended to focus on methodological innovation (Popelka-Filcof et al. 2012b; Scadding et al. in press; Zipkin et al. in press), basing interpretations on the ‘the Provenance Postulate’ (Glascocke et al. 2004; Neff 1998, 2002; Weigand et al. 1977, see Section 1.2 below for further discussion). There remains a bias in geochemical studies towards targeting ochres from known source loci (Eiselt et al. 2011; MacDonald et al. 2012; Popelka-Filcof et al. 2007a, 2009, 2012b; Scadding et al. in press; Zipkin et al. in press), perhaps as no set of analytic procedures or data processing methods has successfully provenanced the diverse geomorphic array of pigments archaeologically known to have been transported to sites and used. Indeed, it seems analytic techniques and methods are best targeted at the distinct attributes of individual ochre sources (Smith and Fankhauser 2009; Scadding et al. in press).

Technological advances are also providing an impetus for ochre research. High precision tomography has recently been applied to iron rich shales to help differentiate deliberate anthropogenic incision by archaic hominins species, from natural fissures or other geological features such as glacial scratching (Jacobson et al. 2013). Again, there is a bias to Pleistocene assemblages in these sorts of studies that are intent on addressing the emergence of behavioural modernity.

In addition to direct ochre research, a number of recent contributions to debate around the emergence of human modernity have used ochre as a jumping off point, interweaving into their narratives the symbolic connotations of pigment use (Henshilwood et al. 2009, 2011; Marean et al. 2007; Wadley 2010, 2013). The assumed symbolic use of ochre is exceedingly difficult to demonstrate archaeologically (Brumm and Moore 2005; Rifkin 2011, 2012; Rossano et al. 2010, 2014:86; Wadley 2001, 2005a, 2005b, 2013; Wynn and Coolidge 2010). Within the small proportion (generally <5%) of anthropogenically modified ochres found in Pleistocene assemblages, engraved pieces with arranged linear incisions that appear to show some level of aesthetic concern, are rare (see Henshilwood et al. 2002; Hodgskiss 2010, 2012; Marean et al. 2007; Mckay and Welz 2008; Rosso et al. 2014:86; Watts 2009) and their correlation to symbolisms is ambiguous.

Symbolic behaviours are an encoding process where items or actions are used to represent something different (Huttenlocher and Higgins 1978). In Australia, Aboriginal cosmology attributes ochre sources to the activities of the ancestral beings that created the landscape (Blundell 2005; Morphy 1989, 1991; Mosby 1993; Vinnicombe 1997). In northern and central Australia, ethnographic studies document ‘highly prized’ and widely traded ochre being selected not only on the basis of deep red/mulberry colour, but also for physical properties such as lustre and metallic sparkle (Smith 2013:276) that were used as ‘... a means of invoking spiritual power’ (Morphy 1989:30-31). Symbolic values such as these are recorded ethnographically as being attached to...
ochre within various functional contexts the world over (Fortis 2010, Rifkin 2012:127), but simply equating archaeological ochres with symbolic behaviours such as artistic and ritual practices is fraught (Hodgkiss 2014; Knight 2010; Wadley 2001, 2010; Watts 2002, 2009, 2010). The use of symbols is a shared experience, not only requiring a capacity for modern thought (Nobel and Davidson 1991; Davidson 2010:S179; Wadley 2001) but also corporate convention and repetition (Brumm and Moore 2005:158).

Rock art, as unequivocal ‘evidence for the emergence of representational, referential behaviour and thus complex symbolism’, has been offered as a means of moving the debate about Pleistocene pigment use forward from inference (David et al. 2013a:3). The major stumbling block to using rock art datasets is a lack of secure chronology. The perfect storm of circumstances needed in order to generate a numeric age determination, definitively associated with rock art (Aubert 2012; Rosenfeld 1993; Watchman 1993, 1997b) is evident in the dearth of widely accepted rock art chronologies globally. In addition, the complex taphonomy of rock art makes establishing sampling biases difficult in relation to stylistic sequences (Nowell and d’Errico 2007).

Models concerning the development of ‘art’ are pervasively Eurocentric, stemming from the geographic location of early archaeological finds (Bicho et al. 2007; Conkey 1984, 2010; Moro Abadia and Gonzalez Morales 2013; Palacio-Pérez 2013:693; Pike et al. 2012). The most plentiful collection of Pleistocene radiometric age determinations are associated with European Upper Palaeolithic parietal art (Moro Abadia and Gonzalez Morales 2013; Valladas et al. 2005). Consequently, the European Upper Palaeolithic is regularly referred to as the earliest evidence of fully developed symbolic behaviour (Lewis-Williams 2002; Mellars, 2005). Although recent research suggests caution in ascribing a blanket deep antiquity to graphic rock art in the region (Combier and Jouve 2014), the general pattern of a time lag between human anatomical and behavioural modernity (McBrearty and Brooks 2000) is consistent with the fossil and rock art records of Europe (Conard 2010; Conard and Bolus 2003).

Rock art has been produced for more than 41 000 years (Pike et al. 2012). This is the minimum age of a red disk motif in a limestone cave in northern Spain determined by uranium-series disequilibrium dating of the overlying calcite. Revolutionary chronometric work in Indonesia, using the same technique, has recently shown that rock art production began in Australasia at least 40 000 BP, and critically, that fully articulated graphic compositions of (endemic) animals were being produced at the same time as the earliest examples of European Upper Palaeolithic art, if not earlier (Aubert et al. 2014:3). Doubtless these recent discoveries will heighten attention in Australasian, where theorists are already looking to the record of Sahul, which offers unique insights in recognising the material expression of behaviourally modern Homo sapiens (Balme et al. 2009; Brumm and Moore 2005; Davidson and Noble 1992; Davidson 2010; Habgood and Franklin 2008; Langley et al. 2011; Tacon et al. 2014; Veth et al. 2011).
1.1.1 Australian Ochre studies

*There is no doubt that systematic use of ochre in Australian sites is as early as the earliest evidence for occupation* (O’Connor and Fankhauser 2001:296)

Among the earliest evidence for the peopling of what is now the Australian continent are ground ‘haematite’ nodules found in stratum dated to \(~\text{53 000 years ago at Madjedbebe (formally Malakunanja II) and Nauwalabila I rockshelters on the Eastern and Southern arms of the Alligator River in Arnhem Land (Roberts et al. 1990, 1993, 1994, 1998). Debate regarding the stratigraphic integrity of these early finds has led most researchers to couch discussions around the timing of the settlement of the Australian land mass to } \geq 44 000 \text{ years ago (Allen and O’Connell 2003; O’Connell and Allen 2004), although these concerns may be overstated (Bird et al. 2002; Hiscock, 2012:25 and recent reviews generally discuss a 50 000 year human history for Sahul (Balme et al. 2009; Davidson 2010; Langley et al. 2011; O’Connor, 2012; O’Connor and Veth 2006; Veth et al. 2011). Irrespective of the exact timing of human colonisation, the first Australians collected and used pigments and evidence for this is present in at least 63 Pleistocene sites across the continent, from what is now the Northern Territory to Tasmania (Figure 1.2, Davidson 2010:S178, his Figure 1; after Habgood and Franklin 2008; Langley et al. 2011:199).}

The unique attributes of the Australian archaeological record of have led scholars to argue that it provides important insights for testing the material correlates of modern cognition (Brumm and Moore 2005) and their abrupt or revolutionary nature (Habgood and Franklin 2008; Hiscock and O’Connor 2006). This is in keeping with the ‘traits list’ approach to identifying material markers of cognitive evolution, chief among which is the use of pigment evident in the grinding or incising of archaeological ochres (Davidson 2010; McBrearty and Brooks 2000). Initially conceived of as an abrupt or revolutionary cultural florescence (Brumm and Moore 2005; Chase and Dibble 1987; Klein and Edgar 2002; Mellars, 2005; Mellars and Stringer 1989), more recently the debate has been reframed to discuss an archaeologically visible ‘package’ of cultural innovations representing modern human behaviour (again including pigment use) that gradually assembled in the African Middle Stone Age and then appeared with anatomically modern *Homo sapiens* elsewhere (Habgood and Franklin 2008:188; McBrearty and Brooks 2000). The international significance of the archaeological record of Australia is that while it is contemporary with the ‘fluorescence’ of materials used to argue for a ‘Human Cultural Revolution’ in Europe (Mellars, 2005:24), only anatomically modern human remains are found in Australia and the very act of reaching Sahul demonstrates that the colonising population were cognitively modern (Balme et al. 2009; Davidson 2010; Veth et al. 2011). The resulting material record may therefore reflect behavioural innovation and adaptation, but does not reflect the development of modern cognition.
When situating this exceptional archaeological record in its global context a few caveats should be noted. In addition to sampling biases in the Australian Pleistocene record (Langley et al. 2011), the ‘uncontested’ colonisation of Sahul by 44 000 BP (O’Connell and Allen 2012, emphasis added) likely represents the timing at which human landscape use rose to a point of archaeological visibility (Hiscock, 2012:25). As stated above, these archaeologically visible materials have consistently included ochre with the general consensus among archaeologists that ‘... the exploitation of pigment sources was universal throughout Pleistocene Australia ...’ (Mulvaney 2012:916). As elsewhere in the world, archaeological interest in Australian ochres has been intertwined with the search for material correlates of complex cognition, especially planning over distance and time (McBryde 1987, 1997a, 1997b, 2000; Mulvaney 1976; Wadley 2013).
Australian ochre studies have always had a distinctly archaeometric focus. The first archaeological accounts of trade and exchange explicitly recognised the need for tools that could provide a spatial dimension to research and suggested the incorporation of methods from the physical sciences in order to ‘illuminate the geographic origin of materials’ (Mulvaney 1976). Following this rationale, David et al. (1993) analysed 33 ochre nodules from five source locations (gravel deposits within creek beds) in the Northern Territory and compared them to 36 ochre samples from an excavated context in the Fern Cave in Queensland. The trace element signatures of these ochres distinctly separated in multivariate space, unsurprising given the former assemblage derives from sandstone geology and the latter limestone. The authors do not discuss the implications of these geological differences, nor local ochre source exploitation. Rather, they viewed this work as a proof of concept for use of the PIXIE/PIGE technique to distinguish the provenance of archaeological ochres. A contemporary study similarly identified PIXIE/PIGE as a preferred technique for the trace element characterisation of ochre because of the total trace element profiles generated (Jercher et al. 1998:397).

Following on from this work Goodall, David and Bartley expanded the study at Fern Cave to include 91 ochre pieces from two excavated contexts and 62 potential ochre sources from the region including geomorphic contexts such as river gravels, (presumably lateritic) ochre surface scatters and ‘block outcrops’ (Goodall et al. 1996:184). Significantly, this study recognised the importance of geochemical and structural data identifying mineralogy using Fourier Transform Infrared Photocalssical spectroscopy in addition to trace element chemistry using PIXE/PIGE. They concluded that a greater variety of mineral pigments were being used in the more recent past and that this was not a reflection of taphonomic factors as elemental proportions did not correlate with the excavation depth of the samples and the ochres were cut into cross sections with only the interior of the sample analysed. No comparison of the excavated ochres and potential sources was made as unspecified methodological issues were being explored (ibid:186).

Around the same time in the South Australian Museum, the geologist Jercher and colleagues were analysing ethnographically well-known, widely traded ochre sources using X-ray Diffraction (XRD) (with Rietveld refinement) and X-ray Fluorescence (Jercher et al. 1998). Similarly, Smith and colleagues were testing a number of different methodologies for analysing the geochemistry of archaeological ochres from excavated contexts in the deserts of Central Australia (Smith and Fankhauser 1996, 2009; Smith et al. 1997, 1998, 2002). Jercher et al. (1998) concluded that structural analyses (such as XRD) were critical in understanding ochre digenesis, the geomorphological environment of source locations. Smith et al. cautioned that a nested analytical approach was required with various resolutions of archaeometric investigation necessary (they used petrography, major and minor oxide concentrations and trace element chemistry) in order to avoid source misattribution. They cite an example from their dataset where excavated ochre from Madjedbebe was assigned to the same geochemical group as the Ulpunyali ochre mine in central
Australia based on trace element chemistry, despite the former being vein haematite and the latter ferruginised sandstone (Smith and Fankhauser 2009:41).

The major archaeological findings of Smith’s work on ochre geochemistry were published in 1998 (Smith et al. 1998 [elegantly summarised in Smith, 2013: Chapter 8]) and still have resonance with archaeometric ochre research today, widely cited as an exemplar study (Eiselt et al. 2011; MacDonald et al. 2008, 2011, 2012; Popelka-Filcoff et al. 2007a, 2008; Zipkin et al. in press). This work realised the potential Mulvaney (1976) had outlined in his synopsis of the archaeology of trade and exchange, that scientific analyses could provide a spatial dimension to the procurement, distribution and use of raw materials over time. Analyses conducted on the ochre assemblage from Puritjarra compared excavated specimens to ethnographically known ochre deposits and other archaeological ochres held in museum collections, differentiating provenance using the multivariate analysis of trace element chemistry. Proffering a ‘nested’ analytic approach, the findings from the study at Puritjarra frankly state interpretations are based on the extrapolation of a pilot program of archaeometric characterisation, from a small number of ochres. From a total of 196 ochre specimens in the stratified shelter deposit, 32 or 16.3% were initially analysed using SEM-EDX. With a clear analytic bias towards red ochres described as ‘high grade’, a subset of only eight specimens, assumed to be from either the Karrku or Ulupinyali mines, went on to further XRD and inductively coupled plasma mass spectrometry. The results were then extrapolated as representative of the 196 excavated ochres that had no further analysis except being classified into seven groups by visual inspections under a low magnification (40x) (Smith et al. 1998:278-9, my emphasis). In other words, the findings of this research, that have had such international resonance, are based on the archaeometric study of only 4% of the excavated ochres from the Puritjarra deposit. The sustained and wide reaching impact of this work, that clearly demonstrates the archaeological value of observing changes in preference for ochres through time and the alternate perspective to regional investigations that this might offer, derives from the fact that archaeological studies of this type have not been replicated in other geographic regions within Australia, and are rare internationally (though see Eiselt et al. 2011). Instead, Australian ochre research has continued a trend towards the advancement of techniques and methods, rather than applying them to archaeological problems.

As well as indicating archaeological potential, Smith and his collaborators’ seminal ochre research showed that there is no one ‘magic bullet’ in regards to methods for the archaeometric analysis of ochre (Smith and Fankhauser 1996, 2009; Smith et al. 1997, 1998, 2002). Therefore, a number of approaches continue to be offered. Green and Watling (2007) used Laser Ablation Inductively Coupled Plasma Mass Spectrometry to differentiate and provenance Australian ochres in respect to the authentication of Aboriginal artworks. This study, as with contemporary research on the provenance of ochres for authentication of artworks using Synchrotron X-ray Diffraction and Particle Induced X-ray Emission techniques (Creagh et al. 2007, 2009; O’Neill et al. 2004), had a technical focus, primarily documenting methodological parameters rather than applying ochre
provenancing to art or artefacts. These studies all used museum and gallery specimens from ethnographically known ochre ‘mines’ and bark paintings to demonstrate that pigments could be differentiated to a compositional group and/or source location based on both geochemical and structural data.

In more recent work applying the same methodology, Scadding et al. (in press) have again targeted ethnographically known ochre mines, this time solely in the Weld Range of Western Australia, incorporating archaeological ochre samples including rock art and ochre from surface finds and excavated contexts. Their results show good discrimination between the isotopic element profiles from Walgie Mia and Little Walgie mines that are within the same geological seams (Smith and Fankhauser 2009:8-9) and demonstrate the potential of this method to provenance archaeological specimens. Importantly, this recent work has shown that trace amounts of Pb in the elemental signature of the Walgie Mia source is critical in distinguishing between provenience locations within the source, something not seen in previous research that used digestion inductively coupled plasma mass on Walgie Mia ochres (Smith and Fankhauser 1996, 2009; Smith et al. 1998).

In northwest central Queensland, in the Selwyn region around Mt Isa and Cloncurry, a program of PIXE/PIGE analysis was undertaken on 14 rock art motifs (23 samples) and three ochre sources (Davidson et al. 2005: their Figure 13.6, p.121) using novel sample preparations (Grave et al. 1999). The chemical composition of rock art paints and ochre sources suggested that decisions about ochre use were not only made with regard to ‘utility and cost of procurements’ (Davidson et al. 2005:124). Clustering of distinctive anthropomorphic motifs with local sources appears to reinforce the findings of Ross (1997), that these geographically restricted anthropomorphic motifs functioned in a different, more bounded way than concentric circle, dot and line motifs with a wider distribution (Davidson et al. 2005). This pigment research was never fully realised and though chemical variability within sources in the region appears less than chemical variance of non-local sources, further work needs to be done in order to untangle ochre and rock art geochemistry and its archaeological implications.

Recent technologically focused work has sought to quantify the precision and accuracy of Neutron Activation Analysis (NAA), again using ochres from ethnographically known sources held in museum collections (Popelka-Filcoff et al. 2012a, 2012b). The results published so far, although preliminary, are concerning for a study that seeks to set up a national ochre chemistry database. The datasets generated independently at facilities in Australia and North America, using k0-NAA and relative comparator NAA (ANSTO and MURR reactors) could not be directly compared by

2 Nee Green (Green and Watling 2007).
3 The term ‘provenience’ is used in archaeometry to delineate the geographic extraction location of a raw material, its discrete geographic ‘find spot’. This is distinct from ‘provenance’ which describes the systematic observation of the chemical/mineralogical composition of an artefact (usually at the resolution of trace element content in parts per million) and that characteristic composition’s relationship to the composition of the raw material(s) from which it has been manufactured (Pollard et al. 2007). The provenance of an archaeological artefact is often assigned to a raw material source or a group of other artefacts without the establishment of ‘provenience’.
multivariate techniques, despite the analytes being 'statistically equivalent' (Popelka-Filcoff et al. 2012a:23). Further, while displaying the same broad trends, comparison of element profiles from 48 Australian ochre samples showed significant differences between the same principle components plots for 11 common elements. Plots of the first two principle components of each NAA dataset discriminated similar compositional groups relative to the known ochre sources, however, the higher resolution k0-NAA data showed tighter groupings with more overlap between clusters (idid:24). In other words, a more complex picture of ochre geochemistry emerges the more elements measured.

No one technique or methodology has been shown to definitively provenance archaeological ochres. Research to date shows that ochre sources and provenience locations exhibit distinct and often unique features, therefore the most successful approach to provenance as with any broader archaeological investigations will be to comprehensively characterise the pigment to identify distinctive features and tailor archaeometric work accordingly. Whether for authentification or anthropological and archaeological research, the description of ochres with various material scientific techniques has proved useful in characterising and discriminating between ochre sources, irrespective of the ultimate assignment of provenance. Yet archaeometric description of the > 63 Pleistocene ochre assemblages known in Australia is very poor (Habgood and Franklin 2008; Langley, et al. 2011, their Table 1).

Even the most conspicuous finds such as the 'ground haematite' argued to be the earliest evidence for human colonisation of the Australian landmass (Roberts et al. 1997:582), are under-analysed. The 'high grade' nature of the Madjedbebe and Nauwalabila I ochre is not quantified, nor is there analysis to support the assertion of mineralogy (haematite) (Jones and Johnston 1985:218-223). Illustrations in scientific publications are rare (c.f. Jones and Johnston 1985, their Figure 9.25:223) and no chemical, structural or use-wear analysis is documented outside of the one museum specimen from Madjedbebe whose trace element chemistry was described by Smith and Fankhauser (1996, 2009).

There is also rarely any analyses provided in support of the often assumed exotic provenance of Pleistocene ochre finds. For example, the red ochre associated with the ~ 40 000 BP Mungo III burial is stated as likely deriving from 200 kilometres away because that was the nearest known ochre source (Johnston and Clarke 1998:117). The assumed exotic context of Pleistocene ochres throughout Australia is increasingly cited as evidence for long distance trade and exchange (Habgood and Franklin 2008:189-90; Veth et al. 2011:212-13) and frequently put forward as evidence of intergroup interaction and identity marking in the form of art production from the time people arrived in Sahul (Balme et al. 2009:64; Veth et al. 2011). All these assertions are so far unsubstantiated by archaeometric analysis.
It is true that pigments used for burials, body paint, colouring artefacts or painting rocks, involved aesthetic and symbolic senses (Mulvaney 2012:916). As outlined earlier, the presence of ochre in archaeological deposits, whether faceted, striated, ground or unmodified, is not itself evidence of symbolic behaviour: The presence of non-local pigment is certainly evidence of forward planning and may be a material expression of cultural landscape and/or potential evidence of social interaction if trade and exchange are implied (McBryde 2000), but only where distances to ochre sources have been established (Smith et al. 1998). Complex symbolism in the form of referential and representational ritual and artistic behaviours (David et al. 2013a) cannot be assumed from the presence of ochre alone, especially when a range of more utilitarian functions are recorded in Australia (Brian 1979; Davies 1846; Plomley 1966; Sagona 1994:23) and across the globe (Fortis 2010, Rifkin 2012:127). A particular ochre source might be important for its cultural affiliation (Blundell 2005; Morphy 1989, 1991: Mosby 1993; Vinnicombe 1997). Equally an ochre’s material properties (greasiness, shine, small particle size, clay content) may make it desirable for utilitarian functions such as medicinal use, protection from heat or cold, as an aggregate in hafting etc. (Rifkin, 2011, 2012 though see Zipkin et al. 2014), or (in the case of small grain size) preferential for artistic and ritual practices (Cole and Watchman 1996; Huntley et al. 2011). It is unlikely that ochres ever functioned solely as utilitarian pigments. However, it is equally unlikely that these esoteric qualities of ochres will be unambiguously demonstrated archaeologically.

Pigment exploitation is widely accepted as evidence that modern behaviours were practiced from the time people enter what is now the Australian landmass (Balme et al. 2009; Brumm and Moore 2005; Davidson 2010; O’Connor and Veth 2006; Veth et al. 2011). A lot of debate has surrounded the timing of the earliest evidence for ‘art’ in Australia (Aubert 2012; Watchman 1993, 1997b). The chief difficulty is extrapolating from evidence of pigment use in the form of grinding or incising of ochre pellets, to the unambiguous production of graphic or stencil forms. There is a variety of circumstantial evidence, chiefly from northern Australian, to suggest that rock art was being produced from the time of colonisation. However, none of these early instances is unproblematic.

O’Connor and Fankhauser (2001) have presented chemical analysis of a red stained limestone slab recovered from excavated strata in the southern Kimberley dated to ~40,000 BP in support a claim for anthropogenic pigment application. Chemistry alone is inconclusive as the ochres are products of geological weathering and have the same constituents as the naturally occurring precipitous iron-oxides found on rockshelter walls and ceilings (Wells et al. 2008). SEM-EDXA spectra showed that pigmented surfaces on the excavated slab have a different major chemical composition from the ochre pellet recovered in the same stratum (O’Connor and Fankhauser

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4 I have avoided the term ‘crayon’ as it implies the direct use of ochre for the creation of iconic imagery (drawing) (Wadley, 2005:1). The term ochre ‘crayon’ is seldom defined where used (cf. Henshilwood et al. 2001:433), and use-wear and/or residue studies are even more seldom supplied in support of the inference. Where use-wear and/or residue studies have been undertaken they demonstrate that ‘crayons’ represent a minute (~0.03%) section of archaeological pigment assemblages (Wadley2005:1 cites Henshilwood et al. 2001).
Composition of the red pigment on the excavated limestone slab was very similar to concentrations of clay matrix ochre from the Karrku quarry in central Australia that were experimentally applied to limestone substrate for comparison (O’Connor and Fankhauser 2001 Tables 1 and 2: 291-2). The elevated concentrations of clay elements (Al, Si, K, Ti) reported for the red staining on the archaeological slab suggests that if it is applied ochre, it is derived from a clay rather than calcite matrix source. This is significant given the dominant limestone geology of the Napier Range, which would produce calcite matrix ochre. Clay elements are mobilised during precipitous mineralisation, not just ochre diagenesis (refer to Chapters Two and Five for further discussion). O’Connor and Fankhauser note that no natural iron staining occurs on the walls or ceiling of Carpenters Gap 1, and that iron staining in the region appears restricted to association with sandstone and siltstone strata (2001:290). This is consistent with the clay-element chemistry of the red pigment on the slab. In conjunction with the location of pigment on every surface of the slab, except for where it was once attached to the wall (O’Connor and Fankhauser 2001:289), this indicates that the artefact is a manuport, irrespective of the anthropogenic or natural origin of the surface pigment.

In Arnhem Land, silicified sandstone blocks, argued to have applied pigment, have been recovered from subsurface stratum radiocarbon dated to ~35 000 BP and ~28 000 BP (Chris Clarkson pers. com 2013; David et al. 2013b). However, analysis of these respective deep red/black and black pigments is yet to be reported and even where recent arguments for the earliest yet known graphic rock markings in Australia have been published (David et al. 2013b) morphological and chemical evidence claimed in support is discussed, but not supplied. For instance, David et al. 2013 state that the small painted or drawn ‘motif’ was subject to microscopic analysis showing ‘differences’ in the pigment across its surface, without presenting micrographs. They claim the ‘motif’ is charcoal without supporting data and in fact state that there was not enough (<0.1mg) carbon in a sample to produce a 14C age determination. They refer to analysing the rock art flake by pXRF and FTIR, but report no data, stating only that calcium oxalate minerals were not measured and this therefore ruled them out as a contaminant for AMS dating (David et al. 2013b:2494-2498). Both pXRF and FTIR would have measured Mn and Mn-oxides, well documented constituents of black rock art pigment (Vázquez et al. 2008) and their absence would support (though not prove) the assertion of a carbon based pigment, yet this is not mentioned. The argument for pigment application in both cases thus far rests on the observance of partial motifs, which is subjective as, in my opinion, none of the slabs show clearly discernible graphics and only one of the slabs has morphological features consistent with applied ochre (David et al.2013:2494, their Figure 1 and personal observation of the Madjedbebe slabs).

5 The ochre pellet has a clay matrix (O’Connor and Fankhauser 2001:293, their Table 3). However, no chemistry for the ochre alone is presented, only composite spectra from its experimental application to limestone. Similarly no comparative chemistry is provided with which to evaluate the proposed chemo-metric method for calculating ochre concentrations from composite limestone + pigment spectra.
Laminated iron-oxides have been found in the strata of mineral accretions on the walls/ceiling of painted rockshelters in northern Queensland. These layers were dated to between 28 000 BP and 23 000 BP using radiocarbon (Campbell et al. 1993; Cole et al. 1995; Mardaga-Campbell et al. 2001). However, these are not associated with visible graphic or stencil art, no morphological data was provided to support the inference of anthropogenic pigment application and again the observance of iron-oxide mineralogy alone is inconclusive.

Taken together this circumstantial evidence, combined with the consistent presence of ochre in the earliest subsurface contexts across Australia and the execution of indisputable stencil and graphic motifs in Indonesia >35 000 BP (Aubert et al. 2014) suggests that not only modern, but symbolic behaviours were practiced by the colonising peoples of Sahul. However, the above review cautions that simply equating the presence of pigments in Pleistocene context with the praxis of symbolic, indeed ritual and referential behaviours is fraught. That unequivocal evidence for complex symbolism is scarce in the Australian archaeological record prior to the Holocene may simply reflect issues of archaeological visibility (Hiscock 2012; Langley et al. 2011; Smith 2013:272). No matter the cause, “... it is difficult to make comparisons between the archaeological record of the first occupation period with later periods for which we have abundant material and a much richer and more diverse record” (O’Connor and Veth 2006:32).

By the time we reach the Holocene nearly every excavated deposit reported in Australia is producing some quantity of preserved ochre, and we know that regionally distinct rock art systems are being produced throughout the Aboriginal nations of Australia at this time (Ross 2013). Yet the majority of Holocene archaeological ochre investigations are either ancillary parts of chronometric studies (Cole and Watchman 1992, 1996; Sale and Watchman 1993; Ward et al. 2001; Watchman et al. 1993, 1997a, 2010; Watchman and Cole 1993), continuations of projects that targeted Pleistocene ochres (Smith and Fankhauser 1996, 2009; Smith et al. 1998, 2002) or concerned with ethnographically infamous ochre ‘mines’ (Popelka-Filcoff et al. 2009, 2012a, 2012b). In much the same way as the trait-list approach to archaeological proxies for modern human behaviour are characterised as under-theorised (Brumm and Moore 2005:158; Henshilwood and Marean 2003:635), archaeological ochre studies, especially in rock art research, have thus far been under-analysed (noting that pigment investigations, especially on a regional scale, have been constrained by costs and the need to take samples back to a laboratory environment for analysis).

The treatment of the Pleistocene of Sahul as a proxy record for human modernity and symbolic behaviours, as with the focus on ethnographically well known ochre mines in archaeometry, has sought the exotic as evidence of exchange networks. Exotic items are more easily recognised archaeologically/archaeometrically and their emphasis may skew interpretations resulting in diffusion⁶ being implied as a dominant social process. In Holocene Aboriginal Australia it is unlikely that ochre ever functioned as a solely utilitarian material because it is derived from the

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⁶ Diffusion here refers to the spread of good ideas rather than colonialist ideologies (McNiven and Russell 1997).
landscape, both the physical and metaphorical (cultural landscape). The cultural importance of ochres might have been overstated in research designs that have sought the exotic and built narratives upon cultural exchange, social interaction and the long distance diffusion of goods and ideas (Brumm 2010, McBryde, 1987, 1997a, 1997b, 2000; Mulvaney 1976).

1.2 Re-examining the Provenance Postulate

_The meaning of the goods and the significance of their source location are explained and maintained over time by the stories that also map the symbolic and geographical world of these long distance transactions_ (McBryde, 1997b:605).

The ‘Provenance Postulate’ articulated by Weigand, Habottle and Sayer in 1977 was rapidly adopted in archaeological research, and has become the staple rationale for the compositional analyses of archaeomaterials. It holds that an artefact can be assigned to the geographically restricted source of the materials from which it was manufactured, so long as the composition difference between source materials exceed the compositional variation within a given source (Weigand et al. 1977:24, emphasis added). Neff (2000:109) restated this as the possibility of assigning a raw material to its source on the basis that there exists some ‘... qualitative or quantitative chemical or mineralogical difference between natural sources that exceeds the qualitative or quantitative variation within each source’ (Wisseman et al. 2002:690). This more recent expression is relevant here because it notes the value of qualitative data and the importance of structural characterisation (see Appendix D), rather than concentrating on the ultimate assignment of a material to a ‘source’ and the geochemical resolution at which this is achieved, something often seen as the measure of success for provenance research (Popelka-Filcoff et al. 2012a). But the most critical qualifier of the ‘Provenance Postulate’ is generally the least often stated in relation to geochemical characterisation, and that is: _elemental analyses are only capable of systematically eliminating possible sources_, because other deposits with identical ‘geochemical fingerprints’ may exist. Therefore, it is possible to rule out a ‘source’ on the basis of elemental composition alone, but not prove source assignment (Malainey 2011:171; Ward 1978; Wilson and Pollard 2001 my emphasis). Further complicating the picture in relation to ochre geochemistry, ‘earth materials’ may have similar chemical profiles and simultaneously distinct mineralogical components (Wisseman et al. 2002:690).

Leaving aside the mechanics of provenance assignment, an oversimplified, but useful dichotomy for understanding its theoretical underpinnings in archaeology is to separate them as falling within either formalist or substantivist paradigms. The formalist perspective highlights the individual within the socio-political trade and exchange system as determining and constraining the distribution and value of an item. A formalist stance predicts that individuals will procure and distribute materials and objects in a cost-efficient manner (similar to the underpinnings of behavioural ecology models adopted in Australian archaeology – c.f. Clarkson 2007: his Chapter
2; Smith 2013: his Chapter 5). The substantivist perspective emphasises the corporate, viewing procurement and distribution of materials and objects as part of complex social processes that function to maintain inter and intra group alliances, establish prestige/status, facilitate access to resources, etc (Dillian and White 2010). Substantivist approaches explicitly attempt to address the symbolic and ideological aspects of trade and exchange networks (Brumm 2010; Dillian and White 2010:5-6; McBryde 1997a, 2000).

Substantivist perspectives have historically informed archaeological interpretations of ochre research, at least implicitly, due to association of ochres with symbolic/ritual behaviours. Australian pigment studies have been informed by ethnographic records which describe ochre being exchanged over distances of hundreds of kilometres (McCarthy 139-40; Mulvaney 1976), an integral material expression of complex exchange networks and even the subject of dedicated procurement expeditions with parties travelling similar long distances to collect ochre from specific sources, despite local pigments being readily available (McBryde 1987; 1997a: 272; Smith, 2013; Smith and Fankhauser 2009:1). Such underpinnings not only imply a substantivist perspective, they emphasise diffusion as the primary mechanism in trade and exchange, the ‘exotic’ representing a transfer of knowledge and meaning especially in respect of ‘sacred’ places and landscapes (Dillian and White 2010:11; McBryde 1997a, 2000).

More recently the model of ‘object biography’ (Gosden and Marschall 1999) has come to prominence, placing the objects/materials themselves as the central focus to define contextual interpretations of artefacts and their materials of manufacture, articulating discrete and often dynamic life histories (Dillian and White 2010:5-6; Message and Fredrick 2012:426). It is this approach that has framed the interpretation of archaeometric data presented in this thesis because it allows fluidity, recognises that trade/exchange are but one of a number of cultural contexts in which objects can be imbued with meaning and that the objects need not be physically modified nor moved in order for this to occur (Gosden and Marshall 1999:174). Indeed, insights into the cultural context of objects and materials are not reliant on the assignment of ‘provenance’.

This research seeks to describe archaeological ochres with material scientific methods and use those characterisations to inform the biography of the object, especially its cultural context, through time and space. Therefore, this research will expressly separate the techniques and methods used to characterise pigments from the application of the ‘Provenance Postulate’. Here, I define characterisation in the alternate framework of provenance as used by collection managers. Understanding the materials from which an artefact is composed, in this case its geochemical composition, greatly enlarges the research potential and scientific significance of the artefact and the archaeological/ethnographic site from which it is derived by enabling comparisons with other objects and sites (Russell and Winkworth 2009).

Under the umbrella of the ‘Provenance Postulate’, previous geochemical ochre research in Australia
has deliberately avoided rock art due to ‘... the problem of dealing with paints as mixtures...and
problems posed by the retouching and over painting of motifs with different pigments’ (Smith et
al. 1998:280). However, these perceived ‘problems’ that may hinder the assignment of processed
pigment to a ‘source’ of raw material, point to the archaeometric importance of characterising
rock art. Most archaeological studies of ochre focus on whether pigment was used at a site and the
implications of this, but not how it was used, limiting interpretations of past behaviour (Hodgskiss
2010:33-44). The nature of composite pigments, which include the selection and procurement of
‘raw’ ochre; the selection of a site and panel; pigment preparation; the form of the motif/gestural
mark and application techniques, mean that there is opportunity for physical evidence of the
cultural context in which rock art was created to be incorporated into its materiality throughout
the processes of its production. As the papers contained in this thesis show, untangling the
taphonomy of rock art pigments is imperative in examining the geochemical signature of cultural
2014—Appendix B).

1.2.1 Previously Unseen: Geochemical Evidence of Cultural Context in Rock Art Production

The concept of culture in anthropology has historically denoted a broad body of beliefs, customary
behaviours and modes of social organisation that are transmitted over generations. While cultural
traditions are known to be resilient through time, it is important to recognise the normality of
change and adaptation to prevailing social and environmental conditions’
(Head et al. 2005:255).

Historically, archaeological ochre research has deployed geochemistry (and occasionally structural
analyses) within the ‘Provenance Postulate’ to try and infer function. Archaeologists have been
preoccupied with determining artefact function from the earliest days of the discipline and this
has been one of the primary drivers of archaeometric investigation (Fullagar 1986; Salmon 1981
cited in Haslam 2006). Here I have selected pigment with at least one known function, deliberately
seeking to illuminate intention in rock art production. The observation of patterning is the primary
means by which archaeologists gain insights into the past intentional interaction of people with
their surroundings and each other. This notion of intentionality underlies typological approaches
in archaeology including stylistic classifications of rock art (sometimesthreatening to undermine
them—see Hiscock and O’Connor 2006; Scarre 2004). Intentionality does not begin and end with
the graphic convention of motifs or ‘gestural marks’ (stencils, finger fluting and the like) (Rosenfeld
1999). Intentionality is present in every aspect of the construction of rock art, from the selection
and procurement of ochre, to the processing of pigment and the way in which it is applied to the
rock surface. Just as ‘... artists can depict anything they wish, but they don’t ...’ (David 2004:71;
Smith 1992), pigments used to produce rock art could be sourced from almost anywhere and
prepared any which way, but they aren’t. Artefacts record intention because they are the net result
of choices from a series of potential end points, the archaeological expression of that intentionality

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being regularity of artefact form (Russell 2004). Choice is not infinite, it is constrained by culture. Thus artefacts are not only evidence of their original intention or function, but also the broader cultural context in which they were produced (David 2004).

Intentionality and cultural landscapes are conceptual spaces that link potential function and praxis (McBryde 1997a; Russell 2004:64). Cultural landscapes are associative (McBryde 1997a) and Aboriginal people see these landscapes ‘...as an intimately connected set of phenomena with both material resources for practical usage and encompassing sentient spirituality’ (Head et al. 2005:257). Meaning may reside anywhere in the landscape and investigating the relationships between natural and cultural places may provide a fuller and more nuanced understanding of the past (Tilley 2004). Rock art is therefore unique material culture, part of a ‘people:Dreaming:land triad’ (David 2004:70). It is at once tangible and intangible; it is simultaneously experienced and timeless because it is a means by which landscapes are socially engaged (David 2000; Rosenfeld and Smith 2002; Rosenfeld 1997). Not only the locations of ochre source therefore, but the location and form (both graphic construction and materiality) of rock art may be explained and maintained, through time, in what McBryde described as ‘storied landscapes’ (1997b). The long lived or ‘near-permanent’ nature of rock art is important as this means that much of it will last beyond the period of its original cultural context of production, leaving marked places in land that pertain to earlier ‘social geographies’ (Rosenfeld and Smith 2002:61-2). Rock art has the potential to offer insights in regards to the reconfiguration of cultural contexts precisely because it is fixed to place, part of the physical and cultural landscape that can be re-socialised (David 2002; Rosenfeld 1997; Taçon 1994).

Ethnographically, post-colonial art production in Aboriginal communities has involved subtle changes in design form, partially facilitated though the transfer of motifs to new materials (Morphy 2009:20). As Frederick has argued (1999: 40), rock art produced in the context of cross-cultural exchange is not always immediately stylistically distinguishable, something demonstrated by a recent study of pigment chemistry using pXRF in Arnhem Land (Wesley et al. 2014). These subtle shifts in art practice have been seen as forms of resistance and subversion during colonial encounters (McNiven and Russell 2002; Russell 2004). While this might be true, it is important to acknowledge the normality of change in cultural systems (David 2000; Head et al. 2005). Though changes in art practice in colonial Australia have occurred through interaction with an outside/invading culture, they are ‘...also clearly continuations of endogenous processes’ (Morphy 2009:20).

Selecting rock art as the core archaeological assemblage in this thesis, the pigments analysed have at least one known function. However, the multi-layered complexity of knowledge in Aboriginal societies is well documented, particularly in respect to the production of art (Morphy 1989, 1991). Rock art may preserve information throughout different stages of its history from its creation
to maintenance and/or re-socialisation via retouch/repainting. Pigment characterisations have a role to play in teasing out layers of intentionality by providing previously unseen patterning. For instance, as Chapter Six demonstrates, rock art produced using the same formal, stylistic convention and the same colour, may be produced using different mineral pigments.

### 1.2.2 Issues of Scale

The different scales at which regional geological and archaeological investigations have historically operated have been observed as hindering effective integration of data and interdisciplinary analyses. Geological investigations scrutinise processes at a landscape scale in regional systems, whereas archaeological investigations extrapolate regional histories from the material records of discrete sites (Linse 1993). Here I propose that archaeological ochre studies can provide bridges across landscape, regional and site specific scales, and offer the methods developed for pXRF analysis as one means of facilitating comparable data scales.

Ochre is a product of geological weathering, the end result of landscape scale processes. Like lithic technologies, ochres are important archaeological evidence because they are durable, found across vast temporal scales and recovered in every known Australian regional prehistoric record in varied contexts as surface and subsurface finds, source quarries and rock art. Ochre has been used to mark inter-regional scale social networks—some of which crossed the continent of Australia in the historic period (McCarthy 139-40; Mulvaney 1976). Ochre is both evidence of trade and exchange networks between cultural groups (McBryde 1987, 1997a, 1997b; Mulvaney 1976; Smith et al. 1998) and the material with which cultural groups differentiate themselves and their country and mark territoriality (Ross 2013; Veth et al. 2011).

The notion of rock art as an expression of group identity and territoriality has been a constant interpretive thread in Australian studies, as has the implication that unpredictable or high-risk ecological conditions and/or low population densities facilitated extended social networks and long distance communication. In contrast, more bounded networks operated in fertile, predictable environs (Rosenfeld 1997:289; Rosenfeld and Smith 2002). The analysis of ochres from excavated contexts has been demonstrated as one means of informing the reconstruction of regional cultural systems, and their expansion or contraction through time (Smith et al. 1998). Changing the material focus of this geochemical investigation from ochre sources to rock art shifts the interpretive focus from implicitly diffusionist views about the trade and exchange evident in highly mobile ochres within the long-range social networks that criss-crossed the Australian landscape in association with song lines/Dreaming tracks, to implicitly territorial, intra-group explanations of rock art as a stationary material that bounded Aboriginal nations and differentiated group identity.

Two things have limited the application of archaeometric, and particularly geochemical investigations of rock art and other archaeological ochres. The primary restriction has been project budgets and the availability of analytical expertise limiting the number of archaeometric
analyses undertaken in assemblages (Neff 1998:321). Secondly, in relation to materials that remain culturally significant such as rock art, destructive sampling for analysis in a laboratory has posed serious ethical considerations (Bednarik 1992; Clottes 1992; Watchman 1992b). pXRF provides an inexpensive and readily accessible method of characterising rock art without a need to remove samples. This method can therefore provide a means with which site specific, regional and even interregional scale archaeometric analysis of rock art and other archaeological pigments can be undertaken.

1.3 pXRF in Archaeology

pXRF has been applied in archaeometry for over 35 years (Guilherme et al. 2008:444) but the last decade has seen a veritable explosion in use of the technique in anthropology related disciplines, particularly for investigating the provenance of archaeological ceramic and obsidian (Aloupi et al. 2000; Forster et al. 2011; Johnson 2012; Nazaroff et al. 2009; Shackley 2002, 2005; Sheppard et al. 2010; Speakman et al. 2011:3483). The recent ubiquity of pXRF has been driven by an increase in commercial availability/decreased prices of ‘hand-held’ instrumentation, colliding with the growing importance of non-destructive methods in contemporary archaeology (Heginbotham et al. 2010:178; Joyce 2011:199). Like no technique before it, the rapid adoption of recent generation hand held pXRF has had an indelible impact on archaeometric research because of its accessibility.

Accessibility has seen pXRF used by both scientists and ‘straight’ archaeologists who may lack a background in scientific method/standard laboratory procedures. Therefore, archaeological use of pXRF has spawned a literature focused on evaluating the technique, and more particularly the scientific merit of methods of its application to archaeological problems (Craig, 2007; Frahm, 2012, 2013; Galli and Bronizzonic 2014; Goodale et al. 2012; Johnson 2012; Potts, 2008; Shackley 2011; Speakman and Shackley, 2013). Added to the wildly varying scientific training of new users, pXRF, like other portable spectrographic techniques, is most often conducted on unprepared or little-prepared sample surfaces thereby re-introducing a number of ‘matrix effects’ that can degrade analytical accuracy (Huntley 2012—Appendix B, Juan F. Ruiz Lopez pers. com. March 2014, Markowicz 2008; Potts et al. 2005; Shackley 2011, Speakman et al. 2011). These ‘matrix effects’ (see Chapter Two) are removed during classic preparations for laboratory XRF by crushing and milling samples followed by the creation of a fused bead (for major elements) or a pressed powder pellet (for trace elements). Analysis of unprepared materials is more complicated, especially in the field, when compared to conventional desktop XRF, as the papers included in the body of this thesis demonstrate (particularly Chapters Two and Five). In short, there is good cause for the close scrutiny of individual pXRF studies, especially those argued to be only ‘internally consistent’ (Speakman and Shackley 2013).

The evaluation of scientific techniques in archaeometry is a necessary means of gauging their efficacy in addressing archaeological problems. The evaluation of pXRF is archaeometrically
uncommon because take-up of the technique has not been motivated by improved analytic resolution or sensitivity — quite the opposite. Recent generation hand-held pXRF analysers are relatively inexpensive, readily available and their ‘non-destructive’ nature has facilitated access to a range of previously ‘off-limits’ artefacts (though see Chapter Four). The dominant use of pXRF, as with most chemical analytics in archaeology, has been provenance studies (Speakman and Shackley 2013). Evaluation of techniques in this area of research is increasingly important as new, or improved (higher resolution) geochemical methods are applied, particularly in respect to the integration of datasets across studies, techniques or laboratories including the comparison of legacy data. The risk associated with multi-technique provenance studies (Frahm 2012:166), and the use of pXRF by scientifically inexperienced researchers, is that unrecognised low-quality or inaccurate geochemical characterisations could be incorporated into datasets leading to ‘source-assignment’ errors: the misattribution of an artefact or archaeomaterial to a group of other artefacts or a source of raw material. Misattribution has the potential to create false archaeological narratives, and in the case of multi-technique studies or inter-study comparisons, to corrupt existing archaeological understandings.

pXRF evaluation has taken the form of the ‘usual’ scientific measures. Most evaluations have focused on:

- **Precision**, the degree to which measurements taken using the same conditions give identical results (Craig et al. 2007; Frahm 2012:167 cites Taylor 1996; Forster et al. 2011; Heginbotham et al. 2010; Speakman et al. 2011) accounting for factors such as instrumental drift (Johnson 2012);

- **Accuracy**, how close a measured value is to ‘the truth’, an accepted or consensus value (Craig et al. 2007; Goodale et al. 2012; Heginbotham et al. 2010; Johnson 2012; Lirtzis and Zacharias 2011; Markowicz, 2008; Malaney 2011:87; Ogburn, 2013; Williams-Thorpe et al. 1999) including quantifying instrumental drift (Heginbotham, et al. 2010; Johnson 2012; Speakman and Shackley 2013); and

- **Sensitivity** an instrumental measurement describing the detection limits of a technique and resolution of semi-quantitative/quantitative data generated (Malaney, 2011:87; Piorek 2008; Speakman and Shackley 2013; Speakman et al. 2011).

A final category touched on in most pXRF evaluations coevally with these traditional scientific concepts, is the most critical assessment criterion for any archaeological application. The concept of **validity** addresses whether or not the variables analysed in fact correspond to the archaeological phenomena one is trying to study (Frahm 2012:170). Validity is a central concept in archaeometry because ‘... analytical characterisation requires a bridge between analytical measurements (elemental concentrations, isotope ratios, proportions of mineralogical phases, etc.) and the archaeological concept of interest ...’ (Neff 1998:323), ‘in other words the characteristic composition, or structure, being measured needs to be relevant to the problem being investigated’ (Plog 1982:75, emphasis added). Any reported application of pXRF should include an explicit
justification for the archaeological validity of its application, at least in the first instance.

The evaluation phase in relation to recent generation pXRF seems to be drawing to a close having produced a significant body of publications from fundamental texts (Potts 2008; Shackley 2011) to detailed instrument specific critiques (Johnson 2012; Speakman and Shackley 2013) and inter-instrument studies (Craig et al. 2007; Heginbotham et al. 2010). Several applications have come to the fore, most notably provenance investigations of archaeological obsidian (Craig et al. 2007; Frahm 2013; Nazaroff 2009; Phillips and Speakman 2009; Speakman and Shackley 2013) including studies in the Australasian region (Galipaud et al. 2014; Golitko et al. 2012; Sheppard et al. 2010). pXRF has been widely adopted for examining archaeological obsidian because the chemical characteristics of the raw material itself are ideal. Variation between obsidian sources is ‘truly huge’ compared to within source variability (Neff 1998:324). Secondly, the reduced suite of elements measured by recent generation, commercially produced, hand held pXRF analysers sits right in the ‘sweet spot’ of discriminate elements that differentiate obsidian sources (Speakman and Shackley 2013). That is, XRF, including pXRF, has optimal accuracy in mid-Z elements. Given current detector (i.e. instrument) limits, precision is best in mid-Z elements which are known to discriminate between obsidian sources (Craig et al. 2007; Nazaroff et al. 2009; Shackley 2002, 2005; Sheppard et al. 2010). Finally, obsidian is as an exemplar material for pXRF because it is texturally uniform and consistently dense.

Other more complex provenance applications have also been demonstrated for pXRF including studies of archaeological basalts (Williams-Thorpe et al. 2003; Williams-Thorpe 2008), ceramics (Forster et al. 2011; Speakman et al. 2011), buildings (Ogburn et al. 2013) and metals (Heginbotham et al. 2010). pXRF has been used to successfully characterise archaeological stuccos and frescos (Gebremariam et al. 2013), chemostratigraphy of excavated sediments (Davis et al. 2012) and in archaeological site prospection (Hayes 2013) and artefact authentification (Galli and Bonizzoni 2014). In Australian archaeology, pXRF investigations have focused on lithic technologies within the traditional application of the provenance paradigm (Attenbrow et al. 2012; Cochrane et al. 2012; Grave et al. 2012) and the characterisation of rock art (Huntley 2012—Chapter Two; Huntley et al. in press—Chapter Six; Wesley et al., 2014).

1.3.1 pXRF and Rock Art Research

The beneficial attributes of non-destructive techniques for rock art analysis have long been expounded in laboratory settings (Edwards et al. 1998; Goodall et al. 1996, 2001). The development and refinement of portable spectrometry has allowed the compositional analysis of objects that have restrictions on destructive sampling (Williams-Thrope 2008) and/or are immobile, such as rock art, which is fixed to place. As with other archaeometric studies, pXRF is the most reported portable spectrographic technique in rock art research. However, in situ characterisation of
rock art has not been confined to pXRF; field portable Raman and Fourier Transform Infrared Spectrometers have been trialed with varying degrees of success (Juan F. Ruiz Lopez pers. com. March 2014; Prinsloo et al. 2013; Tourniè et al. 2010, but see also 1 2009 for complexities of laboratory based analysis) (see preface to Chapter Six, page 144). pXRF has also been used as a complimentary component in archaeological pigment investigations, such as actualistic studies, to describe the ochre sources (d’Errico et al. 2012; Rifkin 2011, 2012).

The first published application of pXRF to rockart appeared in 2005 (Newman and Leondorf 2005). Here pXRF was used in Montana and Wyoming, North America to characterise green, red and yellow pigment motifs and investigate their rumoured historical repainting. The results indicated that Cr was the colour producing constituent of green paint, interpreted as indicating local sources of chromiferous muscovite, specifically the mineral furchsite, were used as pigment. High Pb levels in the yellow motifs thought to be historically repainted were interpreted as evidence of European pigment and the spatial application of pXRF across one motif was further used to demonstrate that only ~80% had been ‘historically retouched’ (ibid:280). This early study flagged the cost-effective nature of field based, in situ rock art analysis. The authors estimated that the equivalent cost of hiring the pXRF unit for four days, over which time they collected 156 spectra, would have allowed laboratory analysis of only 15 equivalent samples (ibid:282).

In the following decade a handful of studies have been published and most echo the findings of this early work. Indeed, Rowe and colleagues (2011:38) were able to analyse 75 motifs within the same rock shelter in a ‘matter of hours’ attesting to the rapid and cost effective nature of data capture. Most studies have been conducted in north America (Bedford 2013; Koenig et al. 2014; Leondorf and Leondorf 2013; Newman and Leondorf 2005; Rowe et al. 2011; Velliky 2013), Australia (Huntley in press —Chapter Six; Huntley 2012 —Chapter Two; Huntley et al. 2014— Appendix D; McDonald et al. 2008, 2014; Wesley et al. 2014) and Spain (Roldán et al. 2010; Neuvo et al. 2012). These studies are summarised here under two categories: the results and interpretations of previous work, and the common methods applied to assist in reaching those interpretations.

Regarding analytic methods, a common strategy and one advocated in this research is spectral acquisition on ‘blank’ or unpainted rock substrate in addition to pigment (Koenig et al. 2014; Leondorf and Leondorf 2013; Newman and Leondorf 2005; Nuevo et al. 2012; Olivares et al. 2013; Rowe et al. 2011; Velliky 2013; Wesley et al. 2014). In relation to the infinitely thin nature of most rock art and the incorporation of the rock substrate into spectra, previous work shows that the idea of simply ‘subtracting’ the background rock matrix of mineralogical heterogeneous stone is not feasible (Olivares et al. 2013; Velliky 2013). In fact, previous work has not quantified, nor addressed the impact on their interpretations, of the mineral heterogeneity of rock substrates (see Chapters Two, Five and Six). There has also been no prior discussion of the geochemical signature of weathering processes in rockshelter environments, nor any attempt to address these.
I explicitly investigated these taphonomic issues in Chapters Two, Three and Five.

Regarding applied studies, red and black pigments have been the most often studied. Researchers such as Bedford 2013, Leondorf and Leondorf 2013, Rold’án et al. 2010, Rowe et al. 2011 and Velliky 2013 have concluded that different sources of red ochre were used to paint motifs within the same site, often the same panel, based on chemical variance within red pigment motifs. No data is supplied to discount these different Fe signatures resulting from differences in pigment thickness or variation in the stone substrate. Rold’án et al. (2010) reported a mixture of Mn and Fe in mulberry/red rock art pigments in the Levant, and their results indicate calcite matrix haematite in red paintings. Leondorf and Leondorf (2013) and Rold’án et al. (2010) are the only authors who report which elements varied in the red ochres they studied and Rold’án and his collaborators alone give relative abundance data.

In respect of the analysis of black pigments, Koenig et al. (2014); McDonald et al. (2014); Newman and Leondorf (2005); Nuevo et al. (2012) and presumably David et al. (2013)7 all found no chemical evidence, such as Mn, in black pigments, interpreting this as evidence for organic, charcoal pigment use. Contrary to this, Rold’án et al. (2010) found strong Mn and Ba signatures in the two black motifs they analysed, concluding manganese oxide pigments were used, whereas Wesley et al. (2014) have argued that lead shot from European weapons was used to produce a black anthropomorphic motif at Urrmarning ‘Red Lily Lagoon’ rock art precinct, western Arnhem Land. Interestingly, Nuevo et al. (2012:4) conclude that a white ‘motif’ (which looks like the stub of wasp nest, rather than a graphic) had very little iron and on this basis suggested it to be organic in composition, rather than investigating clay or calcite mineral pigments ubiquitously reported for rock art (Cole and Watchman 1996; Huntley et al. 2011—Appendix B; Rowe 2001; Sale and Watchman 1993; Ward et al. 2001; Watchman 1990). Many previous studies have shown the archaeological potential of qualitative geochemical description, especially in relation to inferring pigment mineralogy (Koenig et al. 2014; Leondorf and Leondorf 2013; Newman and Leondorf 2005; Wesley et al. 2014) and this potential is not confined to pXRF—portable Raman spectroscopy has also been used in this way (Olivares et al. 2013; Prinsloo et al. 2013; Tournié et al. 2010). However, previous work has not differentiated major mineral phased from motifs of the same colour, a possibility demonstrated in Chapter Six (:144).

1.4 Research Aims and Regional Context

To investigate the cultural context of rock art production in this research, pXRF is integrated into an archaeological analysis of pigments, developing novel methods for the generation and interrogation of geochemical data. Understanding the physical/archaeological context of

7 David et al. (2013:2498) claim to have analysed a ~28,000 BP ‘charcoal’ motif with pXRF (specifically a Thermo Scientific Niton XL3t Gold) – but present no data, stating only that their results showed the presence of calcium oxalate minerals was ‘negligible’.
Similarly, researchers in South Africa have analysed a substrate flake they argue has applied pigment from a rockshelter near Mt Ayliff in the southern cape, the results not yet published (Steyn et al. no date).
materials is imperative for interpreting the geochemical profiles generated. This includes not only the physics of analyses—how the hand held instrument generates element profiles ( Chapters Two and Four)—but also the palaeogeographic environment and specific regional archaeological history of pigments. Rock art pigments and archaeological ochres (surface finds including quarries and those from excavations) have complex taphonomic histories. The chemistry of pigments therefore reflects not only diageneis, but cultural and post depositional contexts. This research seeks to understand the chemical indices of taphonomy to separate (as far as possible) the chemical signatures of environmental and cultural phenomena. The following sections review the archaeological and palaeogeographic context of the two case study areas where pigment characterisations were undertaken.

The rationale for selecting two geographically distinct rock art precincts as case studies was the incremental evaluation and application of pXRF. The opportunity to work within a multi-disciplinary project in the northwest Kimberley was the catalyst for this research. However, the practicalities of fieldwork in remote northern Australia (expense and logistical issues such as the amount of time taken simply reaching sites) necessitated the prior development, evaluation and rigorous field testing of in situ techniques. I selected the Sydney Basin as the setting for this. Firstly, because the common attributes of mineral pigments and sandstone substrates made the materiality and physical contexts of the two rock art assemblages comparable. Methodologies for in situ pXRF analysis developed in one geographic region could consequently be applied in the other. Secondly, my previous research and work experience (in cultural heritage management) has been conducted primarily in the Sydney Basin. I was equipped therefore, to initiate a field program immediately upon commencing my PhD candidacy with useful logistical and archaeological backgrounds, and necessary Aboriginal community consultative experience.

My familiarity with rock art pigments of the Sydney Basin also made it an attractive location to develop, evaluate and field test in situ pXRF. I have undertaken the only characterisations of rock art pigments in the region to date (Huntley et al. 2011— Appendix C). This meant that I had comprehensive pigment characterisation datasets to draw from (Ford 2006; Huntley et al. 2011). Importantly, I was acutely aware of the chemical indices of complex taphonomy in Hawkesbury Sandstone rock art panels (see Chapters Two, Three and Five).

The attraction of working in the Kimberley was not only the rock art assemblage itself, renowned for its volume and complexity, but the amount and quality of legacy data available. The Kimberley region has been subject to the most numerous, varied and highest-quality material science/
archaeometric investigations of rock art in Australia (see Appendix C, Figure 1). The work of conservation scientists based at the Western Australian Museum, combined with the archaeological motivation of establishing a chronology for rock art has resulted in suites of data with which in situ pXRF procedures could be designed, assessed and interpreted (see Chapter Six) (Clarke 1976, 1977, 1978; Crawford and Clarke 1976; Ford et al. 1994; MacLeod and Haydock 2008; MacLeod et al. 1991, 1997; O’Connor and Fankhauser 2001; Randolph and Clarke 1987; Ward et al. 2001; Watchman 1997a, 1997b; Watchman et al. 1997, 2001, 2005).

1.4.1 The Rock Art Assemblages

So far, this chapter has introduced the broad archaeological background of pigment analyses, reviewed international and broader Australian literature and outlined the theoretical underpinnings of this research. This section reviews the regional archaeologies of the Sydney Basin and northwest Kimberley (Figure 1.3). Both rock art precincts have well described stylistic sequence (McCarthy 1967, 1988; McDonald, 1988, 2008; Walsh, 1994, 2000; Welch 1993a, 1993b, 1993c). Both regions have been, or are currently, the subject of more tightly geographically focused, archaeological analyses (Dibden 2011 in the Sydney Basin and Ross and Travers 2013 in the north-west Kimberley). The regional prehistories of the case study areas, including the relative rock art sequences, describe spatial and temporal patterning used to generate hypotheses for the investigation of pigment geochemistry and also provide context for interpreting the resultant elemental datasets.

![Case Study Areas](image)

*Figure 1.3 Case study locations showing iconic examples of their rock art assemblages. Upper inset image: part of a panel of Yowna Gwion at the One Tree Beach2 site, Admiralty Gulf, WA. Lower inset image: Part*

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10 Wunambal name for this motif style – previously ‘Sash Bradshaw’ (Walsh 1994, 2000) or ‘bent knee’ figures (Welch, 1993a, 1993b, 1993c).
of the main panel at the Dingo and Horned Anthropomorph site, Mt Manning, NSW.

Geological Basins are shown in red, data collection points in black.

1.4.1.1 The Sydney Basin

Aboriginal occupation of the Sydney Region appears to have begun in the late Pleistocene, with consistent evidence for basin-wide occupation by the terminal Pleistocene and early Holocene (Attenbrow 2004:335; McDonald 2008:35; Williams et al. 2012:87). The vast majority of sites with numeric age determinations, and assigned chronologies based on the typology of their lithic assemblages, indicate initial use in the late Holocene (ibid). Recent work shows that some preserved sand bodies in the region began forming more than 50 000 years ago (Williams et al. 2012), but assertions that artefacts within these date to 40 000 years or more are generally questioned (McDonald 2008:36; Nanson et al. 1987; Williams et al. 2012:85) with good cause, as stratigraphic integrity seems lacking.

Two major stylistic phases of pigment rock art are described for the Sydney Basin (McCarthy 1967, 1988; McDonald 2008). This broad subdivision was supported by recent, more geographically discrete analyses (Dibden 2011), although chronological parameters for the relative rock art sequence have proven problematic (Huntley et al. 2011; McDonald et al. 2000). Mid to late Holocene ages are suggested for the rock art analysed by pXRF (Chapter Two, Three and Five). Bichrome motifs at Browns Rd29 on the southern Woronora Plateau (Chapter Two) have an inferred age of somewhere between 4000 years ago and the European colonial period (McDonald 2008:249, 343). The motifs examined at Dingo and Horned Anthropomorph were proposed as the first ‘dated’ rock art in Australia based on the extrapolation of numeric ages for ground ochre and pigmentaceous material in excavated contexts (Macintosh 1965:85, see Chapter Five). On this basis, Macintosh argued the horned anthropomorph motifs are ~500 years old and eel motifs ~135 years old. Using a similar rationale, McDonald (2008: 98, 136) proposed that the art in Yengo 1 was produced ~2000 years ago (see Chapter Five for further discussion).

Previous pigment characterisations of Sydney Basin rock art are presented in Appendix C, and further discussion of site specific archaeological contexts is given in Chapters Two and Five.

1.4.1.2 The Northwest Kimberley

Archaeological research in the Kimberley has documented a human habitation record of considerable antiquity, beginning ~45 000 BP (Balme 2000; O’Connor, 1995; Watchman et al. 2005). This region has the potential to answer major questions in Australian and world prehistory regarding the initial settlement of Sahul, the response of populations to major environmental fluctuation, and the timing and material indices of modern/symbolic behaviour (Balme et al. 2009; Brumm and Moore 2005; Davidson 2010; Goebel 2007; Habgood and Franklin 2008; Morwood and Hobbs 1995, 1997; O’Connor 2007; O’Connor and Veth 2006; Veth et al. 2009). Being the closest part of mainland Australia to Asia, the Kimberley is one of few ‘beach-heads’ for the initial
continental colonisation (Morwood and Hobbs 1995, 1997). Many scholars now believe, as I do, that Australia was occupied by 50 000-60 000 years ago (Balme et al. 2009; Davidson 2010; O’Connor 2007; Roberts et al. 1994; Ross and Travers 2013,) although the location and timing of initial colonisation remains unknown. In addition to evidence of ‘early’ human occupation (Balme 2000; Balme et al. 2009; Dortch and Roberts 1996; O’Connor 1995, 1999; O’Connor and Veth 2006; Watchman et al. 2005), the Kimberley boasts a large and complex rock art assemblage with unparalleled iconographic specificity providing insights into past material culture not otherwise preserved (Walsh and Morwood 1999). The rock art of the Kimberley also documents changes in cultural practices through time, including evidence of cross-cultural contact (Morwood and Hobbs 1997; O’Connor and Arrow 2008; O’Connor et al. 2013; Ross and Travers 2013; Walsh, 1997, 2000; Welch, 1993a, 1993c, 2012).

Detailed relative sequences described for the Kimberley have ordered stylistic classifications based on imagery superimposition and observations of differential weathering (Walsh 1994, 1997, 2000; Welch 1993a, 1993b, 1993c)\textsuperscript{11}. The spatial location of rock art styles such as Gwion\textsuperscript{12} figures has been used to argue for deeper antiquity as they seem tethered to what is seen to be a stable geological environment, the King Leopold sandstone (Morwood and Hobbs 2000; Walsh 1997, 2000—though see the discussion in Section 2.2.2 below). Arguments for Pleistocene antiquity of rock art in the Kimberley are based on two studies. One centres on non-iconic pigmentation of a ‘slab’ of shelter matrix and a coeval ochre pellet recovered from a well stratified, radiometrically dated, excavated sequence (O’Connor and Fankhauser 2001). These finds from Spit 47 close to the base of Carpenters Gap 1 have been discussed above (Section 1.1.1, page 16-17). The other, pioneering work that used quartz grains incorporated into mud-wasp nests on a rock art panel to generated ‘direct’ OSL determinations, producing a ‘minimum’ age for the production of a Gwion like anthropomorphic motif (Roberts et al. 1997:697).

The current debate regarding the ‘direct’ ~17 000 BP minimum age for rock art in the Kimberley concerns whether in fact the mud-wasp nests in question overlaid motifs at all (Aubert, 2012:575-578; David et al. 2013a:6-7, Roberts 2000:48, Plate 68). OSL determinations produced from the core of nest KERC5, around 2 cm above the mulberry headdress of a Gwion style anthropomorphic figure, returned a ~17 500 BP minimum age. While single quartz grains from the adjacent nest KERC4 produced minimum ages between ~16 400 BP and ~23 800 BP. Photographs indicate that nest KERC4 is not in fact associated with art, and the association of KERC5 relies entirely on the assumption that the lip of the nest is contemporaneous with its core (Aubert 2012:575-576; Roberts 2000:49). Another complexity with the KERC4 determinations is that there was not enough mud available from the nest to measure environmental dose, so this was extrapolated from the adjacent KERC5 nest. The working assumption therefore in generating the age determinations

\textsuperscript{11} The relative Kimberley rock art sequence described by Walsh and Welch is outlined in Chapter Seven, so is the broader archaeological context of mulberry rock art in northern Australia.

\textsuperscript{12} Current nomenclature for northwest Kimberley rock art is provided in the forward pages of this thesis and outlined in Chapter Seven.
was that the two separate nests were entirely contemporaneous (Aubert 2012:576).

These ‘direct’ OSL ages for rock art production appear anomalous when compared to the Holocene radiocarbon determinations for minimum ages of *Gwion* motifs (n=2) and the carbon bearing substances coeval with paint in the microstrata of mineral accretions from *Gwion* and Irregular Infill Animal motifs (n=2) (Watchman et al. 1997, summarised in Table 1.1 below). The association of the carbon used to generate these age estimates with stylistically identifiable graphic motifs is not in question (Aubert 2012; Watchman 1997), something which seems lost in a recent review of Australian rock art chronology (David et al. 2013a). Queries have been raised about the circumstances under which mineral accretions are closed systems for carbon, but evidence from rockshelter walls and archaeological deposits in the Kimberley suggests that they are (O’Connor and Fankhauser 2001; Watchman et al. 1997; Watchman et al. 2005).

<table>
<thead>
<tr>
<th>Motif</th>
<th>Context</th>
<th>Uncalibrated (Calibrated) (Lab. No.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wanjina (Eye of Frilly Lizard Wandjina)</strong></td>
<td>Charcoal pigment – lowest painted layer</td>
<td>375±35 (1444-1634 CE) (OZD080)</td>
</tr>
<tr>
<td><strong>Wanjina (Simple Wandjina Head)</strong></td>
<td>Beeswax</td>
<td>3780±60 (2457 – 2033 BCE) (OZC343)</td>
</tr>
<tr>
<td><strong>Mambi Gwion (Tassel Bradshaw)</strong></td>
<td>Overlying pigment</td>
<td>1490±50 (538-623 CE) (CAMS 16755)</td>
</tr>
<tr>
<td></td>
<td>Overlying pigment</td>
<td>1490±290 (240-852 CE) (OZB124)</td>
</tr>
<tr>
<td></td>
<td>Underlying pigment</td>
<td>1430±180 (432-779 CE) (OZB351)</td>
</tr>
<tr>
<td><strong>Mambi Gwion (Cane Bradshaw)</strong></td>
<td>Associated with pigment</td>
<td>3880±110 (2559-2149 BCE) (OZB126)</td>
</tr>
<tr>
<td><strong>Irregular Infill Animal</strong></td>
<td>Associated with Pigment</td>
<td>3140±350 (1875-930 BCE) (OZB125)</td>
</tr>
<tr>
<td><strong>Pecked Cupules</strong></td>
<td>Oxalate coating overlying cupules</td>
<td>2220±100 (522 BCE – 3 CE) (OZB024)</td>
</tr>
</tbody>
</table>

**Table 1.1** Summary of 14C age determinations obtained for the Kimberley rock art.

*Note: Motif styles are ordered sequentially by Walsh’s (2000) relative chronology.*

*Data in bold from Watchman et al. 1997:25; data in italics from Morwood et al. 2010:5.*

*Current nomenclature (terminology used in prior publication where different).*

Most of the above radiocarbon determinations overlie rock art, providing minimum age estimates. However, carbon from a mineral accretion underlying a *Mambi Gwion* indicates a maximum age for that motif of ~500 cal. BP (Watchman et al. 1997:25) Significantly, carbons associated with paint
layers of a different *Mambi Gwion* and an Irregular Infill Animal motif produced ages of ~2300 cal. BP and ~1400 cal. BP for their respective painting (ibid). In general terms then, we can begin to propose a pattern of overlap, and therefore coexistence, among *Gwion* and *Wanjina* art in the mid to late Holocene, with minimum OSL determinations of mud-wasp nests indicating earlier *Gwion* styles may have been produced from the Pleistocene. This patterning has again been borne out by recent OSL dating of mud-wasp nests overlying rock art in the northwest Kimberley (*Table 1.2/Figure 1.4* below). On this basis, I think it likely that the pigments research herein deals with mid to late Holocene age rock art. A proposition consistent with the increased numbers of ochres observed in excavated sequences across the Kimberley at this time.

*Figure 1.4. Overview of mud-wasp nest dated using OSL showing a clear association with painted motifs.*
Left: Cages-mock Gwion figure from UP1A. Right: Kangaroo from LM-13.
### Table 1.2 OSL dating of quartz grains from mud wasp nests in Brremangrey, Upper Lawley (Dorre) and Lower Mitchell (Kandiwal) Falls site complexes, northwest Kimberley.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Image/Art style</th>
<th>Accepted grains</th>
<th>Beta dose rate$^a$ (Gy ka$^{-1}$)</th>
<th>Field gamma dose rate$^b$ (Gy ka$^{-1}$)</th>
<th>Cosmic-ray dose rate$^c$ (Gy ka$^{-1}$)</th>
<th>Water content$^d$ (%)</th>
<th>Total dose rate$^e$ (Gy ka$^{-1}$)</th>
<th>Technique$^f$</th>
<th>Statistical Models</th>
<th>Equivalent dose$^g$ (Gy)</th>
<th>Age$^i$ (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Upper Lawley (Dorre)</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>UP1A</td>
<td>Cages figure - Mock Gwion</td>
<td>57</td>
<td>0.921 ± 0.042</td>
<td>0.117 ± 0.004</td>
<td>0.184</td>
<td>1 / 2 ± 0.5</td>
<td>1.25 ± 0.05</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>4.6 ± 0.2</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td><strong>Breemangrey</strong></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BRY3</td>
<td>Armless figure - Wanjina</td>
<td>116</td>
<td>0.879 ± 0.041</td>
<td>0.179 ± 0.004</td>
<td>0.177</td>
<td>1 / 2 ± 0.5</td>
<td>1.18 ± 0.05</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>1.02 ± 0.04</td>
<td>0.86 ± 0.05</td>
</tr>
<tr>
<td>BRY6</td>
<td>Fish - Wanjina</td>
<td>0</td>
<td>0.897 ± 0.041</td>
<td>0.085 ± 0.004</td>
<td>0.177</td>
<td>1 / 2 ± 0.5</td>
<td>1.19 ± 0.05</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>8.7 ± 0.4</td>
<td>7.3 ± 0.5</td>
</tr>
<tr>
<td><strong>The Caverns</strong></td>
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<tr>
<td>CA-7</td>
<td>Argula - Wanjina</td>
<td>55</td>
<td>0.609 ± 0.036</td>
<td>0.128 ± 0.004</td>
<td>0.170</td>
<td>1 / 2 ± 0.5</td>
<td>0.94 ± 0.05</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>2.5 ± 0.1</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>CA-8</td>
<td>Shape - Gwion</td>
<td>88</td>
<td>0.530 ± 0.035</td>
<td>0.120 ± 0.004</td>
<td>0.170</td>
<td>1 / 2 ± 0.5</td>
<td>0.85 ± 0.04</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>21 ± 1</td>
<td>24 ± 2</td>
</tr>
<tr>
<td>CA-9</td>
<td>Gwion figure - Gwion</td>
<td>59</td>
<td>0.530 ± 0.037</td>
<td>0.099 ± 0.004</td>
<td>0.170</td>
<td>1 / 2 ± 0.5</td>
<td>0.83 ± 0.04</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>3.9 ± 0.1</td>
<td>4.6 ± 0.3</td>
</tr>
<tr>
<td><strong>Johns site</strong></td>
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<tr>
<td>JS-10</td>
<td>Figure - Wanjina</td>
<td>126</td>
<td>0.325 ± 0.032</td>
<td>0.088 ± 0.004</td>
<td>0.184</td>
<td>1 / 2 ± 0.5</td>
<td>0.630 ± 0.04</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>1.32 ± 0.04</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>JS-11</td>
<td>Star Yam - Wanjina</td>
<td>67</td>
<td>0.781 ± 0.039</td>
<td>0.109 ± 0.004</td>
<td>0.192</td>
<td>1 / 2 ± 0.5</td>
<td>1.12 ± 0.05</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>0.9 ± 0.2</td>
<td>0.8 ± 0.1</td>
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<tr>
<td><strong>Lower Mitchell (Kandiwal) Falls</strong></td>
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<tr>
<td>LM-13</td>
<td>Kangaroo - Wanjina</td>
<td>42</td>
<td>0.781 ± 0.039</td>
<td>0.097 ± 0.004</td>
<td>0.184</td>
<td>1 / 2 ± 0.5</td>
<td>1.09 ± 0.05</td>
<td>OSL$^h_{50}$</td>
<td>FMM</td>
<td>6.4 ± 0.1</td>
<td>5.8 ± 0.3</td>
</tr>
</tbody>
</table>

$^a$ Concentrations determined from beta counter measurements of dried and powdered sediment samples.

$^b$ Determined from U, Th and K concentrations measured using a portable gamma-ray spectrometer at field water content.

$^c$ Time-averaged cosmic-ray dose rates (for dry samples), each assigned an uncertainty of ± 10%.

$^d$ Field / time-averaged water contents, expressed as (mass of water/mass of dry sample) × 100. The latter values were used to calculate the total dose rates and OSL/TL ages.

$^e$ Mean ± total (1σ) uncertainty, calculated as the quadratic sum of the random and systematic uncertainties. An internal dose rate of 0.03 Gy ka$^{-1}$ is also included.

$^f$ Only one luminescence techniques were applied to these samples. OSL$^h_{50}$ optically stimulated single-grain dating.

$^g$ The statistical model used to determine the dose distribution between aliquots = FMM - Finite Mixture Model.

$^h$ Paleodoses include a ± 2% systematic uncertainty associated with laboratory beta-source calibrations.

$^i$ OSL signal measured using single-grains of quartz - with between 300-700 grains run per sample (depending on the size of the nest) with on average 22% of the grains emitting an acceptable luminescence signal.

$^j$ Uncertainties at 68% confidence interval.
Work conducted by Veitch on the Mitchell Plateau showed evidence for a ‘substantial increase in the regional rate of site usage during the last 3500 years’ (1996:86). The excavated sequences Veitch described date from ~6000 BP and showed a marked increase in cultural debris from ~3000 BP, coincident with the appearance of point technology (Veitch1999a:5, 1999b:32). Ochre within the excavated assemblages was notably more abundant in these recent strata, i.e. <3000 BP (Veitch 1996:74, 76 and 79). To the east of the Mitchell Plateau, the Drysdale River has been described as having little evidence for site use between 22 000–12 000 BP (Morwood and Hobbs 2000; O’Connor and Veth 2006:37). While excavations at rockshelters Drysdale 1 and 3 have produced ground ochre from ~25 5000BP (Morwood and Hobbs 2000:37; personal observation of ochres) the quantities of pigment are small and poor chronological control make it difficult to discuss the implications of these assemblages (see Chapter Seven, Figure 7.1 for locations).

Outside of the northwest Kimberley, on the mainland of the Buccaneer Archipelago to the west, O’Connor recovered ochres throughout the Holocene assemblage in the Widgingarri shelters and noted that the nearest known ‘high grade’ source was 80 kms distant, to the south on Koolan Island. She reports peak ochre discard in the late Holocene (spits <4) with a secondary spike in the mid Holocene strata (O’Connor 1999:78). With regard to general occupation patterns, excavated materials from the Widgingarri I and Koolan 2 shelters showed their continued use between 30 000–24 000 BP when they were several hundred kilometres inland, but both sites appear abandoned between 24 000–20 000 B.P, then reoccupation in the terminal Pleistocene/early Holocene (O’Connor and Veth 2006:37).

In the southern Kimberley along the Fitzroy River at the Mimbi Caves, ochre was found throughout strata of Japi and Riwi sites. In the late Holocene deposit at Japi, the most numerous pieces were recovered from the bottom and central excavated spits (n=39 in spit 7, n=25 in spit 4 and n=35 from spit 3) (Balme 2000:3). Riwi had fewer specimens (n=6 each from spits 7 and 4) with the lowest recovered from the middle of the deposit (spit 8). Based on the age of the excavation horizons in Riwi, the time scales associated with these ochres are Pleistocene and late Holocene (Balme 2000:3-4). Balme again noted a period of site abandonment, though the sequence at Riwi temporally contrasts the Last Glacial Maximum hiatus described by O’Connor and Morwood (above), with a disconformity of textural change in the sediments between the Pleistocene and Holocene strata (Balme 2000:4).

Recent re-excavation at limestone caves in the southern Kimberley including Carpenters Gap 3 (CG3) and Riwi are currently in the analysis stages and no data is yet available regarding the ochre assemblages recovered. New data to hand from CG3 replicates patterning described elsewhere in the Kimberley, and indeed across the Australian continent, with a hiatus in occupation coeval with the Last Glacial Maximum and a sharp increase in evidence for occupation from the mid-Holocene (O’Connor et al. 2014). CG3 was intermittently occupied from ~32, 800 cal. BP (ibid: 18) with
evidence for processes of calcium carbonate dissolutions and re-deposition evident throughout the deposit, particularly in the heavily cemented lower layers (ibid:12). Of note, marine shell artefacts were recovered from the Holocene deposits whose derivation must have been at least 200 km distant (ibid: 21). While this is not as significant as the presence of similar artefacts in Pleistocene contexts in the west Kimberley and Pilbara (ibid: 22, cites O’Connor 1999:60, 121 and Bowdler 1990), it demonstrates the extent of trade and exchange networks that operated at this time, which may be further illuminated by the analysis of coeval archaeological ochres.

In addition to ochres from excavations, five previous projects incorporating pigment characterisation have been undertaken in the Kimberley region. Two of these overlap portions of the northwest Kimberley case study (Thomas 1998; Ward et al. 2001; Watchman, 1997d). The remaining three were conducted to the south and west of the present project area (Clarke 1976; Crawford and Clarke 1976; Ford et al. 1994; O'Connor and Fankhauser 2001.) This previous work was concerned with three major research themes; provenance, chronology and conservation. Specifically, pigment characterisations in the Kimberley have sought to:

- **Provenance** pigment, including the geochemical characterisation of ethnographic sources (Clarke, 1976; Crawford and Clarke 1976; O’Connor and Fankhauser 2001; Thomas 1998);
- Investigate the potential of **direct radiometric dating** (Morwood et al. 1994, 2010; Ward 2001; Watchman 1997a, 1997b, 1997d; Watchman et al. 1997, 2005); and
- Inform the development of **conservation/management** strategies (Clarke, 1976; Ford, et al. 1994; Ward et al. 2001);

The findings of these previous archaeometric pigment characterisations are summarised as follows:

- Red rock art was found to be generally composed of iron-oxide (haematite), while mulberry paint was generally iron-sulphide (jarosite) (Ward et al 2001; Watchman 1997a, 1997b);
- In the case study area, iron-oxide mineralogy has been identified in red **Mambi Gwion** (n=2), ‘Cane’ **Gwion** and (n=1) Yowna **Gwion** (n=1) motifs (Watchman 1997 AIATSIS report; Ward et al. 2001) and red iron-oxide pigments have also been identified in sites containing **Wanjina** motifs to the south, in the Napier Range. XRD was used to attain mineral identifications, including iron-oxides, on homogenised paint layers from Wandjina motifs (Ford et al 1994: 39&60—see Huntley et al. 2014, Appendix D).
- **SEM-EDXA** was conducted on the ochre pellet and pigmented limestone slab from Carpenters Gap 1 to identify iron-oxides. Elevated counts for Mg and P, as well as the presence of clay elements indicate a composite mineralogy for the pigmented surfaces of the limestone slab (O’Connor and Fankhauser 2001:292-3);
- A single yellow rock art paint characterisation is available (Ward et al. 2001: 19). Researchers concluded that a zoomorphic (goanna) motif was composed of a mixture of clay (kaolin), jarosite and goethite minerals. There is a reference to ‘whewellite pigments’

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13 Previous mulberry pigment and mineral accretion characterisations are summarised in **Chapter Seven**
ranging in colour from white to yellow and black in Ford et al.'s study (1994:66) but sample identification is ambiguous. The researchers discuss yellow pigments in stratified paint layers of *Wanjina* flakes and the ‘muddy yellow pigments’ from ‘old (*Wanjina*) sites’ presumably in relation to motifs that were not repainted, but they provide no analyses;

- Most pigments including, red, mulberry, white, and particularly yellow and black, are mixed minerals (Ford et al. 1994; Ward et al. 2001; Watchman 1997a). This is consistent with Clarke’s ethnographic observation that white ochre was mixed with other materials to make coloured paints, including ‘red-brown by mixing with laterite and grey-black by mixing with ground charcoal’ (1976:139);

- P is identified as a consistent constituent of Kimberley rock art and on the pigmented surfaces of the limestone slab form Carpenters Gap 1 (Ford, et al. 1994; Huntley et al. in press/Chapter Six; O’Connor and Fankhauser 2001; Ward et al.). The consistent presence of P is of interest as a variety of sources have attributed the distinctive mulberry pigment hues common to Irregular Infill Animal and *Gwion* motifs to an organic base, possibly tree sap (Crawford 2001:93-94; Morwood et al. 1994:83; Mosby 1993:120-1; Ward et al. 2001:17; Welch 1993a:15);

- No evidence of binders or extenders has been found in prehistoric Kimberley art despite these media being specifically targeted (Ford, et al. 1994:59; Watchman et al. 1997:24);

- White pigments have dominated characterisation research in the Kimberley and are by far the most extensively studied in Australia (Clarke 1976; Crawford and Clarke 1976; Ford, et al. 1994; Huntley et al. 2011: 85-86, Figure 1 – Appendix C; Thomas 1998; Ward et al. 2001; Watchman, 1990, 1997d). These have been found to be either dominantly calcium carbonate or clay minerals – but rarely, if ever, purely one or the other.

- It is thought that in situ, post-depositional mineralogical transitions occur in stratified *Wanjina* paints (Ford et al. 1994, also refer to Huntley et al. in press - Appendix D).

- Ethnographically, white pigments are commonly composed of the distinctive calcium-magnesium carbonate mineral, huntite (Clarke 1976; Crawford and Clarke 1976; Ward et al. 2001; Watchman 1997a and 1997b). However, a lot of mineralogical variability is evident in white pigment that may have significant implications for the determination of provenance (Clarke 1976; Crawford and Clarke1976; Ford, et al. 1994; Huntley et al. 2014 - Appendix D; Thomas 1998; Ward et al. 2001; Watchman, 1997a and 1997b).

### 1.4.2 Archaeological History: Geochemical and Archaeological Implications

There are considerable gaps in our knowledge of paints used by prehistoric artists, with few charaterisations currently available, particularly for yellow, black and orange pigments. The small number of pigment studies conducted for the Sydney Basin and Kimberley rock art assemblages, and the dominance of opportunistic sampling strategies historically deployed, are related to sensitivities of sample collection. Historically it has been necessary to take pigment samples back to the laboratory for study and consequently impact the rock art under investigation, at least in small part. pXRF provides an opportunity to conduct field based, pigment characterisations non-
invasively and can accrue large datasets in a relatively short timeframe (Rowe et al. 2011). At the most rudimentary level the qualitative chemistry described with pXRF can answer the question: ‘what is this paint made from?’ (Newman and Leondorf 2005; Koenig et al. 2014 - see also Chapters Two, Five and Six). Within well-described rock art sequences such as those of the northwest Kimberley and Sydney Basin, even this most basic descriptive chemistry can have a spatial and temporal dimension. As I have argued earlier in this chapter, chemical characterisations can provide an alternate perspective to regional archaeological investigations. Increased opportunity for pigment characterisation has broader connotations too—the materiality of rock art having not only archaeological but also conservation implications.

In Aboriginal Australia, where landscape is innately part of culture, knowledge of the composition of rock art pigments offers researchers insights into the cultural context of its production and maintenance, through time (Clarke 1976; Crawford and Clarke 1976; Mosby 1993; O’Connor et al. 2013; Randolph and Clarke 1987—see Appendix D). For instance, differences in pigment mineralogy within the same colour of the same graphic form such as the white ochres of Wanjina motifs that are known to be carbonate minerals (hunite), oxalates (whewellite), and/or clays (kaolin, illite, halloysite), may indicate something of the cosmological association with an ochre source, the preferential selection of minerals for their material properties, and/or restriction of access to ochre sources. The chemical indices of cultural practice are not straightforwardly separated from purely environmental derivation. For instance, naturally precipitated and anthropogenically applied reduced pigments (mulberry, red, red-brown and orange) will have very similar chemical composition owing to derivation from iron rich minerals. Indeed, ferruginous and deeply weathered sandstone strata are thought to have been exploited as colour constituents in rock art paints (Huntley 2012; J. Huntley et al. 2011; Macintosh 1965; Webb et al. 1994). Similarly, unusually high levels of P in iron-rich pigmentation (O’Connor and Fankhauser 2001, Ward et al 2001, Watchman 1997a) do not necessarily equate to an anthropogenic origin for organic constituents, especially in a monsoonal environment where micro-organic activity is common on rock art surfaces (Ford, et al. 1994; MacLeod and Haydock 2008; MacLeod et al. 1991 - see Chapter Six, Figure 6.8). That said, it is possible to separate cultural and environmental chemical signatures by developing an understanding of the natural processes at work in the environment and their chemical expression.

1.4.3 Regional Environment

One of the defining attributes of rock art is that it is immobile. Taçon has observed that ‘landscapes where rock-art can be found are naturally restricted by the nature of a region’s geology; something obvious but often forgotten’ (2002:124). Here Taçon was referring to the restriction of rock art to geological surfaces suitable for its execution. But the restrictions to rock art imposed by a region’s geology are broader than this, equally obvious, and similarly often forgotten. The geomorphic processes that have helped to shape surfaces suitable for hosting and preserving rock art continue to act upon it once produced (see particularly Chapters Two, Three and Five). In addition, the geological weathering processes that have created the canvas for rock art have also created the
pigments (ochres) used to produce it (McDonald, 2008; Rowe 2001; Watchman 1990) (see Chapters Two, Five and Six). The need to comprehensively understand the geophysical environment in respect of interpreting geochemical profiles of any archaeological pigment, especially the in situ datasets from rock art, cannot be overstated. While centred on geology, this section takes into account other relevant palaeogeographic information in summarising the environmental settings of the Sydney Basin and northwest Kimberley (Figure 1.5).

![Case Study Areas](image)

**Figure 1.5** Case study locations illustrating their geophysical environment. Upper inset shows the King Leopold escarpment from tidal mudflats; lower inset shows the Waratah Rivulet, south Woronora Plateau. Geological Basins are shown in red, data collection points in black.

### 1.4.3.1 The Sydney Basin

The dramatic, rugged, sandstone dominated landscape of the Sydney Basin was regarded by European colonisers in much the same way as its Aboriginal inhabitants, with romanticism and foreboding (McDonald, 2008; Young and Young 1988). The topography of the Sydney Basin is an elongated saucer structure with the gently undulating lowlands of the Cumberland Plain at its centre, rising steeply in the west and more gently in the north and south where characteristic sandstone plateaus are found (Young and Young 1988). The climate of the Sydney region is warm and temperate; orographic effects result in more precipitation and less temperature variation along the coast. Vegetation in the plateaus and valleys where rockshelters included in this research occur is tall open Eucalypt forest (Hazelton and Tille 1990:4-5, see Chapters Two and Five).

The Holocene climate in southeast Australia was relatively stable with environmental changes of a
smaller amplitude and shorter duration than those experienced in the late Pleistocene (Attenbrow, 2004:204). Slightly wetter conditions than those of today persisted between ∼7000 BP and ∼5000 BP, and the overall trend from ∼3800 BP to ∼1500 BP was to cooler, drier conditions. The last 1500–1000 years saw small increases in temperature and rainfall equivalent to those currently experienced. After 3000 BP, the El Niño-Southern Oscillation (ENSO) began to operate as it does now, resulting in more marked seasonality and variation in precipitation patterns. Evidence for the end of cooler and drier conditions in the mid Holocene shows regional variance, but, significantly for the proposed chronology of art production at Yengo 1 shelter in the central Sydney Basin, the transition back to warmer and wetter conditions on the southeast coast began at about 2000 BP (Attenbrow 2002:206-7). The scale of impact from mid-Holocene cooler and drier conditions produced changes in the extent of vegetation communities, rather than a total change of vegetation (Attenbrow 2002:37). Today, large swaths of native vegetation are preserved in National Parks and water catchments due to the poor agricultural value of the skeletal soil and the rugged sandstone topography (Haworth 2003; Nanson and Young 1983; Young and Young 1988).

Land use by original inhabitants in the Sydney Basin was strongly influenced by the rugged sandstone landscape (Haworth 2003). Rock overhangs and caves provided Aboriginal people with opportunities to shelter from the weather and also surfaces on which they could produce rock art (Attenbrow, 2002:43; McDonald 2008). The dominant geology of the region that covers approximately two thirds of the basin, is Hawkesbury Sandstone, a middle Triassic, medium grained, quartzose lithology with thin, spatially constricted shale lenses (Hazelton and Tille 1990). The underlying Narrabeen Group sandstones are restricted to outcrops on the Blue Mountains Plateau and the northern beaches of Sydney, and Basaltic dykes and volcanic plugs occur throughout (Haworth 2003; Hazelton and Tille 1990). Triassic Wianamatta Group shales overlay the Hawkesbury Sandstone and outcrop throughout the plateaus, on the Cumberland Lowlands, and Moss Vale tablelands (Haworth 2003; Hazelton and Tille 1990; Hughes and Sullivan 1983). Lower Shoalhaven series shales and kaolin bearing coal measures underlay the Hawkesbury sandstone and are exposed in escarpments, cliff lines and headlands, principally near the coast (Baker and Uren 1982; Haworth 2003) (Figures 1.6 and 1.7). These shales and coal seams are thought to be the primary source locations for white ochres in the Sydney Basin (Attenbrow 2002:43; Ford 2006; Huntley, 2012/Chapter Two; Huntley et al. 2011/Appendix C).
Figure 1.6 – Two ochre quarries in Booderee National Park, south coast of NSW (2012). Top, left to right: 1) Overview of quarry. 2) Detail of ochre quarry showing finger fluting from ochre extraction top of image. 3) Orange ochre immediately in front of the quarry. 4) Everyday use of the ochre source. Bottom, left to right – 1) Clive Freeman accessing red ochre seam. 2) Detail of the red ochre seam. See Chapter Three for geographic location of Booderee National Park.

Figure 1.7 – Charlie Huntley (age 4) gathering ochre in an exposed Kaolin seam along the Frenleigh Track, New Lambton, Newcastle, NSW.
Detailed descriptions of the geology and taphonomy of Hawkesbury Sandstone rockshelters and their resultant chemical signatures are provided in Chapters Two, Three and Five. Detailed discussion of the taphonomy of rockshelter deposits and related ochre diagenesis for potential sources and subsurface ochre finds are provided in Chapter Five.

1.4.3.2 The Northwest Kimberley

The northwest Kimberley is a vast, rugged region dominated by sandstone terrain of plateaus and gorges. Flat topped benches, ridges, mesas and cuestas are common topographic features. The regional climate is thermochimic. The majority of annual rainfall, around 1450 mm, occurs during the summer monsoon between December and March (Tille 2006:111; Wyrwoll et al. 2007). The Australian-Indonesian summer monsoon is linked to a complex of both regional and global scale considerations in both hemispheres (Denniston et al. 2013; Wyrwoll and Miller 2001:119). Broadly speaking, previous research has indicated that the current monsoon pattern was established following the last glacial maximum around 14 000 BP; precipitation over northern Australia then reached a peak in the early Holocene, decreasing in intensity during the late Holocene (Wyrwoll et al. 2012:127). Regional scale monsoonal-forcing catalysts have been put forward by various research teams to explain early Holocene climate changes including higher sea level/flooding the Indonesian continental shelf and sensible heating of the Australian land mass (Griffiths et al. 2009; Wyrwoll et al. 2012). While causes for Holocene monsoonal variability may be complex, dynamic, and poorly understood, speleothem isotopic and terrestrial sedimentary records of the Indo-Pacific Warm Pool demonstrate increased precipitation in the early Holocene between 11 000 and 7000 BP and 17 000 to 9000 BP respectively (Gagan et al. 2004; Griffiths et al. 2009; Wyrwoll et al. 2007; 2012). Variability in precipitation around 5000 BP in the terrestrial record has been linked to ENSO activity and is reflected in increased charcoal deposition and vegetation disturbance (Gagan et al. 2004: 134).

This is consistent with recent terrestrial work in the northwest Kimberley that suggests a dynamic, variable Holocene monsoonal regime. A period of increased aridity, linked to enhanced ENSO intensity and/or frequency, is thought to have occurred from ~6000 to 1300 BP, with especially dry conditions hypothesised as causing failure of the summer monsoon between 2750 BP and 1300 BP (McGowan et al. 2012). Coincident with the 6000 BP onset of drier conditions, pollen records indicate that the tall grass savannah woodland sclerophyll character of present vegetation communities in the northwest Kimberley has persisted from the mid Holocene to present (McGowan et al. 2012; Tille 2006:112). This patterning is also reflected in terrestrial (Proske et al. 2014) and speleothem records (Denniston et al. 2013) recently collected in the east Kimberley that suggest a strengthened monsoon in the early Holocene. This is followed by a decreased monsoon in the mid Holocene producing close to present vegetation patterns 7000–6500 BP (Proske et al. 2013), decreased precipitation ~4000 BP and a further weakening of the monsoon ~2000–1000 BP (Denniston et al. 2014) with late Holocene aridity thought to have intensified fire activity (Proske et al. 2013).
Kimberley geology consists of a Proterozoic craton bounded at its southern extent by the King Leopold Orogen to the south-west and the Halls Creek Orogen to the south-east (Li 2000). The case study area is dominated by the 1800 million year old King Leopold Sandstone of the Kimberley Group and the overlying basalts of the Carson Volcanics which outcrop on the flanks of Mitchell Plateau (Griffin and Grey 1990). The Mitchell Plateau is a visual backdrop to the study area, not part of it per se. Site complexes investigated by the Change and Continuity project are located in the Lawley (Dorre) and Mitchell (Kandiwal) River catchments to the west and east of the plateau (Ross and Travers 2013:56-59)14.

King Leopold Sandstone is unmetamorphosed and apart from extensive faulting and jointing, it is essentially undeformed except for folding at the margins of the adjacent orogens, an important technical distinction as the more silicified/harder sections of the King Leopold Sandstone cannot therefore be classified as quartzite15. They are quartzarenite, highly silicified sandstone (Schmidt and Williams 2008; Watchman et al. 1997b:23). All quartzarenite strata observed in the northwest Kimberley, regardless of colour, are characteristically texturally ‘mature’ (Williams 2005:118). The more silicified strata expressed distinctive block-form responses to geological weathering and more poorly consolidated, softer, strata display scalloped, cavernous geological weathering, often resulting in extant columns or piers that support silicified block form quartzarenite above (Twidale 1968) (Figure 1.8).

![Figure 1.8](image1.png)

**Figure 1.8** Left to right – (1) Rockshelter on the Kimberley coast at the mouth of the Lawley (Dorre) River showing block-form weathering in its top strata and scalloped cavernous weathering in the bottom strata particularly at the entrance where a cache of ochre and artefacts were found. (2) LMR01b in the lower Lawley (Dorre) River showing block form weathering. (3) LMR01a showing a siltstone horizon of quarried ochre in the foreground and scalloped piers in the upper section of the image. See Chapter Six for the geographic position for the Malauwarra site complex where LMR01a and LMOR01b are located.

The quartzarenite strata not only house rock art, but have also been exploited by Aboriginal people for other cultural practices such as bedrock knapping (Newman, in prep.). The geological context of *Gwion* rock art has been used to argue for Pleistocene antiquity (Morwood and Hobbs

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14 Names in parenthesis are those used currently by the Wunambal Gaambera people

15 Quartzite is a metamorphic rock, hardened by silicification of interstitial material through heat and force applied by pressure of deep burial. Quartzarenite is the hardening of sedimentary stone via the dissolution and precipitation of silica. Silica in quartzarenite is mobilised by water, as is the process for other karstic rock, with either acidity or alkalinity in ground water accelerating this process (Jennings 1983).
2000; Walsh 1997, 2000). However, little if any published research exists on the karstic features of quartzose rocks such as extensive caves, dolines, and tower fields recognised in a number of places in the tropics, including Australia (Jennings 1983; Young 1987:205). The little data available regarding the stability of the Kimberley sandstone environment, and rock art executed on it, indicates surfaces are dynamic and can be relatively fast weathering (c.f. Clarke 1976; Ford et al., 1994; MacLeod and Haydock 2008; MacLeod et al. 1991, 1997) (Figure 1.8).

Surface silicification has been observed as a major factor in the ‘superior state of preservation’ of the red/mulberry motifs in the Kimberley during conservation science research (Clarke 1976:141). The properties of iron dominant pigment minerals make them particularly susceptible to this process, but in my view, any stabilisation would be short to medium term as stabilisation of the immediate surface of strata does not arrest the weathering of the bedrock. As stated above, the same physical and chemical weathering processes affect sandstone bedrock at the same rates however, the degree of silicification in the strata result in different expressions of this weathering. The geological weathering that I observed in the field seemed equally active in both poorly consolidated and silicified units of the King Leopold formation. The more silicified strata expressed angular block form in response to weathering, even at the scale of surface flake exfoliation. Conversely, more poorly consolidated strata showed more scalloped or typically ‘cavernous’ expression of weathering. I also observed a broad continuum of textural gradients in the King Leopold sandstone, from unconsolidated matrices with large sand grains and coarse quartz inclusions, to high siliceous and fine grained strata. The texture of the base geology is separate from the deposition of silica onto the surfaces of the rockshelter/caves. Indeed, silica is not the only precipitous mineral being deposited onto the rock (including art) surfaces (Watchman et al.1997:21 - see Chapter Six for further discussion, Figure 1.9).
Figure 1.9 Rock art panels in the northwest Kimberley showing the complexity of precipitate accretions. Top left – A thick precipitous mineral accretion at Lawley River 3b indicated by pXRF as dominantly gypsum. Top right – Profile of the main panel at LMR01b showing circular surface deposition of percolated minerals, likely salts. Bottom: Overview of the main panel at LMR01b showing purple banded siliceous strata (left) and the extent of surface precipitous iron-oxide (right, image enhanced with Image J D-Stretch, LRE filter, Scale 10).

The geology of the northwest Kimberley is clearly much more complex than the 1:250 000 scale geological mapping suggests (Griffin and Grey 1990). Specifically in respect of pigmentaceous geological units, King Leopold Sandstone contains minor intervals of siltstone and conglomerate (Dowens et al. 2007; Griffin et al. 1990). Restricted outcrops of carbonate rocks such as dolomite have been observed in the study area (Tille 2006:110). The Carson Volcanics which overlay King Leopold Sandstone on the Mitchell Plateau includes interbedded micaceous siltstones with minor pyroclastic rocks and feldspathic sandstones (Dowens et al. 2007:87; Williams, 2005:111). Extensive lateritic duricrusts occur as a result of deep weathering of Carson Volcanics basalts on Mitchell Plateau (Tille 2006:110). All of these locations could provide sources of ochre. The different geological units in the area are all potential pigment sources and may reveal chemically and mineralogically distinctive provenance.
The sparse ethnohistoric information that exists indicates that white hunteite pigments were sourced locally from dark chocolate brown fluvial sediments (Clarke, 1976; Crawford and Clarke 1976—see Appendix D for a further discussion). There is also ethnographic reference to the Aboriginal spiritual importance of a red ochre source at Carlton Hill (Station) located some hundreds of kilometres to the east, close to the Northern Territory border (Crawford, 1968; Mowaljarlai and Vinnicombe 1995). Photographs of the source and samples housed at the Western Australian Museum indicate that it is ferruginous sandstone (Webb et al. 1994), quite unlike other specimens in the collection that derive from the lateritic duricrusts of the Mitchell Plateau16 (Crawford et al. 1982).

1.4.4 Geochemical and Archaeological Implications of Regional Palaeogeographies

The dramatic, rugged, sandstone landscapes of the Sydney Basin and northwest Kimberley are broadly comparable geologically. The Hawkesbury and King Leopold sandstones were formed in similar shallow marine deltaic environments and have been subjected to similar diagenetic processes as they became buried by overlying sediments. Hawkesbury Sandstone is Middle Triassic, ~240 million years old, coarse and uniform in texture, but mineralogically heterogeneous (see Chapters Two and Five). King Leopold Sandstone is Proterozoic, ~1800 million years old, with a continuum of textural units. It appears that coarse strata produce scalloped cavernous forms and the ‘harder’ silicified strata/surfaces create sheared and angular block forms, including ubiquitous flake exfoliation of case hardened surfaces. Critically, responses to the weathering processes in sandstone environs, and their chemical signatures will be the same, no matter their specific morphological expression (refer to Chapters Two and Three for further discussion of weathering processes and their chemical indices).

In the Kimberley, deeply weathered intervals of siltstone and conglomerate in the King Leopold Sandstone and the Carson Volcanics, remnant lateritic duricrusts that cap many of the hills, and especially the ferruginous Laterite (‘bauxite’) of the Mitchell Plateau, and minor ferruginous sandstone occurrences like that observed at the Carlton Hill ochre quarry, all indicate abundant local sources for iron-rich red, mulberry, yellow and even orange ochres (Crawford 1968; Dowenset al. 2007:87; Ian Crawford pers. com. 2012; Griffin and Grey 1990; Mowaljarlai and Vinnicombe 1995; Tille 2006:110; Webb et al. 1994; Williams 2005:111). Ethnographically known pigment sources include the fluvial sediments within riparian zones that contain white ochre nodules of hunteite and clay (Crawford and Clarke 1976) and the lateritic gravels of the Mitchell Plateau Bauxite deposit (Crawford, 1982; Randolph and Clarke 1987; Veitch 1996). In contrast, the Wianamatta Group shales, the youngest and most surficial Triassic stratum of the Sydney Basin, as well as kaolin-bearing coal measures and the Shoalhaven Shales of the lower Sydney Basin offer geomorphically restricted sources of ochre (Baker and Uren 1982; Ford 2006; Haworth 2003; 16 I am preparing a manuscript based on pXRF analysis of twenty-five ochre specimens including the Carton Hill source, specimens from the Mitchell Plateau (gathered by Crawford et al. 1982), Drysdale River Mission, Lombadina Mission, the Lawley River, Kalumburu, Cape Bougainville, Secure Bay and Stewart River.

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Hazelton and Tille 1990). Ochre sources throughout both case study regions are likely mixed minerals, with distinctive geochemical signatures for discrete provenience/extraction locations. Previous archaeological research suggests a mixture of clays (chiefly kaolin) and weathered lenses of Hawkesbury sandstone were used as pigments in the Sydney Basin (Ford, 2006; Huntley et al. 2011; Macintosh 1965). Similarly, ethnography for the Kimberley region suggests admixtures of composite colorants dispersed into clay/huntite media were used to produce paints (Clarke 1976).

The relatively stable temperate climate of the Sydney Basin through the Holocene would have had minimal impact on rock art weathering. Small amplitude acceleration to geological weathering rates and precipitated mineral accretions during periods of increased rainfall may have occurred. Overall Holocene weathering rates for rockshelters and associated art panels is likely to have been relatively consistent. Complementary verification of the stability of weathering rates through the Holocene is also evident in the archaeological visibility of anthropogenically accelerated weathering in previously occupied rockshelters (Hughes and Watchman 1983; Hughes 1978). The stability of ENSO and the return to warmer wetter conditions from ~2000 years ago is not directly evident in the rock art pigments analysed per se because of the coarse nature of any chronological control. However, this provides complementary evidence for dates extrapolated from the Yengo 1 excavation that showed marked increase in discard rates and diversity of cultural debris from this time (McDonald 2008—see **Chapter Five**). This could be further extrapolated to refine the <4000 BP age suggested for the well preserved bichrome rock art on the Woronora Plateau (**Chapter Two**) (Dibden 2011; McDonald 2008).

The monsoonal Holocene paleoclimate of the northwest Kimberley was much more varied and would have heavily influenced geological weathering of rockshelters and rock art taphonomy. In northern Australia following the aridity of the last Glacial maximum, wetter conditions with a strengthened monsoon in the early Holocene appear to be followed by a period of increased aridity linked to enhanced ENSO in the mid Holocene (between 7000 BP and 4000 BP), and the possible collapse of the summer monsoon ~2500–1000BP. This would have had a measurable impact on geological weathering processes and rock art taphonomy. Increased aridity and lower precipitation might have created short term instability in rock art weathering increasing granular disintegration and enhancing the effects of insulation and associated physical flaking. In the medium term, decreased moisture in sandstones would have slowed surface silicification of rock art and other mineral precipitates such as gypsum accretions and case hardened rockshelter surfaces. The chronological control necessary to investigate this further is lacking and new archives such as the mineralogy of surface accretions will be useful areas for further research (see Huntley et al. 2014—**Appendix D**). The simplistic equation of increased climatic aridity to the collapse of Aboriginal cultural traditions represented by an abrupt ‘change’ in rock art styles from Gwion to Wanjina, such as that recently presented by McGowan et al. (2012) are not well argued and less well supported by the current evidence. McGowan et al. (2012) seem to entirely ignore the continuous mid to late
Holocene archaeological record present in subsurface contexts throughout the Kimberley region (Balme 2000; Morwood and Hobbs 2000; O’Connor 1999, O’Connor and Veth 2006; O’Connor et al. 2014; Veith 1996, 1999a, 1999b). Further, modelling by Wyrrwoll and others cautions against simplistic interpretations that correlate terrestrial records and palaeomonsoonal intensification by outlining the dynamism of hemispheric scale forces (Wyrrwoll et al. 2007; 2012) and recent work in the Kimberley has show there may be diversity in environmental responses within the region (Denniston et al. 2013; Proske et al. 2014). Climatic variability of the amplitude experienced in the Kimberley in the Holocene would be expected to have considerable cultural impact, and could have resulted in the expansion or contraction of group territories and/or restricted accesses to, or changes in, the source of ochres. But the archaeological record shows continuous Aboriginal presence in the region throughout this time, with the potential that further work may unpack people’s response to climate (Williams 2013; William et al. 2010, 2013). We are speaking here about adaptations within a dynamic cultural system, not societal collapse.

The seasonal extremes in precipitation provided by the monsoon in northern Australia mean that the formation of mineral skins and other precipitates are likely rapid and seasonally episodic. For this reason, previous pigment characterisation and conservation work conducted in the Kimberley has specifically targeted data collection in both the wet and dry seasons (Ford et al. 1994). Studies of white pigment from Wanjina motifs has shown hydrology is a major taphonomic agent for post-depositional mineralogical transitions of pigments and mineral accretions (MacLeod et al. 1994, 1997; MacLeod and Haydock 2008). Exposure to water was also cited as the major conservation threat regarding the deterioration of huntite and layered pigment application in Wanjina art (Clarke, 1976; Crawford and Clarke 1976). The major catalytic effects of water have been further supported by studies into the microclimate and hydrological regimes of shelters (Gliberto, 2000), including studies in the northwest Kimberley (MacLeod and Haydock 2008; MacLeod et al. 1997).

In relation to the taphonomy of archaeological ochres, water inundation could be expected to accelerate and facilitate weathering processes and increase the mobility of soluble elements, all of which may cause mineral transition particularly in the lower section of excavated contexts where seasonal water inundation occurs.

The diagenetic chemical signature of ochres is discussed further in Chapter Five and mineral phase transitions are discussed in Appendix D.

1.5 Research Aims

In addition to understanding, evaluating and producing novel techniques in applying pXRF to rock art, the broad archaeological objectives of this research were to:

- Provide insight into the cultural context of rock art production by illuminating artists’ choices of pigment and how these choices might vary over time and space. This includes major mineral constituents and composite paint recipes evident in geochemical profiles.
• Offer an alternate perspective, complementary strands of evidence, and more fine-grained data to be interwoven into the development of a more robust chronology for the two rock art assemblages (via the comparison of ochres from excavated context and rock art pigments).

• Demonstrate how archaeologically significant information can be drawn from the qualitative and semi-quantitative geochemical characterisation of archaeological ochre, especially rock art pigments, and that this data can provide an alternate chronological and behavioural perspective in regional studies, irrespective of the assignment of provenance.

Ancillary outcomes of this research provide data relevant to future conservation and management practices by:

a) characterising the material properties of pigments and other site fabrics such as rockshelter substrates, mineral accretions, ochre surface finds and excavated ochres (Chapters Two, Three, Five and Six),

b) critically considering the potential impact of methods like pXRF that produce ionising radiation on other techniques from the archaeological sciences (Chapter Four), and

c) describing comparative tolerances of chemical precision and accuracy of in situ pXRF and legacy data from other, laboratory based techniques (Chapters Two, Five and Six).

1.5.1 Thesis Structure and Case Study Specific Research Aims

This thesis has been completed ‘by papers’ whereby the substantive chapters contained within are in the format of journal articles/book chapter contributions submitted to peer reviewed academic publications. Thesis Chapters have either been published (Chapters Two and Six, see Appendix B); accepted into press (Chapter Three, though no proof has yet been provided); or are currently under review in the listed target journals (Chapters Four and Five). Care has been taken to minimise (as far as practicable) any repetition that may occur by the requisite contextual and methodological sections of Chapters Two to Six which take the form of ‘stand alone’ original research outputs17. Some repetition in manuscripts that have arisen from a single research program with consistent overarching aims, and some repetition within the contextual section of manuscripts derived from the same case study are perhaps inevitable18. The scope of each journal article/book chapter encapsulates a discrete segment of the overall project. As with a traditional monograph thesis, each chapter flows in a logical progression, building on the ideological and/or methodological work set out in preceding chapters. However, in an obvious departure from a traditional monograph a discrete methodology chapter is not provided. The reasons for this

17 While attempts were made to refer to the limitations of pXRF outlined in detail in (Huntley 2012—Chapter Three), consistent feedback during peer review for this and other chapters necessitated some repetition in discussing the physics of pXRF (matrix effects) and the resulting chemical signatures of these. Referees consistently commented that they did not want to be referred back to previous publications, requesting instead that a salient summary of ‘matrix effects’ relevant to archaeological samples be outlined in each publication in order to make them ‘self-contained.’

18 There is also repetition in abbreviations within the document. Abbreviations appear at the first use of terminology, however, abbreviations may repeat in the first use of a term in each self contained publication (Chapters Two to Six).
are twofold: firstly, a formal methodology section outlining the experimental conditions of
darchaeometric analyses is necessarily contained within all publication outputs (Chapters Two
to Six); secondly, the central focus of this research has been to evaluate and apply pXRF to the
characterisation of rock art pigment. It has therefore been an aim of the research to develop
novel methods and provide a considered protocol for in situ pXRF analysis in rock art studies (see
Chapter Seven).

This Introduction (Chapter One) has discussed the broad archaeological, scientific and
environmental background for the research program. Following on from the literature review and
overview of conceptual/theoretical frameworks, I have outlined the rationale for research over
two study areas and described their regional archaeological and palaeogeographical contexts. I
conclude by outlining the objectives and ancillary outcomes of the overall research project.

For clarity, the body of this thesis is split into two sections. PART I includes three technically
focussed papers that evaluate the archaeological utility of pXRF for rock art applications. Chapter
Two concurrently addresses research questions for the regional prehistory of the project areas,
and Chapters Two and Three coevally provide information relevant to rock art conservation
and management. While Chapter Four presents a case study relevant to all collection and site
managers, outlining the potential effects of pXRF on other archaeological science methods.

Chapter Two presents a re-formatted version of the published article:

Huntley, J. (2012). Taphonomy or Paint Recipe: In situ portable X-ray fluorescence analysis
of two anthropomorphic motifs from the Woronora Plateau, New South Wales. Australian
Archaeology, 75 (December), 78-94. ISSN 0312-2417

The aim of this paper is to evaluate in situ pXRF analysis of rock art against legacy data from
the same panel and the same motifs (Appendix C). The physics of XRF for in situ rock art
investigations is explained, as is site specific taphonomy, to develop an understanding of exactly
what is captured in pXRF spectra. Here I propose a novel method of isolating, interrogating and
interpreting geochemical profiles in order to separate cultural and environmental processes using
‘Indicator Element’ suites. Where the chemical indices of anthropogenic and natural processes are
one and the same, for instance where weathered sandstone is used in the paint recipe, I applied
pXRF spatially across the rock art panel to differentiate anthropogenic pigment from natural
geomorphic processes, highlighting the power of field based analysis.
Chapter Three presents a re-formatted version of the book chapter currently in press:


Building on the evaluation of pXRF for rock art applications in the preceding paper this book chapter broadens the discussion of archaeometric value, explicitly considering the conservation and management potential of non-invasive methods, appraising the strengths and limitations of pXRF in tandem with Micro-Computed Tomography. Without necessarily advocating the use of either technique, we introduce the types of data that can be generated in respect of the material properties of rock art sites. We expect this chapter will help Indigenous communities, archaeological scientists and rock art researchers to critically consider the potential of non-invasive methods for investigating, conserving and managing rock art.

Chapter Four presents a re-formatted version of the journal article currently under review:


This paper extends the evaluation of pXRF from rock art research to all archaeological applications by considering the impacts various subfields of the archaeological sciences, and the analytic techniques they use, can have on one another when working in conjunction on the same problems and/or materials. The non-destructive nature of XRF has been cited as the principle reason for an explosion in the use of hand held spectrometers for archaeological investigations over the last 15 years. We present evidence to the contrary. Our experiment demonstrated that irradiation at durations and intensities commonly used when analysing the geochemistry of artefacts and site fabrics can have a measurable impact on luminescence signal, and could lead to over estimates in age determinations in some situations.
PART II includes two papers outlining different novel methods for applying pXRF to rock art. The innovative approaches developed for in situ characterisation of archaeological pigments establish ways that archaeologists can address questions relevant to understanding regional prehistories.

Chapter Five presents a re-formatted version of the original research article currently under review:


In this paper, I develop a method for comparing rock art pigments with ochres from excavated contexts concluding that qualitative/semi-quantitative pXRF data can rule out a relationship between rock art and other archaeological pigments, but does not have the required precision to robustly establish that they may be the same. In addition, a ‘high quality’, faceted red ochre nodule recovered from the deposit at Dingo and Horned Anthropomorph (D&HA) shelter: white and cream hand stencils, cream and pink ochre ‘washes’ and a porous red ochre nodule recovered from Yengo 1 (Y1) shelter are the first Ca matrix, archaeological pigments yet described in the Sydney Basin. Radiocarbon determinations from the deposit at Yengo 1 associated with the Ca matrix red ochre indicates these pigments have been exploited since the mid Holocene (McDonald 2008:98). Further, the presence of Ca ochres in both sites shows these pigments were used in social contexts argued to be dominantly ritual and secular respectively (D&HA, Macintosh 1965: 85 - Y1, McDonald 2008:13940). Thus the results demonstrate the ways that geochemical data can provide additional strands of chronological and behavioural evidence with which to enhance our understanding of regional prehistories

Chapter Six presents a re-formatted version of the original research article currently in press:


This article presents a method that can differentiate between the two major mineralogies of mulberry paint used in Kimberley rock art, in the field, non-invasively. The significance of this method is that it can be subsequently applied across the region to provide insights into the choices of artists who selected both haematite and jarosite pigments, and thereby change or continuity in the cultural context of rock art production through time and space. The significance of this method is that it can differentiate between pigments in motifs executed in the same colour and style. The article also makes a major contribution to the northern Australian prehistory with the first
archaeological description of a mulberry ochre quarry — showing that mulberry ochre (haematite with a clay matrix) occurs in small siltstone horizons within King Leopold Sandstone and indeed, that ochre quarries occur locally, in caves with large rock art assemblages.

Chapter Seven presents a summary of the research project, including the detailed analytic protocol that should be used to generate scientifically robust geochemical datasets from rock art pigment, in the field, via pXRF.

In accordance with the examination requirements of the University of New England, a single consolidated list of References Cited is presented at the end of the thesis. Please note that the additional works contained in the Appendices include separate bibliographies at the end of each (Appendix C and Appendix D respectively).

Appendix A summaries the pXRF field analysis protocol for rock art developed during the Sydney Basin case study and subsequently applied during the northwest Kimberley case study. It is specific to the Bruker Tracer III-V instrument used, rather than the general principles and recommendations made in Chapters Five, Six and Seven.

Appendix B presents offprints of the published articles included as Chapters Two and Six.

Journal articles derived from, although peripheral to, research undertaken in the two case study areas of this doctoral project are provided as Appendices C and D. These articles are included as relevant context for (Appendix C in relation to Chapters Three and Four), and extensions of (Appendix D in relation to Chapter Seven), the research questions explored in the thesis.

Appendix E supplies the two geochemical datasets included as Supplementary Online Material for the journal article presented as Chapter Six.