DEVELOPMENT OF A SPECTROSCOPIC METHOD FOR THE NON-DESTRUCTIVE ANALYSIS OF AUSTRALIAN ABORIGINAL OCHRE MATERIALS

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for my family...

i. **Declaration:**

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Kate Colyer May 2015

ii. Acknowledgements:

On the first day of my PhD, I never could have imagined that the end point would see me here. So much has changed, both personally and academically, and it is quite overwhelming to think that this chapter of my life is closing. I also could never have imagined that out of a full thesis, this page would be the hardest to write! Yet here I am, almost paralysed by the fear that I will forget someone deeply important to the process, and concerned that any words I use will simply be inadequate in expressing my heartfelt thanks. So let me start by firstly sincerely apologising to anyone I may have forgotten – please know that your contribution and support was deeply appreciated.

On a professional level, there are many people to thank. A number of individuals and institutions have shared their knowledge and equipment with me throughout this process, and without them many of the results presented here would not have been possible. Thank you to Associate Research Professor David Beatie from The Ian Wark Research Institute for the use of and assistance with the raman instrument, to Peter Self from the Commonwealth Scientific Industrial Research Organisation for the use of and assistance with in-situ X-ray diffraction experiments, to Professor Jani Matisson and Pamela Solomon, formally from Flinders University, for their assistance with and use of the thermal gravimetric analysis instrument, and Dr Rachel Popelka-Filcoff and all the staff involved with the undertaking of neutron activation analysis at The Australian Nuclear Science and Technology Organisation.

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As well as supervisors, fellow students shape not only life at university but life outside. I have had the pleasure of being included in a number of groups throughout this project and have worked closely with many students. My heartfelt thanks to you all for the memories we have made along the way. Special mention to Adam Blanch and Anders Barlow, both now Drs, for accepting me as an intruder into the pink room, and to Lauren Hyde for sharing many a Subway lunch with me. A special mention is also necessary for Samuel Wallace – a dear friend from honours and beyond – thank you for the many pizza nights, the laughter and the tears, and for a friendship that will last a lifetime.

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iii. **Summary:**

This thesis details the work undertaken towards and the results obtained from the development of a portable and non-destructive technique for the analysis of Australian Aboriginal ochre materials. Many of the methods traditionally utilised for analysis are limiting due to their cost, lack of portability, the sample requirements and the destructive nature of analysis. This thesis explores these traditional methods before developing and optimising a spectroscopy based technique that reduces or eliminates many of these and other limitations.

Chapter one explores the historical context of pigments. It investigates what a pigment is chemically and visually, whilst exploring many of the pigments used throughout the ages and their evolution over time across the globe. This chapter then discusses early pigments commonly utilised in Australia, and focuses on ochre as the main pigment used by Aboriginal Australians. This study focuses on the significance of ochre to the Aboriginal culture, the chemistry of ochre and the factors that influence its varied colour, and how the structure of ochre changes with heat treatments. This chapter investigates previous scientific studies conducted on ochre and similar pigments across the globe. It explores the work of others and investigates the analytical methods and instrumentation used for analysis, the results obtained from this work, and the advantages and disadvantages of each technique utilised.

Chapter two focuses on the characterisation of ochre samples via the use of commonly utilised traditional analytical techniques including X-Ray diffraction analysis, neutron activation analysis, infrared analysis, Raman spectroscopy and thermal gravimetric analysis. The analysis concentrates on ten samples obtained by the mining commission chosen because their colour and composition varied, their province was known, they were from a trusted source and they had been used in previous studies thus allowing for accurate comparisons. It details the experimental methods used for the work completed for this project. It denotes the sample type, locality and province studied, the chemical composition of standards, the instrument models used for any analysis, and the modes of operation and specific parameters used. These samples are analysed using the traditional methods of analysis discussed in chapter one, and results are presented.

Chapter three is a preliminary study into the use of a newly emerging instrument known as the X-Rite i1Pro. This instrument is UV-based, portable and non-destructive, and its application to ochre and similar pigments is novel. This chapter discusses the technical aspects of the instrument and the experimental setups utilised before exploring the feasibility of such an application by studying a range of haematite and goethite standards of known mixture compositions. This chapter explores the instruments' ability to detect colour and distinguish between samples of varying colour, before determining the accuracy and reproducibility of these measurements. Experiments then move from standards to the mining samples discussed previously and this chapter presents the results of their analysis with this new and emerging technique. The range of samples is then expanded to include some from an

ethnographic collection, and are also analysed utilising a traditional, laboratory lased, bench top grade UV-vis, with the results of the two instruments compared. Work expands to establish a suitable model for the prediction of sample composition, again centring on a range of haematite and goethite standards of known mixture compositions and investigates a number of statistical methods of analysis. Studies include single wave length analysis, a model based on ΔE, and multiple linear regression analysis. The results of each model are presented here. This chapter also investigates the effect of a variety of sample preparation methods to explore the suitability of this instrument to artefacts and images of unknown origin. It explores the effect of sample thickness, and application method including the use of a variety of binders. Statistical analysis is completed in this chapter.

Chapter four focuses on the effect of the substrate on the i1Pro results, as it is hypothesised that factors such as surface roughness and colour may influence the spectra obtained. A number of wood and stone based substrates are investigated, and the prediction models developed in chapter three are applied.

Chapter five explores the application of the X-Rite i1-Pro system to a number of well-provenanced raw ochre materials from well-known sites significant to Aboriginal Australians. This chapter aims to determine if the inter-site variation is smaller than the intra-site variation, and if the samples analysed from each site can be statistically linked with the hope that unknowns could be tested and preliminarily provenanced. This chapter presents background information, sample information, experimental methods and the results of the study including statistical analysis. The same raw ochre samples are then analysed utilising neutron activation analysis and the results of the two methods are compared.

Chapter six is a case study focusing on the application of the X-Rite i1-Pro system to toas of cultural significant to Aboriginal Australians. This chapter presents background information on the significance of the toas, sample information, experimental methods and the results of the study. Results include the statistical analysis of the spectra obtained, and comparisons between the ochre found on the toas and material identified as possible source material.

Chapter seven presents the conclusions reached from the research detailed here. It also presents hypotheses for ongoing work, and future directions for this and associated projects.

Appendix A presents a study completed into the formation of haematite via the dehydration of goethite. This is culturally significant as many sources and indeed colours of ochre were held in higher regard than others by Aboriginal Australians, and an understanding into the chemistry of alteration was necessary. This appendix presents background and sample information, as well as experimental techniques and results obtained from the use of both thermal gravimetric analysis studies and X-Ray diffraction analysis.

Appendix B presents a case study into the accumulation of a dust-like particle on the surface of Aboriginal Rock Art at Arkaroo Rock in the Flinders Rangers South Australia. Background information and photographs, experimental techniques and results of the analysis utilising

microscopy, X-ray diffraction, thermal gravimetric analysis and colour analysis with the X-Rite i1pro is presented here, along with subsequent statistical analysis. The results of this appendix were presented at International Symposium on Archaeometry, Tampa, Florida. This work has been published in The Open Journal of Archaeometry.

Appendix C presents supporting data – necessary for the details of the thesis and reference but not specifically relevant to each chapter or section.

iv. **Table of contents:**

v. List of abbreviations:

AAS – Atomic Absorption Spectroscopy

ACIR – Autocorrelation Infrared

ANSTO – Australian Nuclear Science and Technology Organisation

ATR – Attenuated Total Reflectance

ATR-FTIR – Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy

CCDs – Charge-Coupled Devices

CHNS – Carbon, Hydrogen, Nitrogen, Sulphur

CSIRO – The Commonwealth Scientific and Industrial Research Organisation

DRIFT – Diffuse Reflectance Infrared Fourier Transform Spectroscopy

DSC – Differential Scanning Calorimetry

DTA – Differential Thermal Analysis

ED-XRF – Energy Dispersive X-ray Fluorescence

EDS – Energy Dispersive Spectrometers microanalysis

EDX – Energy-Dispersive X-rays analysis

ESEM-EDX – Environmental Scanning Electron Microscope - Energy-Dispersive X-rays analysis

FIR – Far-infrared Spectroscopy

FTIR – Fourier Transform Infrared Spectroscopy

GCMS – Gas Chromatography Mass Spectrometry

HPLC – High Pressure Liquid Chromatography

ICP-AES – Inductively Coupled Plasma Atomic Emission Spectroscopy

ICDD – International Centre for Diffraction Data

ICP-AES – Inductively Couple Plasma Atomic Emission Spectroscopy

ICP-MS – Inductively Coupled Plasma Mass Spectrometry

INAA – Instrumental Neutron Activation Analysis

IR – Infrared

IRM – Isothermal Resonance and Magnetic Susceptibility

LA-ICP-MS – Laser Ablation Inductively Coupled Plasma Mass Spectrometry

LD – Limit of Detection

Micro-ATR – Micro-Attenuated Total Reflectance

MEU – Minor Early Use

MLU – Minor Late Use

NAA – Neutron Activation Analysis

NIPALS – Nonlinear Iterative Partial Least Squares

NRA – Nuclear Reaction Analysis

PCA – Principal Component Analysis

PIGE – Particle Induced γ-Ray Emission

PIGME – Programmed Inert-Gas Multi-Electrode

PIXE – Particle Induced X-ray Emission

RBS – Rutherford Backscattering Spectrometry

RQPA – Rietveld Quantitative Phase Analysis

SEM – Scanning Electron Microscopy

SEM-EDX – Scanning Electron Microscopy Energy Dispersive X-ray Spectrometry

SR-XRD – Synchrotron Radiation X-ray Diffraction

TGA – Thermo Gravimetric Analysis

TOF-SIMS – Time of Flight Secondary Ion Mass spectrometry

Unc. – Uncertainties

WD-XRF – Wavelength Dispersive X-ray Fluorescence

XRF – X-ray Fluorescence

XRD – X-ray Diffraction

vi. **List of figures:**

vii. **List of tables:**