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Characterisation of Ochre Sources in South Australia by Neutron Activation Analysis (NAA)

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Abstract

This paper summarises the recent characterisation of several South Australian ochre sources by neutron activation analysis (NAA). NAA provides trace and major elemental composition for the samples, and through subsequent multivariate analyses allows conclusions based on the original geochemistry of the sources to be made. 65 samples from 13 sources in South Australia were analysed. Elements important in distinguishing between sources were identified and further studies for characterisation of South Australian ochre have been outlined.

Introduction

Ochre (iron oxide pigment) is found in cultural contexts across Australia in artefacts, decoration and ritual. Ochre is a vital material in Aboriginal Australia and is used in cultural contexts from objects to body decoration. Although ochre figures prominently in Aboriginal Australian culture today, very little is known about the extent of quarrying and exchange of the material in the past. Certain sources of ochre have significance due to connections with Dreamtime stories and landscapes, as well as due to ochre qualities such as colour and covering strength (Clarke 1976; Clarke and North 1991a, 1991b; Jercher et al. 1998; Jones 1984a, 1984b, 2007). While local communities utilised some of these ochre sources, others had significance
beyond the immediate region. Known ethnographic information about some ochre sources documents travel of hundreds of kilometers to a source at a specific time of year for ochre mining (Clarke and North 1991a, 1991b; Keeling 1984). However, many ochre procurement routes are lost to history and are no longer used in the present.

This paper discusses recent applications of neutron activation analysis (NAA) and the provenance postulate specifically for South Australian ochre sites. This manuscript investigates the possibility of applying the provenance postulate to sources as part of a larger framework of ochre analysis in Australia.

**Samples**

Within South Australia, many ochre quarry sites have been documented through historic and ethnographic studies. In the 1980s-1990s researcher Margaret Nobbs (1996) identified about 20 of these sites through her research into the rock art of South Australia. As part of a study on ochre analysis in the 1990s Mike Smith and Barry Fankhouser (2009), at the Australian National University, also documented some of the sites that Nobbs had previously identified. These two studies, in combination with the South Australian Museum collections, provided a foundation for the characterisation of ochre quarries across Australia and specifically in relation to South Australian sites.

Ochre quarry samples were the focus of this study, and samples did not include those found in archaeological contexts. In order to develop the foundation database for archaeological examples, the characterisation of known and suspected ochre quarry sites used by Indigenous Australians must be completed as a reference data set. Once this is established, archaeological ochre results can be compared to the quarry sites and conclusions drawn on the cultural exchange of ochre. This study analysed varying numbers of samples from 13 South Australian ochre quarry sites (Table 1), which provides a foundation for subsequent archaeological sample studies, which are currently undergoing analysis in 2012.
Table 1 Sources and number of samples investigated in this study from identified ochre sources in South Australia.

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of samples</th>
<th>Region</th>
<th>Description of ochre</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulloo Creek</td>
<td>2</td>
<td>Olary</td>
<td>Dark red-brown clay</td>
<td></td>
</tr>
<tr>
<td>Clayton</td>
<td>2</td>
<td>Marree</td>
<td>Red powder</td>
<td></td>
</tr>
<tr>
<td>Moana (Ochre Cove)</td>
<td>14</td>
<td>Barker</td>
<td>Range of colour from pink to red</td>
<td></td>
</tr>
<tr>
<td>Mount Hayward</td>
<td>6</td>
<td>Flinders Ranges</td>
<td>Purple-red</td>
<td></td>
</tr>
<tr>
<td>Mount Howden</td>
<td>1</td>
<td>Curnamona</td>
<td>Red and slaty</td>
<td></td>
</tr>
<tr>
<td>Ochre Cliffs</td>
<td>4</td>
<td>Copley</td>
<td>Pink to dark red</td>
<td>No documentation of use by Aboriginal people</td>
</tr>
<tr>
<td>Lyndhurst</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overland Corner</td>
<td>6</td>
<td>Renmark</td>
<td>Red and yellow</td>
<td></td>
</tr>
<tr>
<td>Pernatty Lagoon</td>
<td>2</td>
<td>Torrens</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>Pine Point</td>
<td>13</td>
<td>Yorke Peninsula</td>
<td>Copper King Mine</td>
<td></td>
</tr>
<tr>
<td>Puttapa Gap</td>
<td>4</td>
<td>Copley</td>
<td>Copper King Mine</td>
<td></td>
</tr>
<tr>
<td>Rockleigh</td>
<td>6</td>
<td>Eastern Adelaide Plain</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>Tombstone Dam</td>
<td>3</td>
<td>Central Lakes</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>Wangiana</td>
<td>2</td>
<td>Curdimurka</td>
<td>Red and yellow</td>
<td></td>
</tr>
</tbody>
</table>

The sample numbers from each site vary depending on their sampling history by previous researchers and by the availability of samples in the South Australian Museum collections. The majority of the sites have documented ethnographic or historical information on their use. However, no documentation currently exists on the use by Aboriginal communities of two sites in this study, Mount Howden and Ochre Cliffs Lyndhurst, which have been identified as having high quality ochre. Figure 1 displays the locations of the ochre sources analysed in this study.
Many archaeometric studies are based on the concept of the “provenance postulate”, first referred to in the literature by Weigand in 1977 (Weigand et al. 1977). This postulate defines the inter- and intra-source variation between sources and provides the basis for multivariate statistical analyses used for calculating similarities and differences between compositional groups. This postulate underpins many investigations into using chemical composition to trace potential movements of cultural material in the past by comparison of inter- and intra-site variance.
**Neutron Activation Analysis**

Neutron activation analysis (NAA) has been utilised in archaeological studies for the past five decades, covering many diverse types of archaeological material and site locations (Speakman and Glascock 2007). Advantages of this radioanalytical method include its high precision, accuracy and ability to measure both trace (parts per million) levels and major (percentage) concentrations of elements. Recent developments in both relative comparator and the $k_{\theta}$-NAA technique have led to the application of elemental characterisation and analysis of ochre pigments in other locations worldwide (Eiselt et al. 2011; Popelka-Filcoff et al. 2007).

NAA was carried out on 65 ochre samples from varying contexts in South Australia. The samples were irradiated in the 20 MW OPAL research reactor and the analysis was performed using the $k_{\theta}$-method of standardisation ($k_{\theta}$-NAA) (Bennett 2008; Popelka-Filcoff et al. 2012). From the bulk sample, approximately 50mg was taken for each of the short and long irradiations, the combination of which allowed for the measurement of 40+ elements from each sample. Sample preparation, irradiation, decay and counting procedures followed standard procedures at the NAA facility (Bennett 2008). Data were transformed to log$_{10}$ values and normalised for Fe concentration using methods based on earlier studies (Popelka-Filcoff et al. 2012). Multivariate data analysis was performed using methods similar to those recently published, and used principal components analysis in the GAUSS routines (Eiselt et al. 2011), as have been used in previous ochre studies (Popelka-Filcoff et al. 2008).

**Results and Discussion**

Of the elements reported, 35 were used in the final analysis. Only a few elements were not used in analysis and those that were eliminated were due to incomplete data across the sample set. Missing values for these elements were due to the values being below detection limits. The principal components analysis was able to account for 95% of the total data set variability in the first 10 vectors. Elements that demonstrated the most variability included arsenic, zinc, caesium, europium, vanadium, antimony,
manganese and sodium. Of these elements, arsenic, zinc, vanadium and sodium provided the most discrimination between the source samples. Bivariate plots of these elements were investigated for analysis of the South Australian ochre sources. Where sample numbers were large enough (greater than 4, as defined by the mathematics), ellipses were drawn in the 90% confidence interval to indicate source groupings.

An examination of the plots indicates patterns in the data and trends (Figures 2-3). Figure 2 shows a plot of $\log_{10}$ As vs $\log_{10}$ Zn. A few sources fall into distinct groups with relatively high Zn content, which include Mount Hayward, Puttapa Gap and Lyndhurst. The relationship between these sites is in agreement with the relative close proximity of the sites geographically in the Flinders Ranges area of South Australia. The remaining groups that can be separated include Overland Corner, Rockleigh and Pine Point, which also present varying locations around South Australia. Samples from Moana are dispersed over a large region of the plot. This distribution may reflect the inherent variability within the site as well as the disturbances this site has received in contemporary times with its use as a rubbish dump. The remaining sites have relatively small numbers of samples owing to the limitations in sample collection. For these, Clayton associates closely with Overland Corner, and Mount Howden with Lyndhurst, and Pernatty Lagoon with Pine Point. With only one or two samples from these sites it is difficult to ascertain trends on associations and variability within these sites and this needs to be developed further before definite conclusions can be made about these sites.

The identification of arsenic and zinc and similar plots with vanadium demonstrate that transition metals are important in distinguishing ochre sources in South Australia. Substitution of these elements into the Fe-oxides of ochre may be an indication of the original genesis and geochemistry of the ochre sources. After defining the patterns for each source, subsequent samples from archaeological and other contexts can be attributed and provenanced to the original quarries.
Figure 3 is a plot of $\log_{10} \text{Na}$ and $\log_{10} \text{Sb}$ for the same sample set. As in the previous figure, a majority of the samples cluster together, with some distinct outliers. Mount Hayward is again clearly distinct from the remaining groups. However, Puttapa Gap and Lyndhurst are not as closely related based on these elemental concentrations. Of the remaining sources, Rockleigh, Bulloo Creek, Overland Corner and Pine Point can be clustered into individual groups. Again, Moana is distributed more widely than some of the other groups. Classification of sources for which only a small number of samples were available was not well defined and relationships with other groups could not be established.

The identification of the elements that can be used to distinguish between sources can be used in future work with archaeological samples, as well as a way to understand the geochemical variability between source sites. Further archaeological samples will be analysed as funding and time permit.
**Figure 3** $\log_{10} \text{Na} \text{ vs } \log_{10} \text{Sb}$. Ellipses are at the 90% confidence interval. Sample groups with more than 4 samples are drawn with ellipses.

**Conclusions**

This initial study on the ochre sources of South Australia characterises some of the major and ethnographically known ochre sources in the state. Several of the elements used in the characterisation of ochre sources were identified and trends in arsenic, antimony, sodium and zinc were used to classify samples into statistically defined groups. Groups were able to be defined where a sufficient number of samples were available. Where only a small number of samples were available, groups could not be defined and more samples would need to be analysed to allow a full assessment of group relationships to be made. Of those with larger groups of samples, the provenance postulate could be applied to differentiate ochre sources.
Future Work

Future studies include further NAA analyses of sources as samples permit, and comprehensive analysis of these sources with known sources Australia-wide. Further data on ochre from archaeological contexts can also be used to compare with source data and to draw conclusions on potential use and exchange of ochre in South Australia and beyond.

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References


ABSTRACTS

Characterisation of Binders in Aboriginal and European Painted Works using Pyrolysis Gas Chromatography Mass Spectrometry

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Binders are the components of paints used to bind pigments and adhere them to the object (Surowiec 2008:293). The materials used as binders vary greatly across cultures. For instance, binders traditionally used by Indigenous Australians include bracket orchid juice, native Australian beeswax and grass tree resin, whereas traditional European binders typically consist of linseed oil, sandarac and egg white (Vandenabeele et al. 2000:263). It is known that after European settlement in Australia Indigenous peoples began incorporating European-style binders into their work, together with their own traditional binders; however, when and how this transition occurred is still unclear (Tworek-Matuszkiewicz 2012). The ability to chemically characterise the binders used by each culture, and distinguish between them, has the potential to provide great insight into the history of binders as used before, during and after European settlement in Australia. Such characterisation would also provide information on how to best restore and conserve Indigenous painted works from various time periods.

Extensive characterisation of European binding media has been conducted previously; however, there has been very little investigation into traditional Aboriginal binders (Blee et al. 2010:745). The aim of this study is to use pyrolysis gas chromatography mass spectrometry (py-GCMS), a technique...
commonly used in painting analysis, to characterise binders from both European and Aboriginal cultures, and hence determine if they can be chemically distinguished from each other. Py-GCMS involves the rapid vaporisation of a sample, such as paint, by high temperatures to form small volatile compounds that are subsequently separated and detected to determine the exact chemical composition of the sample (Bull 2008; Chiavari et al. 2003:544). This technique, although destructive, is capable of analysing extremely small samples (down to 1 nanogram), and hence allows objects of cultural significance to be analysed without visible damage and without compromising the integrity of the works. This technique also requires very minimal sample preparation, and hence the possibility of loss or contamination of the very small samples available is minimised, providing another advantage for use in the investigation of valuable works. Finally, the technique is capable of analysing a wide range of complex, non-volatile organic compounds, and hence can be applied to the wide range of binders used (De la Cruz-Canizares et al. 2005:179).

This research will involve optimising the py-GCMS technique to analyse a range of different binding media, before compiling a library of the chemical fingerprints of binders typical of each culture, against which painted works from the South Australian Museum can be compared to determine the binders they contain. The traditional Aboriginal binders that will be used for the optimisation and library compilation are bracket orchid juice, native Australian beeswax, grass tree resin and macadamia nut oil, because these natural products have been used extensively in Aboriginal painted works (Blee et al. 2010:745; Cole and Watchman 1993:355; Ryan 2006:4). The European binders that will be analysed include linseed oil, tempera (egg white), sandarac, manila copal, manila elemi and shellac. This will allow at least one plant resin, one oil and one wax to be analysed from each culture, and hence ensure the library will cover a range of binders.
Once this library has been compiled it is hoped that a series of Aboriginal painted clubs of the time period in question from the South Australian Museum, including a fighting club, sword club and throwing club as well as a spear thrower from various regions, will be analysed using the technique, in order to determine if this analysis would be effective for use on artefacts which may contain complex mixtures of binders. This data will be used for historical research and conservation and restoration investigations.

References


Chiavari, G. and S. Prati 2003 Analytical pyrolysis as diagnostic tool in the investigation of works of art. *Chromatographia* 58(9):543-554.


