

Profiling nineteenth-century Australian potteries: Approaches to provenancing ceramics and identifying potting practices

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This study explores the advantages of using chemical characterisation to investigate provenance and manufacturing processes at two colonial potteries: the Thomas Ball Pottery in the Sydney Brickfields, and Irrawang in the lower Hunter Valley, New South Wales. A total of 64 earthenware sherds were analysed using X-ray fluorescence spectroscopy (XRF) and 11 lead-based glazes using Raman microspectroscopy to determine the composition of the ceramic bodies (fabrics) and glazes respectively. XRF and statistical analyses of the fabrics confirmed that sherds from the two Potteries could be discriminated. Raman microspectroscopy was used to identify glaze inclusions such as quartz, feldspar and haematite. These characterisations of both bodies and glazes are part of ongoing research to develop chemical profiles of known potteries, creating a reference database for the wider identification of Australian colonial pottery products and potting practices.

INTRODUCTION

Analytical chemistry provides a variety of techniques for chemically characterising artefacts. Combining elemental and mineralogical studies of ceramics can provide complementary information on the composition of ceramic bodies and surface treatments to explore issues such as authenticity, degradation and artefact function, as well as marketing, trade and consumption based on ceramic provenance. Identification of raw materials and their processing can also offer insights into how European ceramic traditions interacted with the Australian environment during the development of local potting practices.

In the Americas and Europe ceramic chemical characterisation has continued to develop since the archaeometric boom of the 1950s, motivated by issues of provenance, trade, and colonial socio-economic and political relationships. Investigating adaptation of European pottery technologies by colonists in the development of colonial potting traditions has provided significant insights into cultural systems. In some cases, comparisons between the technologies of homeland and colony, once the use of local resources has been established, demonstrate the re-interpretation of European material forms by colonists (Iñáñez et al. 2008; Olin and Blackman 1989; Olin and Sayre 1975, 1978; Rodríguez-Alegria et al. 2003).

Production, trade and consumption of local versus imported ceramics have long been of interest in Australia (Fahy 1967, 1971; Fahy and Birmingham 1987; Ford 1995; Graham and Graham 1979; Ioannou 1986). The use of chemical techniques to provenance Australian-made pottery and identify associated production processes is gaining increasing recognition, evidenced by the recent emphasis on analytical chemistry in consultancy reports and theses on colonial ceramics from New South Wales (Kelloway 2008, Pitt 2010). For instance, Butcher et al. (2007) used element oxide compositions of ceramic bodies as determined by the electron microprobe (EMPA) to distinguish between locally made, unprovenanced Parramatta pottery and imported British colonial ceramics. The results highlighted differences in mineralogy and element oxide concentrations of the two groups. Similarly, Kelloway (2006) determined the element oxide composition of Irrawang glazes using scanning electron microscopy (SEM) to investigate aspects of glaze production. The source of colour variation in glazes was identified

and a glaze recipe estimated based on the chemical and historical data.

This paper reports the initial findings of an ongoing investigation into colonial ceramic products in New South Wales from c.1788–1850, aimed at providing a guide and reference base (chemical profiles) for future chemical studies. Sherds from the Thomas Ball Pottery, Sydney Brickfields, and the Irrawang Pottery, lower Hunter Valley were characterised using numerous techniques. The results of two techniques are presented here: X-ray fluorescence spectroscopy (XRF) of the ceramic bodies and Raman microspectroscopy of the glazes. The XRF elemental data was used to develop chemical profiles of the Potteries for inclusion in a reference library for future provenance studies. Raman microspectroscopy was performed on the glazes to identify glaze inclusions as another reference for provenance work.

PROVENANCE AND MANUFACTURING PROCESSES: AN AUSTRALIAN CONTEXT

Locally-made colonial ceramics were advertised in the early nineteenth century as domestic and utilitarian ware, such as dairy and food preparation vessels, water carafes and filters, toilet wares, garden urns, tableware and ginger beer bottles, to name a few. High status tableware was imported, usually from Britain – high status pottery if made locally was apparently sold privately. Distinctive local wares can often be associated with a specific pottery on typological grounds but such attributions are sometimes questioned (Owen 2001). Where the attributes are not unique and no potter's mark is present, locally made colonial ceramics are catalogued as just that.

Typological provenancing has particular limitations where few early colonial potteries have survived urban expansion, limiting the amount of available comparative reference material (Gilbert et al. 1993; Monette et al. 2007). Australian exceptions include the non-urban excavated site of James King's Irrawang Pottery (Birmingham 1976, forthcoming), the regional Lithgow Pottery (Evans 1981; Higginbotham 1982) and rare urban manufacturing sites such as that of potters Jonathan Leake and Thomas Ball in the Sydney Brickfields (Casey 1999: 7, 2010; Casey & Lowe 2007, 2009).

Chemical characterisation has the ability to discern ceramics originating from different potteries as well as manufacturing regions when typological analysis is inconclusive (Neff 2000: 106-121). Conversely, it can also identify ceramics with the same production origin, and so refine the typological categories that form the basis of sampling. Manufacturing processes can also be investigated by analytical chemistry. The identification of mineral inclusions and colorants, and the estimation of firing temperatures using techniques like Raman spectroscopy and scanning electron microscopy can provide information on raw material selection, ceramic paste/body and glaze preparation and firing processes (Colomban et al. 2006; Pollard et al. 2007: 109-113, 118-120; Smith and Clark 2004; Vandenabeele 2004). Combined, these approaches can be richly informative on the development of colonial potting traditions within the wider cultural context of environmental and resource awareness.

DETERMINING PROVENANCE

At the core of provenance studies is the *provenance postulate*. This postulate poses that determining an artefact's origin relies on inherent differences among possible sources beyond the observed variation within each source, be it a qualitative or quantitative elemental and/or mineralogical dissimilarity. A range of factors must be considered in establishing these differences, including analytical accuracy and precision in conjunction with sampling, natural variation within sources and post-depositional effects (Neff 2000: 107-106; Weigand et al. 1977: 24; Wilson 1978: 220).

In order to source ceramics to particular potteries, ideally reference groups of known provenance need to be characterised and compared to specimens of unknown origin. Kiln material is particularly valuable for establishing reference groups because of its known provenance. If samples of known origin are unavailable, the *criterion of abundance* method can be used, which assumes that pottery is most frequently found close to its location of manufacture (Neff 2000: 112; Wilson 1978: 220). Compositional disparities amongst samples and sources relate to issues including access to raw materials and processing, artefact function and post-depositional environment, all of which impact chemical signatures (Freestone et al. 1985: 171, 1994, Owen and Day 1998, Wilson 1978: 223). Manufacturing techniques are highly significant to ceramic sourcing. Clay levigation, the addition of tempers and colorants, the mixing of differently prepared and/or sourced clays all influence the final composition of a product causing dilution or enrichment of elements and minerals (Arnold 1992: 159-161; Blackman 1992, Buxeda et al. 2003; Neff 1988, 1989; Papachristodoulou et al. 2006: 351). Since the characterisation of ceramics is the sum influence of the events that acted upon them from creation through to recovery and analysis, the chemical signatures of source groups are a reflection of all these influences (Neff 2000: 117-121).

TECHNIQUES

Today the technological suite available to archaeologists is extensive, extending well beyond the earlier range of petrographic methods based on thin-sections and heavy mineral analysis. It encompasses amongst others: neutron activation analysis (NAA), inductively-coupled mass-spectrometry (ICP-MS), X-ray fluorescence spectroscopy (XRF) and Raman spectroscopy.

X-ray Fluorescence Spectroscopy

One technique long used to provenance pottery is X-ray fluorescence spectroscopy (XRF). XRF provides the concentrations of elements present in samples, based on the emission of characteristic X-rays (secondary/fluorescence) by atoms within the specimen when it is bombarded with an X-ray beam (primary X-rays). Elements present in major (>1 per cent), minor (0.1-1 per cent) and trace (<0.1 per cent) concentrations can be ascertained based on the interpretation of the intensities of emitted characteristic radiation. The results can be used alongside distributional and multivariate statistical analyses to determine archaeologically meaningful patterns. XRF offers both non-destructive and destructive analyses. To obtain a homogenous sample and reduce particle size and mineralogical effects, ceramic samples are normally powdered and either pressed into a pellet or made into glass according to the analytical elements desired (Pollard et al. 2007: 93-123).

Raman Spectroscopy

Raman spectroscopy is a non-destructive technique used for the characterisation of samples at a molecular level. In contrast to XRF, which only determines the elements present and their concentrations, Raman spectroscopy provides structural information which distinguishes between different forms of compounds, for example, between the iron oxides haematite and magnetite. When a laser beam hits a sample, laser light is scattered in one of two ways. The majority of the scattered laser light will have the same energy before and after it was scattered by the sample (inelastic or Rayleigh scattering); however, a much smaller amount of light will have lost or gained energy when it interacted with the specimen (elastic or Raman scattering). The output is a spectrum that records the energy shift (reported in Raman shift, cm^{-1}) of the scattered light. These differences in energy are related to the characteristic vibrations of molecular bonds between atoms present in the sample. The pattern of peaks present in the spectrum is used to identify bonds and thus compounds in ceramics (Long 2002). Examples of Raman spectra are presented in Figure 3. Raman spectrometers are often coupled to a microscope, allowing microscopic analysis with the size of the laser beam (lateral resolution) in the order of $1 \mu\text{m}$ (Kelloway et al. 2010: 3). This then allows the identification of inclusions in glazes and glasses by comparing unknown spectra with known reference spectra of various compounds.

COLONIAL POTTERY PRODUCTION IN NEW SOUTH WALES

To provide a reference base for future chemical studies dealing with the provenance of Australian made ceramics this paper focuses on the analysis of ceramic bodies and glazes from two potteries in New South Wales: the Thomas Ball Pottery (c.1801–1823) and James King's later Irrawang Pottery (c.1832–1852).

The Thomas Ball Pottery

The pottery belonging to Thomas Ball was located in the Brickfields area of Sydney, now 710–722 George Street, Haymarket, and operated from c.1801–1823 (Casey & Lowe 2009). Ball, who described himself as the first to commence a pottery in the colony, built a kiln and used an adjacent garden to dry his wares. During Ball's operations, other potters, like Samuel Skinner, also began production in the area (Lawson

1971; Ford 1995; Casey 1999: 7). Little more is known of the Ball Pottery from the historical record but archaeological excavations proved more informative on production processes and the types of wares produced (Casey 2010; Casey and Winnett 2010; Pitt 2010).

The excavated wares are mostly coarse fabrics, thinly lead-glazed (Figure 1(a)). The forms are domestic and utilitarian, and contemporary advertisements indicate that supplies such as red lead and glaze colorants were imported. Particularly distinctive are the buff-bodied lead-glazed ceramics decorated on a yellow background with brown and green zigzags – confirmed by SEM as derived from iron and copper oxide respectively.

The Irrawang Pottery

The Irrawang Pottery is located in the flood plain of the Williams River in the lower Hunter Valley, a region rich in clays (Uren 1973), and was one of many ventures of owner James King, operating from c.1832–1852 (King 1835, 1852). The Pottery continued with stoneware sales only (wine demijohns and ginger beers) until 1855 (Birmingham 1976). The Hunter District Water Board resumed the eastern part of the estate in the 1960s and the Pottery now forms part of the overflow and spillway from the Grahamstown Reservoir. Like the Ball Pottery, the Irrawang Pottery is known from both archaeological excavation and historical research (Birmingham 1976, forthcoming).

Domestic and utilitarian wares were produced at Irrawang, including milk pans (Figure 1(b)), chamber pots, wine jars and ginger beer bottles. The first products were lead-glazed earthenware, followed by lead and salt-glazed stoneware. Pots were primarily wheel-turned with labour and machinery predominately British in origin. Staffordshire moulds and some glazing materials were also imported. A number of wares produced at Irrawang were retrieved through excavation, with documentary evidence providing a longer list of the wares sold (Bickford 1971; Lawson 1971; King 1844; Jack and Liston 1982).

Historical information about King’s ceramic production and glazing processes, as well as his clay sources, is sparse. Clay was widely available in and near Irrawang: contemporary and later observers commented on clay from the area, including the importation of white clay from Stroud, in the 1960s the Geological Survey found clay in numerous test pits in and beyond the Irrawang area, the excavation found a rich clay zone near the so-called clay pit on site and kaolin sources in the region were also surveyed (Baker and Uren

1982; Macle hose 1977 [1839]; *Maitland Mercury* 1865; Kelloway 2008; Uren 1973).

Chemical characterisation of lead glazes in 2006 confirmed (Kelloway 2006) that the colour variations in the lead glazes – ranging from yellow through to dark brown (‘black’) – were produced by varying the amount of iron oxide in the glazes. Greater concentrations of iron oxide produced darker colours when fired in an oxidising atmosphere.

EXPERIMENTAL METHODOLOGY

Samples

All samples were lead-glazed earthenware, ranging from buff to orange, red and brown fabrics (Figure 1, Table 1). A total of 59 Irrawang rim sherds classified as milk pans, and five Ball sherds of various forms were selected for fabric analysis by XRF. The five Ball sherds were rim, base and body fragments, selected while excavations were in progress. Seven Irrawang glazes and four Ball glazes were analysed with Raman microspectroscopy. The Ball glazes included two yellow-orange glazes and two brown glazes. The Irrawang glazes included one yellow, three brown, and three dark brown glazes.

Table 1: Total number of samples analysed by X-ray Fluorescence and Raman spectroscopy.

	Irrawang Pottery	Thomas Ball Pottery
X-ray Fluorescence Spectroscopy	59	5
Raman Spectroscopy	7	4

Sample Preparation and Analysis

XRF

A sample from each sherd was prepared as a homogenised powder (for detail on this process see Kelloway 2008) and subsequently transformed into a glass bead at the XRF Laboratory, Solid State and Elemental Analysis Unit, University of New South Wales (Norrish and Hutton 1969). Loss on ignition values were also acquired, which account for the loss of volatiles during fusing. A total of 12 element and element oxide concentrations were determined: iron (Fe_2O_3), manganese (MnO), titanium (TiO_2), calcium (CaO), potassium (K_2O), sulphur (SO_3), phosphorous (P_2O_5), silicon (SiO_2), aluminium (Al_2O_3), magnesium (MgO), sodium (Na_2O) and zinc (Zn).

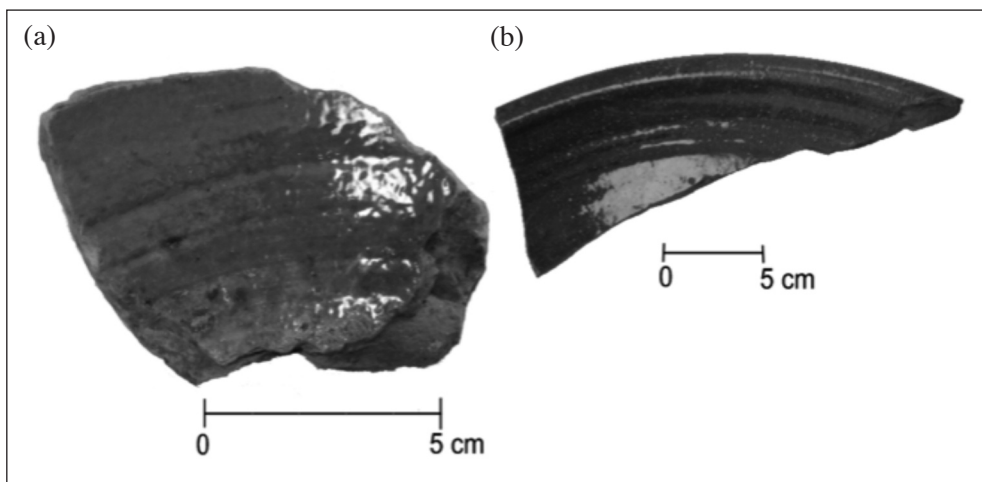


Figure 1(a): Lead-glazed earthenware body sherd manufactured at the Thomas Ball Pottery in the Sydney Brickfields, c. 1801–1823.

Figure 1(b): Lead-glazed earthenware milk pan rim sherd produced at Irrawang in the lower Hunter Valley, c. 1832–1852, New South Wales.

Raman Microspectroscopy

All samples were prepared as cross-sections embedded in epoxy at the Australian Centre for Microscopy and Microanalysis, University of Sydney (Kelloway 2006). Raman spectra were collected using a Renishaw inVia Raman spectrometer fitted with a Leica DMLM microscope using a 50× objective. An argon ion laser emitting at 514 nm was used at various laser powers (~1-7 mW at the sample), with 1 accumulation of 10 s over a spectral range of 2000 to 100 cm⁻¹.

Data Interpretation

XRF

Principal Components Analysis (PCA) is a multivariate statistical analysis tool commonly used to determine patterns in archaeological data. PCA was used to interpret the XRF results (Table 2) and was carried out using the GAUSS program routines supplied by the University of Missouri Research Reactor Archaeometry Laboratory (Columbia, MO, USA) (Glascok 1992: 19-21). SO₃, P₂O₅ and Zn were excluded from the analyses as most SO₃ and Zn concentrations were below the minimum value of detection and P₂O₅ is typically affected by burial (Freestone et al. 1985, Pillay et al. 2000: 55-6, Tsolakidou and Kilikoglou 2002: 570). Two Na₂O values below the level of detection were substituted with 0.55 of the estimated detection limit of that element (Baxter 2003: 121). The data were re-summed and Aitchison's log-centred ratio transformed before PCA (Aitchison 1986: 141; Aitchison et al., 2002; Baxter 1992, 2003: 75-77; Baxter and Freestone 2006). Bivariate plots were also used.

Raman Microspectroscopy

Cosmic ray peaks (spectral artefacts identified as randomly occurring sharp narrow peaks) were removed using *GRAMS AI* (Version 8.0, Thermo Electron Corp, Waltham, MA, USA).

Raman inclusion spectra were identified by comparing unknown spectra with known reference spectra of various compounds.

RESULTS AND DISCUSSION

XRF

The means and standard deviations of the element oxide concentrations as determined by XRF and loss on ignition values for the samples according to pottery source are given in Table 2. Discrimination between the two sources was achieved with both PCA and bivariate plots based on the XRF data.

Figure 2 presents the plot of the first and second principal components (PCs) of the Irrawang and Ball ceramics resulting from PCA, accounting for 89.71 per cent of the variation in the dataset. Both the Ball and Irrawang fabrics form distinct groups. Analysis of the contributions to variation by each element oxide for each principal component showed that Na₂O was a significant contributor to the separation of the two Pottery groups. The Na₂O content of the Ball ceramics is less than that of the Irrawang sherds, observed in Table 2. The separation of the groups was also well represented in a plot of MgO and Na₂O (not presented here) during analysis using bivariate plots. The sub-groups of the two Pottery clusters correlate to differences in fabric colour, namely, buff versus orange, red and brown fabrics. Table 2 shows that within each group, the subgroups are significantly distinguished from each other by their Fe₂O₃ content.

The dissimilar geochemistry of Ball and Irrawang ceramics reflected in the XRF results is the chemical consequence of different raw materials and other production practices, as well as other factors. This includes variations in source materials, recipes and clay processing, such as levigation and mixing, as levigation and mixing. Although the Ball sample size is small compared with the Irrawang sample population it significantly illustrates the potential of chemical

Table 2: Descriptive statistics for the Thomas Ball and Irrawang Potteries' XRF results (weight percentage oxide)

	Fe ₂ O ₃	MnO	TiO ₂	CaO	K ₂ O	SO ₃	P ₂ O ₅	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	Zn	Loss on Ignition
THOMAS BALL POTTERY													
<i>All Samples (n=5)</i>													
Mean	3.10	0.01	1.10	0.12	0.86	0.00	0.14	72.03	19.90	0.35	0.01	0.00	1.95
Standard Deviation	1.46	0.00	0.08	0.12	0.21	0.00	0.13	4.58	3.94	0.06	0.01	0.00	1.88
<i>Buff Fabrics (n=2)</i>													
Mean	1.53	0.01	1.08	0.25	1.05	0.00	0.26	67.43	23.98	0.41	0.02	0.01	3.97
Standard Deviation	0.00	0.00	0.05	0.07	0.11	0.00	0.15	3.50	2.29	0.02	0.01	0.01	0.71
<i>Red/Orange/Brown Fabrics (n=3)</i>													
Mean	4.15	0.01	1.12	0.04	0.73	0.00	0.07	75.10	17.19	0.30	0.01	0.00	0.60
Standard Deviation	0.37	0.00	0.10	0.01	0.14	0.00	0.00	0.78	0.87	0.02	0.01	0.00	0.19
IRRAWANG POTTERY													
<i>All Samples (n=59)</i>													
Mean	4.75	0.02	1.35	0.23	1.04	0.00	0.03	74.22	15.69	0.61	0.95	0.00	0.72
Standard Deviation	1.36	0.01	0.21	0.08	0.56	0.01	0.01	2.41	3.04	0.10	0.37	0.00	0.37
<i>Buff Fabrics (n=12)</i>													
Mean	2.46	0.01	1.21	0.11	2.00	0.00	0.04	71.04	20.37	0.75	0.40	0.00	1.19
Standard Deviation	0.65	0.01	0.38	0.07	0.42	0.00	0.01	2.49	2.74	0.11	0.32	0.00	0.43
<i>Red/Orange/Brown Fabrics (n=47)</i>													
Mean	5.34	0.02	1.39	0.27	0.79	0.00	0.03	75.03	14.49	0.57	1.09	0.00	0.60
Standard Deviation	0.71	0.01	0.13	0.04	0.21	0.01	0.01	1.59	1.63	0.06	0.23	0.00	0.24

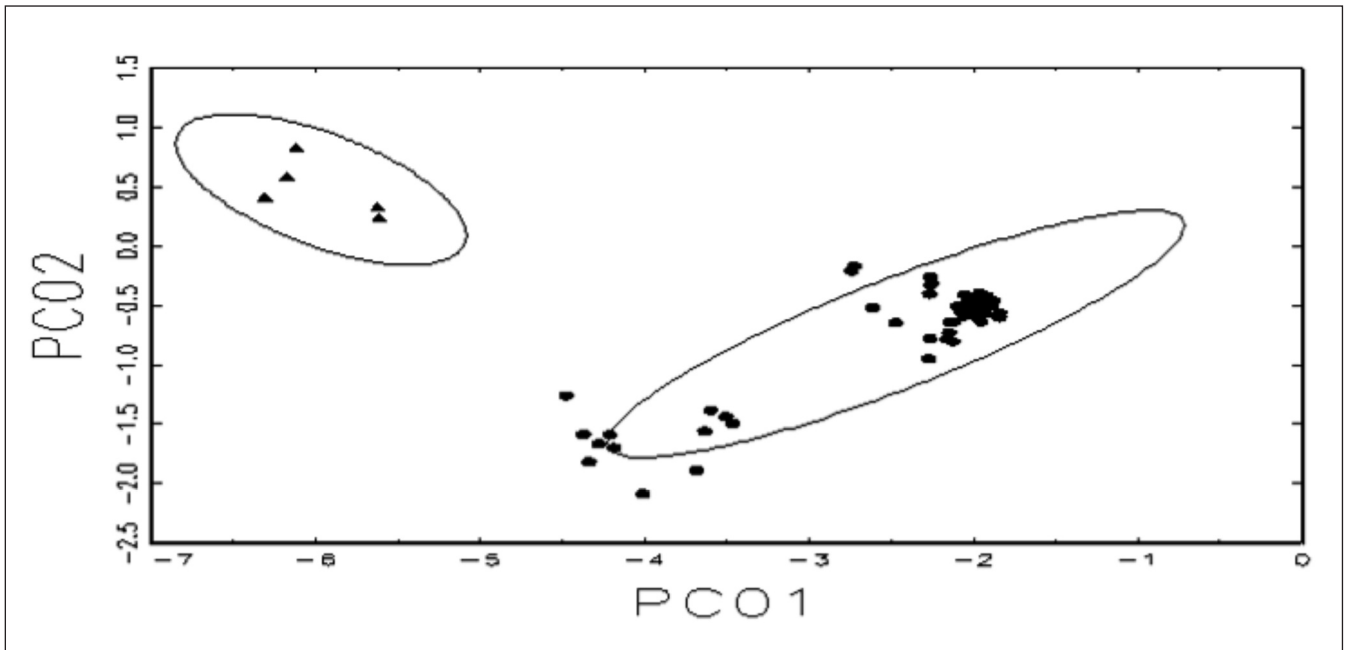


Figure 2: Plot of the first and second principal components resulting from Principal Component Analysis of the dataset. The Ball (\blacktriangle) and Irrawang (\bullet) ceramics form distinct chemical groups. The first principal component (PC01) accounts for 73.85 per cent of variation and the second principal component (PC02) for 15.86 per cent. The circles are indicative of 90 per cent confidence limits.

characterisation for distinguishing the products of different potteries in the Australian context. The next step – analysing more samples from identified kilns – will add to this chemical reference set for future comparative work, providing a basis for exploring the origins of sherds excavated on household and other consumption sites. Other techniques like instrumental neutron activation analysis (INAA) are also being used to develop this reference database, providing trace element concentrations, highly valuable fingerprinting elements (Glascok 1992: 11). Chemically characterising these samples with additional techniques also widens the comparative research applicability of the database.

Raman Microspectroscopy

Both the Irrawang and Ball ceramics are lead-glazed. With the exception of one sample, TBL 006, the Ball glazes are thin with uneven colouring, i.e. yellow/orange glazes with dark patches rich in iron oxide. TBL 006 represents a thicker even-coloured dark brown glaze with a finer body, macroscopically closer to Irrawang specimens.

The Ball glazes are generally thinner than the Irrawang glazes and microscopically also contain a qualitatively greater number of inclusions, indicating differences in potting practices. In both cases the inclusions derive not only from the glazing materials but also potentially from the slip and/or body. The presence/absence of minerals can be used to provenance ceramics. Examples of spectra collected during this study are presented in Figure 3. In both sets of glazes the following inclusions were identified: α -quartz, haematite, feldspar metamorphic zircon (Caltech 2008; Legodi and de Waal 2007; Société Française de Minéralogie et de Cristallographie 2006; Zoppi et al. 2005). Igneous zircon (Xian et al. 2004) and cristobalite were present in Irrawang glazes but not observed in Ball glazes. Similarly, cassiterite (tin oxide, SnO_2) was present in Ball but not in Irrawang glazes (Colomban et al. 2001). Cassiterite was likely added to the glaze as an opacifier. Tin oxide was also found in Ball glazes by Pitt (2010). In the Irrawang glazes the number of haematite grains qualitatively increased in the darker brown glazes, confirming the use of iron as a colorant (Kelloway

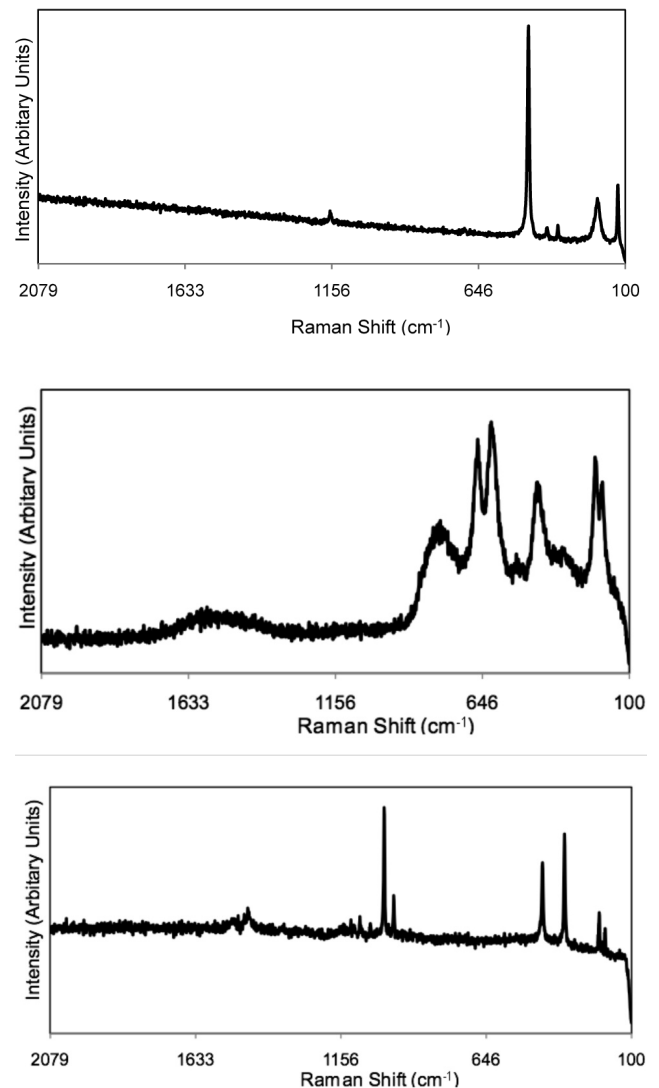


Figure 3. Examples of representative Raman spectra from inclusions identified in the glazes: (top) quartz, (middle) haematite and magnetite, and (bottom) metamorphic zircon.

2006). The presence of different inclusions in the glazes from each Pottery is indicative of dissimilar potting strategies, particularly access to raw materials and their processing.

CONCLUSIONS

This study successfully distinguished between two sets of sherds representing two Australian colonial potteries. Ceramic bodies from the Thomas Ball Pottery in Sydney and the Irrawang Pottery in the Hunter River region were discriminated based on XRF determinations of element oxide concentrations. The dissimilar geochemistry results from variations in potting practices, including the use of different raw materials, amongst other factors. Disparities were echoed in the Raman microspectroscopy results. The Ball glazes included cassiterite, not found in the Irrawang samples, while igneous zircon and cristobalite, absent in the Ball specimens, were present in the Irrawang glazes. These inclusion differences could be used in future to provenance ceramics. The glazes from the two Potteries also visibly varied in quality, those from Irrawang thicker with more even coloration.

While variations in chemical signatures reflect different potting practices, artefact function and depositional factors, the investigation of these individual influences where relevant require more targeted studies. What is important in this paper is that the products of these two potteries can be distinguished. This is a first step in the creation of a chemical reference base for future comparative studies. Other analytical methods now in use to analyse Australian-made archaeological ceramics include INAA and mineralogical mapping of sherds with Raman spectroscopy, adding complementary data sets. Chemical sourcing of pottery has obvious applications in many colonial and inter-colonial marketing, consumption and social identity studies. It also has specific relevance to how successive potters in different parts of Australia explored and manipulated new environments to develop their age-old potting skills.

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