15

Melting Moments: Modelling archaeological high temperature ceramic data

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Abstract

A fundamental concept in compositional studies in archaeology is that an elemental fingerprint most broadly reflects region- or area-specific petrogenetic conditions (the provenance postulate). In this study, a sample population from a single shipwreck assemblage of trade ceramics (stoneware jars from East and Southeast Asia), can be separated into clear compositional groups. While the multivariate elemental definition of these groups is not controversial, their interpretation is. The study uses a method of elemental data optimisation where mathematical and statistical techniques are combined to explicitly evaluate the significance of these groups. Contrary to expectations, group elemental signatures emerge as hybrids of provenance and temperature. The results highlight the value of explicit modelling approaches to archaeological ceramic elemental datasets, as well as underscore the general influence of temperature on stoneware compositional profiles.

Keywords: Principal components analysis, polynomial regression, data optimisation, ICP-OES, provenance postulate, East and Southeast Asia

Introduction

In the elemental analysis of archaeological ceramics the ‘provenance postulate’ remains a major conceptual link between geochemical pattern and archaeological interpretation (Olin et al. 1978; Kolb 1982; Maggetti et al. 1984; Jones 1986; Vitali and Franklin 1986; Ferring and Perttula 1987; Mason and Keall 1988; Middleton et al. 1992; Mommsen et al. 1992; Mallory-Greenough et al. 1998; Neff 2000; Wilson and Pollard 2001; Gomez et al. 2002; Hein et al. 2002; Grave 2004). Experimental studies of earthenwares have shown that interpretation can be complicated by additional factors such as technological treatment

or post-depositional alteration (Matson 1971; Kilikoglou et al. 1988; Gosselain 1992; Cogswell et al. 1996; Buxeda i Garrigos 1999; Buxeda i Garrigos et al. 2001; Matsunaga and Nikai 2004; Schwedt et al. 2004). These qualifications of the provenance postulate have largely dismissed firing temperature as a variable with any substantial effect on elemental composition. As a result archaeological ceramic elemental profiles are generally considered unalterable by the varying temperature regimes required for the successful production of a ceramic vessel.

A major difference between clay compositions used for earthenware and stoneware relates to the relative concentration of elements (fluxes) that lower or raise the melting (eutectic) point. Mismatch between firing temperature and flux-rich clays can result in vessel failure with development of excessive glass phases and gas formation ('bloating') causing partial or complete vessel collapse ('slumping'). For stonewares — vitreous ceramics fired between ~1100-1400°C — the relatively low concentrations of fluxing elements allow firing in the higher temperature ranges required without premature melting and slumping of the ceramic vessel (Kerr and Wood 2004).

Most archaeological characterisation work on high-temperature ceramics from East and Southeast Asia has adopted the provenance postulate (and associated caveats) more or less uncritically (Impey and Tregear 1983; Guo and Li 1986; Liu 1986; Pollard and Hall 1986; Pollard and Hatcher 1986; Yang and Wang 1986; Stenger 1992; Yap and Hua 1992; Pollard and Hatcher 1994; Hughes et al. 1999; Chen et al. 1999). However elsewhere, I have shown that the high firing temperatures required for stoneware production can have a measurable effect on composition (Grave et al. 2000). The observations underpinning that argument were limited to a small population of decorated vessels and the kaolinitic white clays they were produced from, from a single production centre in central northern Thailand, using a sensitive but relatively low-dimensional technique (PIXE/PIGME). Here I evaluate a more robust elemental dataset for a shipwreck assemblage of stoneware jars from several East and Southeast Asian production centres in order to demonstrate the importance of firing temperature as a variable that structures the elemental composition data derived from high-temperature ceramics (Grave et al. 2005a). An analytic advantage for elemental analysis of stoneware storage jars is that these fabrics are typically derived from clay sources that tend to be more elementally complex than the clays used for white bodied 'fine' ceramics. Greater compositional complexity increases the likelihood of detecting the range of factors that modulate elemental signatures.

The objectives of this paper are twofold and interrelated. The first is to evaluate the significance of compositional groups in this assemblage. The second more methodological objective is to provide a means to explicitly test this multivariate dataset against a number of working hypotheses.

Limitations

This study is an empirical presentation and interpretation of relative data patterns and trajectories rather than an effort to reconstruct 'original' ingredients or technological parameters. The complex relationship between composition and eutectic point, for example is beyond its scope. Therefore I have dispensed with the convention of reporting elements as oxides and make no attempt to relate empirical observations of elemental behaviour to absolute estimates of initial clay composition or firing temperature.

Background

East and Southeast Asian archaeological assemblages of the last thousand years or so typically contain stonewares from a wide range of production centres of varying technical proficiency. Stoneware technology, initiated in China prior to the first millennium AD, was widely adopted in East Asia and mainland Southeast Asia from the early second millennium AD (Hayashiya and Hasebe 1966; Impey 1972; Mikami 1972; Medley 1976; Li 1990; Stevenson and Guy 1997). This technology was responsible for goods that defined the character of one of the most extensive trade and exchange systems of the pre-modern period (Bronson 1990), a system fed by numerous small production centres, that gave rise to some of the largest industrial-scale specialised production complexes of the pre-modern world (Harrison 1986; Long

1992; Valdes et al. 1992; Dupoizat 1996; Descantes et al. 2002). The ready spread of stoneware technology can be at least partly attributed to the relative ease with which the temperatures required can be achieved. Stoneware kilns ranged from simple in-ground bank kilns to larger more elaborate hill-side brick structures ('Dragon' kilns) (Vallibhotama 1974; Hughes-Stanton and Kerr 1980; Garnsey and Alley 1983; Shaw 1985; Liu 1986; Hein and Barbetti 1988; Ho 1990; Impey 1996; Grave et al. 2000).

The current work is part of a wider research project to understand the impact of the transition from the pre- to early-modern economy in East and Southeast Asia. Stoneware compositional data from high resolution chronological contexts (shipwrecks) can be used as an archaeological proxy for changes in craft organisation for East and Southeast Asia and is detailed elsewhere (Grave et al. 2005b). Here I focus on achieving an appropriate level of analytic detail to articulate these production dynamics.

Methodological considerations

The provenance approach to ceramic elemental analysis is best applied where an extended system of trade/exchange is thought to have operated over a region, and would seem ideally suited to East and Southeast Asian archaeological stoneware assemblages. The advantage of establishing an unambiguous geochemical signature is that it provides a means independent of more formal criteria such as typology to distinguish between different production centres, even where the actual source area or centre remains unknown. This characteristic is especially useful where popular forms were widely emulated, as is the case for the numerous competing centres of Asian stoneware production (Brown and Sjostrand 2002).

Analytical requirements normally involve a) a relatively large and representative sample population, b) instrumental technique(s) that can provide accurate and precise (reproducible) measurement of elements; and c) a large number of elements for a high dimensional dataset to maximise identification of elements or elemental suites that are distinctive of different production centres. Substantial technical advances in measurement sensitivity as well as greater flexibility and availability of analytic facilities have no doubt contributed to the growth in popularity of this approach. Criticism of the adoption of novel analytical techniques may be justified where there is no proven advantage in larger numbers of elements or higher sensitivity measurements.

Recently, Baxter and Jackson (2001) suggested that technical developments, rather than archaeological requirements, have driven the move to use increasingly large numbers of elements that may needlessly complicate interpretation. They introduce the idea of data optimisation and adopt a multivariate modelling solution that seeks the most parsimonious explanation of data structure by reducing the number of elements required to maintain sample relationships (Krzanowski 1987). While most techniques of multivariate analysis involve data reduction, a drawback of this method is that its criteria are focussed on the sample or object side of a dataset. A major shortcoming is that it discounts the interpretative potential of elemental/variable behaviour for understanding overall data structure.

Schematic Models

Out of the extensive empirical and experimental work on the factors contributing to ceramic compositional signatures, three major themes emerge: provenance; technological modification (usually focussed on additive or subtractive technologies); and post-depositional alteration. Assessing these major compositional models (provenance, technological and environmental alteration) requires both internal and independent evaluation criteria:

- The type of structure(s) (shape) of the sample;
- The behaviour of elements that describe this structure;
- A measure of statistical goodness-of-fit for elemental behaviour;
- Expectations for an observation independent of elemental behaviour that would unambiguously support a specific hypothesis such as the provenance postulate.

For the typical multidimensional interpretative environment used for high-dimensional datasets — principal components analysis (PCA) — the schematic appearance of these themes can be broadly defined, based on expectations of data structure and behaviour (Figure 1; Grave et al. 2005a). In this technique, contiguity is essential for group identification. In a normally distributed sample group, shape tends to be ellipsoidal, with deviations from normality reflected in more or less distorted group shapes. In a multi-group sample the orientation of group ellipsoids to each other reflects the degree of similarity or distinctiveness between the underlying geochemistry of each group.

Figure 1. Schematic representation of models discussed in the text: a: provenance — groups defined by distinct elemental suites operating independent of each other and reflecting different parent catchments; b: technological alteration — varied technological treatments producing a number of groups that are subsets of elemental range and orientation of parent catchment; c: post-depositional alteration — elemental signature of parent catchment altered by interaction with mobilised elements of a different catchment to produce a new hybrid signature

For provenance-determined data structure, group range and shape is primarily influenced by the distinctive geochemistry of different catchments. This difference is reflected in independent group orientation as well as distribution (Figure 1a). Where systematic differences in technological modification is the dominant influence, such as removal of or addition of inclusions, separation between groups will be constrained by the orientation and elemental range of the parent geochemical signature (Figure 1b). Finally, post-depositional alteration, where a distinctive provenance-determined signature is altered by a subsequent geochemically distinct depositional environment, will produce a hybrid elemental signature (Figure 1c). Without good control over these subsequent processes, post-depositional alteration may obscure the relationship to unaltered groups from the same parent catchment.

Material and Methods

Sample Population

Typical archaeological contexts involve anything from decadal to centuries-old accumulations of ceramic debris that may reflect a wide range of production centres, each of which can vary greatly in technical proficiency over time. In order to circumvent these issues, this study uses a representative sample population of stoneware storage jars, from an absolutely dated historical context, the Spanish Manila galleon, ‘Nuestra Señora de la Concepción’, wrecked August 1638 in the northern Marianas Islands while on the return leg to Acapulco from the Philippines (Mathers et al. 1990). In line with the ‘time capsule’ nature of the wreck, the jar assemblage is of limited typological range but appears to represent a number of production centres (Rinaldi 1990). Prior to sampling, scaled digital imaging recorded jar type. A portable circular diamond saw was used to remove samples from an inconspicuous area (typically from the base) of 157 jars.

ICP-OES Analysis

The applicability of inductively coupled plasma-optical emission spectrometry (ICP-OES) to compositional analysis of stonewares has been reported elsewhere (Grave et al. 2005a). The technique relies on superheated plasma (8000–10000° centigrade) to reduce compounds to atomic constituents. The current generation of optical emission spectrometers uses a charge-coupled detector (CCD) to measure the optical properties of the plasma. After spectral splitting, the intensities of light wavelengths that are element-specific are simultaneously measured as an analogue of elemental concentrations. Typically ICP-OES enables both a high sample throughput (100–200 per day) and long periods between routine servicing. Theoretically, ICP-OES is capable of simultaneously measuring up to 70 elements of the periodic table but in practice is normally used for only 20–30 elements.

The method requires careful sample preparation (removal of surfaces with a tungsten carbide high speed burr and ultrasonically cleaned) followed by drying and powdering (grain size <10 microns) in a tungsten carbide ball mill (SPEX 5000) for 10 minutes. Samples are then reduced to an aqueous solution through digestion of a small amount of sample powder (200 mg) with a high pressure microwave system (Milestone Ethos Plus) and a combination of hydrofluoric and nitric acids based on a modified EPA method. Following digestion the aqueous samples are loaded into an auto sampler for nebulisation and ICP-OES analysis (a radial Varian Vista MPX ICP-OES system).

SEM Analysis

The physical and mineralogical characteristics of a representative subsample were examined using scanning electron microscopy (SEM). This involved carbon coating fresh fracture surfaces of samples under vacuum and examination for SEM and X-ray element-specific mapping using a Joel 35C SEM equipped with an energy dispersive spectrometer.

Accuracy and Precision

For ICP-OES measurement performance is gauged by reference to external standards to determine precision and accuracy experimentally. Ideally these standards are as closely matched to the general matrices of the actual samples as possible. Because no internationally accepted standards exist for stonewares, replicates of two standard reference materials (SRM) from the U.S. National Institute of Standards and Technology (NIST) (SRM679 Brick Clay and SRM2711 Montana Contaminated Soil) were used. These clay and soil standards were selected because they roughly approximate the matrices of the archaeological samples and cover a wide range of elements. Table 1 gives experimental recoveries for the NIST standards against their certified/published values. Of a total of 41 measured elements we retain 33 elements that have very good measurement precision ($\leq 10\%$). Twenty four of these compare well with NIST certified/published SRM values ($\leq 25\%$), indicating a good level of measurement accuracy.

Multivariate Analysis

Multidimensional data reduction with principal components analysis (PCA) enables standardization of widely divergent elemental ranges (z-scoring) such that the majority of data variation is accounted for on the first few components ((Pollard 1986; Tangri and Wright 1993; Neff 1994). Each successive component describes variation not otherwise accounted for. Typically, with highly structured ceramic compositional data, the first 4 components describe at least 70% of total variation (Grave et al. 2005a). As PCA highlights the most significant structures as well as the contribution of elements in a reduced number of dimensions, it facilitates graphic (scatterplot) interpretation (Tufté 1983; Grave et al. 2000).

A strength of PCA is its intrinsic ability to mathematically isolate distinct features of a dataset by component (i.e. it does not require a priori assumptions about data structure). In anthropometric studies of cranial data, for example, PCA is used to distinguish a general size feature (typically accounted for on component 1) from other diagnostic (and non-size related) data structures on subsequent components (Hennessy and Moss 2001; Adriaens and Verraes 2002; Bruner and Manzi 2004). For archaeological ceramics this capacity — the relationship between elemental pattern and a general feature — has not

Element	ICP-OES Emmission line (nm)	SRM 679 (n=40)				Element	SRM2711 (n=30)			
		Average (ppm)	% Stdev	NIST Cert/Pub	% Stdev		Average (ppm)	% Stdev	NIST Cert/Pub	% Stdev
Ba	493.408	462.55 ± 6.06		432.2 ± 2.27	107.02	Ba	537.3 ± 3.98		726 ± 5.23	74.01
Bi	222.821	73.3 ± 7.05				Bi	18.96 ± 7.6			
Ca	317.933	1559.94 ± 5.44		1628 ± 0.8	95.82	Ca	18781.21 ± 4.67		28800 ± 2.78	65.21
Cd	226.502	0.52 ± 7.95				Cd	3.94 ± 2.45		41.7 ± 0.6	9.45
Ce	418.659	102.8 ± 7.72		105 ± —	97.9	Ce	62.4 ± 4.35		69 ± —	90.43
Co	228.615	27.09 ± 6.77		26 ± —	104.19	Co	9.5 ± 2.95		10 ± —	95
Cr	276.653	88.63 ± 6.35		109.7 ± 4.47	80.79	Cr	35.06 ± 2.69		47 ± —	74.6
Cu	324.754	33.3 ± 6.95				Cu	103.65 ± 2.69		114 ± 1.75	90.92
Fe	238.204	92552.26 ± 5.72		90500 ± 2.32	102.27	Fe	25864.25 ± 2.47		28900 ± 2.07	89.5
Ga	417.204	29.8 ± 5.98				Ga	13.96 ± 2.88		15 ± —	93.07
Gd	342.246	20.46 ± 6.22				Gd	7.29 ± 2.75			
Hf	264.141	4.05 ± 14.47		4.6 ± —	88.04	Hf	4.85 ± 9.15		7.3 ± —	66.44
K	766.491	24445.25 ± 6.99		24330 ± 1.93	100.47	K	22249.12 ± 1.94		24500 ± 3.26	90.81
La	379.477	48.79 ± 5.54				La	25.99 ± 1.98		40 ± —	64.98
Li	670.783	75.89 ± 8.47		71.7 ± 8.65	105.84	Li	21.09 ± 5.11			
Lu	261.541	2.98 ± 6				Lu	0.95 ± 3.75			
Mg	280.27	7483.58 ± 5.95		7552 ± 1.16	99.09	Mg	6906.31 ± 4.02		10500 ± 2.86	65.77
Mn	257.61	1810.85 ± 6.01		1730 ± —	104.67	Mn	607.9 ± 2.95		638 ± 4.39	95.28
Na	588.995	585.33 ± 7.78		1304 ± 2.91	44.89	Na	4795.66 ± 2.05		11400 ± 2.63	42.07
Nb	309.417	12.89 ± 7.36				Nb	9.67 ± 4.01			
Nd	401.224	23.83 ± 5.85				Nd	11.5 ± 2.04		31 ± —	37.1
Ni	231.604	59.09 ± 6.3				Ni	17.42 ± 4.37		20.6 ± 5.34	84.56
Pb	220.353	16.68 ± 8.77				Pb	1106.35 ± 2.45		1162 ± 2.67	95.21
S	181.972	293.59 ± 10.95				S	381.68 ± 1.48		420 ± 2.38	90.88
Sc	335.372	23.03 ± 5.61		22.5 ± —	102.36	Sc	8.19 ± 1.67		9 ± —	91
Sr	407.771	72.87 ± 5.69		73.4 ± 3.54	99.28	Sr	185.14 ± 1.88		245.3 ± 0.28	75.47
Th	283.73	48.86 ± 6.12		14 ± —	349	Th	17.65 ± 3.43		14 ± —	126.07
Ti	334.941	5722.7 ± 6.1		5770 ± 5.72	99.18	Ti	2682.23 ± 2.82		3060 ± 7.52	87.65
V	311.07	188.4 ± 6.33				V	84.96 ± 2.59		81.6 ± 3.55	104.12
Y	371.029	37.5 ± 5.69				Y	18.57 ± 1.71		25 ± —	74.28
Yb	328.937	5.15 ± 6.08				Yb	2.51 ± 1.15		2.7 ± —	92.96
Zn	213.857	115.82 ± 5.91		150 ± —	77.21	Zn	298.53 ± 2.19		350.4 ± 1.37	85.2
Zr	343.823	150.16 ± 5.83				Zr	107.71 ± 3.09		230 ± —	46.83

Table 1. Statistics for the accuracy and precision of the ICP-OES analysis showing total number of elements used in this study and optimal spectral lines in nanometers (nm). Averages based on number of replicates (n=#) with % standard deviations (calculated by taking the standard deviation for the element and dividing it by the element mean X 100. The purpose of this calculation is to make the standard deviation figures directly comparable between elemental concentrations that can differ by orders of magnitude). Data for the certified standards NIST 679 and 2711 includes % standard deviations and % recoveries (calculated by dividing the mean of the NIST value by 100 then dividing the unknown by this result). Highlighted elements are those that are both precise and accurate. Reported but non-certified data are without errors shown by —.

been explored. The significance of a generalised feature lies in the possibility that group differentiation on the first component would reflect a property that if demonstrated, would apply to all samples, irrespective of origin, technical treatment or environmental effects. In other words more specific effects, such as provenance-specific patterning, should be sought on subsequent components.

Polynomial Regression Analysis and 'goodness of fit'

Determining the probability either that the first principal component isolates a generalised effect, or of the best fit between the data and a particular model, requires statistical (rather than mathematical) evaluation. Regression analysis and its associated R^2 score is an effective way to test both (Fan and Gijbels 1996). The non-linear transformations involved in PCA require a polynomial regression approach. For modelling, a hypothesised governing property of the multidimensional behaviour of elements determines their respective positions along one axis (e.g. valence state, atomic weight, physical behaviour) against the first component order of elements on the other axis (the response). The fit of a line through the observed points of this model provides a measure of the extent to which the model explains the distribution of elements. This is given by an R^2 value, an estimate of the proportion of the variation in the response around the mean that can be attributed to the model rather than random error. An R^2 value of 1 reflects a perfect fit and an R^2 value of 0 means that the fit predicts the model no better than the overall response mean. For evaluating how well a general phenomenon is isolated on the first component, then, this should be reflected in a high R^2 score. Conversely, if the first component reflects compound effects, then this should produce a low R^2 value.

Preliminary Modelling Expectations

Having defined the test population, method and quality of instrumental measurement, and the multivariate and statistical means to evaluate data structure and elemental behaviour, we can now turn to defining provisional expectations for each of the three schematic models presented earlier.

Model A (Figure 1a): Provenance postulate — elemental signature that reflects spatially and geologically discrete production centre:

- Groups defined by distinct elemental suites operating independent of each other and reflecting local petrogenetic conditions (i.e. each group defined by a different elemental trajectory in multidimensional space).
- Independent correlates: typology — each group has distinct typological attributes.

Model B (Figure 1b): Technological modification of elemental signature (e.g. addition or subtraction of inorganic or organic inclusions):

- Group defined by distinct elemental suite that reflects change in compositional range as a result of technological alteration. Different technological treatments can produce a number of groups constrained within the same provenance-specific elemental trajectory.
- Independent correlates: physical evidence for additions; correlations with independent measurements of elemental behaviour (e.g. elemental enrichment associated with purposefully added inclusions).

Model C (Figure 1c): Post-depositional alteration of elemental signature (e.g. environmental enrichment/depletion):

- Elemental signature(s) altered by interaction with mobilised elements to produce a new hybrid signature. If a many-to-one relationship, then this effect would tend to blur provenance-related distinctions.
- Independent correlates: evidence of accretion of salts in pore spaces, dissolved minerals.

Results

Variation in summed elemental totals for each sample conflates both systematic as well as random effects. Because of the difficulties in separating the two, sample measurements were normalised to Σ 50000 ppm. PCA indicates that the normalised dataset is highly structured. It readily separates into five discrete groups on the first two components, with the eigenvalues for these components accounting for almost 65% of overall variation (Figure 2; Table 2). In the accompanying variable plot for these components two elemental trends are evident. The first ranges from high K samples to high Ca samples and describes groups 1–3 and 5 along component 1. The second distinguishes high Ti from the K-Ca trend and separates group 4 samples along component 2. No further new groups are evident on subsequent components.

Polynomial regression of the accompanying elemental plot produces a low R^2 value suggesting that, while the object plot clearly distinguishes 5 groups, there is little correlated behaviour between variables. Optimisation of these results determines how many elements can be removed while retaining group integrity. This step involves iterative removal of redundant or noisy elements using improvements in the polynomial R^2 value as a guide. Elements that exhibit little systematic behaviour due to poor measurement statistics or because of sample outliers are obvious targets for exclusion by optimisation.

Following R^2 optimization the revised dataset was reanalysed by PCA (Figure 3). The results show a substantial 15% improvement in the variation accounted for by the first two components (from ~65% to ~80%). Little substantive difference is evident in the group object scatterplot of component 1 and 2. The polynomial regression R^2 values for the accompanying element plot shows an improvement from 0.3 to almost 0.9 indicating a high level of descriptive efficiency in the element-reduced dataset. While element end members in the optimised dataset appear to retain a high level of redundancy, removal of any of these reduced the R^2 value.

Figure 2. PCA scatterplot of the first two components for the non-optimised dataset showing structure of objects (above) and elements with polynomial regression and R^2 value (below).

Element	Group 1 (n=76)		Group 2 (n=55)		Group 3 (n=9)		Group 4 (n=8)		Group 5 (n=9)	
	Average (ppm)	% Stdev	Average (ppm)	% Stdev	Average (ppm)	% Stdev	Average (ppm)	% Stdev	Average (ppm)	% Stdev
Ba	422.02 ± 9.02		259.77 ± 13.67		290.18 ± 22.98		336.48 ± 8.41		96.61 ± 66.76	
Bi	10.64 ± 19.74		15.71 ± 17.06		16.87 ± 11.5		9.95 ± 27.34		22.13 ± 3.57	
Ca	1598.43 ± 39.44		1907.34 ± 86.12		2766.31 ± 25.78		1611.54 ± 33.79		6154.27 ± 16.68	
Cd	0.12 ± 41.67		0.17 ± 58.82		0.23 ± 104.35		0.18 ± 105.56		0.2 ± 50	
Ce	112.91 ± 13.78		75.84 ± 18.54		65.39 ± 13.46		98.62 ± 8.51		14.57 ± 45.16	
Co	36.16 ± 38.61		39.58 ± 87.37		29.36 ± 24.66		64.23 ± 44.89		21.84 ± 39.1	
Cr	18.95 ± 18.58		31.19 ± 15.2		55.16 ± 21.32		78.58 ± 4.16		46.76 ± 39.61	
Cu	10.98 ± 84.97		10.72 ± 29.01		20.3 ± 23.4		18.55 ± 7.98		28.49 ± 17.16	
Fe	17721.7 ± 9.86		22723.89 ± 10.97		24199.6 ± 4.58		17658.06 ± 3.53		28563.38 ± 3.2	
Ga	20.04 ± 11.58		18.92 ± 10.15		19.73 ± 9.38		34.11 ± 5.69		16.11 ± 24.89	
Gd	8.7 ± 19.31		8.79 ± 24.8		7.54 ± 4.77		7.55 ± 4.64		6.62 ± 9.06	
Hf	6.28 ± 18.95		4.32 ± 20.6		3.04 ± 21.05		6.26 ± 14.22		0.44 ± 88.64	
K	21173.59 ± 8.6		14541.7 ± 11.93		9591.28 ± 13.95		16081.24 ± 9.36		2033.69 ± 49.14	
La	60.38 ± 13.66		37.11 ± 15.33		27.56 ± 6.57		42.96 ± 9.57		6.39 ± 32.86	
Li	23.6 ± 12.5		30.63 ± 15.18		35.42 ± 23.94		73.34 ± 11.82		8.24 ± 23.91	
Lu	1.79 ± 20.11		1.73 ± 26.59		1.38 ± 7.97		2.48 ± 46.37		1.19 ± 14.29	
Mg	2923.27 ± 33.21		4653.08 ± 38.36		6802.83 ± 40.01		5231.36 ± 17.86		6326.63 ± 21.92	
Mn	391.38 ± 14.5		269.23 ± 71.17		430.49 ± 29.39		122.31 ± 34		587.61 ± 31.79	
Na	939.81 ± 19.56		1069.87 ± 17.75		700.24 ± 11.57		399.69 ± 8.12		2229.85 ± 29.4	
Nb	13.81 ± 12.45		10.31 ± 12.22		8.53 ± 11.02		18.29 ± 6.94		5.31 ± 21.85	
Nd	18.77 ± 9.27		16.01 ± 11.74		16.24 ± 10.1		26.95 ± 5.42		10.51 ± 27.88	
Ni	10.33 ± 20.52		14 ± 23.5		29.95 ± 20.8		27.21 ± 6.5		11.97 ± 22.81	
Pb	42.13 ± 19.7		30.67 ± 58.59		17.51 ± 7.65		31.36 ± 15.11		7.63 ± 199.87	
S	69.97 ± 80.92		116.93 ± 120.5		322.26 ± 102.23		136.42 ± 45.59		154.08 ± 84.62	
Sc	10.23 ± 8.31		10.4 ± 10.29		12.3 ± 15.12		14.99 ± 6.14		12.58 ± 7.63	
Sr	46.14 ± 12.85		46.3 ± 32.57		42.59 ± 16.29		50.64 ± 7.72		84.27 ± 32.27	
Th	25.97 ± 6.85		22.46 ± 6.68		20.78 ± 3.37		24.95 ± 5.85		14.19 ± 4.72	
Ti	3964.48 ± 10.23		3736.79 ± 11.27		4160.76 ± 11.62		7290.77 ± 5.79		3323.87 ± 28.53	
V	72.37 ± 11.52		81.03 ± 14.18		100.59 ± 19		173.94 ± 5.85		110.65 ± 18.98	
Y	33.93 ± 13.79		25.77 ± 13.74		24.22 ± 6.77		33.57 ± 9.06		11.06 ± 22.6	
Yb	3.69 ± 12.2		2.85 ± 9.82		2.71 ± 6.27		3.68 ± 7.61		1.86 ± 15.59	
Zn	77.4 ± 16.46		79.17 ± 30.83		70.28 ± 35.84		76.51 ± 17.03		34.92 ± 16.15	
Zr	130.05 ± 15.22		107.71 ± 13.75		108.39 ± 9.76		213.24 ± 19.87		52.08 ± 22.37	

Table 2. Summary statistics for the five elemental groups of stoneware jars identified through ICP analysis. Averages based on number of replicates (n=#) with % standard deviations (calculated by taking the standard deviation for the element and dividing it by the element mean X 100).

Figure 3. PCA scatterplot of the first two components for the optimised dataset showing structure of objects (above) and elements with polynomial regression and R^2 value (below).

Ten elements were discarded to produce the optimised dataset. These include elements at concentrations well below those of the standards or not represented in them and those that are likely to have poor measurement characteristics (Cd, Gd, Lu, Pb). However, they also include elements in concentrations for which measurement is either precise or both accurate and precise (Co, Mn, Na, S, Sr, Zn). Three of these elements can be discounted because of outlier behaviour (Co: a single sample in group 2 with significantly elevated levels, >250 ppm), S (significantly enhanced, >500 ppm) for several group 2, 3 and 5 samples and Zn (elevated levels, >150 ppm) in three group 1 and 2 samples). The remaining elements Mn, Sr and Na otherwise appear statistically normal (i.e. have good measurement statistics and are not subject to outlier distortion).

Elevated concentrations of these elements characterise group 5. Mn and Na, relatively abundant components of sea water, could be expected as precipitates from post-depositional sea water infiltration (Rodshkin and Ruth 1997). A more complex argument needs to be mounted for Sr, a trace element that normally tracks Ca. Structural similarities allow substitution of Sr into the Ca molecular lattice. This relationship is charge dependant and environmentally sensitive (Porder et al. 2005). The Ca/Sr ratio is substantially higher (Sr depleted) than in the remaining groups (average group 1–4 Ca/Sr ratio: $43.15 \pm 8.72\%$; group 5 Ca/Sr ratio: 73.03). As Sr-depleted-Ca in group 5 is consistent with a marine rather than terrestrial source, this distinction also suggests possible sea water infiltration. In other words group 5 samples may be more porous, less vitrified and therefore affected by post-depositional precipitates than the remaining groups.

Scanning electron microscopy (SEM)

Low and high magnification SEM and X-ray mapping of fresh carbon-coated fracture surfaces was used to assess the likely extent of post-depositional chemical alteration of a selection of fabrics from each group. All groups exhibit extensive vitrification, closed pore spaces and the development of gas bubbles (Figure 4a). Contrary to expectations from the elemental profiles, Group 5 samples appear to be more vitrified with larger coalescing bubbles than the remainder and have no evidence of post-depositional precipitates (Figure 4b). Group 5 samples also contained numerous fine and coarser Ca- and Na-rich mineral inclusions. These inclusions retained clear (unmelted) grain boundaries and were part of the original pre-fired fabric (Figure 4c and d). No samples from the other groups contained inclusions of comparable composition, size or preservation.

Figure 4. Representative jar types for each of the 5 compositional groups discussed in the text (all to scale).

Discussion

Returning to the three models we can now re-evaluate these results.

Model A (provenance postulate):

For model A, the independent attribute of jar form provides a check on whether the five compositional groups are likely to come from different centres (Figure 5). Groups 1 and 2 share a jar form that is indistinguishable in style and decorative detail (Figure 5, group 1, group 2). This close similarity suggests the same potters rather than emulation of a popular jar form by two centres. The significance of the compositional separation will be returned to below. Group 2 also includes several examples of a second smaller form representing a distinctive fabrication convention (two-piece shoulder joined type (Figure 5, group 2, sample 351). Together, group 1 and 2 account for the majority of the sample population suggesting that these jars were a predominant type available to Spanish ships leaving Manila in the early 17th century. Based on comparison with published data, group 1 and 2 forms have a likely origin in a southeastern Chinese production complex in Fujian or Guandong Province (Hogervost 1982; Southeast Asian Ceramic Society (West Malaysia Chapter) 1985; Harrison 1986; Long 1992; Valdes et al. 1992; Dupoizat 1996). The remaining groups represent about 5% each of the total sample. The possible spatial significance of this relatively low figure can be gauged from group 3. This group includes a range of types derived from production centres in more distant Thailand (Brown 1988; Brown and Sjostrand 2002), suggesting that the other small groups may also reflect more distant production centres (Figure 5, group 3). Group 4 samples (Figure 5, group 4) are of a distinctive type without sufficiently good parallels to nominate a source area but we can infer a single production region from the relatively homogenous form and the distinctiveness of the titanium-rich composition of this group. For group 5 (Figure 5, group 5) large elemental differences coupled with stylistic anomalies (less well-defined neck and rim; less symmetrical body indicating greater degree of hand finishing) suggest that this group, though broadly similar in form to the most common type shared by groups 1 and 2, is an emulation and does not originate in the same production complex.

Figure 5. The Boiling Point model: polynomial regression analyses and R^2 values for boiling point data (y axis) compared with order of elements (x axis) on the first component from the PCA of the optimised dataset. Note that the very high value for the 3rd regression reflects the low number of elements and is retained primarily for heuristic value. Contrast this with the high values for regressions 1 and 2, each with ~10 elements extending across the component and boiling point range.

Model B (technology):

The results from the PCA of the optimised dataset were used to determine if a generalised feature was captured in the order of elements along the first component (effectively detrending the PCA 'horseshoe' distribution inherent in the eigenvalues themselves). A strong correlation is evident between component-ordered elements and boiling point data (Aylward and Findlay 1983). Several iterations to improve the polynomial R^2 value result in not one but three regression solutions for the component 1 order of elements against their boiling points (Figure 6). Two of these correlate with elemental order from left to right and an overall decrease in boiling point. The third describes low boiling point elements in what is otherwise the high boiling point side of the plot. While only trace elements are represented at elevated boiling points, the third trend runs counter to this with low boiling point major, minor and trace elements in the otherwise high boiling point end of the first component. This generalised boiling point behaviour is consistent with progressive volatilisation of elements under increasingly high temperature firing regimes. In this scenario the enhancement of a limited suite of low temperature elements in the high temperature end of the component reflects development of an extensive K-Y-Ba-rich felspathic glass phase depleted in other low temperature elements (Kopeikin 1960; Yakovleva and Beznosikova 1960).

Figure 6. Scanning electron micrographs of representative group fabrics. Above, high magnification stoneware fabric typical of groups 1–4 (a); and fabric typical of group 5 (b). Both show evidence of extensive glass formation with gas bubbles but note the group 5 sample appears more evolved with larger areas of glass and coalesced gas bubbles. Below, low magnification X-ray maps of the same area of a group 5 fabric preserving (c) Ca- and (d) Ca/Na-rich minerals with clear grain boundaries.

Model C (environmental effects):

Post-depositional alteration does not appear to have had appreciable influence on the stoneware fabrics of the sample population. In contrast to relatively porous earthenwares with a greater potential to take up elements mobilised in ground water, the stonewares all exhibited extensive glassy phases (i.e. non-continuous pore structures) that appear impervious to penetration by ground water or salts. Even assuming some degree of alteration undetectable by SEM, the samples of this study, immersed in salt water for almost 400 years, shared the same conditions of temperature and salinity, and have been treated in the same manner for museum storage, such that post-depositional alteration should affect all samples equally.

Summary

For the 'Concepción' stoneware assemblage, the geographic provenance of compositional groups cannot be disengaged from systematic differences produced by firing temperature. The first component of the PCA analysis for the optimised dataset isolated a generalised temperature-related behaviour; polynomial regression analysis highlighted the explanatory efficiency of the boiling point model and underscored the potential pitfalls in optimisation techniques, such as proposed by Baxter and Jackson (2001), that arbitrarily remove ostensibly redundant elements. In this study the elemental end members of the optimised PCA that appeared to contain a high level of redundancy in fact represent a complex relationship between temperature and fabric composition.

Of the three ceramic elemental hypotheses (provenance, environment and technology) two can be accommodated within the dataset (Figure 7). While provenance (Model A) can be demonstrated to account for group distinctions, firing temperature differentials (Model B) represent the most parsimonious explanation of data structure.

Figure 7. PCA scatterplot of the first two components for the optimised dataset showing structure of objects with hypothetical schemas superimposed (labels follow Fig. 1).

If, as proposed, groups 1 and 2 come from the same production centre then they appear to reflect a complex production environment. The close typological similarity of both groups suggests they were produced by the same potters. However, if the distinction between them primarily relates to differences in firing technology then this suggests that the products of a single pottery workshop were sent to at least two kilns with different firing characteristics. This level of complex organisation has good historical antecedents for the operation of large pottery production centres in Southeastern China from at least as early as the 17th century (Sung 1966).

Group 3 consists of vessels that are of entirely different types and are typical of production centres in Thailand. This group, about the same distance on the first component from group 2 as group 2 is to group 1, also appears to reflect a lower firing temperature technology. Group 4, both compositionally and typologically distinct from the remaining groups, represents a class of jar from yet another, (?) more distant, production complex but that more closely matches the higher temperature range of group 1 and 2 and therefore is more closely related technologically (e.g. northern China, Vietnam).

Group 5, the most compositionally distant of the groups, broadly conforms to the most common jar type of groups 1 and 2 but diverges in typological details. Model C (post-depositional salt water enrichment), suspected to be responsible for this distance, was not sustainable. SEM data indicates levels

of vitrification comparable or even more developed than for the remaining groups. In group 5 the low-temperature end member is also richest in fluxing elements (Ca, Mn and Na) that would lower the eutectic point and promote melting at lower temperatures. The presence of Ca/Na rich minerals with distinct boundaries in the group 5 fabrics suggests that while extensive melting had occurred this was curtailed before a full glass phase could develop. The survival of minerals composed of low boiling point elements further supports group 5 as a low temperature end member best explained in Model B. Group 5 wares appear to be the product of a firing technology with significantly lower temperatures than represented, for example, in the distance between the Southern Chinese groups 1, 2 and Thai group 3 samples. As an adaptation of high temperature firing technology to clays with high flux, low melting-point characteristics more typical of earthenware compositions, group 5 appears to represent a stoneware firing technology where stoneware was adapted to a less than optimum clay type.

Conclusions

Temperature plays a role in elemental sequestration of stoneware ceramic datasets. This observation underlines the opportunities for a better quantitative understanding of the differences between both contemporary and successive stoneware firing technologies of a region. It also highlights the potential of this approach as an analytical proxy for complex technological organisation (e.g. the apparent decoupling of potters of a common jar type from multiple firing complexes with different temperature characteristics). These conclusions tend to contradict conventional modelling assumptions for archaeological ceramic elemental datasets with provenance/temperature effects perhaps more widespread than previously supposed. If so, these types of signatures may prove of broader utility in other archaeological settings for identifying systematic techno-cultural differences between production centres or regions.

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References

- Adriaens, D. and W. Verraes. 2002. An empirical approach to study the relation between ontogeny, size and age using geometric morphometrics. In P. Aerts, K. D'Août, A. Herrel and R. V. Damme (eds), *Topics in functional and ecological vertebrate morphology*. Maastricht: Shaker Publishing.
- Aylward, G. H. and T. J. V. Findlay. 1983. *SI chemical data*. Milton, Queensland: Wiley.
- Baxter, M. J. and C. M. Jackson. 2001. Variable selection in artefact compositional studies. *Archaeometry* 43(2):253–268.
- Bronson, B. 1990. Export porcelains in economic perspective: The Asian ceramic trade in the 17th century. In Ho Chuimei (ed.), *Ancient ceramic kiln technology in Asia*, pp 126–151. Hong Kong: Centre of Asian Studies.
- Brown, R. M. 1988. *The ceramics of Southeast Asia, their dating and identification*. 2nd ed. Singapore, Oxford University Press.
- Brown, R. and S. Sjostrand. 2002. *Maritime archaeology and shipwreck ceramics in Malaysia*. Kuala Lumpur: Department of Museums and Antiquities.
- Bruner, E. and G. Manzi. 2004. Variability in facial size and shape among North and East African human populations. *Italian Journal of Zoology* 71:51–56.
- Buxeda i Garrigos, J. 1999. Alteration and contamination of archaeological ceramics: The perturbation problem. *Journal of Archaeological Science* 26:295–313.
- Buxeda i Garrigos, J., V. Kilikoglou and P. M. Day. 2001. Chemical and mineralogical alteration of ceramics from a late Bronze Age kiln at Kommos, Crete: The effect on the formation of a reference group. *Archaeometry* 43(3):349–371.
- Chen, T., J. G. Rapp Jr, Z. Jing and N. He. 1999. Provenance studies of the earliest Chinese protoporcelain using instrumental neutron activation analysis. *Journal of Archaeological Science* 26:1003–1015.
- Cogswell, J. W., H. Neff and M. D. Glascock. 1996. The effect of firing temperature on the elemental characterization of pottery. *Journal of Archaeological Science* 23:283–287.
- Descantes, C., H. Neff and M. D. Glascock. 2002. Yapese prestige goods: The INAA evidence for an Asian dragon jar. In M. D. Glascock (ed.), *Geochemical evidence for long-distance exchange*, pp 229–256. Westport, Conn.: Greenwood Publishing Group.
- Dupoizat, M.-F. 1996. Asian stoneware jars. In J.-P. Desroches, F. G. Casal and F. Goddio (eds), *The treasures of the San Diego*, pp 222–251. New York: Elf Aquitaine International Foundation/National Museum of The Philippines.
- Fan, J. and I. Gijbels. 1996. *Local polynomial modelling and its applications*. London: Chapman and Hall/CRC.
- Ferring, C. R. and T. K. Perttula. 1987. Defining the provenance of red slipped pottery from Texas and Oklahoma by petrographic methods. *Journal of Archaeological Science* 14:437–456.
- Garnsey, W. and R. Alley. 1983. *China: Ancient kilns and modern ceramics: A guide to the potteries*. Canberra: Australian National University Press.
- Gomez, B., H. Neff, M. L. Rautman, M. D. Glascock and S. J. Vaughan. 2002. The source provenance of Bronze Age and Roman pottery from Cyprus. *Archaeometry* 44(1):23–36.
- Gosselain, O. P. 1992. Bonfire of the enquiries. Pottery firing temperatures in archaeology: What for? *Journal of Archaeological Science* 19:243–259.
- Grave, P. 2004. Elemental characterisation of Tepe Yahya Iron Age ceramics. The Archaeology of Resistance and Integration. In P. Magee (ed.), *Excavations at Tepe Yahya, Iran, 1967–1975, Volume IV: The Iron Age Settlement*, pp 62–80. American School of Prehistoric Research Bulletin 46. Cambridge, Mass.: Peabody Museum, Harvard University.
- Grave, P., M. Barbetti, M. Hotchkis and R. Bird. 2000. The stoneware kilns of Sisatchanalai and Early Modern Thailand. *Journal of Field Archeology* 27(2):169–182.
- Grave, P., L. Lisle and M. Maccheroni. 2005a. Multivariate comparison of ICP-OES and PIXE-PIGE analysis of East Asian storage jars. *Journal of Archaeological Science* 32(6):885–896.

- Grave, P., M. Maccheroni and L. Lisle. 2005b. The transition to the early modern economy in East and Southeast Asia, 1400-1750 AD: Production and exchange of storage jars. In Cheng Pei-kai (ed.), *Proceedings of the international conference: Chinese export ceramics and the maritime trade, 12th–15th centuries*, pp 163–186. Hong Kong: Chinese Civilisation Centre, City University of Hong Kong.
- Guo Yanyi and Li Guozhen 1986. Song Dynasty Ru and Yaozhou green glazed wares. In *Scientific and technological insights on ancient Chinese pottery and porcelain, Proceedings of the International Conference on ancient Chinese pottery and porcelain, Shanghai Institute of Ceramics*, pp 153–160. Beijing: Science Press.
- Harrison, B. 1986. *Pusaka: Heirloom jars of Borneo*. Singapore: Oxford University Press.
- Hayashiya, S. and G. Hasebe. 1966. *Chinese Ceramics*. Rutland, Vermont and Tokyo: Charles E. Tuttle.
- Hein, A., A. Tsolakidou and H. Mommsen. 2002. Mycenaean pottery from the Argolid and Achaia: A mineralogical approach where chemistry leaves unanswered questions. *Archaeometry* 44(2): 177–186.
- Hein, D. and M. Barbetti. 1988. Sisatchanalai and the development of glazed stoneware in Southeast Asia. *Siam Society Newsletter* 4(3):8–18.
- Hennessy, R. J. and J. P. Moss. 2001. Facial growth: Separating shape from size. *European Journal of Orthodontics* 23(3):275–285.
- Ho Chuimei (ed.), 1990. *Ancient ceramic kiln technology in Asia*. Hong Kong: Centre of Asian Studies, Hong Kong University.
- Hogervost, A. 1982. Stoneware storage jars (Martavans). In C. L. van der Pijl-Ketel and J. B. Kist (eds), *The ceramic load of the 'Witte Leeuw' 1613*, pp 220–245. Amsterdam: Rijksmuseum.
- Hughes-Stanton, P. and R. Kerr. 1980. *Kiln sites of ancient China: An exhibition lent by the People's Republic of China*. London: Oriental Ceramic Society.
- Hughes, M. J., K. J. Matthews and J. Portal. 1999. Provenance studies of Korean celadons of the Koryo Period by neutron activation analysis. *Archaeometry* 41(2):287–310.
- Impey, O. 1972. *A tentative classification of the Arita kilns*. In *International symposium on Japanese ceramics*. Seattle.
- Impey, O. 1996. The early porcelain kilns of Japan: Arita in the first half of the seventeenth century. Oxford: Clarendon Press.
- Impey, O. and M. Tregear. 1983. Provenance studies of Tanqui porcelain. *Trade Ceramic Studies* 3: 102–118.
- Jones, R. E. 1986. Techniques and methodology in characterisation and provenance work. In R. E. Jones, *Greek and Cypriot pottery: A review of scientific studies*, pp 15–56. Athens: The British School at Athens.
- Kerr, R. and N. Wood. 2004. *Chemistry and chemical technology*. Cambridge, Mass.: Cambridge University Press.
- Kilikoglou, V., Y. Maniatis and A. P. Griminas. 1988. The effect of purification and firing of clays on trace element provenance studies. *Archaeometry* 30(1):37–46.
- Kolb, C. 1982. Ceramic technology and problems and prospects of provenience in specific ceramics from Mexico and Afghanistan. In J. S. Olin and A. D. Franklin (eds), *Archaeological ceramics*, pp 193 – 208. Washington: Smithsonian Institution Press.
- Kopeikin, A. A. 1960. The effect of fluxing additions on the structure and properties of semiporcelain. *Glass and Ceramics (Historical Archive)* 15(10):531–536.
- Krzanowski, W. J. 1987. Selection of variables to preserve multivariate data structure, using principal components. *Applied Statistics* 36(1):22–33.
- Li Jiazhu. 1990. The evolution of Chinese pottery and porcelain technology. In W. D. Kingery (ed.), *Ceramics and civilisation: Ancient technology to modern science*, Volume 1, pp 135–62. Westerville, Ohio: The American Ceramic Society.

- Liu Zhenqun. 1986. Investigations of the kilns and firing processes of pottery and porcelain in Chinese past dynasties. In *Scientific and technological insights on ancient Chinese pottery and porcelain, Proceedings of the International Conference on ancient Chinese pottery and porcelain, Shanghai Institute of Ceramics*, pp 295–300. Beijing: Science Press.
- Long, K. N. 1992. Typology and classification of jars. In C. O. Valdes, K. N. Long and A. C. Barbosa (eds), *A thousand years of stoneware jars in the Philippines*, pp 168–199. Manila: Jar Collectors (Philippines).
- Maggetti, M., H. Westley and J. S. Ofin. 1984. Provenance and technical studies of Mexican majolica using elemental and phase analysis. In J. B. Lambert, *Archaeological chemistry III, advances in chemistry series* 205, pp 151–191. Washington DC: American Chemical Society.
- Mallory-Greenough, L. M., J. D. Greenough and J. V. Owen. 1998. New data for old pots: Trace-element characterization of ancient Egyptian pottery using ICP-MS. *Journal of Archaeological Science* 25:85–97.
- Mason, R. B. and E. J. Keall. 1988. Provenance of local ceramic industry and the characterization of imports: Petrography of pottery from medieval Yemen. *Antiquity* 62(236):452–463.
- Mathers, W. M., H. S. Parker III and K. A. Copus (eds), 1990. *Archaeological report: The recovery of the Manila galleon 'Nuestra Señora de la Concepción'*. Sutton, Vermont, USA: Pacific Sea Resources.
- Matson, F. R. 1971. A study of temperature used in firing ancient Mesopotamian pottery. In R. H. Brill (ed.), *Science and Archaeology*, pp 65–79. Cambridge, Mass.: The MIT Press.
- Matsunaga, M. and I. Nikai. 2004. A study of the firing technique of pottery from Kaman-Kaleoyuk, Turkey, by synchrotron radiation-induced fluorescence X-ray absorption near-edge structure (XANES) analysis. *Archaeometry* 46(1):103–114.
- Medley, M. 1976. *The Chinese potter: A practical history of Chinese ceramics*. Oxford: Phaidon.
- Middleton, A. P., M. R. Cowell and E. W. Black. 1992. Romano-British relief-patterned flue tiles: A study of provenance using petrography and neutron activation analysis. In *Sciences de la Terre et Ceramiques Archeologiques, Experimentations, Applications* 16, pp 49–59. Saint Louis a Cergy: Institut Geologique Albert de Lapparent.
- Mikami, T. 1972. *The art of Japanese ceramics*. New York: Weatherhill.
- Mommsen, H., T. Beier, U. Diehl and C. Podzuweit. 1992. Provenance determination of Mycenaean sherds found in Tell el Amarna by neutron activation analysis. *Journal of Archaeological Science* 19: 295–302.
- Neff, H. 1994. RQ-mode principal component analysis of ceramic compositional data. *Archaeometry* 36: 115–130.
- Neff, H. 2000. Neutron activation analysis for provenance determination in archaeology. In E. Ciliberto and G. Spoto (eds), *Modern analytical methods in art and archaeology, chemical analyses series* 155, pp 81–134. New York: John Wiley and Sons.
- Olin, J. S., G. Harbottle and E. V. Sayre. 1978. Elemental compositions of Spanish and Spanish-colonial majolica ceramics in the identification of provenience. In G. F. Carter (ed.), *Archaeological chemistry II, advances in chemistry series* 171, pp 200–229. Washington DC: American Chemical Society.
- Pollard, A. M. 1986. Multivariate methods of data analysis. In R. E. Jones, *Greek and Cypriot pottery: A review of scientific studies*, pp 56–83. Athens: The British School at Athens.
- Pollard, A. M. and E. T. Hall. 1986. Provenance studies of oriental porcelain by chemical analysis. In *Scientific and technological insights on ancient Chinese pottery and porcelain, Proceedings of the International Conference on ancient Chinese pottery and porcelain, Shanghai Institute of Ceramics*, pp 377–381. Beijing: Science Press.
- Pollard, A. M. and H. Hatcher. 1986. The chemical analysis of oriental ceramic body compositions: Part 2 — greenwares. *Journal of Archaeological Science* 13:261–287.
- Pollard, A. M. and H. Hatcher 1994. The chemical analysis of oriental ceramic body compositions: Part 1: Wares from North China. *Archaeometry* 36(1):41–62.

- Porder, S., A. Paytan and P. M. Vitousek. 2005. Erosion and landscape development affect plant nutrient status in the Hawaiian Islands. *Oecologia* 142:440–449.
- Rinaldi, M. 1990. The ceramic cargo of the 'Concepción'. In W. M. Mathers, H. S. Parker III and K. A. Copus (eds), *Archaeological report: The recovery of the Manila galleon 'Nuestra Señora de la Concepción'*, pp 398–528. Sutton, Vermont USA: Pacific Sea Resources.
- Rodshkin, I. and T. Ruth. 1997. Determination of trace metals in estuarine and sea-water reference materials by high resolution inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry* 12:1181–1185.
- Schwedt, A., H. Mommsen and N. Zacharias. 2004. Post-depositional elemental alterations in pottery: Neutron activation analyses of surface and core samples. *Archaeometry* 46(1):85–101.
- Shaw, J. C. 1985. The kilns of Lan Na or northern Thai ceramics. In *Technical workshop on ceramics (T-W4), Bangkok and Chiang Mai, Thailand, December 1–12, 1985*. Bangkok: Southeast Asian Ministers of Education Organisation, SEAMEO Project in Archaeology and Fine Arts.
- Southeast Asian Ceramic Society (West Malaysia Chapter) (ed). 1985. *A ceramics legacy of Asia's maritime trade: Song Dynasty Guangdong wares and other 11th to 19th century trade ceramics found on Tioman Island, Malaysia*. Singapore: Oxford University Press.
- Stenger, A. 1992. Sourcing and dating of Asian porcelains by elemental analysis. In P. Wegars (ed.), *Hidden heritage: Historical archaeology of the overseas Chinese*, pp 315–331. Amityville, New York: Baywood Publishing Co.
- Stevenson, J. and J. Guy. 1997. *Vietnamese ceramics: A separate tradition*. Chicago: Art Media Resources/Avery Press.
- Sung Ying-Hsing. 1966. *Chinese technology in the seventeenth century* (trans. E.-T. Zen Sun and S.-C. Sun). Mineola, New York: Dover Publications.
- Tangri, D. and R. Wright. 1993. Multivariate analysis of compositional data: Applied comparisons favour standard principal components analysis over Aitchison's loglinear contrast. *Archaeometry* 35(1): 103–15.
- Tufte, E. 1983. *The visual display of quantitative data*. Cheshire, Conn.: Graphics Press.
- Valdes, C. O., K. N. Long and A. C. Barbosa. 1992. *A thousand years of stoneware jars in the Philippines*. Manila: Jar Collectors (Philippines).
- Vallibhotama, S. 1974. The Khmer ceramic kilns of Ban Kruat and their preservation. *Our Future* 2:30–33.
- Vitali, V. and U. M. Franklin. 1986. New approaches to the characterization and classification of ceramics on the basis of their elemental composition. *Journal of Archaeological Science* 13:161–170.
- Wilson, L. and A. M. Pollard. 2001. The provenance hypothesis. In D. R. Brothwell and A. M. Pollard (eds), *Handbook of archaeological sciences*, pp 507–517. Chichester: John Wiley.
- Yakovleva, M. E. and A. V. Beznosikova. 1960. The microstructure of earthenware and semiporcelain fired at 1100–1300. *Glass and Ceramics (Historical Archive)* 15(9):483–490.
- Yang Wenxian and Wang Yuxi. 1986. A study of ancient Jun ware and modern copper red glaze from the chemical compositions. In *Scientific and technological insights on ancient Chinese pottery and porcelain, Proceedings of the International Conference on ancient Chinese pottery and porcelain, Shanghai Institute of Ceramics*, pp 204–210. Beijing: Science Press.
- Yap, C. T. and Y. Hua 1992. Principal component analysis of Chinese porcelains from the Five Dynasties to the Qing Dynasty. *Zeitschrift für Naturforschung* 49a:1029–1033.