

Emma K. Bartle,<sup>1</sup> B.Sc. and R. John Watling,<sup>1</sup> Ph.D.

## Provenance Determination of Oriental Porcelain Using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)\*

**ABSTRACT:** The sale of fraudulent oriental ceramics constitutes a large proportion of the illegal artifact and antique trade and threatens to undermine the legitimate international market. The sophistication and skill of forgers has reached a level where, using traditional appraisal by eye and hand, even the most experienced specialist is often unable to distinguish between a genuine and fraudulent piece. In addition, current provenancing techniques such as energy-dispersive X-ray fluorescence (EDXRF) spectrometry and thermoluminescence (TL) dating can result in significant damage to the artifact itself. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), a relatively nondestructive analytical technique, has been used for the provenance determination of materials based on geographical origin. The technique requires the production of a laser crater, *c.* 100  $\mu\text{m}$  in diameter, which is essentially invisible to the naked eye. Debris from this crater is analyzed using ICP-MS, with the results forming the basis of the provenance establishment protocol. Chinese, Japanese, and English porcelain shards have been analyzed using this protocol and generic isotopic distribution patterns have been produced that enable the provenance establishment of porcelain artifacts to their country of production. Minor variations between elemental fingerprints of artifacts produced in the same country also indicate that it may be possible to further provenance oriental ceramics to a specific production region or kiln site.

**KEYWORDS:** forensic science, forensic chemistry, laser ablation-inductively coupled plasma-mass spectrometry, provenance determination, elemental analysis, oriental ceramics, Ming porcelain, Imari porcelain, chemometrics

Pottery manufacture in China dates back to before 500 BCE, making this country one of the first to produce kiln-fired ceramics. China is also one of the first countries to produce porcelain, with the first plain-glazed porcelains being produced during the Tang dynasty (618–906). While these porcelains were relatively inferior in color and quality, significant refinement in the porcelain manufacturing process, optimization of clay mixtures, and development of firing techniques eventually produced porcelains of high-quality marble-like whiteness and a clear and brilliant finish (1,2).

By the start of the Ming dynasty (1368–1644), the manufacturing process had been optimized, and the porcelains from this period were regarded as the crowning achievements of Chinese ceramics. Porcelain is produced by firing a mixture of white china clay (kaolin) and china stone (petuntse) to temperatures over 1300°C. A pottery manufacturing center was developed in Jingdezhen, in the Jiangxi province, and the majority of porcelain production took place there. Jingdezhen, on the river Ch'ang, was geographically well placed for the development of the industry. It is surrounded by the mountains of Jiangxi and watered by two rivers. Kaolin and petuntse were readily available locally and the rivers facilitated the transport of raw materials to the kilns (3).

It was during the Ming dynasty that the use of blue underglaze painting on white porcelain was introduced. This blue decoration proved to be highly successful and popular, and demand both from within the imperial court and foreign trade increased immensely.

These blue and white porcelain wares became known as the finest product of the Chinese potter worldwide (2).

Toward the end of the Ming period, the quality of porcelain produced declined and the demand of the imperial court and foreign trade receded. Genuine pieces manufactured during the Ming period have become extremely valuable, with prices remaining high over the past centuries (3).

Porcelain production first began in Japan at the very end of the Momoyama period (1573–1615) in the Hizen province of Kyushu, the southernmost of the four main islands of Japan. Up until the mid-17th century, Japanese porcelain was produced for imperial and domestic use only. Porcelain produced in Arita first entered the world market in the mid-17th century, when civil wars in China led to a decline of the Ming dynasty (4). These events gave rise to a hiatus in the production of porcelain at Jingdezhen with the Chinese unable to satisfy world demand, and their monopoly of the porcelain trade was lost. It was at this time that porcelain production in the Hizen province had reached its peak in terms of quality, and the large industry within Arita was capable of satisfying the European, Indian, and South-East Asian market in quantity. The porcelain came to be known as "Imari porcelain," the name taken from the port from which the export porcelain was shipped (5).

Imari porcelain was produced using clay from the Izumiyama deposit, in Arita. The clay was in the form of porcelain stone, consisting mainly of sericite and quartz, which was the end product of weathering of a metamorphosed primary acid volcanic rock. The chemical composition of the raw clay in the Izumiyama deposit was similar to the clay mixture used during the Ming dynasty by the potters at Jingdezhen. For this reason, porcelain stone from Izumiyama was used unmixed (5).

The past decade has witnessed the prices being paid for Chinese Ming and Japanese Imari porcelain increase significantly, and forgers have proliferated in the hope of making huge, illicit

<sup>1</sup>Centre for Forensic Science, The University of Western Australia, Crawley, WA 6009.

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profits. Black-market trade in cultural material, such as oriental ceramics, is covert and hence the exact value of the market is unknown. However, it is estimated that the annual illegal trade of antiquities internationally *c.* \$2 billion (6). The illicit trafficking of cultural material, specifically ancient South-East Asian artifacts, is comparable with the illegal trading of drugs, firearms, and tobacco, with recent reports from across the globe revealing that gangs dealing in money laundering and drug smuggling are also trafficking fake and looted antiquities. Experts estimate that *c.* 20% of Chinese material entering the international art market is fraudulent (6,7).

The majority of fraudulent oriental ceramics are produced solely for the purposes of being sold as authentic and deceiving the consumer. These fakes have become so sophisticated that even experienced specialists can have trouble distinguishing a genuine object from a counterfeit. With this surge in both the quality and quantity of the forgeries, robust scientific methods for the authentication of ceramics need to be developed and put into use (8).

One of the most efficient and reliable methods of authenticating oriental ceramics is through provenance with respect to geographical origin. This involves the use of chemical characterization. Provenance studies rely on the hypothesis that different raw materials and/or batch compositions are used for ceramics produced at different kiln sites, or the same kiln site but different time periods of manufacture, giving the products individual chemical compositions. The literature on the trade routes within ancient China and Japan confirms this hypothesis as in those times the transport of raw materials was extremely difficult, forcing potters to make use of local materials (9).

Studies have been published on the authentication of oriental ceramics; however, a robust nondestructive *in situ* method is yet to be developed. Researchers at the City University of Hong Kong have developed a method using the thermoluminescence (TL) test (8). Today, this is the most common way of scientifically establishing the age of oriental ceramics. The method relies on measuring the excited states of atoms caused by natural radiation in the environment. Although commonly used, this method is destructive, requiring the removal of a core measuring 3 mm in diameter from the artifact. This results in a decrease of both the monetary and cultural value of the porcelain piece. Secondly, the TL test is only accurate within a 20% margin for porcelain (8). Additionally, forgers have now developed methods to overcome the TL test and are artificially aging their forgeries by using irradiation (10).

Leung and colleagues investigated the use of energy-dispersive X-ray fluorescence (EDXRF) spectrometry for provenance establishment and dating ancient Chinese porcelain (9,11). This method was successful in differentiating between ceramics produced at different kiln sites; however, the technology was unable to discriminate between ceramics from the same kiln site but fabricated at different times. An additional limitation is that the energy of the X-rays used make only limited depth penetration possible and consequently only the glaze can be analyzed.

Therefore, the provenance of oriental ceramics, using EDXRF, is based solely on the chemical composition of the glazes. This is a major problem as it has been established that potters used several kinds of glaze materials within the same dynasty in Jingdezhen. Consequently, the ceramic body, which is produced using local materials at the different kiln sites and that varies in composition over time, stands a significant potential to yield more robust information for identifying provenance than analysis of the glaze.

Inductively coupled plasma-mass spectrometry (ICP-MS) has been well documented as a powerful provenance determination tool, with the potential to uniquely classify samples of the same

type, but different origins. It allows analysis for a wide range of elements for maximum discrimination, with extremely sensitive detection limits. ICP-MS can be used with two methods of sample introduction: solution and solids by laser ablation. ICP-MS is used to generate isotope distribution patterns for all samples, also known as an elemental “fingerprint,” which is unique to the sample (12,13).

The use of conventional ICP-MS for the provenance determination of ancient Chinese porcelains has been investigated by Li et al. (14–16). This requires the sample to be in the form of an aqueous solution. Thirty-nine trace elements were determined and the technique proved successful in differentiating between ceramics from different geographical origins. However, conventional ICP-MS has many limitations. Dissolution itself can be time consuming and, depending on the nature of the analyte, certain elements can be lost by volatilization or through hydrolysis and precipitation. Potential contamination by reagents and incorporation of particulate airborne material can also cause additional problems (13). More significantly, solution ICP-MS is destructive to the sample, which is not ideal in the case of high-value antiquities.

For laser ablation (LA)-ICP-MS, a laser is coupled to an ICP-MS instrument and a solid sample is directly analyzed following the ablation of tiny craters (*c.* 100  $\mu\text{m}$  in diameter). This eliminates the need for removal of significant masses of sample from the ceramic artifact, making it a relatively nondestructive technique.

This paper details an investigation of the potential of LA-ICP-MS for provenance determination of Chinese and Japanese porcelain with respect to geographical origin. Isotope distribution patterns (fingerprints) for the fired clay have been established and used to classify the artifacts to their country of manufacture. Detailed statistical analyses of the data have confirmed the differences in trace element composition of porcelains from different geographical origins to be statistically significant.

## Materials and Methods

### Instrumentation

All measurements were carried out using a thermo electron plasma quad III ICP-MS. Sample introduction was by laser ablation to allow for direct sampling of the ceramic material. Ablation was achieved using a 266 nm Cetac LSX-200 laser ablation unit (Cetac, Omaha, NE). The ablation cell was coupled to the ICP torch, and argon was used as a carrier gas. The instrumental settings were optimized using a NIST 610 glass standard.

Materials were examined using bright-field microscopy (Zeiss Axioscope II microscope) with a  $\times 10$  objective. Images were obtained using a Zeiss Axiosan digital camera (The Netherlands).

### Samples and Standards

Japanese shard material was provided for the investigation by the Kyushu Ceramics Museum, Arita, Saga prefecture, Japan. The shards were from a selection of kilns that produced blue-and-white porcelain during the Imari period. Chinese shard material was loaned from The Percival David Foundation of Chinese Art in London. The shards were from ceramics known to have been produced in Jingdezhen in the 14–16th centuries. For comparison purposes, a range of English blue-and-white porcelain was also used in the investigation. A Spode Blue-and-White Italian Olive Dish was used as an in-house reference standard. In addition, six 20th-century English porcelain artifacts were donated for use from a private collection. The latter pieces were all manufactured at

TABLE 1—Details of porcelain shard samples.

Country of Production	Region of Country	Number of Kilns Sampled	Period (Century)	Number of Samples
China	Jingdezhen	1	14th–16th	18
Japan	Amakusa Islands	4	17th–18th	74
Japan	Arita	14	17th–19th	76
Japan	Imari	2	17th–18th	28
Japan	Seto	1	17th	26

Stoke-on-Trent, England. The production kilns, periods of manufacture, and number of samples of the Chinese and Japanese shard material are given in Table 1.

### Sample Preparation

Owing to the limited sizes of the Chinese and Japanese porcelain shards, the main reproducibility study was conducted using the in-house reference ceramic, a Spode Italian Olive Dish (2004/SP1). Once the elemental homogeneity of this had been established, a limited study was undertaken on the Chinese and Japanese shard material to also confirm their elemental homogeneity. The reproducibility of both the clay and the glazes was investigated.

The dish was placed in a plastic bag and broken using a hammer. The head of the hammer was covered in Glad Wrap™ to prevent contamination by the metal surface. Ten pieces of medium-sized debris were randomly selected for analysis. This study was undertaken to ensure that elemental homogeneity was both tested and confirmed by analyzing randomly chosen areas of the original ceramic. Using pliers, covered in Glad Wrap™, a small sample was broken randomly off each piece of selected debris. This meant that a reproducibility study could be undertaken for both a single small region of the ceramic and over the bulk of the artifact itself. A similar procedure was used to sample the Chinese and Japanese porcelain shards. Although this sampling protocol is suitable for shard material only, due to its destructive nature, the literature indicates research into the future development of an *in situ* sampling device that could be used to sample a whole porcelain artifact (17).

The samples were embedded in resin that was prepared using a ratio of 50:1 mL of Casting Resin (Kirkside Products, Osborne Park, WA) to catalyst (methyl ethyl ketone peroxide 37%, Kirkside Products). The samples were placed into the center of the copper molds, arranged on a glass plate, and the resin mixture was poured into the molds. The mixture was left to set overnight. After this, the solid resin stubs were removed from the molds and polished to a flat surface using a rotating lap. The analytical surfaces of the stubs were first polished using a rough silicon carbide paper (500 mesh, 20 μm), and subsequently a smooth surface was produced using high-grade silicon carbide paper (800 mesh, 12.5 μm). Following this procedure, each stub was placed in an individual beaker, initially filled with 18 meg Ω water, and ultrasonicated for 15 min, to remove any adhering particulate material.

### Sample Analysis

Multielement analysis was undertaken using LA-ICP-MS. Samples were ablated for 60 sec at 10 Hz, with a laser energy of 55%, a fluence of 32 J/cm<sup>2</sup>, and 100 μm spot size. A scanning pattern was used, with a scan rate of 30 μm/sec. Data were collected using the scan mode. The ICP-MS was optimized, using the NIST 610 glass

TABLE 2—Isotopes determined using LA-ICP-MS to facilitate interisotope correction and interference correction.

<sup>9</sup> Be	<sup>55</sup> Mn	<sup>73</sup> Ge	<sup>98</sup> Mo	<sup>114</sup> Cd	<sup>140</sup> Ce	<sup>162</sup> Dy	<sup>182</sup> W	<sup>202</sup> Hg
<sup>42</sup> Ca	<sup>59</sup> Co	<sup>75</sup> As	<sup>101</sup> Ru	<sup>115</sup> In	<sup>141</sup> Pr	<sup>163</sup> Ho	<sup>184</sup> W	<sup>203</sup> Tl
<sup>44</sup> Ca	<sup>60</sup> Ni	<sup>82</sup> Se	<sup>102</sup> Ru	<sup>118</sup> Sn	<sup>146</sup> Nd	<sup>166</sup> Er	<sup>185</sup> Re	<sup>204</sup> Pb
<sup>45</sup> Sc	<sup>63</sup> Cu	<sup>85</sup> Rb	<sup>103</sup> Rh	<sup>120</sup> Sn	<sup>147</sup> Sm	<sup>169</sup> Tm	<sup>190</sup> Os	<sup>205</sup> Tl
<sup>46</sup> Ca	<sup>64</sup> Zn	<sup>88</sup> Sr	<sup>105</sup> Pd	<sup>121</sup> Sb	<sup>151</sup> Eu	<sup>172</sup> Yb	<sup>191</sup> Ir	<sup>206</sup> Pb
<sup>48</sup> Ti	<sup>65</sup> Cu	<sup>89</sup> Y	<sup>106</sup> Pd	<sup>125</sup> Te	<sup>152</sup> Sm	<sup>174</sup> Yb	<sup>192</sup> Os	<sup>207</sup> Pb
<sup>49</sup> Ti	<sup>66</sup> Zn	<sup>90</sup> Zr	<sup>107</sup> Ag	<sup>126</sup> Te	<sup>153</sup> Eu	<sup>175</sup> Lu	<sup>193</sup> Ir	<sup>208</sup> Pb
<sup>51</sup> V	<sup>69</sup> Ga	<sup>91</sup> Zr	<sup>108</sup> Pd	<sup>137</sup> Ba	<sup>157</sup> Gd	<sup>177</sup> Hf	<sup>195</sup> Pt	<sup>209</sup> Bi
<sup>52</sup> Cr	<sup>70</sup> Ge	<sup>93</sup> Nb	<sup>109</sup> Ag	<sup>138</sup> Ba	<sup>158</sup> Gd	<sup>178</sup> Hf	<sup>197</sup> Au	<sup>232</sup> Th
<sup>53</sup> Cr	<sup>71</sup> Ga	<sup>95</sup> Mo	<sup>111</sup> Cd	<sup>139</sup> La	<sup>159</sup> Tb	<sup>181</sup> Ta	<sup>200</sup> Hg	<sup>238</sup> U

LA-ICP-MS, laser ablation-inductively coupled plasma-mass spectrometry.

standard, before use. The NIST 610 glass standard was used for both instrument optimization and also analyzed routinely during the analytical protocol to allow for corrections, caused by instrumental drift, to be undertaken. The samples were analyzed in replicates of 10, with a gas blank being measured before each sample analysis. The isotopes determined in this study to facilitate interisotope correction and interference correction are detailed in Table 2. The final isotopes used in the study for provenance establishment are listed in Table 3. While the choice of isotopes does not obviate all potential isobaric overlap interference, it ensures that optimum sensitivity and percentage interference in these instances is trivial and easily corrected for using a conventional iterative approach. Consequently, the study isotope choice is considered appropriate as interference is either statistically insignificant or can easily and accurately be corrected for.

## Results and Discussion

### Reproducibility

*Reproducibility of the Isotope Distribution Signature of the Clay*—The interelement association patterns (spectral fingerprints) for replicates of the five sampled pieces of 2004/SP1 are given in Fig. 1.

The results indicate that the isotope distribution profiles of the clay in a porcelain artifact can be expected to be extremely reproducible, making it an ideal medium for provenance determination studies by LA-ICP-MS. The porcelain tested in this reproducibility study is a modern piece, and hence the manufacturing and refining processes will be very closely controlled. Because raw clay is mined as a natural material, it will contain mineral inclusions and impurities that would affect the quality and color of the final fired ceramic. During the refining processes, these are removed, leaving only the pure, fine white clay mineral fraction. Using this fraction will not only improve the homogeneity and physical integrity of the final fired ceramic but will ensure that a pure white product is produced.

TABLE 3—Isotopes selected for use in the study for provenance establishment of oriental ceramics using LA-ICP-MS.

<sup>9</sup> Be	<sup>53</sup> Cr	<sup>66</sup> Zn	<sup>88</sup> Sr	<sup>120</sup> Sn	<sup>141</sup> Pr	<sup>159</sup> Tb	<sup>172</sup> Yb	<sup>205</sup> Tl
<sup>44</sup> Ca	<sup>55</sup> Mn	<sup>69</sup> Ga	<sup>89</sup> Y	<sup>121</sup> Sb	<sup>146</sup> Nd	<sup>162</sup> Dy	<sup>175</sup> Lu	<sup>208</sup> Pb
<sup>45</sup> Sc	<sup>59</sup> Co	<sup>73</sup> Ge	<sup>90</sup> Zr	<sup>138</sup> Ba	<sup>152</sup> Sm	<sup>165</sup> Ho	<sup>178</sup> Hf	<sup>209</sup> Bi
<sup>49</sup> Ti	<sup>60</sup> Ni	<sup>75</sup> As	<sup>93</sup> Nb	<sup>139</sup> La	<sup>153</sup> Eu	<sup>166</sup> Er	<sup>181</sup> Ta	<sup>232</sup> Th
<sup>51</sup> V	<sup>68</sup> Cu	<sup>85</sup> Rb	<sup>98</sup> Mo	<sup>140</sup> Ce	<sup>158</sup> Gd	<sup>169</sup> Tm	<sup>184</sup> W	<sup>238</sup> U

LA-ICP-MS, laser ablation-inductively coupled plasma-mass spectrometry.

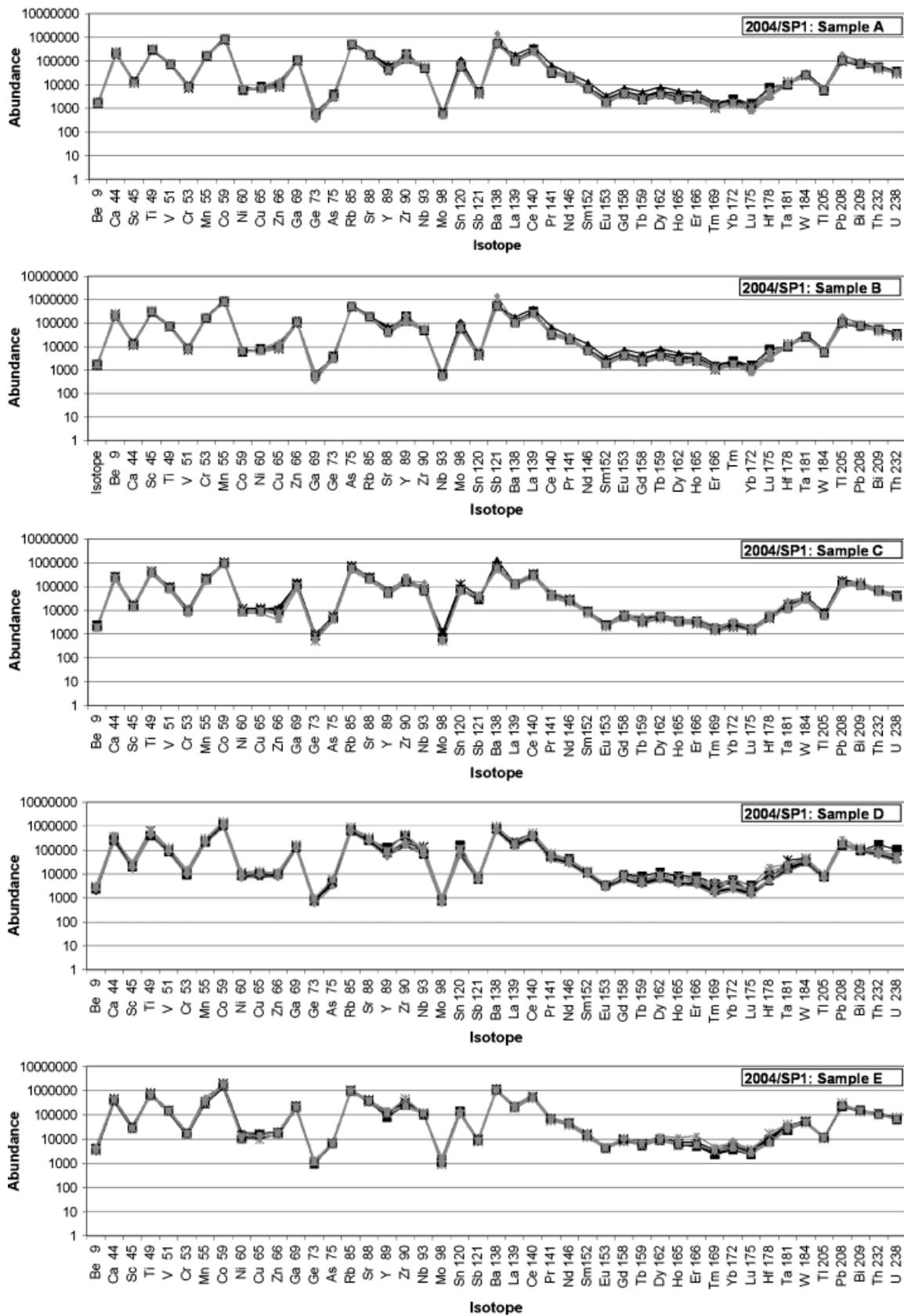


FIG. 1—Isotope distribution fingerprints of the Spode Olive Dish detailing 10 replicates of samples A–E.

Manufacturing processes used by the ancient Chinese and Japanese cultures were all manual and hence the ancient porcelains may not be as homogenous as the modern artifacts. Although the

refining process used nowadays is essentially identical in principle, the efficiency and reproducibility of the ancient one may not be as good as the steps were all undertaken manually. For this

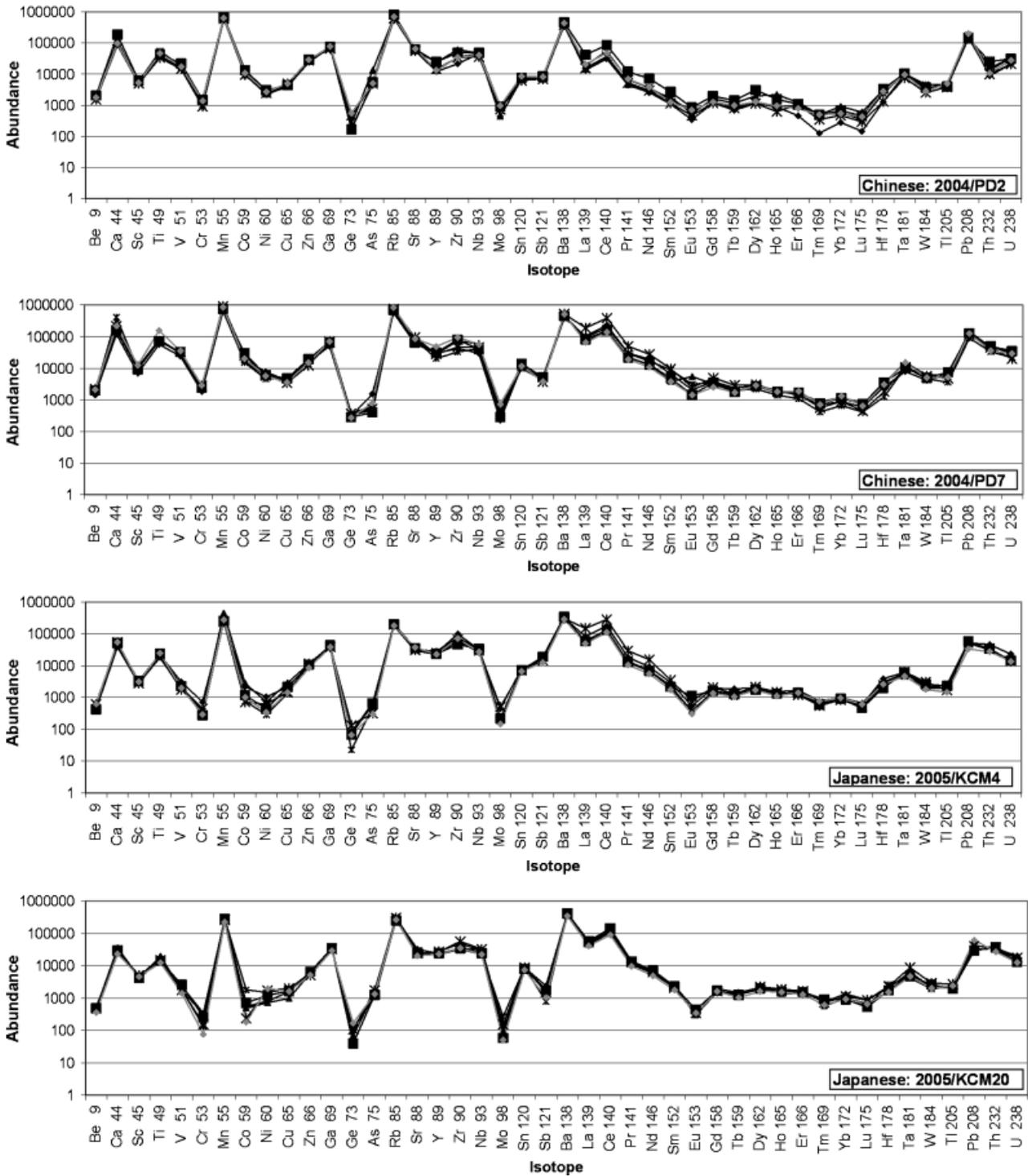


FIG. 2—Isotope distribution fingerprints for replicates of the clay bodies of two Chinese shards (2004/PD2 and 2004/PD7) and two Japanese shards (2005/KCM4 and 2005/KCM20).

reason, an additional reproducibility study was undertaken using a selection of Chinese and Japanese shard material. Spectral fingerprints for a selection of these shards are detailed in Fig. 2. The four samples were chosen to illustrate as close a match as possible between material from the two countries, and while similarities are apparent it is still easily possible to distinguish generic differences between Chinese and Japanese material to establish the country of origin.

The manual refining process used was based on gravitational separation, whereby the porcelain rocks were crushed to a fine powder, which was placed in large tanks of water. Mineral inclusions, which had not been powdered as finely as the clay, and other unwanted heavy and coarse material sank to the bottom of the tank and the finer particles remained in suspension in the water. This fine suspension was then separated, allowed to settle over time, and the precipitated fine clay was used in the produc-

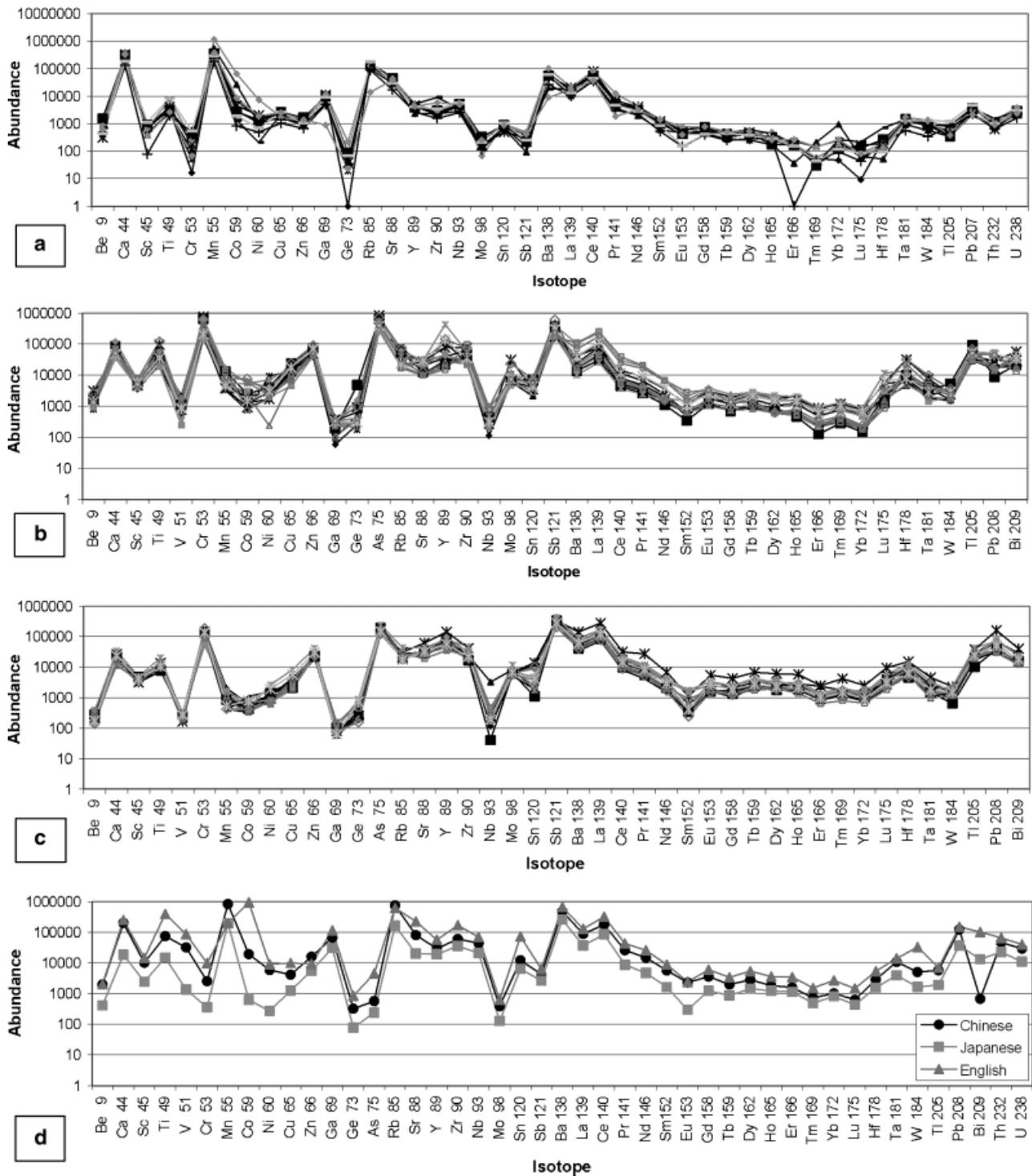


FIG. 3—(a) Isotope distribution fingerprints for the clear glaze of a 15th-century Chinese porcelain shard; (b) isotope distribution fingerprints of the clay bodies of 14 Chinese porcelain shards, produced in Jingdezhen, between the 14th and 16th centuries; (c) isotope distribution fingerprints of the clay bodies of 13 Japanese porcelain shards, produced in Arita, between the 17th and 19th centuries; (d) generic isotope distribution fingerprints for the clay bodies of Chinese, Japanese, and English porcelain.

tion of porcelain. The resulting homogeneity of the clay is reflected in the results from the reproducibility study undertaken as part of this investigation.

The isotope distribution patterns for the Chinese and Japanese porcelain indicate that, even though the manufacturing process was not as controlled as similar modern processes, the clay used in these ceramics is still homogenous, with only minor variations in

isotope ratio profiles. The high reproducibility of the porcelain isotope signatures, both modern and ancient, enhances the possibility for LA-ICP-MS to provide a new technique for use in the provenance determination of oriental ceramics.

*Reproducibility of the Isotope Distribution Signature of the Glaze*—The isotope signatures of ten replicates of the clear glaze of a Chinese porcelain shard are shown in Fig. 3a.

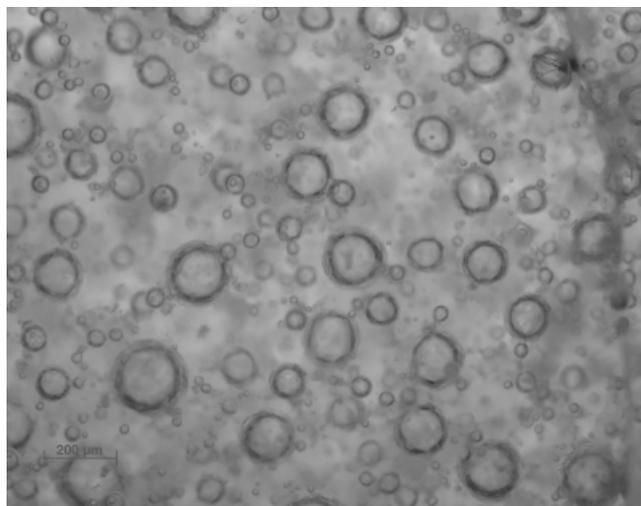


FIG. 4—Bright-field image of the glaze surface taken at  $\times 10$  magnification, detailing the abundance and layering of gas bubbles in the glaze.

Although a generic isotope signature is easily apparent, the reproducibility of the interelement association patterns in the glaze is not as good as for the porcelain body. This relative lack of reproducibility is a reflection of inhomogeneity in the glaze composition and thickness and the application methods used. Guan glaze was used to underglaze blue-and-white Chinese porcelains, and is characterized by a heavy crackle. The crackling of the glaze was a deliberate effect used by the potters, caused by underfiring of the glaze that produced thousands of gas bubbles during the firing process, which are then unable to escape through the viscous glaze, as the ingredients do not melt completely. The result is a clear glaze with air pockets (Fig 4). This image was taken using a bright-field microscope and demonstrates not only the number of gas bubbles trapped within a small area of glaze but also the layering of the air pockets.

The position of the gas bubbles in the glaze is nonsystematic; consequently, when the laser ablates the glaze, it actually ablates a mixture of glaze material and air pockets. The randomness of the gas bubbles means that a different percentage mixture of glaze and gas will be ablated each time, giving rise to a different mixture of ions passing into the mass spectrometer. In addition, as a result of underfiring the glaze, the glaze ingredients do not melt and mix completely. Thus, inclusions of nonmelted glaze ingredients will also cause differences in the elemental fingerprint, leading to a nonuniform medium.

#### *Provenance Determination of Porcelain Shard Material*

*Comparison of Shard Material from the Same Origin*—The high reproducibility of isotope distribution patterns for the main clay body of ceramic shards means that, using LA-ICP-MS, there is a significant probability of being able to establish robust provenance identification protocols for porcelain shards. Ming porcelain was produced at Jingdezhen using clay-mined locally, and because this was not completely suitable to produce porcelain directly it was mixed with locally mined petuntse and feldspar. Consequently, the trace elemental composition of this starting material would be expected to be similar over the entire period of Ming porcelain production. However, as a result of individual potters and factories mixing their clays, there will be differences in the relative amounts of the three main ingredients, which will result in small differences in the elemental composition of the

porcelain bodies over time and facilitate provenance identification. This observation is exemplified in Fig. 3*b* where, although the isotope distribution pattern for the rare-earth elements is similar for all shard material, indicating geographical and geological coprovenance, variations in the isotope distribution patterns of the more common elements are apparent indicating different periods or sites of manufacture.

Similar manufacturing relationships also exist for Japanese porcelain shards. The isotope distribution patterns for 13 Japanese shards are detailed in Fig. 3*c*. These shards are all from pieces of Imari porcelain, produced in Arita. It is well documented in the literature that the porcelain produced in Arita at this time used clay mined from the local Izumiyama Quarry (18). Owing to the high quality and unique composition of the porcelain stone from this deposit, it was used unmixed. Because of this aspect, it would be logical to assume that the trace element composition of the porcelain produced in the area would remain unchanged with time. Fortunately, however, weathering and slight compositional variations in the clay in different areas of the quarry resulted in minor, but identifiable, differences in trace element composition of the artifacts produced during the lifetime of the quarry.

*Comparison of Shard Material from Different Countries*—The high reproducibility of the isotope distribution profiles of the clay bodies of the porcelain shards, and the consistency of elemental profiles between shard pieces from different ceramics produced in the same country, suggests that isotope distribution patterns could be used to indicate generic differences between porcelains from different countries. This consistency of elemental fingerprint pattern could ultimately be used as a general classification mechanism to relate unprovenanced oriental ceramics to their country of origin.

Generic elemental fingerprints for Chinese, Japanese, and English porcelain are detailed in Fig. 3*d*. A visual comparison of these three patterns confirms that easily recognized differences do exist in the interelement relationships of porcelains from these countries.

Principal components analysis (PCA) is a statistical technique used to identify populations within a data set. Elemental data are taken to produce orthogonal vectors that can be plotted on two-dimensional plots, showing the relative difference between samples across the two axes (vectors). PCA can be used to try and prove the hypothesis that the samples are not from the same source, for example the porcelains were produced in different countries. For this reason, it is important that the elements used in the PCA will offer the maximum discrimination between samples. If discriminatory elements are used and the populations still cluster together, it can be concluded that they were originally part of the same population and the samples are therefore coprovenanced.

A plot of the first two vectors in the PCA analysis is detailed in Fig. 5. The total variability within the samples is described in the two vectors. Ten samples of each porcelain source were used for the PCA. The PCA incorporates all analyte isotopes. The plot confirms that the data can be separated into three isolated populations, corresponding to the Japanese, Chinese, and English porcelains, and that the porcelain can be identified with its country of production. Further PCA analysis can be undertaken, using porcelain samples from a single country, to further differentiate between different regions of production and kiln sites.

## **Conclusions**

The excellent reproducibility of the spectral fingerprints and consistency of isotope distribution profiles of clay bodies of porcelain from the same country confirms that LA-ICP-MS can be

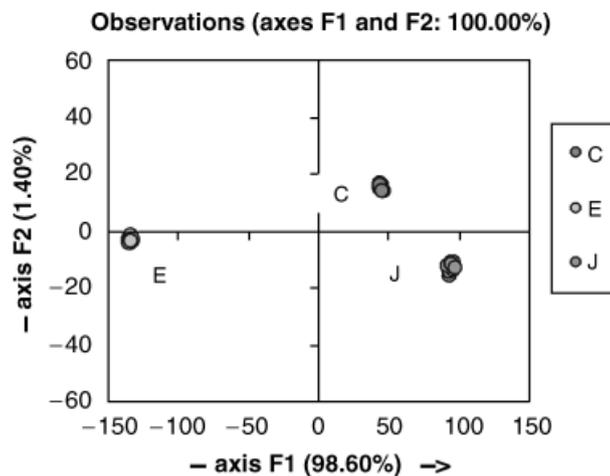


FIG. 5—Principal component analysis plot confirming the separation of the porcelain shard samples into three isolated populations: Chinese (C), English (E), and Japanese (J).

used to identify and classify unprovenanced oriental porcelains to their country of production. The high sensitivity, low detection limits, and relatively nondestructive nature of this analytical technique are also advantageous given the high monetary value of Chinese Ming and Japanese Imari porcelains. Minor variations in the spectral fingerprints of porcelains from the same country can be attributed to variations in production methods both over time and between individual potters, indicating a potential to further provenance oriental porcelains to specific production kilns using isotope distribution profiles.

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Additional information and reprint requests:

Emma K. Bartle, B.Sc.  
Centre for Forensic Science  
M420, The University of Western Australia  
35 Stirling Highway  
Crawley, 6009 WA  
E-mail: [ebartle@optusnet.com.au](mailto:ebartle@optusnet.com.au)