CENTRE FOR FORENSIC SCIENCE

THE UNIVERSITY OF WESTERN AUSTRALIA

Provenance Determination and Authentication of Oriental Porcelain using LA-ICP-MS

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Types of oriental porcelain studied

Chinese Ming Porcelain

•It wasn't until the Ming Dynasty (1368-1644) that potters perfected the art of making porcelain.

• Porcelain is made by firing a mixture of kaolin to temperatures above 1300°C.

•The pieces they produced were translucent. They also began experimenting with underglaze blue decoration.

• All porcelain was produced in the town of Jingdezhen.

• Porcelain was produced for both imperial use and for export.

Porcelain bowl with armorial-style decoration, from Jingdezhen, Jiangxi Province, China. Ming Dynasty, AD 1600-20 (Photo: British Museum)

Porcelain plate with design of tiger, from Arita, Japan. Edo Period, AD 1650-1670s (Photo:British Museum)

Japanese Imari Porcelain

• Porcelain production first began in Japan at the very end of the Momoyama Period (1573-1615).

• It was produced in the region of Arita, Kyushu.

• Potters employed the same method as the Chinese, with the use of blue decoration painted onto a white body and clear glaze applied over the top.

• The porcelain came to be known as Imari porcelain, as it was exported from the port of Imari.

Fake or the real thing?

• Nowadays, pieces of authentic Chinese Ming and Japanese Imari porcelain are very valuable and fetch high prices at auctions worldwide.

This Chinese blue and white 'Dragon and Phoenix' moonflask measures only 45.2cm tall. It was sold by auction at Sotheby's, Hong Kong, in 2005 for a hammer price with buyer's premium of US$4.42 million

• As a consequence, over the past decade there has been an increase in the production of imitation Oriental porcelain. Many of these artefacts are being sold undetected amongst authentic pieces for hundreds of thousands of dollars.

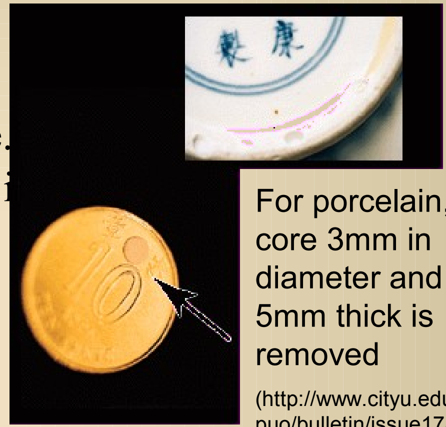
• With this black market trade of imitation relics growing and becoming more competitive, the sophistication and skill of forgers has reached a level whereby even the most experienced specialist is unable to distinguish between a genuine and fraudulent artefact using the old-fashioned appraisal by eye and hand.

• The most famous forgery was a porcelain vase produced by Master Mao. Master Mao artificially aged a modern-day fake using a number of techniques and took it to be examined by a panel of experts at The Palace Museum, Beijing, which holds the world's greatest collection of Chinese Ming porcelain. The panel agreed that it was an authentic Ming vase, and offered him a small payment to put it in the museum collection. Master Mao explained that it was actually a fake, however the imitation was of such high quality that they didn't believe him and instead accused him of saying that so that he could take it to sell on the Black Market for a higher price than they were offering him. To this day the fake remains in the museum's collection.

Current Scientific Methods of Authentication…and why they are no longer good enough

- **Thermoluminescence (TL) Testing –**

  This technique is used to try and authenticate porcelain by estimating it’s age. does this by measuring the excited state of atoms caused by natural radiation i the environment. It is based on the premise that the older the porcelain is, the less likely it is to be a fake.



For porcelain, a core 3mm in diameter and 5mm thick is removed

(http://www.cityu.edu.hk/puo/bulletin/issue17/e1704.html)

Problems with this method –

- **It is destructive!** It requires you to drill a 3mm core sample from the artefact. This not only decreases it’s monetary value, but also causes visible damage!
- Forgers are now artificially aging their porcelain using x-rays

2. Energy Dispersive X-Ray Fluorescence (EDXRF) –

This technique is used to try and authenticate porcelain by measuring the elemental composition of the major elements present. This is then compared to the elemental composition of authentic pieces. It is based on the premise that if the elemental composition is the same then it is authentic.

Problems with this method –

- X-rays can only penetrate the glaze layer and so the authentication is based on the composition of the glaze alone. According to the literature, potters used different glaze mixtures during the Ming Dynasty and hence it is hard to authenticate by analysing only this.

Reasons for provenancing oriental porcelain

• In Japan, Imperial law dictated where porcelain stone was to be mined. For example, all Imari porcelain was made using clay mined from the Izumiyama Quarry. Porcelain produced in different eras was sourced from different quarry sites. Trade of this clay between pottery manufacturers and countries was forbidden.

(a) Izumiyama Quarry, Arita-shi, Japan. This quarry was where porcelain stone was mined from for the manufacture of Imari porcelain. Because only one clay source was used it is expected that all Imari porcelain should show similar elemental compositions.
(b) An excavated chamber from the Nabeshima-Hanyou kiln (18-19C). Samples from this kiln site have been analysed as part of the study.

(c) Takahamayaki Jhugoyama dragon kiln. This kiln, now overgrown but completely preserved, was in use until mid 18th Century. Dragon kilns consisted of a row of chambers built on an incline. A fire was lit in the bottom chamber and heat traveled upwards through the different chambers, resulting in different firing temperatures within each chamber.

(d) The view from the entrance looking into the chamber. Ceramic pieces would be stacked into each of the chambers.

• In China, porcelain was produced in the town of Jingdezhen, which was surrounded by the mountains of Jiangxi and watered by two rivers. Transport was not readily available during those days, and hence potters had to make use of locally mined materials. Hence, all Ming Dynasty porcelain produced in Jingdezhen was made using this local clay.

Research aims and objectives

To develop a method, using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) for the provenance determination & authentication of oriental ceramics by:

- Establishing that differences in trace element composition will exist between ceramics of different geographical and periodical origins, and that these differences are reproducible, allowing the determination of the artefact's country of production.

- Investigate the differences in trace element composition of raw clay and glaze materials used at different kiln sites in China and Japan, and see if characteristic patterns can be established that would allow for pieces to be provenanced to a particular kiln site.

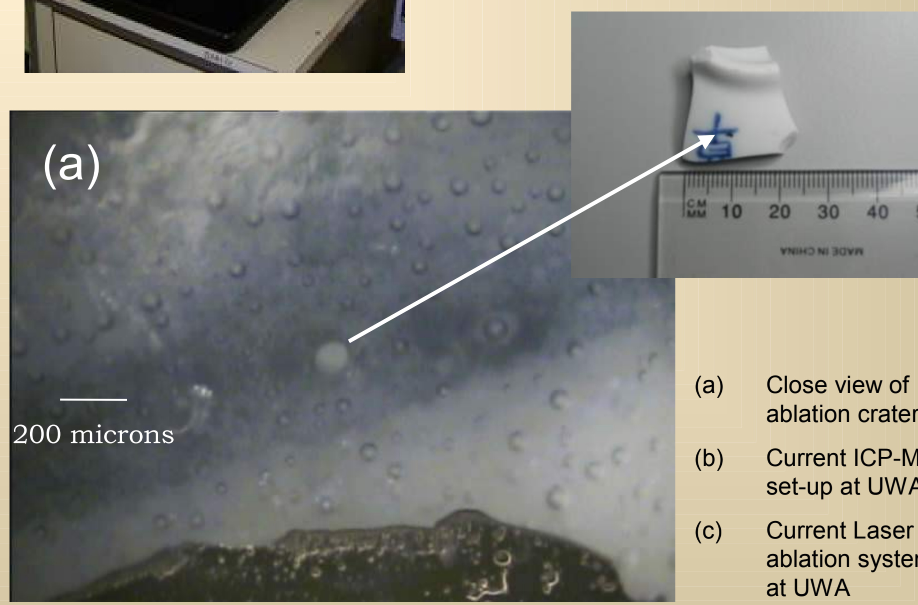
- Establish if a relationship exists between the trace element composition between the raw clay/glaze materials and the final fired ceramic. This would be useful in cases where reference shard samples from a particular kiln site are unavailable for analysis but samples of the raw material, which can be taken from the quarries, can be used instead.

- Compile the results from analysis of the trace element composition of clay/glaze/pigment of reference porcelain shards (loaned from a number of international museums) into a database, which porcelain pieces of unknown or questioned origin can be compared to.

Laser Ablation ICP-MS

- The porcelain sample is placed inside the sample cell, and a laser beam is fired onto the surface. This laser beam causes a crater to form, and the debris from this crater is transported into a plasma by a vacuum system. The high temperature of the plasma (7000°K) causes the porcelain debris to completely break-up and ionise. These ions are transported into the mass spectrometer (MS). The MS contains a detector which is used to measure which ions are present and their abundances, and generates a computer output with this information. This information is graphed and referred to as the elemental "fingerprint" for that particular porcelain sample.

- The main advantage of this technique over the other current scientific methods of authentication is the crater formed is only 100µm, making it invisible to the naked eye!

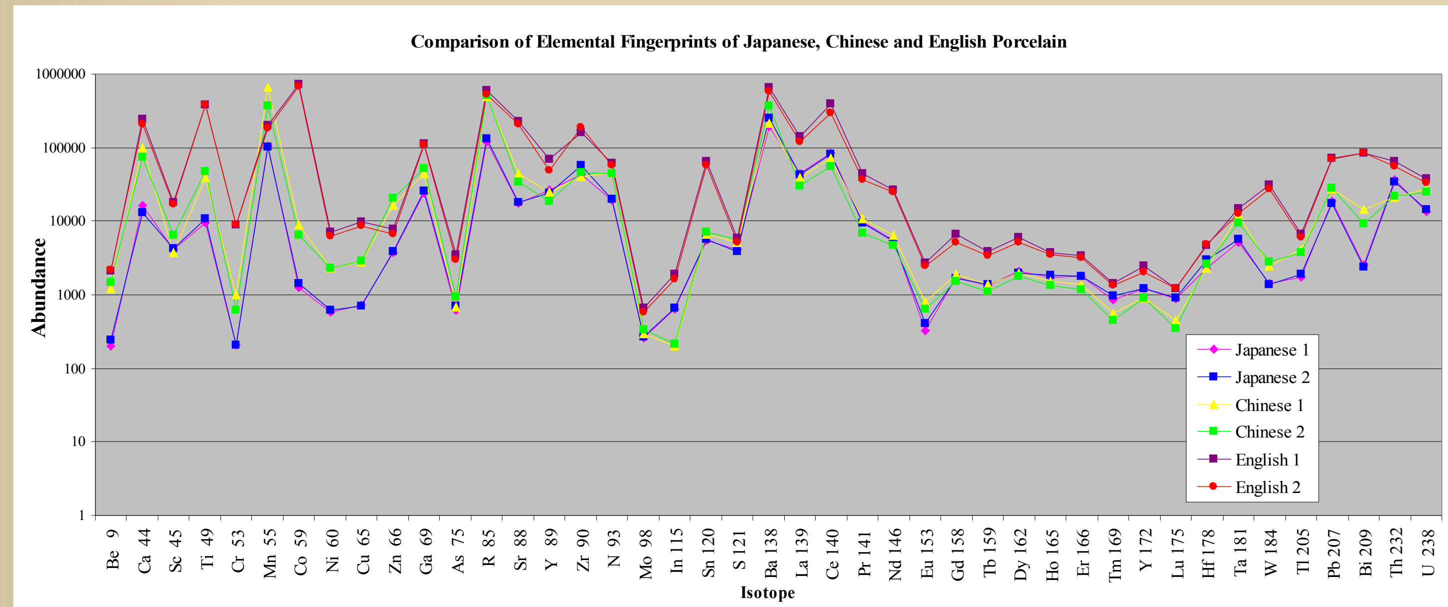


(a) Close view of ablation crater

(b) Current ICP-MS set-up at UWA

(c) Current Laser ablation system at UWA

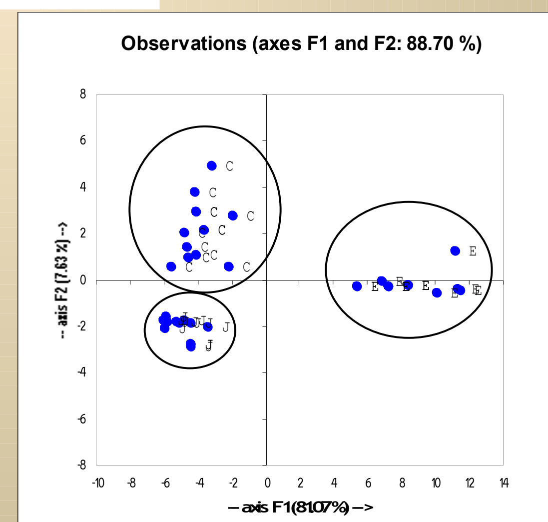
Preliminary results 1: Establishing the country of origin of the raw clay materials



(a) Elemental fingerprints of two samples each of Chinese, Japanese and English Porcelain.

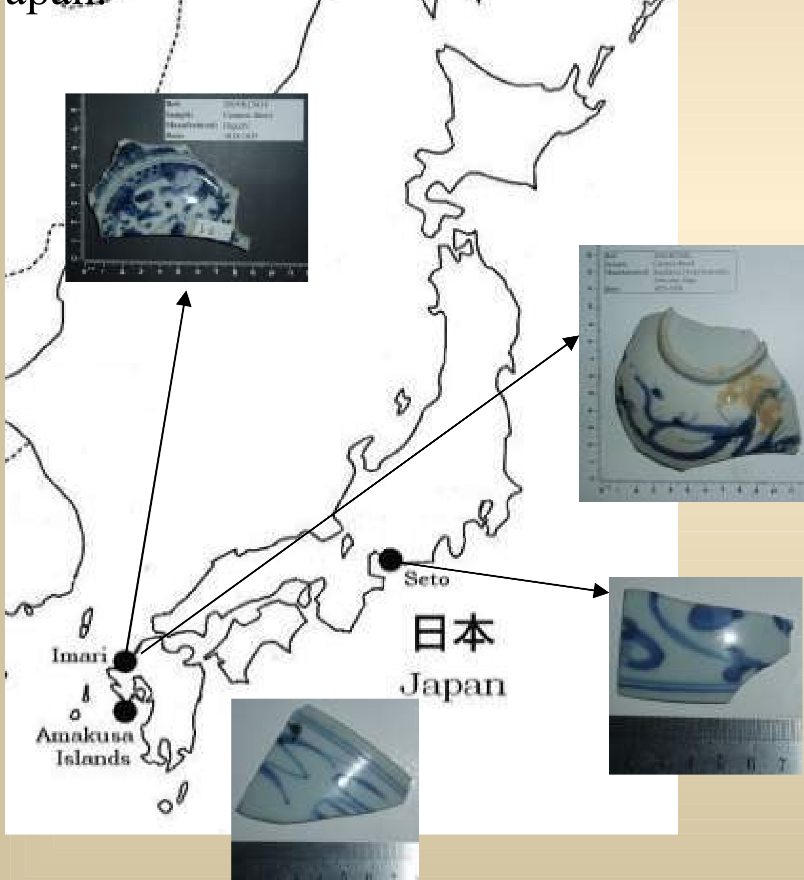
(b) Principal Component Analysis showing the clear separation of porcelain shards into their country of origin, where C = China, J = Japan and E = England

- Samples of clay from Chinese, Japanese and English porcelain artifacts were analysed using LA-ICP-MS
- Differences in the elemental profiles of porcelain produced in different countries are evident
- Chemometrical anaysis demonstrates these differences are statistically significant, and confirms the porcelain samples can be separated into three distinct groups based on country of origin

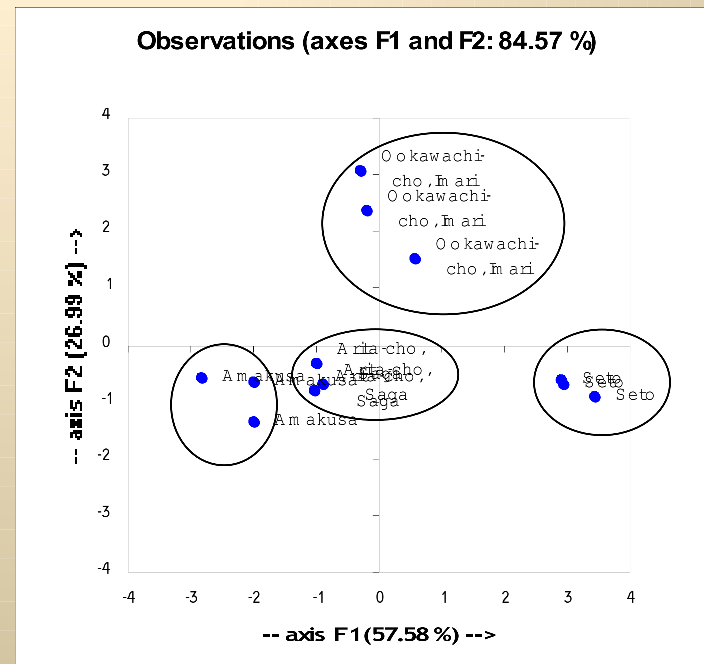


Preliminary results 2: Tracing the origin of porcelain back to a specific region of Japan

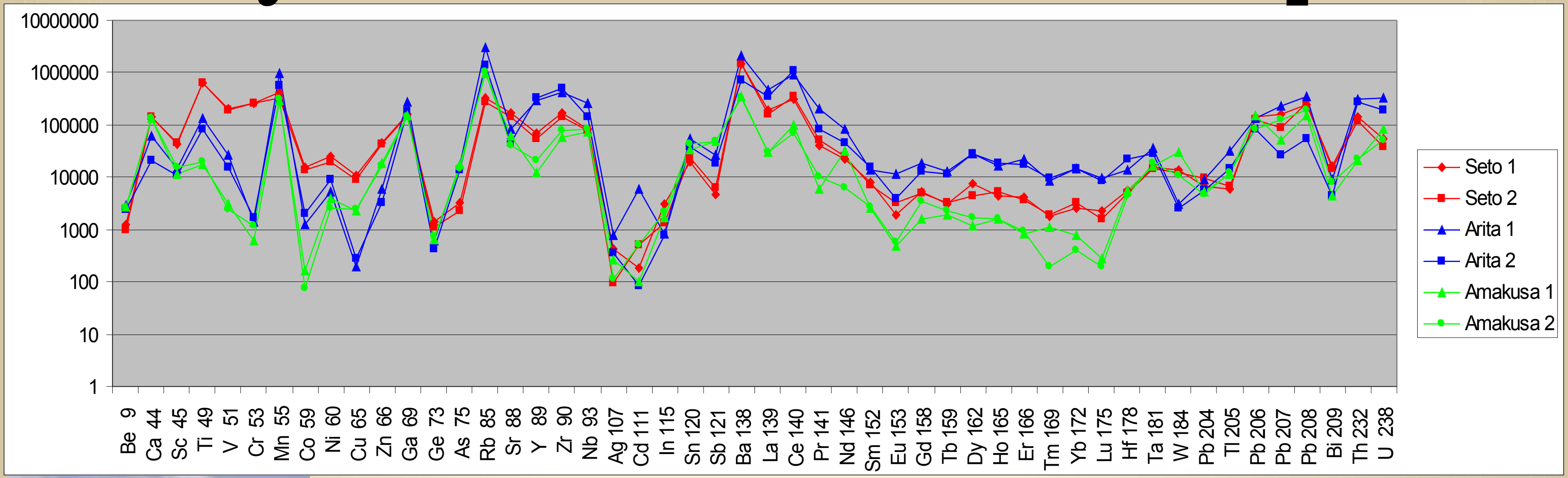
There are four main porcelain production areas in Japan – Arita, Imari, Amakusa Islands and Seto. Visually, porcelain produced from all of these areas is quite similar however LA-ICP-MS has been used to identify differences in trace elemental composition of clay from these four areas, allowing porcelain artefacts to be traced back to a specific region of production within Japan.



•Chemometrical analysis demonstrates these differences are statistically significant, and clearly separated the porcelain into four groups which correspond to the four porcelain producing areas



Preliminary results 3: Comparison of raw clays from different sites in Japan



(a) Izumiyama Quarry – the source of porcelain stone for Imari porcelain

(b) Clay storage sheds at Takahama kiln, Amakusa Islands

(c) Clay storage sheds at Izumiyama Quarry, Arita

- Raw clays were collected from different kiln sites in Arita, Seto and the Amakusa Islands
- These were analysed using LA-ICP-MS
- The elemental fingerprints indicate differences exist in the trace element distribution of clays from different origins
- A relationship between the trace element composition of the raw clays and the final fired ceramics have been established

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