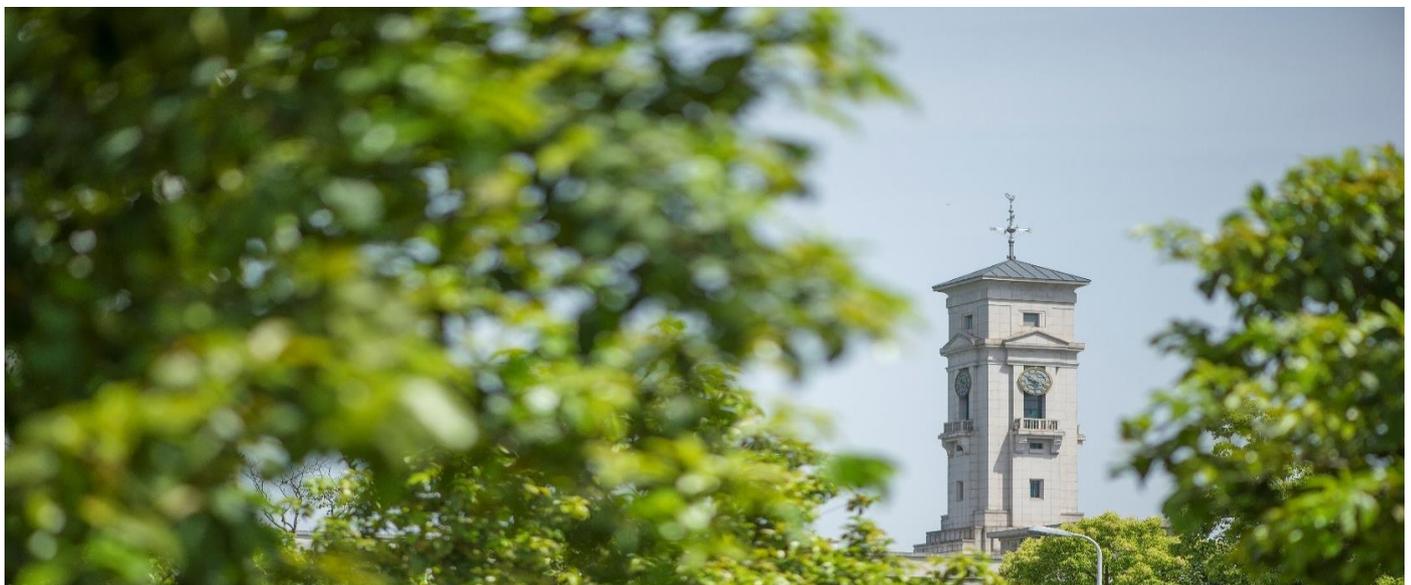


# Isotopic investigations of Chinese ceramics

Julian Henderson, Hongjiao Ma, Jianfeng Cui, Renjie Ma, Hongyan Xiao



**University of  
Nottingham**

UK | CHINA | MALAYSIA

University of Nottingham Ningbo China, 199 Taikang East Road, Ningbo, 315100, Zhejiang, China.

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## Isotopic investigations of Chinese ceramics

Henderson J.<sup>1,2</sup>, Ma. H.<sup>1,2,3</sup>, Cui, J.<sup>4</sup>, Ma R.<sup>4</sup>, Xiao H.<sup>4</sup>, Liu, Y-J<sup>4</sup>

<sup>1</sup> Department of classics and archaeology, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

<sup>2</sup> University of Nottingham - Ningbo China, 199 Taikang East Road, Ningbo, 31500, China

<sup>3</sup> Institute of Cultural Heritage and History of Science & Technology, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing, 100083, China.

<sup>4</sup> School of Archaeology and Museology, Peking University, Beijing, 100871, China,

### Abstract

This chapter provides insights into Chinese ceramic technologies of both bodies and glazes as well as provenance by using isotopes applied to a number of case studies.

The use of Sr isotopes to investigate Chinese high fired Celadon wares and Blue and white Jingdezhen porcelain (Jiangxi province) has revealed a clear distinction associated with the fluxes used in the glazes: plant ash in celadons and limestone in Jingdezhen glazes, something that is not clear from major element analysis. Furthermore the technique is able to suggest by implication the nature of the silica source used in the glazes- normally weathered granitic rocks or metamorphic rocks (porcelain stone) which also contains Sr. This leads to an isotopic mixing line of the 2 Sr-rich components and is proof that 2 Sr -rich components were mixed in the manufacture of limestone glaze. This is not the case for plant ash glazes. Eventually the technique may be used in provenance studies. Like Sr isotope analysis, lead isotope analysis relies on there being a lack of or a minimal change in the isotope ratios when the raw materials are heated. Lead isotope analysis links the use of lead in glazes to the original metal ore and if a kiln uses a distinctive lead source in its glazes it can provide a provenance for the pottery. This has been very successful in distinguishing Chinese Tang sancai wares made in the Huangye, Huangbao, Liquanfang and Qionglai kilns.

## **1 Chinese high fired ceramics: stoneware, porcelain and celadon**

Generally speaking, three terms are used in literature for Chinese high fired ceramics, namely stoneware, porcelain and celadon. Stoneware is a term which refers to the degree of sintering and is used to describe high fired ceramics with a firing temperature normally higher than 1100°C. (Earthenwares are ceramics with a less vitrified body and are fired below 1000°C.) In the context of Chinese ceramics, the term stoneware is usually used to describe early high fired ceramics occurring from the Shang dynasty (1600—1046 BC) to the Tang dynasty (618-907 AD). They tend to have a thin glaze with a colour ranging from brown via green to grey. The green glazed Yue wares, which were made near Ningbo in Zhejiang province dating to the Five Dynasties (907-960) and Song Dynasty (960-1279), are typical stonewares of this type.

Porcelain is a term exclusively used to refer to the white colour of high fired ceramics, but for studies of ancient Chinese ceramics it has a much wider meaning. Because in the Chinese language there are only two words to describe ceramics, Ci ‘瓷’ for high fired ceramics and Tao ‘陶’ for low fired ceramics, many Chinese authors tend to describe all high fired ceramics as porcelain unless there is a specific name for a certain type of wares. The so called protoporcelain is an example of this, it was a direct translation from Chinese word 原始瓷, meaning primitive high fired ceramics. The best description of protoporcelain as a material is stoneware (Krahl 2011).

White porcelain was a great Chinese invention. The manufacturing technology of white porcelain was transmitted eastwards to Korea and to Japan, and westwards to Europe leading to the development of a porcelain industry in other parts of the world. Some early white porcelain dating to the late period of Northern Dynasties (420-581A.D) was very thick and coarse, and the

manufacture of most early white porcelain adopted the technique of applying a white slip between glaze and ceramic body to make the ware look white by covering the grey sometimes yellowish ceramic body (Zhu et al. 2009; Li 1998 23-100). The first fine porcelains appeared in northern China in early 7<sup>th</sup> century (Wood 1999) and it wasn't until the early 10<sup>th</sup> century that porcelain was made in southern China.

Celadon was a word derived from the French, first used in the 17<sup>th</sup> century to describe ceramics with a jade-green glaze from China, Korea and Japan (Kerr and Wood 2004). It is now used to describe any high fired ceramics with a green coloured glaze.

The three terms used to describe Chinese high fired ceramics, stoneware, porcelain and celadon, are therefore defined by their appearance.

## **2 The raw materials and kilns used**

The raw materials for making ancient Chinese high fired ceramics can be broadly divided into two categories, the weathered acid igneous rocks used in south China and the sedimentary coal clay used in north China (Guo 2007). The differences in the raw materials used in south China and north China is due to the continent of China being fused some 200-250 million years ago from two blocks with different geological histories (Wood 1999). This led to different ceramic technologies in the North and South. In the South celadons were made from porcelain stone, a pulverized altered igneous rock consisting of clay and fine grained mica, a hydrous silicate of potassium and aluminium,; the potassium acted as a flux. True porcelain is made from a high firing refractory kaolin clay ('china clay') mixed with alkali feldspar (such as albite) and quartz: they derive strength partly from their vitrified bodies. The northern Chinese kaolin deposits are sedimentary and lack the alkali fluxes, resulting in a less translucent body

because the formation of a vitreous phase is minimal. Feldspar, quartz, calcite or dolomite were used (Guo 2007).

The kilns used in south China normally had a long chamber and they were commonly built upon the slopes of hills; they are known as dragon kilns (Wood 1999, 33-35). The elevation of the kiln chamber and its position on a hill slope led to a natural path for the air inside the kiln, transmitting the flame along the whole length of the kiln to the top. Kilns used in the north were normally built on flat landscapes with a circular shaped chamber and a chimney at the back (known as through draft). They are known locally as *mantou* kilns because they resemble northern steam baked bread rolls (Wood 1999, 95). Their plan can also resemble a horse-shoe shape and 18 such Northern Song (960-1127 CE) kilns have been excavated at Yaozhou, Shaanxi province (Henderson 2000, 171-176, Fig. 4.33) associated with comprehensive evidence for various phases of pottery production in a workshop. The fuel used to fire kilns was wood in both North and South China. Even in north China, where coal was commonly available, it was not used as fuel for firing ceramics until the mid-late northern Song dynasty, which, for most northern kiln sites, was the last phase of their ceramic production (Li 1998).

## **2.1 Coloration**

Ceramics with a coloured glaze or coloured decoration were not common in China prior to the Yuan Dynasty (1279-1368). Monochrome white ware porcelain and green ware celadon were the major products consumed and appreciated in the Chinese domestic market before the 14<sup>th</sup> century. The green colour of celadon is coloured by iron (He et al. 2015, Emami et al 2019) probably present as both oxidized ( $\text{Fe}^{3+}$ ) and reduced ( $\text{Fe}^{2+}$ ) ions. However, the colour is also affected by translucency and in Yue celadons is augmented by precipitation of anorthite crystals at the body-glaze interface and also sometimes in areas rich in aluminium and potassium oxides (Vandiver et al 1989, 358). Scattering of

light from beneath the surface of Song Dynasty Longquan celadon glazes, and therefore brilliance, also occurred because of the presence of wollastonite crystals in calcium oxide rich areas (Vandiver and Kingery 1984, 615). Tang Dynasty Changsha pale yellow wares made for export, and found on the Belitung shipwreck in large numbers, were decorated with green and brown vapour, foliage, floral and animistic patterns (Liu 2011). Monochrome Changsha copper red glazes were also produced in the Tang Dynasty (Wood 1999, 169). Another Tang Dynasty polychrome decorated (green, brown and more rarely blue) ware was lead glazed *sancai* (tri-colour) ware (Rawson 2012, Shen et al 2019).

The Yuan dynasty (1279-1368), established by Mongol conquerors, was the time when there was a fluorescence in coloured ceramics, with glaze coloration and designs being developed further over the course of the Ming (1368-1644) and Qing (1644-1912) Dynasties. The pigments used were based on three transition metal colorants, cobalt, iron and copper. Under glaze painting, over glaze painting, coloured glaze and the combination of the three were the major techniques used for decorating ceramic wares. By controlling the concentration of the pigment and the firing atmosphere in the kiln, different colours and effects can be created using the same colouring elements. Cobalt colorants are associated with a range of impurities including Fe, Mn, As, Ni; Zn and Bi. The Fe:Mn ratio changes from the Yuan to Ming Dynasties indicating that the origin of the cobalt also changed, one origin possibly being the Middle East (Wen et al 2007) and later Europe when used for the decoration of Chinese *famille rose* porcelain (Giannini et al 2017). Copper red was produced under reducing conditions in the Changsha wares by nano-scale copper crystals (Li et al 2016). The green glaze of Changsha yellow wares was also sometimes opacified with tin oxide (Shen et al 2018).

In the following, the use of isotopic techniques to investigate Chinese ceramics will be described. By using practical examples it will demonstrated how each

technique provides distinct kinds of characterizations that can tell us about their production technologies and provenances.

### **3 The use of isotopes to investigate Chinese high fired ceramics**

#### **3.1 The principles**

The determination of isotopes in high fired Chinese ceramics provide a fingerprint for the relative geological ages of raw materials used in production processes and can be used to shed light on the identity of raw materials used. This is therefore not the same as providing *a priori* a provenance to the production site. If one or more raw material was local to the primary production site then isotope research can potentially provide a provenance for the material made there. If provenance is being investigated it relies on there being sufficient contrast in the geological formation age of the raw materials used to make archaeological materials for it to be possible to provide a match. Finally, it is helpful to map variations in isotope signatures across the landscape (e.g. for Pb, Sr and Nd) in order to compare them with isotopic analyses of archaeological materials and potentially provide a provenance.

Strontium and neodymium isotope analysis to investigate ancient vitreous materials was pioneered by European scholars for ancient glass (Wedepohl and Baumann 2000, Freestone et al. 2003, Henderson et al. 2005). After initial scientific exploration, it was decided that the application of Sr isotope analysis to ancient glass (and therefore other vitreous materials like glazes) should be based on two assumptions which are important for producing valid results. Firstly, Sr has a low relative mass difference between its isotopes and it is not susceptible to redox reactions (Faure 1986). As a result there is no detectable fractionation (the relative partitioning of heavier and lighter isotopes) that could distort the results during the various processes of production, especially at high temperatures. Therefore, the Sr isotope compositions of the raw materials should be passed down to the glass (or glaze) that was produced from the raw

materials that were used to make it. Secondly,  $\text{Sr}^{2+}$  substitutes for  $\text{Ca}^{2+}$  in calcium-bearing minerals such as plant ash, calcium carbonate and, especially, aragonite (in shells), so that the Sr isotopic signature of the glass or glaze should be mainly derived from the raw material(s) which introduced the calcium content. If the calcium was introduced in the form of plant ash, the Sr isotopic signature should be derived from the bio-available Sr isotope signature of the place where the plant originally grew (as determined by the geology). If the calcium was introduced in the form of shell fragments such as in beach sand or other carbonate minerals contained in the sand used for making glass, the Sr isotope signature should be the modern (Holocene) value of seawater when the shell and carbonate formed.

Neodymium isotopes are used as an important indicator of the provenance of siliciclastic sediments in geological studies. The utility of this provenance method lies in the apparently low diagenetic mobility of rare earth elements and in distinct Sr–Nd characteristics of different crustal source terrains (McLennan et al. 1993). These features make Nd isotopes suitable to determine silica sources such as sand or quartz pebbles that may have been used in the manufacture of ancient glass or glaze. The neodymium in glass and glaze is likely to have originated from the heavy mineral content of the silica source used for making glass. Since the early days of applying Sr–Nd isotopic analysis to ancient glass, it has been developed as a very promising method for provenance studies (Henderson et al 2010, Ganio et al 2013, Degryse 2015, Henderson et al, 2020). A big data base is crucial for any method to work, especially isotopic provenance. Therefore over the last twenty years, or so, Sr–Nd isotopic data for glass of a range of ages but also for likely raw materials has been produced around the world. The provenance of ancient glass using Sr–Nd isotopic signatures is beginning to reach a level of maturity and to answer some important questions about raw material use, provenance and mixing in a way that trace element analysis, another sensitive technique, can't always. Apart from glass and glaze,

other vitreous materials that could potentially benefit from Sr-Nd isotope analysis are faience and enamels. Other isotopes that have been applied recently to the study of ancient glass are B isotopes (Devulder et al 2014) and Sb isotopes (Lobo et al 2013). However, these isotopic techniques are still to realise their full potential.

### **3.2 The use of Sr-Nd isotopes to investigate Chinese high fired ceramics (For experimental conditions see Supplementary information)**

The application of Sr-Nd analysis to Chinese high-fired ceramics was originally inspired by the works on ancient glass, but due to the different nature of the two materials and associated production technologies Sr-Nd isotopic, studies of Chinese high-fired ceramics have gone down a somewhat different path in recent years. The earliest Sr-Nd isotopic analyses of Chinese high fired ceramics were meant to be used for more or less the same purpose as the Sr-Nd study of ancient glass, to provenance them. Li et al. (2005) first explored the potential of Sr isotope analysis in a Chinese ceramic provenance. Ceramic body samples from two distinct types of stoneware made using raw materials from different geological contexts, Yaozhou (Shaanxi province) Tang Dynasty (618-907) tri-colour wares and Song Dynasty (960 – 1279) Jizhou (Jiangxi province) black wares, were analysed for their Sr isotopic compositions, and the results showed a clear difference between the two materials showing that the calcium-bearing raw materials used to make them derived from different geological contexts. After this initial success, the same group of researchers (Li et al. 2006) applied Sr and Nd isotopic analysis to the ceramic bodies of other Tang dynasty (618-907 AD) tri-colour wares produced at the Yaozhou kiln (Shannxi province) and the Gongyi kiln (Henan province), as well as modern replicas; the results showed again that isotope analysis could differentiate between the three groups of materials clearly. Li et al. (2008) applied Sr isotopic analysis to two types of ceramics that occurred in the same geographical area but that were produced over two thousand years apart: white wares from earliest state from Erlitou,

Henan province (1900–1500 BC) and white porcelain from Gongyi, Henan province dating to the Tang dynasty (618–907 AD). They did this so as to test the assumption that the two pottery types were made by exploiting the same kaolinite clay deposit in Henan province. The results showed that they were made using kaolinite clay but that the origins of the clay used was different. This suggested that the prestigious white pottery wares used in Erlitou may have been produced at a different location and transferred from outside the area for a specific purpose.

However, currently the real strength of Sr-Nd isotopic analysis of Chinese ceramics does not reside in its use as a provenance tool. There are other techniques, such as trace element analysis (laser ablation inductively coupled plasma mass spectrometry), which can just as well be used instead of the more expensive Sr-Nd isotopic analysis for provenance studies; trace element analysis uses far smaller samples than Sr-Nd isotope analysis. The specialised application of Sr-Nd isotopic analysis to Chinese ceramics is that it can provide clues which can be used to work out recipes used in the manufacture of Chinese high-fired ceramics in a way that no other technique can at the moment. This is not to say that Sr-Nd isotope analysis of Chinese high fired ceramics may not one day also become a crucial provenance tool.

Throughout history, Chinese high fired ceramics, such as different types of stonewares and celadon (see Figs 1 and 2), have nearly all been made with a calcareous glaze. Two high calcium materials, limestone and plant ash, were commonly suggested as the fluxes used in the recipes and therefore the source of calcium in glazes. However, apart from a few exceptions, it is never clear for most ancient Chinese glazes which specific calcareous material was used in a particular recipe. This situation has prevented scholars from achieving a clear understanding of how the technology of ancient Chinese high fired glazes developed over time. Strontium isotopic signatures ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) together with the

strontium to calcium ratios ( $\text{Sr} \times 10^3/\text{Ca}$ ) and Sr concentrations are just the right tools to tackle this issue, because different calcareous materials, limestone, plant ash and shells, each have characteristic values for the three parameters. There are other calcium sources in nature, such as fluorite and bone ash. They would have introduced significant amounts of other elements, such as F and P, along with Ca, if they had been used as the calcium source in a glaze recipe. Since no high F and high P glaze has been found, they are not candidates for the calcium source in ancient Chinese high fired glazes. Moreover, nearly all ancient Chinese ceramic production sites were located in inland areas, so the possibility of seashells being used as a calcium source in glaze recipes is also excluded – if shells were used this would be revealed by a ‘modern’ Sr isotope signature. Therefore at the moment the key question to answer using this technique is the identification of the calcium flux used in ancient Chinese glaze recipes, plant ash or limestone.



Fig 1 Jingdezhen glazed blue and white porcelain; the glaze was made using a limestone flux.

The concentrations of  $P_2O_5$ , MgO and sometimes MnO had been used as indicators in trying to identify the source of calcium for a certain glaze recipe (Guo 2007). However, due to the heterogeneous nature of plant ashes, the content of  $P_2O_5$ , MgO and MnO hardly ever gave a clear answer to the question. On the other hand, the three values normally associated with Sr isotopic analysis,  $^{87}Sr/^{86}Sr$ , the strontium to calcium ratio ( $Sr \times 10^3/Ca$ ) and Sr concentrations are fundamentally different for limestone and plant ash as elaborated below so this is a way of distinguishing between the two.

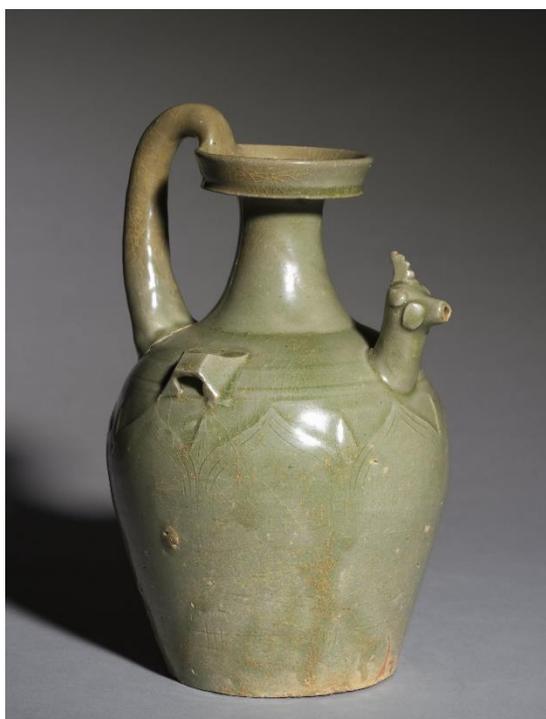


Fig 2 Yue ware; the glaze was made using a plant ash flux.

The  $^{87}Sr/^{86}Sr$  for limestone should be the same as the  $^{87}Sr/^{86}Sr$  of seawater when the limestone was deposited, which is generally lower than modern seawater with a  $^{87}Sr/^{86}Sr$  value of 0.7091, while the  $^{87}Sr/^{86}Sr$  value of plant ashes would reflect the bio-available  $^{87}Sr/^{86}Sr$  for the place where the plant grew. With the assumptions that plant ashes that were used would have grown near the ceramic production site and that bio-available  $^{87}Sr/^{86}Sr$  of a certain location would not change unless major ecological changes occurred, bio-available  $^{87}Sr/^{86}Sr$  retrieved near ancient production sites should normally be enough to provide a

reference  $^{87}\text{Sr}/^{86}\text{Sr}$  value. The strontium to calcium ratios ( $\text{Sr} \times 10^3/\text{Ca}$ ) for limestone and plant ash are also largely different. Turekian and Kulp (1956) reported the strontium to calcium ratios ( $\text{Sr} \times 10^3/\text{Ca}$ ) of over a hundred limestone units sampled worldwide: the average  $\text{Sr} \times 10^3/\text{Ca}$  was 1.5. On the other hand, the  $\text{Sr} \times 10^3/\text{Ca}$  of plants should be the same as the soils in which the plants grow, which is around 10 (Capo et al. 1998), because plants do not discriminate between  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  when taking them up from soils. Similarly there should be no change in relative levels of Sr and Ca when plants are ashed. Therefore, the  $\text{Sr} \times 10^3/\text{Ca}$  of a plant ash should have more or less the same value as that in the soils. Barkoudah and Henderson (2006) reported the major, minor and trace elements of 25 plant ashes sampled in Syria with Sr isotope results for them showing clear contrasts between northern and southern Syria (Henderson et al 2009). The  $\text{Sr} \times 10^3/\text{Ca}$  ratios for them averages 9.6. Therefore, the claim that  $\text{Sr} \times 10^3/\text{Ca}$  for plant ash is nearly an order of magnitude higher than that of limestone should be a secure one, with the former being around 10 and the latter being around 1.5. Because plant ashes have much higher  $\text{Sr} \times 10^3/\text{Ca}$  than limestone, when introducing the same amount of Ca in the glaze the amount of Sr brought in by plant ash should also be much higher. Therefore, as demonstrated above, strontium introduced into glaze by limestone should be very different from that introduced by plant ash in terms of their strontium isotopic signature and elemental features.

Unlike the situation in ancient western glasses where the Sr in the glass was mostly contributed from one source (plant ash for plant ash glass [Henderson et al 2010] and beach sand for natron glass [Degryse 2015]), in Chinese high fired ceramic glazes, the Sr was normally contributed from two sources: the silica source and the calcareous flux (Ma et al. 2014, Li et al. 2019). Theoretically speaking for any material made by fusing two or more raw materials with different Sr isotopic compositions ( $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration), its Sr isotopic

composition should be a mixture of Sr isotopic compositions of the two or more raw material components according to the equation below.

$$\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M = \frac{Sr_A Sr_B \left( \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_B - \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_A \right)}{Sr_M (Sr_A - Sr_B)} + \frac{Sr_A \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_A - Sr_B \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_B}{Sr_A - Sr_B} \quad (\text{Equation 1})$$

Where  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M$  and  $Sr_M$  are Sr isotopic ratio and Sr concentration of the mixture, and  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{A,B}$  and  $Sr_{A,B}$  are Sr isotopic ratio and Sr concentration for the two mixing components.

Because the Sr isotopic ratio and Sr concentration ( $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{A,B}$  and  $Sr_{A,B}$ ) for the mixing components are constant, the equation could be simplified as

$$\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M = \frac{a}{Sr_M} + b \quad (\text{Equation 2})$$

The equation  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M$  against  $Sr_M$  is a hyperbola and is dependent on the weight ratio between component A and component B (Figure 3)

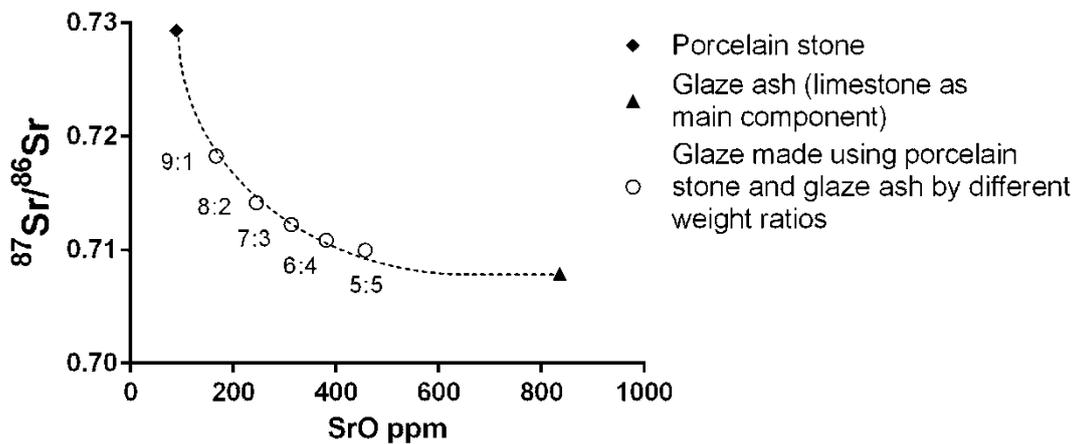


Figure 3 the hyperbolic mixing line of Sr isotopic compositions of glaze made by two raw material components (redrawn from Li et al. 2019, figure 2)

Because the siliceous raw material used in western glass making in Late Bronze Age Mesopotamia was quartz pebbles which do not contribute Sr to the glass melt at all, it is safe to assume that the Sr content of that glass was introduced in one calcium bearing component of the raw material (the plant ash). But this assumption has to be refined for Chinese high-fired ceramic glaze studies, in two ways. On the one hand, when the silica source and calcareous flux with similar Sr contents but different  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures are mixed when making glaze, the Sr isotopic composition of the glaze should be a mixture of values contributed from the two raw materials according to equation 1. Due to the variations of the Sr contents and  $^{87}\text{Sr}/^{86}\text{Sr}$  in the amount of raw materials used, Sr isotopic analysis of samples taken from different shards of a same type of glaze should always display a diagonal line in a plot of  $^{87}\text{Sr}/^{86}\text{Sr}$  against reciprocal of Sr ppm (or a hyperbola in a plot of  $^{87}\text{Sr}/^{86}\text{Sr}$  against Sr ppm). Moreover, the extrapolated ends of the mixing line should point to the Sr isotopic compositions of the raw materials (Li et al. 2019): see Fig 3.

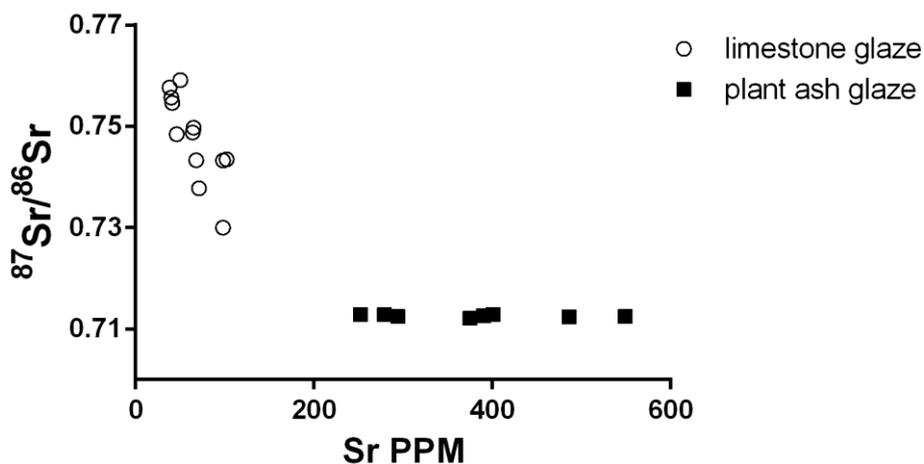


Figure 4 Different characteristics of  $^{87}\text{Sr}/^{86}\text{Sr}$  versus Sr ppm in limestone and plant ash glazes. The mixing line for limestone glaze can be seen but a mixing of the two raw materials can not be seen in the pattern of Sr isotopic compositions for multiple plant ash glaze data because the Sr contribution from the siliceous material is negligible according to Equation 2 (redrawn from Ma et al. (2014) figure 1).

On the other hand, when the calcareous flux contributes the vast majority of Sr to the glaze, which is normally over 400 ppm as is the case for plant ash glaze, the pattern for  $^{87}\text{Sr}/^{86}\text{Sr}$  against Sr ppm when plotted would approximate to a horizontal line with consistent  $^{87}\text{Sr}/^{86}\text{Sr}$  values near that of the calcareous flux (Fig 4). This is because the contribution of  $^{87}\text{Sr}/^{86}\text{Sr}$  from the silica source in the glaze, which normally contributes less than 100 ppm Sr, would be close to negligible according to equation 1 (Ma et al. 2014). Therefore according to the plotted line in Fig 4, we should be able to estimate how much Sr was introduced into a glaze by the shape of the line and to estimate the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the calcareous flux by extrapolation.

By using the signature values of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\text{Sr} \times 10^3/\text{Ca}$  for limestone and plant ash and with the help of plotted  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration data, the calcareous flux used in a number of Chinese glaze recipes, which had been unclear and sometimes confusing due to ambiguous historical records, have been worked out. Ma et al. (2016) showed that the Ming dynasty (1368-1644 AD) *Blanc De Chine* glaze (Fig 5) and Qing dynasty (1636-1912 AD) blue-and-white glaze produced at Dehua, Fujian province were fluxed with different calcareous fluxes: the former by calcareous plant ash and the latter by limestone. This result is in accordance with available historical records. In this study, it was also discovered that two recipes were used for making blue-and-white porcelain glazes during the late Ming and early Qing dynasties at the Wun Yiu kiln in Hong Kong: calcareous plant ash was the flux for one recipe and limestone for the other. It was suggested that the reason why two recipes were used was that the workshop was run by two families, and the two families used different recipes for their products. Li et al. (2016) studied the Sr isotopic compositions of the bodies of Southern Song (1127-1279 AD) imperial Guan wares (a prestigious thick glazed celadon – see Fig 5) and two sources of raw materials found near the manufacturing site. The authors suggest that the raw materials used for imperial

Guan wares were both high aluminium clays but that the difference in the Sr isotope compositions between the wares, and therefore the raw materials used, was due to the refinement and levigation processes which had changed the mineralogical composition of the refined clay used to make the wares. Xu et al. (2018) studied the Sr isotopic compositions of the black glaze and its possible raw materials in Song dynasty Jizhou wares (black glazed stonewares produced in Jiangxi province), and concluded that the black glaze of Jizhou wares was made by fusing local high aluminium clay, high silica plant ash and a small amount of iron colorant. Ma et al. (2019) studied the Sr isotopic compositions of glazes produced in various periods (10-17<sup>th</sup> Century AD) at Longquan, Zhejiang province. According to the results the authors concluded that the famous Longquan celadon glaze was a glaze fluxed with a calcareous plant ash rather than the previously widely accepted idea that it was fluxed with limestone. Shen et al. (2019) studied the glazes and possible raw materials used to make Tang to Northern Song dynasty (10-12<sup>th</sup> Century AD) Yaozhou celadon wares (Fig 5), and concluded that the glaze was fluxed with plant ash produced from vegetation growing on the local Loess Plateau. A recipe recorded in the early 20<sup>th</sup> century, records that a local calcareous rock was used. It is still being used to make modern replicas, so the local calcareous rock must have been introduced much later than the date of the ancient Yaozhou celadon samples.



Figure 5 Some ceramic types that have been studied for Sr isotopic analysis: Ming dynasty (1368-1644 AD) Blanc De Chine from Dehua (left), Southern Dynasty (1127-1279 AD) Guan ware (middle) and Five dynasties period (907-960 AD) Yaozhou ware (right)

With more and more isotope results for high-fired Chinese glaze recipes being produced, it is approaching the time for one of the most important questions in Chinese ceramic studies to be answered: when and how did limestone glaze replace plant ash glaze to make Chinese high-fired ceramics? We know that Chinese high-fired ceramic glaze began as plant ash glaze when proto-porcelain emerged (Kerr and Wood 2004), and we know that in the 18<sup>th</sup> – 19<sup>th</sup> centuries AD, and even today, that the traditional glaze for hand-made wares was limestone based. There is no doubt that limestone glaze was a more advanced technology compared to plant ash glaze for the purpose of coating high-fired ceramics. It is more predictable, easier to control, the raw material is easier to get, it is easier to mass produce glazed ceramics and ecologically more friendly. So there must have been a transitional period when limestone glaze was first invented somewhere, the technology started to spread out and it was replaced with the out-dated plant ash glaze over a much larger geographical area. Ceramics are among the few things that we know were mass produced, extensively traded, domestically and over long distances in ancient times and are still available in large quantities and are well preserved. Answering this specific question can provide us with a very unique perspective on how technology evolved in ancient Chinese society, and how different it was from technological upgrades and technological evolution today?

Compared to the extensive application of Sr isotopic analysis of Chinese high-fired ceramics, the application of Nd isotopic analysis is very much under-developed. Apart from some early attempts using this technique for provenance (Li et al. 2005, Li et al. 2006, Li et al. 2008), in the last ten years there have been

very few new advances in this area. However, Nd isotopes are very powerful for identifying the silica source used to make ancient vitreous materials, so it should be a very promising for identifying the siliceous raw material used in certain ceramic bodies and glaze recipes. So, given time, more research using Nd isotope analysis to investigate the technology and provenance of Chinese high-fired ceramics should bear fruit, potentially providing more information about silica sources and, in combination with Sr, provenance.

### **3.3 A role for lead isotope analysis?**

#### **3.3.1 The principles (For experimental conditions see Supplementary Information)**

Lead has 4 isotopes, namely  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ . Because the latter three isotopes are radiogenic and their abundances depend on the geological age of the lead, lead has a large range of natural isotopic compositions. Thus, lead isotope ratios are used in archaeological chemistry to trace lead-containing artifacts back to their ore source (Gale and Stos-Gale, 2000; Pollard, 2006).

So far, lead isotope analysis is the most effective method for the provenance study of lead-bearing objects such as metals, lead-silica glass and lead glazed ceramics. Between the 1960s and 1980s, Brill and others introduced this method into archaeology to identify the source of ancient lead raw materials used (Brill and Wampler, 1966). Gale and Stos-Gale (1982, 1989, 2000) in particular developed it further. In the 1990s and later doubts were raised about the feasibility of lead isotope analysis due to a claimed process of fractionation causing severe problems in the interpretation of the results by disrupting the ratios and therefore the characterization of the lead-rich material which led to a famous controversy in archaeological science (Muhly 1995; Budd et al.1995; Budd et al. 1996, Pollard and Heron, 1996; McGill et al, 1999, Qin et al 2004). The controversy settled down after Budd et al. announced that their simulation

experiments did not show measurable isotopic alteration using Thermal Ion Mass Spectrometry (McGill et al, 1999).

Cui and Wu's (2011) experiments to imitate non-equilibrium evaporation during metallurgical processing of lead showed that the process altered the lead isotopic ratios of the remaining liquid. However, they found the process to be minimal so that in most ancient metallurgical processes lead isotopic fractionation can be ignored. So with this in mind, lead isotope analysis is still the most useful method for identifying the provenance of the lead-bearing artifacts.

Four lead isotopes can be examined by plotting three groups of the four ratios ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ). In general, if there is no overlap between groups, the source of the lead mine can be defined by using two sets of isotope ratios. Some scholars have pointed out that because of the linear correlation between the two isotope ratios in archaeological materials - it is only for a general qualitative investigation of archaeological events - only one set of isotope ratios need be used. However, lead ores are common in China, especially in the Central Plains. Therefore, by using the ratio of 204 as the denominator, commonly used in geochemistry, and 206 as the denominator commonly used in archaeology for a two-dimensional map analysis, the overlapping effect in lead isotope archaeology cannot be avoided. This usually causes unnecessary trouble when data processing.  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ , are daughter isotopes and are the final radioactive decay products of U and Th of decay chains beginning with  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  respectively.  $^{204}\text{Pb}$  is the only non-radiogenic lead isotope. The single-stage evolution model of lead isotope presented by Holmes and Houtormans (Holmes 1946) assumes that the regional distribution of U, Th and Pb is uniform at the initial stage of the Earth's formation. Moreover, the ratios of U/Pb and Th/Pb in mines show regional differences. In such a closed system, U and Th decay continuously to form Pb unless the ore deposit is mined. The lead isotope ratio ( $a_0=9.307$ ,  $b_0=10.294$ ,  $c_0=29.476$ ) of the Canyon Diablo meteorite

represents the original lead isotope composition at the initial stage of the Earth's formation, from which the isochron equation can be derived (Patterson 1956). In other words, the scatter diagram of  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  in ore samples with the same geochron will be a straight line.

In sum, when the ratios cluster together or if the scatter diagram of  $^{207}\text{Pb}(^{208}\text{Pb})/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  is in a straight line, we can infer that these samples might have the same sources.

### **3.3.2 Application of lead isotopes to the provenance of Chinese lead glazes**

Due to the high lead contents of lead glazed ceramics, one can use lead isotope analysis to investigate the source of lead materials used in glaze preparation. Mason et al (1992) and Wolf et al (2003) carried out pilot studies in applying lead isotope analysis as a provenance study of Islamic lead glazed pottery. In recent years, lead isotope analyses of 7<sup>th</sup>-10<sup>th</sup> century glazed pottery in East Asia have been extensively carried out. First Cui et al. (2010) found that the lead isotope ratios of earthenware Tang Sancai lead glazes from two Tang Dynasty kilns, the Huangye kiln in Henan province and the Huangbao kiln in Shaanxi province did not overlap with each other, which indicates that the two kilns used different lead sources for their glazes. Some examples of Tang sancai tricolour ware are shown in Fig. 6.



Fig. 6 Tang Dynasty (618-907) glazed ceramics from Chinese archaeological sites. 1. Hungye kiln jar (IIIT5H25:39); 2. Tricolour Liquanfang kiln jar (TIHIB: 46); 3. Liudingshan cemetery-hu (I M5:28); 4. Tricolour Huangbao kiln camel; 5 and 6: Tomb of prince Yide, horse and rider, hunting figures tricolour (QYD1-1-1-3-3 and QYD1-1-1-3-7)

A further study showed that the lead source used by the Huangbao kiln came from the geochemically-defined Northern China province, while the lead source used by the Huangye kiln came from geochemically-defined Yangtze Province – see Fig 7 (Cui et al. 2010; Shen, et.al., 2019).

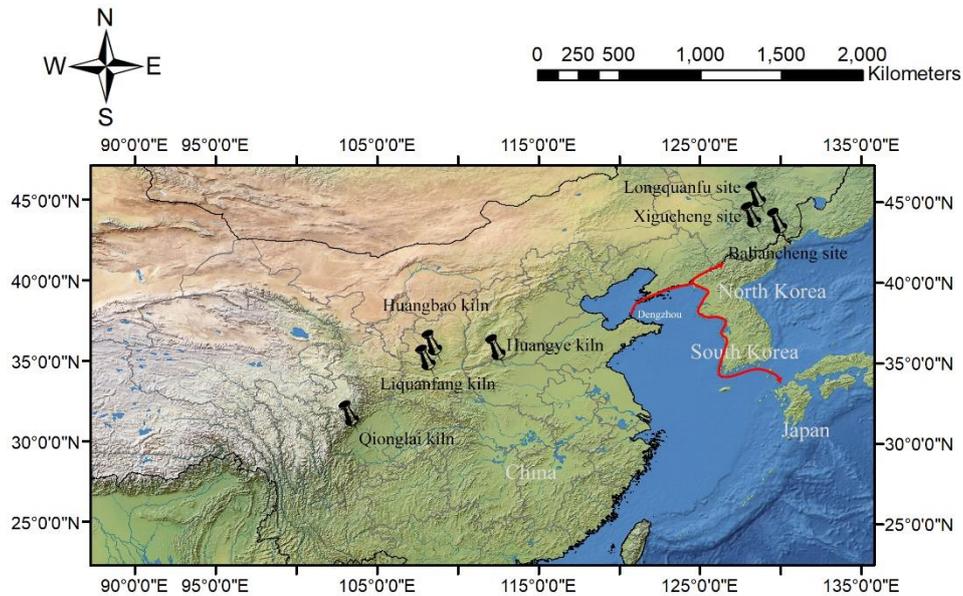


Figure.7 Locations of major Tang Sancai kiln sites

Tatsumi and Furihata (2011) pointed out that the glaze of Nara (Japan) tricolor pottery was mostly made with a Japanese lead ore, and samples unearthed from the late 6<sup>th</sup> century Asuka Ike (飛鳥池) site partially used lead material similar to that used in the Huangye kiln. Analyses of Bohai glazed pottery unearthed at Kraskino, southern Russia dating to the Tang Dynasty (618-907 AD) shows that the lead materials used in the pottery came from many sources, including Japanese and Chinese lead ores (Furihata et al. 2015).

In Peking University (PKU), the lead isotope database of Tang Sancai wares has been constructed since 2010. Up to now, we have produced primary lead isotope ratio diagrams of Tang Sancai potteries. The database includes all important kiln sites for Tang Sancai that have been excavated (fig.7). As shown in Fig. 8, the lead isotope ratios of Tang Sancai samples from Huangye, Huangbao, Liquanfang and Qionglai kilns clearly cluster and can be roughly divided into four groups.

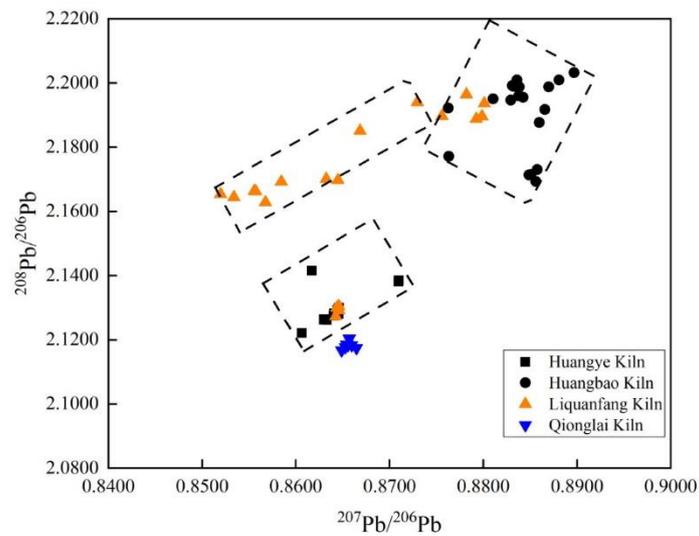
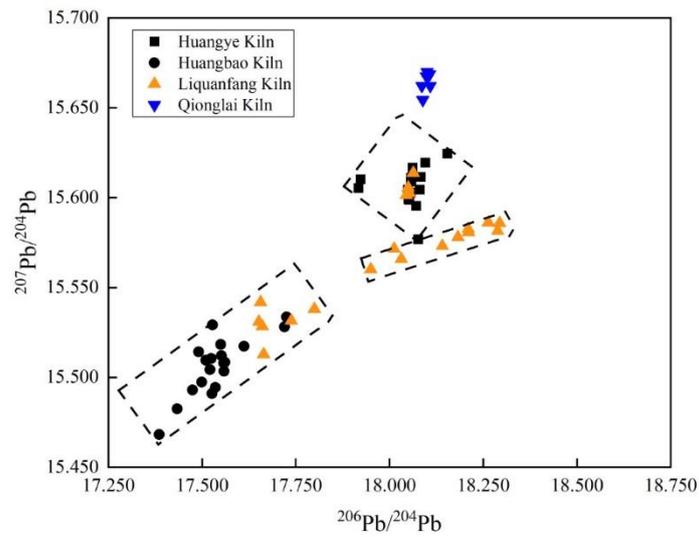


Figure 8 Lead isotope ratios for Tang Sancai glaze samples from four kiln sites

Thus when lead isotopes are determined in Tang Sancai pottery glazed wares excavated from a range of archaeological sites and compared to the results for kiln sites held in the PKU database, we may be able to provide their exact provenance.

## **4 Conclusions**

Chinese high fired ceramics include celadon and porcelain wares made as early as the 5<sup>th</sup> century AD with a peak in the Ming and Qing dynasties. The wares were copied widely leading to blue and white (and other decorated) wares becoming very popular in the 18<sup>th</sup> and 19<sup>th</sup> centuries. The scientific analysis of Chinese high fired ceramics allows us to answer a range of questions about the production technologies used to make these important wares and in some cases about their provenance. Isotopic analyses have indicated what raw materials were used in (bodies and) glazes, how they were sometimes refined, how different sources of calcium were sometimes mixed, and by defining lead isotope signatures for kilns a provenance for lead-rich glazed wares is obtained.

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## Supplementary Information

### Strontium isotope analysis

The most reliable techniques for isotope determination of silicate materials such as glass and glazes are solution based Thermal Ionization Mass Spectrometry (TIMS) and high resolution or multi-collector inductively coupled mass spectrometry (HR or MC-ICP-MS). These techniques require research samples to be taken off the original wares using tools that avoid contamination, such as those with a tungsten carbide edge. The samples then need to be spiked, dissolved and purified in a clean preparation laboratory (class 100, laminar flow) for instrumental analysis. Approximately 0.3 grams of the powdered glaze is weighed out for analysis. Standard silicate dissolution is undertaken and the strontium fraction is separated using an ion exchange column (Ganio et al. 2012). The strontium isotope compositions and concentrations can be determined by TIMS using a Thermo Scientific Triton multi-collector mass spectrometer, in this case at the Natural Environmental Research Council funded Isotope Geosciences Laboratory in the UK. At this facility the NBS 987 Sr standard gave an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.710281 \pm 0.000005$  (1s, n =16), the accepted value is 0.710250, to which these data collected were normalised. For neodymium a J&M Nd internal standard gave a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.511108 \pm 0.000005$  (1s, n =4) and these data are normalised to a value of 0.511123. Typical blanks are below 150 pg for strontium. A recent comparison between J&M and the La Jolla international standard was carried out and La Jolla gave a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.511846 \pm 0.000003$  (1s, n=6) (accepted value 0.511860) while J&M gave  $0.511103 \pm 0.000001$ , (1s, n=10).

## **Lead isotope analysis**

Lead isotope measurement is usually carried out by thermal ionization mass spectrometry (TI-MS) or multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). With the improvement of MC-ICP-MS, the advantages of it in lead isotope measurement are more and more obvious. At present, MC-ICP-MS has been applied to measure the lead isotope ratios of most ancient leaded samples.

The advantages of MC-ICP-MS includes a faster measurement process and a more accurate result which is more than one order of magnitude higher than that of TI-MS. (Pollard et al., 2006). What's more, the pre-treatment of samples becomes much simpler, especially for the leaded glazed pottery.

Here we report the sample preparation process used in Peking University. Due to its high sensitivity and accuracy, MC-ICP-MS has been increasingly widely applied to detect heavy metal isotopes. Previous work on the lead isotope analysis of bronze artefacts using MC-ICP-MS showed the need for a simpler sample preparation than TIMS (thermal ionization mass spectrometry) (Niederschlag et al. 2003). The pre-treatment of MC-ICP-MS need only dissolve the sample in the pure nitric acid (Baker et al. 2006), analysed lead isotope ratios in archaeological silver and copper with MC-ICP-MS using bulk dissolution without lead purification. Their results indicated that bulk solution analyses without lead purification on all samples agree within error with the TIMS data, suggesting that problems for MC-ICP-MS due to isobaric interferences and/or mass bias variations due to the presence of matrix elements are insignificant. Therefore, it is possible to analyse for lead isotopes by bulk dissolution using MC-ICP-MS.

The step-wise pre-treatment procedure in this study is as follows: (1) small fragments are chipped from the glaze using a sharp scalpel; (2) the sample is dissolved in pure nitric acid in a 50ml glass beaker, leaching the solutions; (3)

the clear solution is diluted in a 100ml flask using deionized water; (4) the solutions are measured to detect the lead content using ICP-AES; (5) according to the lead content results. The solutions are diluted down to the tolerance limit of the instrument, which is  $1\mu\text{g} / 1$ ; (6) the thallium (Tl) standard solution-SRM997 is added to the solutions; (7) the sample is measured on the MC-ICP-MS. Determined from repeated analyses of SRM981, the overall analytical error ( $2\sigma$ ) for all lead isotope ratios was less than 0.06%. The standard deviation of the mean values for the 20 measurements of each of the five ratios made during the analysis of one sample was less than 0.02%.

### **LIA Data processing**

The four lead isotopes can be examined by plotting three groups of ratios. In general, if there is no overlap between groups, the source of the lead mine can be defined by using two sets of isotope ratios. Some scholars have pointed out that because of the linear correlation between the two isotope ratios in archaeological materials - it is only for a general qualitative investigation of archaeological events - only one set of isotope ratios need be used. However, lead ores are common in China, especially in the Central Plains. Therefore, by using the ratio of 204 as the denominator, commonly used in geochemistry, and 206 as the denominator commonly used in archaeology for a two-dimensional map analysis, the overlapping effect in lead isotope archaeology cannot be avoided. This usually causes unnecessary trouble when data processing.  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ , are daughter isotopes and are the final radioactive decay products of U and Th of decay chains beginning with  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  respectively.  $^{204}\text{Pb}$  is the only non-radiogenic lead isotope. The single-stage evolution model of lead isotope presented by Holmes and Houtormans (Holmes 1946) assumes that the regional distribution of U, Th and Pb is uniform at the initial stage of the Earth's formation. Moreover, the ratios of U/Pb and Th/Pb in mines show regional differences. In such a closed system, U and Th decay continuously to form Pb unless the ore deposit is mined. The lead isotope ratio ( $a_0=9.307$ ,  $b_0=10.294$ ,

$c_0=29.476$ ) of the Canyon Diablo meteorite represents the original lead isotope composition at the initial stage of the Earth's formation, from which the isochron equation can be derived (Patterson 1956). In other words, the scatter diagram of  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  in ore samples with the same geochron will be a straight line.

In sum, when the ratios cluster together or if the scatter diagram of  $^{207}\text{Pb}(^{208}\text{Pb})/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  is in a straight line, we can infer that these samples might have the same sources.