

LEAD ISOTOPE ANALYSIS OF TANG SANCAI POTTERY GLAZES FROM GONGYI KILN, HENAN PROVINCE AND HUANGBAO KILN, SHAANXI PROVINCE*

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Through the use of MC–ICP–MS, this study analyses the lead isotope ratios of 19 Tang Sancai pottery glazes unearthed from the Gongyi and Huangbao kiln sites. According to their different lead isotope ratios, the two kilns can be grouped separately. The research also suggests that the Gongyi and Huangbao kilns are independent production centres of Tang Sancai in the Tang Dynasty. The data from the Huangbao kiln indicates that the lead in the glazes originates from the Northern China geochemical province, while the data from Gongyi kiln suggests its source as the Yangtze geochemical province. Furthermore, the results obtained for the Tang Sancai pottery indicate that the lead sources for glaze making of these two kilns were very consistent, which suggests that lead isotope analysis could be a helpful method to identify the kilns producing Tang Sancai artefacts.

KEYWORDS: TANG SANCAI POTTERY, GLAZE, LEAD ISOTOPE ANALYSIS, GONGYI KILN, HUANGBAO KILN

INTRODUCTION

Tang Sancai, as the name suggests, is the renowned Chinese glazed pottery produced in the Tang Dynasty (AD 618–907), especially during the High Tang period (AD 650–755). *Sancai* refers to the three main colours used in the glazes of these potteries; namely, green, yellow and white. Many other colours, such as blue, brown and so on, are also used in these kinds of pottery glazes. So far, three kilns have been discovered in China as the major source of Tang Sancai potteries. These are Gongyi kiln in Henan Province (Gongyi Conservation Institute of Henan Province 2000; Henan Provincial Institute of Cultural Relics and Archaeology and China National Institute of Cultural Relics 2005, 2007), Huangbao kiln (Zhuo 1992) and Liquanfang kiln in Shaanxi Province (Zhang and Li 1999; Shaanxi Provincial Institute of Archaeology 2008) (Fig. 1).

Scientific analyses have been undertaken on Tang Sancai pottery artefacts to study their provenance: most have focused on the chemical composition of the bodies (Miao and Lu 2001; Lei *et al.* 2005, 2007; Li *et al.* 2006). According to these results, the chemical characteristics of these three kilns are distinct from one another. That means that each kiln has its own source of raw materials. For provenancing of the glazes, Feng *et al.* (2005) and the present authors (Cui and Lei 2009) did some pilot studies, which indicated that elemental analysis of the glazes could be an effective method for the studying the source of the pottery.

Tang Sancai, as a lead glaze, is known for its high composition of PbO, usually more than 50% (Li 1998), which makes it ideal to use lead isotope analysis as the most direct way to study the

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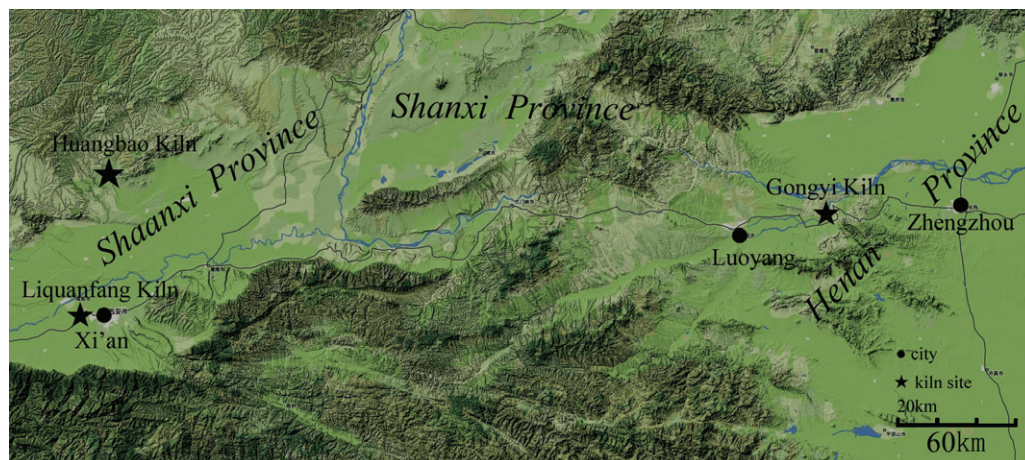


Figure 1 The geographical distribution of the three main Tang Sancai kilns.

provenance of the glaze. This method has been applied on the ore source study of lead glazed pottery by some Western scholars since the 1990s (Wolf *et al.* 2003). Until now, no similar work has been conducted in China. For the purpose of collecting more primary evidence from each kiln and establishing a database for the identification of the unknown Tang Sancai samples, this study has analysed the lead isotopes of some Tang Sancai glazes from Gongyi kiln and Huangbao kiln.

METHODOLOGY

Lead isotope ratios were measured using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) of the type VG Elemental in the School of Earth and Space at 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 more simple sample preparation than TIMS (thermal ionization mass spectrometry) (Niederschlag *et al.* 2003). The pretreatment 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 pretreatment 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 50 ml glass beaker, leaching the solutions; (3) the clear solution is diluted in a 100 ml 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 $1 \mu\text{g l}^{-1}$; (6) the thallium (Tl) standard solution-SRM997 is added to the solutions; and (7) the sample is measured on the MC-ICP-MS.

Determined from repeated analyses of SRM981, the overall analytical error (2σ) for all lead isotope ratios was less than 0.06% (see Table 1). The standard deviation of the mean values for

Table 1 The results of 12 runs for SRM981 determination and the average analytical error

Run number	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
1	0.9145	2.1662	16.945	15.496	36.705
2	0.9146	2.1673	16.922	15.477	36.677
3	0.9144	2.1667	16.944	15.494	36.713
4	0.9147	2.1675	16.948	15.503	36.734
5	0.9144	2.1662	16.949	15.499	36.716
6	0.9144	2.1661	16.943	15.492	36.699
7	0.9141	2.1655	16.945	15.491	36.696
8	0.9141	2.1655	16.937	15.482	36.677
9	0.9141	2.1656	16.944	15.488	36.692
10	0.9142	2.1660	16.949	15.495	36.713
11	0.9143	2.1661	16.944	15.492	36.704
12	0.9143	2.1662	16.944	15.492	36.703
Analytical error (%)	0.03	0.04	0.06	0.04	0.03

Table 2 Lead isotope ratios for the Tang Sancai glazes from Huangbao kiln and Gongyi kiln

	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<i>Huangbao kiln</i>					
T 12	0.8836	2.2010	17.535	15.494	38.595
T 01	0.8870	2.1988	17.491	15.514	38.459
T 03	0.8849	2.1714	17.521	15.504	38.045
T 11	0.8866	2.1917	17.475	15.493	38.299
T 13	0.8860	2.1877	17.528	15.529	38.346
T 02	0.8838	2.1988	17.527	15.491	38.538
T 27	0.8832	2.1989	17.558	15.508	38.609
T 49	0.8843	2.1955	17.550	15.518	38.531
T 08	0.8881	2.2009	17.433	15.483	38.369
<i>Gongyi kiln</i>					
G 01	0.8606	2.1221	18.154	15.624	38.526
G 08	0.8630	2.1264	18.081	15.604	38.449
G 18	0.8642	2.1277	18.051	15.599	38.406
G 20	0.8641	2.1282	18.057	15.603	38.428
G 24	0.8646	2.1299	18.062	15.617	38.471
G 26	0.8645	2.1292	18.057	15.609	38.446
G 31	0.8640	2.1275	18.053	15.599	38.408
G 36	0.8645	2.1296	18.062	15.615	38.465
G 39	0.8630	2.1262	18.071	15.595	38.424
G 05	0.8617	2.1415	18.077	15.577	38.712

the 20 measurements of each of the five ratios made during the analysis of one sample was less than 0.02%.

RESULTS

Nineteen glaze samples from Tang Sancai potsherds have been analysed in this study. The results are given in Table 2. The data are also shown on the $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ plots shown in Figure 2. All the samples were randomly selected from 100

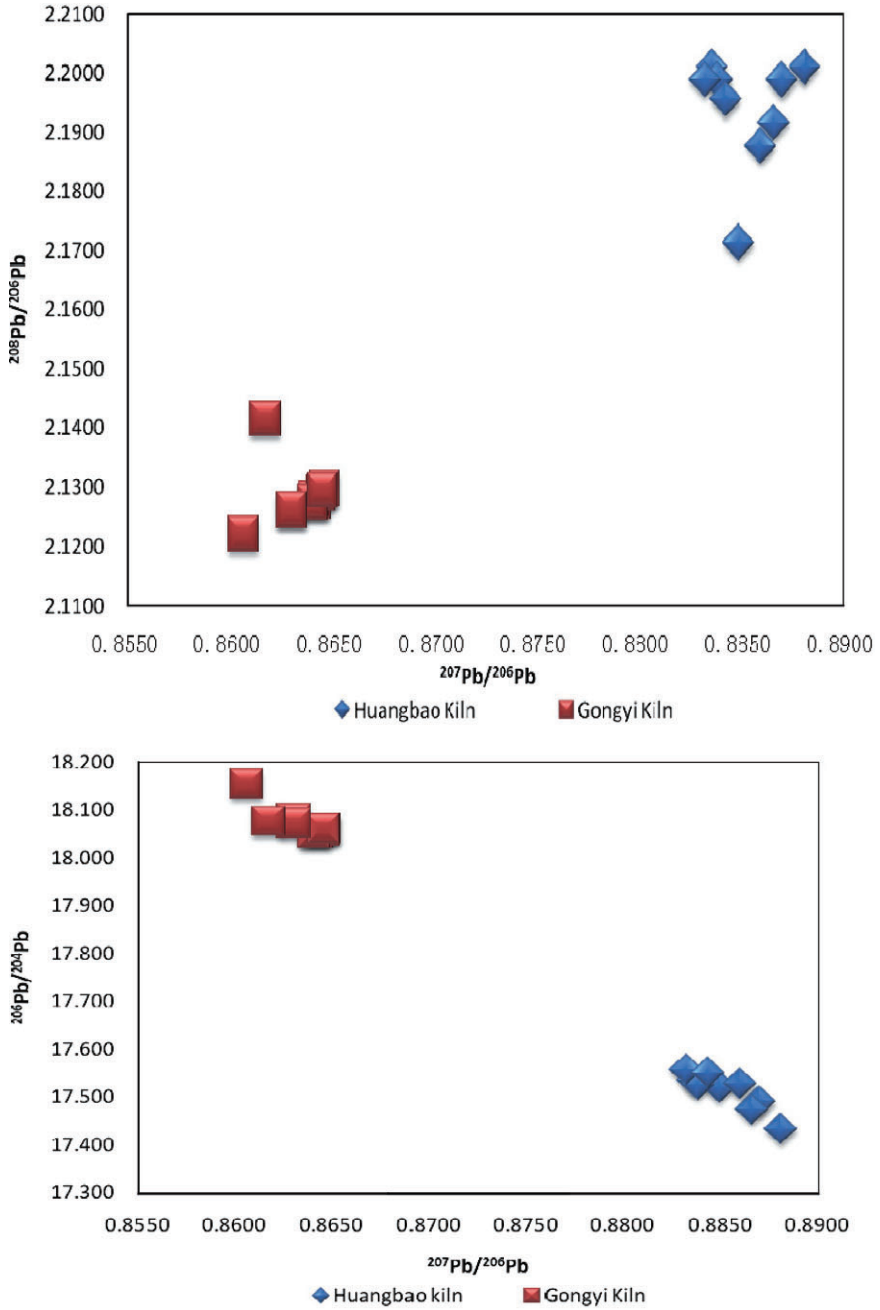


Figure 2 Lead isotope ratios for Tang Sancai pottery glazes from Huangbao kiln and Gongyi kiln.

potsherds to make the representation as wide as possible. The colours of the glazes include green, yellow, blue and brown, and all glazes are transparent. The bodies of all samples are white. The chemical compositions of some yellow glazes have been reported in our recently published paper (Cui and Lei 2009). One of the authors has also reported the chemical compositions of the bodies (Lei *et al.* 2007).

DISCUSSION

It can be concluded from these results that the two kilns had lead ore sources that were very distinct from each other, which is also proved by the elemental analyses of the glazes. According to the lead isotope ratios for the glazes, the two kilns can be grouped separately, with each kiln exploiting a different ore source. The results also suggest that Gongyi kiln and Huangbao kiln were independent centres for Tang Sancai production during the Tang Dynasty.

Based on the lead isotopic characters for ores and rocks, Zhu recognized three main geochemical provinces in China—the so-called Northern China province (NC), the Yangtze province (Y) and the Southern China province (SC) (see Fig. 3; see also Zhu 2001). As the difference in the values of the lead isotopic ratios is the result of the dissimilar history of geological evolution, the lead isotopic compositions of these three large geological blocks can be clearly distinguished from each other, with $^{206}\text{Pb}/^{204}\text{Pb}$ values of 16.2–17.8 for NC, 17.8–18.4 for Y and 18.4–19.8 for SC (Zhu 1995).

According to our results for the lead glazes, the values of $^{206}\text{Pb}/^{204}\text{Pb}$ of the Huangbao kiln are all lower than 17.8 and those of the Gongyi kiln are between 17.8 and 18.4. Therefore, it can be concluded that lead in the glaze of pottery from the Huangbao kiln was probably from the Northern China province, while that in the glazes of pottery from the Gongyi kiln was probably from Yangtze province.

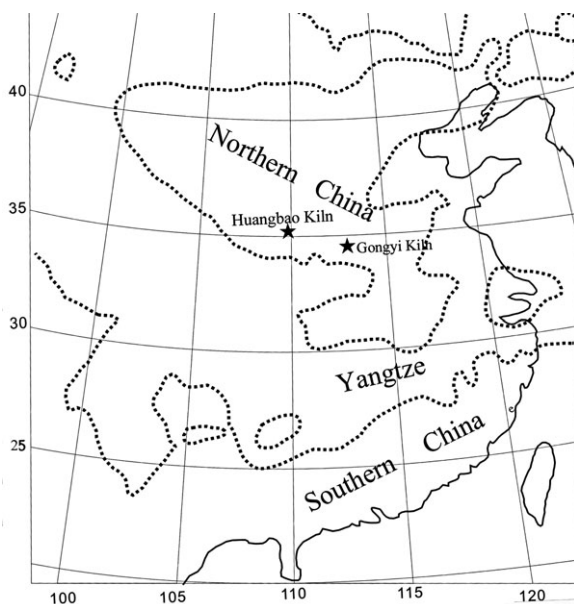


Figure 3 A sketch map showing the three main lead isotopic provinces in China (after Zhu 2001).

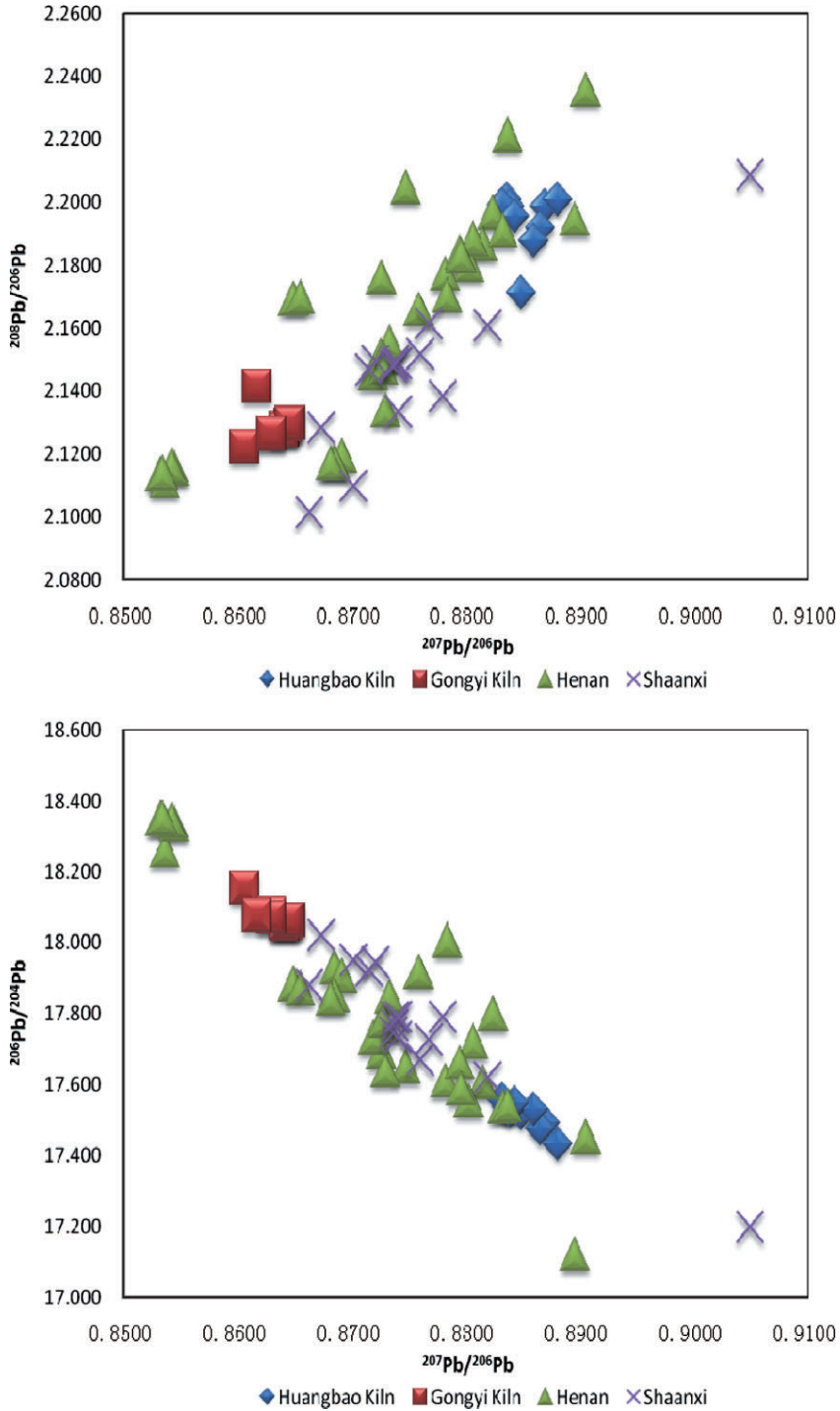


Figure 4 Lead isotope ratios for Tang Sancai pottery glazes from Huangbao kiln and Gongyi kiln, and a comparison with the data for lead ores from Henan Province and Shaanxi Province.

The fields of these lead isotope analysis (LIA) data for the two kilns are all very small, especially for the Gongyi kiln. The nine points from the Gongyi kiln almost overlap together in all the figures. This indicates that the lead isotope ratios for the glazes will be a useful fingerprint for the provenance of the pottery.

In order to identify the original ore source of these lead glazes, we compared our data with those for modern lead ore data published by various geological departments (see Fig. 4). But almost no LIA data of modern ores match the data from the two kilns, which may be due to the insufficiency of LIA data from these two provinces. Therefore, it still remains a puzzling fact that only few LIA data of lead ores have been published, despite the abundance of lead ores in both of the two provinces. Although the exact provenance of the lead in the glazes has not been located, it is worth noting that lead isotope analysis could be a very useful means to relate those Tang Sancai artefacts unearthed from archaeological sites to their producing kilns.

CONCLUSION

In conclusion, the ore source of the lead used at the Gongyi and Huangbao kilns can be easily distinguished according to the lead isotope ratios for the Tang Sancai glazes. Although the exact location of their sources remains to be explored, the data from the Huangbao kiln show that the lead in the glazes may come from North China, while the data from Gongyi kiln indicate that its lead bears the characteristics of South China. Furthermore, the results obtained for the Tang Sancai pottery indicate that the lead sources for glaze making of these two kilns were very consistent, which suggests that lead isotope analysis could be a helpful method to provenance the Tang Sancai artefacts to their producing kilns.

Finally, in order to get more information about the LIA characterizations and to build a database of lead isotope ratios for Tang Sancai glazes from kilns, we will analyse more potsherds from these two kilns in the future. In the meantime, samples from Liqianfang kiln will be also analysed, and we will also attempt to analyse some Tang Sancai artefacts of uncertain origin (such as those from archaeological sites of tombs, shipwrecks etc.) to discover their production centres.

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