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# Western technical traditions of pottery making in Tang Dynasty China: chemical evidence from the Liquanfang Kiln site, Xi'an city

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## A R T I C L E I N F O

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## 1. Introduction

Tang Sancai is a renowned low-fired glazed pottery produced in China during the Tang Dynasty (AD 618–907). The term 'sancai' refers to the three colours used in the glazes, namely green, vellow and white. However, the colours of the glazes used to decorate the wares of the Tang dynasty were not limited in number to these three, as blue and brown examples were also made (Chinese Ceramic Society, 1983). During the Tang period, a large number of Tang sancai ceramics were exported to and imported from Central Asia and the Near East. These multicoloured glazed ceramics were viewed as especially prestigious in the Islamic world, increasingly becoming a popular style in Islamic ceramic. With the development of bilateral trade between China and the Islamic world, deep interests were aroused among potters in both regions to imitate each other's styles of pottery (Ma, 2009). Since the 8th century, Islamic potters produced large numbers of lead-glazed ceramics, the resemblance of which is so similar to the authentic Tang sancai that sometimes it is hard to tell them apart just by their appearance. Lead glazes began to be used in the Warring-State, Parthian and Roman periods respectively, but the lack of archaeological

#### ABSTRACT

This study is based on the SEM-EDS and LA-ICP-AES analyses of a sample of twenty-nine Tang sancai sherds unearthed from the Liquanfang site, Xi'an city. The results indicate that ceramics with yellowish bodies are calcareous and those with red bodies were made of ferruginous clays. The use of calcareous clay in Tang sancai bodies is otherwise unknown in Chinese history, which suggests that the technique of Tang sancai making at this site might have been influenced by ceramic technology from the Near East or Central Asia. The paper therefore argues that the traditional approach of treating calcareous clay as the main characteristic of pottery made in the ancient Near East or Central Asia is not necessarily accurate. It is likely that some calcareous Tang sancai ceramics were made in the capital city of the Tang dynasty. © 2010 Elsevier Ltd. All rights reserved.

excavations has obscured the origins of and relationships between these early lead glazes (Kerr and Wood, 2004: 474–488; Kingery and Vandiver, 1986; Tite et al., 1998).

During the past two decades, extensive scientific studies based on the analysis of chemical compositions of porcelain bodies and glazes have been conducted in order to distinguish Tang sancai from its Central Asian and Near Eastern reproductions (Rawson et al., 1989; Wood et al., 2007, 2009; Mason and Tite, 1994). The most effective way to analyse the ceramic bodies nondestructively is through XRF. Until now, the analytical results show that most Tang sancai ceramics excavated in the Near East are made of kaolinitic clay, which is high in alumina (usually higher than 25% Al<sub>2</sub>O<sub>3</sub>), while ancient Islamic ceramics are mainly made of calcareous clay with high lime contents (usually higher than 10% CaO) (Kingery and Vandiver, 1986). Calcareous clay had been used in the Near East since the Neolithic period (Wood et al., 2007), but since there is a dearth of calcareous clays in China, they were seldom used in pottery making in ancient China (Kingery and Vandiver, 1986). Therefore, it is traditionally thought that lime and alumina can be regarded as the two major characteristic oxides that allow distinguishing authentic Chinese Tang sancai from its Islamic imitations.

So far, five kiln sites producing Tang sancai ceramics have been found in China. Among them, during the Tang dynasty period, the Gongxian kilns in Henan, and the Huangbao and Liquanfang kilns in



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Fig. 1. A map of mainland China, showing the five main Tang sancai kiln sites.

Shaanxi are the most important ones (see Fig. 1). All ceramics from the Gongxian and Huangbao kilns are made of white kaolinitic clay (Li, 1998), and archaeological and chemical research have ascertained the Gongxian kilns as the major source of exported Tang sancai ceramics (Rawson et al., 1989).

In 1999, the Liquanfang kiln site was discovered by a team from the Shaanxi Archaeological Institute in the western suburbs of Xi'an city (Shaanxi Provincial Institute of Archaeology, 2008). The Tang sancai excavated from this site bears different characteristics from those found at the Gongxian and Huangbao sites: the major colours of bodies found at this site are red and light yellow, which means that different raw materials may have been used to make ceramics in this kiln.

### 2. Samples

In this study, 29 Tang sancai sherds from the Liquanfang site (15 with red bodies and 14 with yellowish bodies) were analyzed using LA-ICP-AES to investigate their composition and raw materials. The glaze colours of the samples include green, brown and yellow. Fig. 2 shows a photograph of some samples. According to the archaeological reports, there is no stylistic difference between ceramics with a red body and those with a yellow one (Shaanxi Provincial Institute of Archaeology, 2008).

#### 3. Analytical methods

#### 3.1. SEM-EDS

Four samples were observed in cross sections using scanning electron microscopy (SEM) to study their microstructures. The compositions of their bodies, slips and glazes were semiquantitatively determined by energy dispersive spectrometry (EDS) combined with SEM. Analyses were performed using a FEI Quanta2000 operating at 15 kV, with the electron beam defocused to  $200-500 \ \mu m$  to average a large area.

#### 3.2. LA-ICP-AES

We analyzed quantitatively all the Liquanfang sherds for their bodies' chemical compositions using Laser Ablation Inductively



Fig. 2. Some Tang sancai sherds from the Liquanfang site, used as samples.

#### Table 1

The results of some major and minor elements for three repeat analyses of NIST 610 and Corning B glass standards, by LA-ICP-AES. Published values are from Pearce et al. (1997) and Brill (1999), for NIST 610 and Corning B, respectively.

	Na <sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	$Fe_2O_3$
NIST 610	13.03	0.09	2.23	71.56	0.04	11.92	0.09	0.09
	13.13	0.09	2.20	71.62	0.04	11.75	0.08	0.08
	13.14	0.09	2.19	71.65	0.04	11.82	0.08	0.08
Average	13.10	0.09	2.21	71.61	0.04	11.83	0.08	0.09
STD	0.06	0.00	0.02	0.04	0.00	0.08	0.00	0.01
RSD	0.48	4.00	0.99	0.06	0.00	0.72	2.96	7.02
Published	13.35	0.07	2.04	69.98	0.06	11.45	0.08	0.06
Corning B	16.10	1.06	4.64	62.58	0.97	9.08	0.12	0.40
	16.17	1.06	4.59	62.74	0.94	8.94	0.11	0.38
	16.16	1.06	4.59	62.70	0.93	9.00	0.11	0.39
Average	16.14	1.06	4.61	62.68	0.95	9.01	0.11	0.39
STD	0.04	0.00	0.03	0.08	0.02	0.07	0.00	0.01
RSD	0.24	0.05	0.57	0.13	2.28	0.74	3.48	1.76
Published	17.0	1.03	4.36	62.26	1.00	8.56	0.09	0.34

Coupled Plasma Atomic Emission Spectrometry (LA-ICP-AES). In this study, a LEEMAN-Prodigy ICP-AES with a NEW-WAVE laser ablation system was used to carry out the analyses. Eighteen elements were determined in the bodies, including Al, Fe, Mg, Ca, Na, K, Ti, Mn, Ba, Sr, Cu, Zn, Sr, Ce, La, Y, Yb, Zr. The data were quantitatively controlled by using standard reference materials, Corning B and NIST 610 glass standards. The analytical details and calibration method are presented elsewhere (Cui and Zhang, 2007), and the results are listed in Table 1. The SiO<sub>2</sub> data were calculated by subtracting the sum of all other elements in weight percent oxides from 100%. For the major and minor elements, most relative standard deviations are less than 1%, and for trace elements less than 5%. The data recoveries for major elements are commonly  $100 \pm 5\%$ , and for minor and trace elements commonly 100  $\pm$  20%. Table 1 gives results of some major and minor elements for three repeat analyses of NIST 610 and Corning B glass standards.

Because these reference standards are all for glass, we tested the applicability of our approach by preparing two samples of modern ceramic sherds by acid-dissolved methods. We then determined their compositions by means of ICP-AES, as well as by LA-ICP-AES. The results are found to be comparable within  $2\sigma$  relative error (see Table 2).

#### 4. Results

#### 4.1. SEM-EDS

Four samples were analyzed using SEM-EDS. Samples X29 and X32 have yellowish bodies, while X02 and X15 have red bodies. The glaze colours of X29/X02 are green and those of X32/X15 are yellow/brown. Back-Scattered Electron (BSE) images of X02 and X32 are shown in Fig. 3(a–d). They illustrate that the microstructures of all samples are constituted by three parts: glaze, slip and body. Table 3 shows the major element contents for these three parts of each sample, as determined by SEM-EDS.

#### 4.1.1. Glazes

The SEM-EDS results show that all samples are low-fired leadglazed ceramics. The PbO contents are all about 45%, and the contents of CaO in the glazes with yellowish bodies is higher than in the glazes with red ones. Two sherds with green glazes have more than 1% copper oxide. The brown ones have no detectable copper contents, but their iron oxide content is higher than 3%. The results reaffirm what has been previously observed by other scholars (Rawson et al., 1989; Wood et al., 2007; Li, 1998), i.e. that the colouring element of the brown glazes is iron, while the colorant of green glazes is copper.

#### Table 2

The comparative results for ICP-AES and LA-ICP-AES, of two modern ceramics.

Sample number	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	K <sub>2</sub> 0	CaO	Ва	Sr	Mn	Ti
MC1*	14.78	1.75	0.19	0.42	2.80	0.13	392	23	106	5204
MC1^	15.06	1.70	0.20	0.47	2.95	0.12	383	27	95	5581
MC2*	14.05	1.87	0.23	0.37	1.47	0.20	309	70	110	7820
MC2^	14.25	1.90	0.25	0.40	1.46	0.15	297	73	122	8047

\*Acid-solution ICP-AES

^LA-ICP-AES.

### 4.1.2. White slips

In all four ceramics, there is a layer of white slip between the body and the glaze. The compositions determined by SEM-EDS show that the slip has higher aluminium content than both the body and the glaze, which indicates that the main ingredient of the slip is kaolinite. White slips on the bodies were widely used for Tang sancai making in the Gongxian kilns, which is probably the main source of Chinese sancai in the Near East. According to the former study, the Liquanfang kilns might have a strong relationships with Gongxian kilns. For instance, several sancai sherds of white bodies were found in the Liquanfang kilns. The chemical analysis suggest that these white body sherds have the same source as those found in the Gongxian kilns (Lei et al., 2007).

In the Islamic world, white slips were also widely used on the body of ceramics. According to the recent report by Wood et al. (2009), Islamic ceramics unearthed from Samarra in Iraq were mostly coated with a white slip under a lead glaze. Using kaolinite to form a slip layer between the translucent calcareous glazes and the bodies was a common decorative method for coarse high-fired ceramics in the northern part of ancient China. However, Islamic sancai ceramics used very quartz-rich, rather than clay-rich, white slips with their lead-glazed wares.

#### 4.1.3. Bodies

The most important finding of the SEM-EDS analysis regards the use of different raw materials for the differently coloured bodies from the Liquanfang kiln site. The raw materials used for producing the red bodies are ferruginous clays with high iron contents, and those used for the yellowish bodies are calcareous with high calcium contents. The discovery of calcareous ceramics among Tang dynasty pottery products is a noteworthy phenomenon. Generally speaking, the use of calcareous clay for pottery making was a craft tradition in the ancient Near East, while in ancient China the main types of clay for pottery production include kaolinite, china stone and ferruginous clay with high iron content. Up to now, ceramics with calcareous bodies were only found in Northwest China during the Neolithic periods, especial in the Gansu and Qinghai regions. These ceramics were probably made of loess which are rich in carbonates in the Loess Plateau. However, after the Neolithic period, no archaeological evidence of Chinese ceramic bodies made of calcareous clay has been reported. As Sundius (1959) pointed out, 'it is noteworthy that this knowledge seems to have been forgotten after the Yang Shao epoch.' In ancient Chinese ceramic technology, calcareous material was usually being used only for the glaze. This is the first time that a calcareous ceramic was found in the glazed ceramics production of ancient China.

#### 4.2. LA-ICP-AES

Twenty-nine bodies of Tang sancai sherds from the Liquanfang site were chemically analyzed using LA-ICP-AES. The results are shown in Table 4. Table 5 shows the comparison of the means of all



Fig. 3. The BSE images of the sherd sections.

elements present in these two kinds of ceramics, which indicates that the contents of most oxides in these two types of pottery are significantly different.

Fig. 4 is a plot of the concentrations of CaO vs.  $Al_2O_3$ , and Fig. 5 one of the concentrations of CaO vs. Sr. These bivariate plots indicate clear differences between the two body types. Fig. 4 shows some variation in the alumina content and a relatively stable lime content in the red bodies, while there is a negative correlation between CaO and  $Al_2O_3$  in the yellowish bodies. This suggests that

# Table 3 Chemical results determined by SEM-EDS.

				·						
	Cu0	Na <sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	PbO	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	$Fe_2O_3$
X29										
Glaze	1.1	0.7	0.6	7.6	36.0	46.5	1.9	2.9		2.7
Slip		1.1	1.6	19.4	45.1	17.4	4.3	4.5	1.0	4.6
Body		1.3	4.6	15.2	53.7		3.1	11.8	0.7	9.1
X32										
Glaze		0.5		11.0	32.0	48.6	0.9	3.7		3.2
Slip		0.9	1.4	22.9	46.8	20.4	2.8	2.8		2.1
Body		1.9	4.8	15.5	53.7		2.9	12.2	0.7	8.3
VOD										
X02					<b>.</b>					
Glaze		0.6	0.9	8.4	34.5	47.1	1.3	1.9		5.4
Slip		1.2	1.3	21.3	44.7	23.7	2.9	1.1		3.9
Body		1.9	2.6	17.9	58.4		3.7	2.1	1.1	12.3
V1E										
A15	2.0	0.0	~ .	44.0	25.0		4.0	4.0		~ ~
Glaze	2.8	0.6	0.4	11.0	35.8	44.2	1.2	1.3		2.3
Slip		1.1	1.2	25.8	52.7	9.5	3.0	1.2	1.6	4.1
Body		1.5	2.7	17.9	59.9		4.0	2.5	1.0	10.5

the reduction of Al<sub>2</sub>O<sub>3</sub> contents in the yellowish bodies occurred due to the increase of CaO contents. In Fig. 5, the data points of the red bodies almost cluster together, while the data for the yellow ones show some positive correlation. In the red bodies, the strontium content is relatively consistent around 250 ppm, while in the yellowish bodies strontium reaches from 500 to 900 ppm. There is a close geochemical relationship between strontium and calcium, and the increase of strontium contents in the yellowish bodies is probably due to the introduction of the calcium-rich component. The situation is similar for MnO vs. CaO (Fig. 6). In the red bodies, the manganese oxide varies from c. 700-1100 ppm, while in the yellow ones manganese oxide is mostly present at about 1200-1500 ppm. Significantly, MnO and Sr have a positive correlation suggesting their common origin in the raw material (Fig. 7). The iron oxide content, in contrast, is lower in the yellowish bodies than in the red ones, suggesting that manganese is not correlated with iron. It can be concluded that the manganese and strontium in the yellowish bodies were introduced together with the calcium oxide.

The results indicate that the two body types from the Liquanfang site were made from different but similar raw materials. The range of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios is from 3.09 to 3.69 for red bodies, and from 3.43 to 3.81 for yellowish bodies. The mean value is 3.27 for red body and 3.66 for light yellow body ceramic, only a little higher than that of the red one. All bodies have Fe<sub>2</sub>O<sub>3</sub> contents higher than 5%, with the red ones having on average 7.6 wt% Fe<sub>2</sub>O<sub>3</sub> and the yellow ones on average 6.2 wt% Fe<sub>2</sub>O<sub>3</sub>. Judging from the relatively similar Si:Al ratios, these two bodies may be based on a similar type of clay.

Та	ble	4				
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LA-ICP-AES results of the bodies of Tang sancai sherds from t	the Liquanfang site.
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Sample ID	Na <sub>2</sub> O	MgO	CaO	$Fe_2O_3$	$Al_2O_3$	SiO <sub>2</sub>	K <sub>2</sub> O	TiO <sub>2</sub>	BaO	MnO	Cu	Zn	Sr	Y	Ce	Yb	Zr	Gd	Sc
Red body																			
X02	1.99	2.68	2.93	6.59	18.12	63.21	3.44	0.77	0.099	712	68	113	262	55	107	6	120	41	17
X08	1.85	2.89	3.02	7.30	18.33	62.01	3.40	0.90	0.101	773	68	116	251	45	108	5	158	41	18
X17	1.77	3.05	3.11	7.48	18.92	60.59	3.89	0.91	0.094	794	74	135	228	45	107	5	166	44	19
X74	1.60	3.15	3.13	8.52	18.61	60.07	3.55	0.95	0.114	905	327	264	250	45	141	4	134	47	18
X19	1.97	3.13	3.14	7.95	19.15	59.70	3.63	1.03	0.096	1124	70	120	263	52	161	6	321	45	19
X79	1.74	3.10	3.20	8.65	19.59	58.91	3.49	0.99	0.124	836	102	163	282	46	184	5	108	49	19
X46	1.80	3.03	3.28	7.16	18.80	61.09	3.46	1.13	0.100	816	59	134	247	95	140	8	199	53	17
X04	2.07	2.96	3.32	6.94	18.77	61.10	3.72	0.82	0.099	792	89	113	251	58	88	6	126	41	17
X78	1.64	3.26	3.42	8.53	19.12	59.62	3.15	0.93	0.098	963	72	162	242	58	131	5	220	47	18
X38	1.89	2.67	3.46	7.28	18.03	62.03	3.55	0.76	0.137	666	99	129	272	34	98	4	178	39	14
X15	1.92	2.71	3.55	6.55	17.34	63.33	3.53	0.79	0.090	687	61	98	282	33	80	4	100	35	15
X16	1.84	3.10	3.64	7.69	19.25	59.44	3.74	0.95	0.102	1026	71	118	259	49	107	5	141	44	18
X75	1.77	3.07	3.73	7.77	18.47	60.51	3.45	0.91	0.120	792	59	130	259	38	167	4	124	46	17
X80	1.83	3.05	3.81	7.57	18.28	60.89	3.30	0.90	0.133	789	58	214	275	50	128	5	149	46	16
X77	1.62	3.20	4.18	8.04	18.69	59.67	3.33	0.89	0.128	1094	210	109	277	49	113	5	132	45	17
Light yellow	/ body																		
X50	2.26	4.08	11.42	5.37	15.34	57.42	3.06	0.72	0.101	1076	146	105	538	46	98	5	132	35	13
X29	1.60	4.82	11.70	6.87	15.11	55.18	3.31	0.93	0.121	1715	105	130	660	33	70	3	170	37	14
X53	1.95	4.48	12.02	6.30	15.55	55.35	3.12	0.79	0.106	1462	74	111	644	38	121	4	102	37	14
X56	2.04	4.18	12.31	5.91	15.23	56.37	2.88	0.76	0.091	1191	106	121	479	45	118	5	138	37	13
X62	1.97	4.17	13.32	5.90	14.93	55.80	2.80	0.72	0.103	1318	77	87	759	39	99	4	112	35	14
X61	1.98	4.77	14.10	6.13	14.50	54.89	2.54	0.73	0.089	1356	52	132	841	39	139	4	207	39	13
X32	1.61	4.63	14.42	6.95	15.04	53.68	2.32	0.88	0.125	1498	74	172	896	41	135	4	164	42	15
X47	2.04	4.92	14.47	5.71	15.08	53.00	3.61	0.68	0.121	1346	64	102	876	40	84	4	186	36	14
X58	1.97	5.68	14.77	6.47	14.78	52.35	2.64	0.78	0.107	1356	79	115	765	37	141	4	221	39	14
X66	1.96	5.37	15.01	5.92	14.28	53.57	2.74	0.76	0.103	1313	70	99	769	143	113	15	158	42	13
X-II	1.90	4.53	15.07	6.00	14.85	53.58	2.61	0.90	0.095	1319	76	114	613	43	78	5	230	35	13
X67	2.11	4.82	15.12	6.17	14.25	53.96	2.44	0.72	0.101	1263	74	98	766	33	127	3	129	36	13
X64	1.93	5.52	15.70	5.85	13.95	53.17	2.75	0.79	0.095	1239	51	89	818	32	138	3	84	39	13
X63	1.82	5.25	18.39	6.84	14.38	49.36	2.64	0.81	0.116	1431	74	125	909	37	161	3	113	41	15

(The data from  $Na_2O$  to BaO are in wt%, others in ppm).

One of the authors and his colleagues (Lei et al., 2005) analyzed the trace elements of the same samples by means of INAA. The results indicate that the trace element patterns of the Liquanfang ceramics are close to each other, but different from the sherds of other kiln sites. Although there are some distinctions between red bodies and yellow ones, they are clustered together in the statistical plot. Compared to the red bodies, the results for the yellow ones show that they were all diluted by a similar amount, which means that some material might have been added into the yellowish bodies that did not contain any of the 21 elements analyzed. Thus, these two bodies may have been made from the same clay, while their compositional differences may be due to the addition of some calcareous material to the yellow-coloured ceramics.

### 5. Discussion

The Tang sancai ceramics from the Liquanfang sancai site show two characteristics. First, their glazes are lead-bearing low-fired

#### Table 5

Summary of the chemical data (means, standard deviations and Si/Al ratios) for the two coloured groups.

Oxides	Red ( <i>n</i> = 15)		Light yellow ( $n = 14$ )				
	Mean (wt%)	Std. Dev. (wt%)	Mean (wt%)	Std. Dev.			
Na <sub>2</sub> O	1.82	0.14	1.94	0.17			
MgO	3.01	0.19	4.80	0.51			
CaO	3.40	0.34	14.13	1.87			
Fe <sub>2</sub> O <sub>3</sub>	7.60	0.66	6.17	0.47			
$Al_2O_3$	18.63	0.57	14.80	0.47			
SiO <sub>2</sub>	60.81	1.35	54.12	1.98			
K <sub>2</sub> O	3.51	0.19	2.82	0.35			
TiO <sub>2</sub>	0.91	0.10	0.78	0.08			
BaO	0.11	0.02	0.11	0.01			
MnO	0.09	0.02	0.14	0.02			
Si/Al (in oxides)	3.27	0.17	3.66	0.12			

glazes, which are common for sancai productions, including western imitations of Tang sancai wares (Wood et al., 2007, 2009).

Second, the analytical results by SEM-EDS and LA-ICP-AES show that two types of bodies were used at the Liquanfang kiln site to make Tang sancai ceramics. One was calcareous and firing to a light yellow colour, and the other was ferruginous clay with high iron content, firing red. The trace element patterns (Lei et al., 2005) and the proportions of several important components such as alumina, potash, and iron oxide indicate that they were made from the same type of clay, but with the yellow-firing bodies diluted by the addition of a relatively clean component rich in lime and magnesia, and trace elements such as manganese and strontium.

Xi'an city is located in the Loess Plateau, and the loess contains a high CaO contents in its composition, usually from  $5\% \sim 30\%$ . Thus loess could be the major choice of material for the pottery making in Liquanfang kiln, especial for the yellowish bodies. But







Fig. 5. A bivariate plot of CaO vs. Sr content of the bodies.

the loess has higher silica content than the common clay, as it is a kind of silt-clay. The average SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the Shaanxi loess is about 4.6 (Liu, 1965; also Gallet et al., 1996), which is much higher than the results of all Liquanfang bodies. This makes it unlikely that the clay used for the ceramic bodies in Liquanfang was loess. As Zhou et al. (1964) point out, 'in addition to several exceptions, during the Neolithic period, most materials used to make pottery are red, black clays and sedimentary soils, not loess.' In fact, loess was used as a ceramic body material only in the Gansu and Qinghai regions in China during the Neolithic period. In the Xi'an area, no archaeological evidence for loess-based ceramics has been found up to now. The clay used for the red bodies in Liquanfang kiln is a red ferruginous clay. Ferruginous clay is widely available around Xi'an City, and large numbers of ceramics made from these clays were dated from the Neolithic period to the Iron Age (Chinese Ceramic Society, 1983). Thus, the raw material used for making the red bodies is likely to come from the Xi'an local area, while in our opinion there is less likelihood for the yellowish-firing ceramics to be made from naturally occurring clay/loess.

#### 5.1. Calcareous clay in Tang sancai production

The use of calcareous clay in Tang sancai production in China is particularly noteworthy. Rawson et al. (1989) distinguished between imported Tang sancai ceramics and their Near Eastern imitations by means of chemical analysis, pointing out that the difference in body types between Tang sancai and Near Eastern ceramics is the most useful tool to separate and identify them. Near



Fig. 6. A bivariate plot of CaO vs. MnO content of the bodies.



Fig. 7. A bivariate plot of Mn vs. Sr content of the bodies.

Eastern ceramics usually have higher contents of CaO. Calcareous clay has been used in the production of ceramics since 6500 BC (Kingery and Vandiver, 1986), and a high CaO contents in the bodies characterise ceramics made in the Near East or Central Asia. In contrast, in ancient China, the most widely used types of clay for making ceramics are kaolinitic or illitic clays, china stone and semirefractory red clays, which all have lower CaO contents (for comparison, see the summary of chemical compositions of ancient Chinese ceramics by Li, 1998). Thus, the finding of calcareous clay used for making Tang sancai ceramics represents a unique and potentially important discovery.

In general, the Tang sancai wares exported to the West were made of kaolinitic clays with high alumina contents. Before the excavation of the Liquanfang kiln site, most scholars focused on the Tang sancai with white hard bodies that were fired at a higher temperature than the lead-glazed Near Eastern wares. In addition, due to their similar appearance, some yellowish bodies could be easily confused with white ones unless chemical analysis was carried out. As a result, up to now, the calcareous clay used in the making of Tang sancai has not attracted enough attention. The pottery we analyzed was excavated from the kiln site, which points to its local origin, and it is unlikely that the raw materials used for making it were shipped from as far away as Central Asia or the Near East.

As mentioned above, the clay used to make yellowish bodies is very similar to the one used for the red ones, and differs from it primarily in its elevated lime content. This increased lime content can be due to several possible reasons, including the exploitation of naturally lime-rich clays, the geological mixing of lime-rich or slightly dolomitic material to the original red clay, and intentional addition of such material by the potters.

Xi'an city is located in the Loess Plateau, and there are numerous loess sources around the city. This loess is a windblown deposit rich in calcium carbonate, sand and other components from weathered rocks (Liu, 1985, pp. 4–8). The lime content of the loess in Shaanxi province varies mostly from 5% to 30% (Liu, 1965). Thus, the lime content of the yellowish bodies is consistent with the use of such loess. However, as mentioned above the clay used to make the red ceramics is clearly not loess, and the yellowish ceramic was made from a clay very similar to the red one apart for its lime content. Therefore, we do not believe that the yellowish bodies were made from loess. Hitherto, no geochemical evidence indicates that there is a semi-refractory red clay deposit with high CaO content in China. However, a so-far unknown natural process to enhance the CaO contents in the clay used to produce the yellowish bodies can not be excluded completely, such as the dissolution of calcium

carbonate from loess layers and its re-deposition in some deposits of red clay.

Alternatively, the high lime content in the yellowish bodies could be caused by the intentional mixing of some calcareous material to the local red clay, which would suggest that the CaO content was presumably deliberately increased by the potters. This may have been done because the potter was familiar with the behaviour of calcareous clay, and mixed some calcium-bearing additions to the local red clay to obtain an analogous material. This would have been beneficial particularly for the ceramics with lightcoloured transparent glazes, since calcareous clays fire to a pale yellow ceramic even if they have nearly the same content of iron oxide than ferruginous clays that would fire a dark red. Molera et al. (1998) discuss the mechanism of this effect, and it is likely that the ancient potters were aware of the phenomenon, even if they did not know the underlying chemical reasons.

The sections studied so far do not show traditional temper inclusions such as limestone particles or crushed shells, common in lime-tempered western ceramics (see Fig. 3a-d). Instead, any additive appears to have been extremely fine-grained. We have some indications regarding the nature of this material from the chemical analyses of the bodies as presented here, and in Lei et al. (2005). The concentrations of most oxides and nearly all trace elements in the yellow ceramics is lower by an average of 20% of their value in the red ceramics, while lime is increased from 3.4 wt% in the red ceramics to an average of 14.1 wt% in the yellow ceramics. A few other components are also enriched in the vellowish bodies: magnesia is 4.8 wt%, compared to 3.0 wt% in the red ceramic, manganese oxide is up from 0.09 wt% to 0.14 wt%, and strontium is up from around 250 ppm in the red ceramics to around 800 ppm in the yellow ones (see Fig. 5). Silica is lower in the yellow ceramics than in the red ones, but only by about 10% of its original value (c. 54 wt% in the yellowish bodies, compared to 61 wt% in the red ones), thus less diluted than the other oxides and trace elements. This had been noted earlier, in the discussion of the ratio of silica to alumina in the two groups. From this we can conclude that the added material consisted primarily of lime, but also contained magnesia, some silica, soda, manganese oxide, and strontium.

One possibility is that the added lime-rich material was washed wood ash, a raw material commonly used in Chinese glaze preparation and therefore familiar to the Tang sancai potters. Wood ash compositions vary widely between different tree species and pedological environments; also, not many wood ash analyses are published. However, Chen et al. (1986: 237, Table 3) provide the composition of washed wood ash from Fujian province, reporting an average composition of c. 11 wt% silica, 2.9 wt% alumina, 40.5 wt% lime, 5.7 wt% magnesia, and 2.8 wt% manganese oxide, in addition to minor concentrations of potash and phosphorous oxide (around 2 wt% each), and a loss on ignition of 32 wt%. Most wood ashes are also rich in alkali oxides; however, the washing of the ash selectively removes the water-soluble alkali components of the ash (Wood, 2009; see also Rehren, 2008), resulting in a lime-dominated and very fine-grained residual material that can be easily mixed into any clay without leaving visible temper inclusions. In the context of European glassmaking and the question of raw materials there, it is known that the manganese and phosphate content of wood ash varies widely. Apart from the components listed, wood ash is a rather pure material, and will not contain any significant concentrations of the trace elements measured by Lei et al. (2005), explaining the constant dilution factor observed in our samples for all trace elements determined.

Alternatively, as pointed out by one of the reviewers of this paper, the additive may have been a very fine-grained burnt lime. This would solve one particular problem associated with the suggested wood ash addition, namely the high cost of procuring sufficient wood ash to be used as a substantial additive in bulk ceramic production (cf. Wood, 2009). Limestone is geochemically relatively variable, and apart from the common dolomitic component responsible for an increased magnesia content can also contain small but significant amounts of strontium or manganese. Thus, the chemical pattern observed between the two groups of Tang sancai is equivocal in this respect. Further research, including strontium isotope analysis is necessary to further reduce the number of possible interpretations.

#### 5.2. Liquanfeng as a possible source for exported sancai ceramics

According to historical records, the ancient name for the kiln site was the Liquan Block of Chang'an city (Shaanxi Provincial Institute of Archaeology, 2008). When the Persian government was defeated by the Arab Empire and forced into exile to China in AD 677, the Tang Government built a Persian Temple as the residence for the Persian emperor-in-exile in the capital city of Chang'an. The community grew as more Persian immigrants came, and it is possible that among them, some western potters settled down in Chang'an city and started making Tang sancai with local raw materials, or influenced the local Chinese potters in this direction. The discovery of a large number of fired and unfired sancai pottery figurines in the shape of 'foreigners' at the kiln site indicates that the potters working here were familiar with foreign people. Furthermore, glass cullet was also unearthed from the kiln site, indicating an imported Near Eastern technology. The XRF results for these glass fragments show that they are mainly soda-lime-silica glass, the typical Western traditional glass. This evidence directly associates the Liquanfang kiln with a Near Eastern influence (Jiang, 2007). It can thus be reasonably hypothesized that the production of Tang sancai with light yellow bodies may have been inspired by potters emigrated from Western or Central Asia who had brought with them their traditional technical styles and recipes for ceramic bodies and glaze compositions.

The discovery of calcareous sancai ceramics made in China also suggests that it is quite possible that some Near Eastern or central Asia sancai finds made of calcareous clay were not necessarily made locally in that area as imitation wares, but may have been imported from China. In view of the evidence for the production of calcareous ceramic with lead glazes in the capital of Tang-period China, it is no longer possible to differentiate between authentic Chinese sancai and its Western imitations by their CaO contents alone. The possibility that some ceramics with high lime contents could originate from the Liquanfang kiln site should also be taken into consideration, requiring a more refined understanding of the chemical characteristics of the different sancai-producing sites and regions.

#### 6. Conclusions

The main sancai products made at the Liquanfang kiln site are very different from the common sancai ceramics with white bodies and a high alumina content. They can be categorized into two types: one has a light yellow calcareous body and the other a red body made of ferruginous clay. The chemical composition of 29 analyzed samples suggests that both types were made using the same or a very similar clay, but with the addition of about twenty percent by weight of a lime-rich fine-grained substance, such as washed wood ash or very fine burnt limestone. This addition resulted in a clay paste which when fired formed the yellowish bodies. A natural or geological mixing of lime to a ferruginous clay can not be excluded, but appears less likely at our current knowledge of the geology around Xi'an. Preliminary SEM-EDS analyses of four cross sections show the use of an alumina-rich slip between the ceramic body and the glaze, and the use of a lead-rich recipe for the glaze production.

\This study revises the old concept of regarding a calcareous composition as the main characteristic of pottery made in the ancient Near East and Central Asia. This study has shown that some Tang sancai wares were also made from calcareous ceramics in the capital city of the Tang dynasty. Thus, it is possible that some calcareous sancai-like ceramics dating to the 8th century AD, wherever they were found, were made at the Liquanfang site in Chang'an city.

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#### References

- Brill, R.H., 1999. Chemical Analyses of Early Glass. Vol. 2, The Tables. Corning Museum of Glass, Corning, New York.
- Chen, X., Huang, R., Jiang, L., Yu, L., 1986. The structural nature of Jianyang hare's fur Temmoku imitations. In: Shanghai Institute of Ceramics (Ed.), Scientific and Technological Insights on Ancient Chinese Pottery and Porcelain. Science Press, Beijing, pp. 236–240 (in Chinese).
- Chinese Ceramic Society, 1983. History of Chinese Ceramics. Cultural Relic Publishing House, Beijing (in Chinese).
- Cui, J.F., Zhang, H., 2007. LA-ICP-AES analysis of some pottery of Longshan and Erlitou cultures. In: School of Archaeology and Museology in Peking University, Henan Provincial Institute of Cultural Relics and Archaeology (Eds.), Archaeological Discovery and Research at the Wangchenggang Site in Dengfeng (2002–2005). Elephant Press, Zhengzhou, pp. 645–656 (in Chinese).
- Gallet, S., Jahn, B., Torii, M., 1996. Geochemical characterization of the Luochuan loesspaleosol sequence, China, and paleoclimatic implications. Chemical Geology 133, 67–88.
- Jiang, J., 2007. Glass ingots excavated from the Liquanfang tri-color Kiln site of the Tang dynasty in Xi'an city. In: Gan, F.X. (Ed.), Study on Ancient Glass along the Silk Road. Fudan Press, Shanghai, pp. 176–180 (in Chinese).
- Kerr, R., Wood, N., 2004. Science and Civilization in China. In: Chemistry and Chemical Technology, Part 12, Ceramic Technology, vol. 5. Cambridge University Press, Cambridge, pp. 474–488.

- Kingery, D., Vandiver, P., 1986. Ceramic Masterpieces: Art, Structure, and Technology. The Free Press, New York.
- Lei, Y., Feng, S., Feng, X., Fan, D., Xu, Q., Sha, Y., Cheng, L., Chai, Z., Jiang, J., Zhou, Z., Zhang, S., Liao, Y., 2005. Study on the compositional differences of Tang sancai from different kilns by INAA. Journal of Archaeological Science 32, 183–191.
- Lei, Y., Feng, S., Feng, X., Chai, Z., 2007. A provenance study of Tang sancai from Chinese tombs and relics by INAA. Archaeometry 49 (3), 483–494.
- Li, J.Z., 1998. A History of Science and Technology in China, Volume of Ancient Pottery and Ceramic. Scientific Press, Beijing (in Chinese).
- Liu, T.S., 1965. Chinese Loess Deposit. Science Press, Beijing, pp. 202–227 (in Chinese).
- Liu, T.S., 1985. Loess and the Environment. Science Press, Beijing, pp. 4–8 (in Chinese).
- Ma, W.K., 2009. The influence of Chinese porcelain on the Islamic pottery of the earlier Abbasid dynasty. In: Luo, H.J., Zheng, X.M. (Eds.), Conference Proceedings of 2009 International Symposium on Ancient Ceramics. Shanghai Scientific and Technological Literature Publishing House, Shanghai, pp. 570–576 (in Chinese).
- Mason, R.B., Tite, M.S., 1994. Beginning rouse, sharping, pp. 576 576 (in Chinese), Archaeometry 36 (1), 77–91.
- Molera, J., Pradell, T., Vendrell-Saz, M., 1998. The colours of Ca-rich ceramic pastes: origin and characterization. Applied Clay Science 13 (3), 187–202.
- Pearce, N., Perkins, W., Westgate, J., et al., 1997. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. The Journal of Geostandards and Geoanalysis 21 (6), 115–144.
- Rawson, J., Tite, M.S., Hughes, M.J., 1989. The export of Tang Sancai wares: some recent research. In: Transactions of the Oriental Ceramic Society: 1987–1988, vol. 52. Oriental Ceramic Society, London, pp. 39–61.
- Rehren, T.h., 2008. A review of factors affecting the composition of early Egyptian glasses and faience: alkali and alkali earth oxides. Journal of Archaeological Science 35 (5), 1345–1354.
- Shaanxi Provincial Institute of Archaeology, 2008. The Kiln Site of Tricolor-Glazed Pottery at Liquanfang in Chang'an Capital City of Tang Dynasty. Cultural Relics Publishing House, Beijing (in Chinese).
- Sundius, N., 1959. Some aspects of the technical development in the manufacture of the Chinese pottery wares of pre-Ming age. Bulletin of the Museum of Far Eastern Art 33, Stockholm. 107–123.
- Tite, M., Freestone, I., Mason, R., Molera, T., Vendrell-Saz, M., Wood, N., 1998. Lead glazes in Antiquity – methods of production and reasons for use. Archaeometry 40, 241–260.
- Wood, N., 2009. Some implications of the use of wood ash in Chinese stoneware glazes of the 9th–12th centuries. In: Shortland, A., Freestone, I., Rehren, T.h. (Eds.), From Mine to Microscope: Advances in the Study of Ancient Technology. Oxbow Books, Oxford, pp. 51–61.
- Wood, N., Doherty, C., Owen, M.R., 2009. A technological study of Iraqi copies of Chinese Changsha and Chinese sancai wares found at Samarra. In: Luo, H.J., Zheng, X.M. (Eds.), Conference Proceedings of 2009 International Symposium on Ancient Ceramics. Shanghai Scientific and Technological Literature Publishing House, Shanghai, pp. 154–180.
- Wood, N., Tite, M.S., Doherty, C., Gilmour, B., 2007. A technological examination of 9–10th century AD Abbasid blue-and-white ware from Iraq, and its comparison with 8th century AD Chinese blue-and-white sancai ware. Archaeometry 49 (4), 665–684.
- Zhou, R., Zhang, F.K., Zheng, Y.F., 1964. Scientific summary of the ceramic technology in Yellow River drain area from Neolithic to Shang-Zhou age. Acta Archaeological Sinica 64 (1).