

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Journal of Archaeological Science

journal homepage: <http://www.elsevier.com/locate/jas>The exploration of Sr isotopic analysis applied to Chinese glazes: part one[☆]Hongjiao Ma^a, Julian Henderson^{a, *}, Jane Evans^b^a Department of Archaeology, University of Nottingham, University Park, Nottingham NG7 2RD, UK^b NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

ARTICLE INFO

Article history:

Received 4 March 2013

Received in revised form

26 July 2013

Accepted 12 August 2013

Keywords:

Chinese glaze

Raw materials

Strontium isotopes

TIMS

ABSTRACT

Ash glaze and limestone glaze are two major glaze types in southern Chinese ceramic technology. In this study strontium isotope compositions were determined in ash glaze samples from the Yue kiln dated to between the 10th and 12th centuries AD, limestone glaze samples from Jingdezhen dated to between the 15th and 18th centuries AD and ceramic raw materials from Jingdezhen. The Sr isotopic characteristics of limestone glaze and ash glaze are completely different. The Sr isotope characteristics of limestone glaze is characterised by low Sr concentrations, large $^{87}\text{Sr}/^{86}\text{Sr}$ variation, and a two component mixing line. On the other hand the strontium isotope characteristic of ash glaze samples is characterised by a consistent $^{87}\text{Sr}/^{86}\text{Sr}$ signature and high Sr concentrations with a large variation. The different Sr isotope compositions for the two types of glazes are a reflection of the various raw materials involved in making them. The Sr isotopic composition has been altered by the refinement process that the raw material was subjected to. It was found that the mineralogical changes caused by the alteration are reflected in the Sr isotope results. The potential of Sr isotopic analysis of Chinese glazes is evaluated according to the results produced by this, the first such study.

© 2013 The Authors. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Glaze is a functional and decorative layer of glass that seals the surface of ceramics. The high quality glaze of Chinese ceramics was one of the key features that made it so popular around the world and led to it becoming part of a global trade system. To understand the ancient production processes that created this substance, many scientific analytical investigations have been carried out. In this study Sr isotope analysis is used to investigate Chinese high fired glazes, from the time when this technology was at its pinnacle of development in order to understand the technology of the raw materials used and their provenance. Sr isotopic analysis is a long established technique in geology, but only in the last decade has it been applied to the investigation of ancient glass. The present study serves the purpose of exploring this technique's applicability in the context of Chinese high fired glaze.

Like many other things, the development of high fired ceramics in China was divided into a northern zone and a southern zone by

the *Qin'ling* Mountain range. The South led the way most of the time, due to easier accessibility of refractory ceramic raw materials in the southern geology. Two types of high fired glaze were most important in the history of southern Chinese ceramics: limestone glaze and ash glaze.¹ Ash glaze was the dominant high fired ceramic coating from 3rd century AD until 14th century AD, and then limestone glaze became the commonest from the mid-14th century AD onwards (Kerr and Wood, 2004). Limestone glaze and ash glaze are both thin layers of opaque to translucent glass, and porcelain stone (weathered acid igneous rock) was the common raw material used to make both glaze types. The difference in the two types of glaze was the flux component. Botanic ash was the flux used in ash glaze, and glaze ash (a mixture of a major component of calcium carbonate powder and botanic ash) in limestone glaze. In the present study, limestone glaze from Jingdezhen, ash glaze from the Yue kiln and porcelain raw materials from Jingdezhen were chosen as isotopic samples to address the research questions.

[☆] This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

* Corresponding author. Tel.: +44 115 951 4840; fax: +44 (0)115 951 4812.

E-mail address: julian.henderson@nottingham.ac.uk (J. Henderson).

¹ Limestone glaze and ash glaze are frequently described as porcelain glaze and lime glaze. However the present research context to prevent the term 'lime' and 'porcelain' from causing confusions, the fluxes involved for making these glazes—limestone and botanic ash are used.

2. Background to Sr isotope analysis on vitreous materials

The pioneering work of applying Sr isotopic analysis to glass was done by Wedepohl and Baumann (2000). In this work they demonstrated how the $^{87}\text{Sr}/^{86}\text{Sr}$ signature and the elemental concentration of Sr should be interpreted in terms of raw materials used for making the glass. They stated that the bulk of the Sr content in glass derived from the lime-bearing portion of the raw material. They also stated that the Sr isotopic composition of imperial period Roman natron glass, which is typical of 350–500 ppm Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ signature of around that of modern seawater (0.70918), can be attributed to the use of marine molluscan in beach sand; limestone would be expected to introduce a much lower Sr concentration in the glass of c. 100–200 ppm. Wedepohl and Baumann's pioneering work is more scientific speculation than a final statement because they only provided the Sr compositions of 5 samples for one type of glass to back up their theory. But their speculation caught the attention of scientists of ancient glass, and a number of studies investigating strontium isotopes in ancient glass soon followed.

Freestone et al. (2003) studied the Sr isotopic signatures of three types of glass from four sites, for which the source of raw materials was basically known from previous compositional researches. In this study, the authors demonstrated in more detail how the isotopic compositions of glass should be interpreted in terms of the raw materials used. From the glasses from *Bet She'an* and *Bet Eli'ezer* in Israel, which are believed to have been made from natron and coastal sand, they retrieved a similar result to the samples tested by Wedepohl and Baumann. All the samples contain a high Sr concentration and a $^{87}\text{Sr}/^{86}\text{Sr}$ signature of around that of modern seawater. From the natron glass samples from Ashmunein, Egypt, which are believed to have been made from natron and limestone-bearing sand, they found the Sr contents to fall between 100 and 200 ppm just as Wedepohl and Baumann had speculated. From the plant ash glass samples from Baniyas, Israel, a high content of Sr (c. 400 ppm) and a $^{87}\text{Sr}/^{86}\text{Sr}$ signature of between 0.707723 and 0.707797 were found. This Sr composition was interpreted as being determined by plant ash, which is capable of introducing high Sr concentrations and a $^{87}\text{Sr}/^{86}\text{Sr}$ signature derived from the underlying geology on which the plant grew.

Henderson et al. (2005) is another exploratory work that contributed to the early understanding of how Sr concentrations and the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures reflect the raw materials used in ancient glass production. This work was the first to compare the Sr isotopic compositions of raw materials with raw glass from the primary glass-making factory site at al-Raqqa, Syria. In this study 4 natron glass samples and 7 plant ash glass samples along with 2 quartz pebble samples and 2 plant samples from the vicinity of the site were subjected to Sr isotopic analysis. The Sr compositions of the 4 natron glass showed that feldspar could be another end member in the natron glass Sr balance. The Sr isotopic compositions of the quartz pebbles verified the suggestion made by Wedepohl and Baumann that they would contribute in a negligible way to the Sr isotopic composition in glass. The 2 plant samples analysed in the study were *Alhagi maurorum medik*; these were harvested close to the glass factory site and their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are about the same as found in the plant ash factory raw glasses, so it confirmed the assumption that plant ash glass inherited its Sr isotopic composition from the ashed plant (the lime-bearing component).

Degryse et al. (2010) is another work that concerns the basics of Sr isotopic application to glass. This work showed that in a (Scottish) temperate climate the Sr composition of botanic ash could be affected not only by the underlying geology but sometimes also by the hydrology of the immediate area where the plants grew.

Although there were other Sr isotope analyses on ancient glass, the aforementioned four works provide the basic knowledge in this area.

Although this study is probably the first application of Sr isotopes to Chinese glazes, it is not the first use of Sr isotopic analysis in the investigation of Chinese ceramics. Li et al. (2006) studied the trace elements and Sr–Nd isotopic compositions of 13 visually indistinguishable Tang dynasty Sancai ceramic body samples to provenance them according to their geochemical characteristics. 11 of these samples were from the two most important Sancai production sites (5 from Gongxian kiln and 6 from Yaozhou kiln), and 2 were modern fakes. The results showed that Sr–Nd isotopic compositions not only provide a better distinction between ancient Sancai wares from different production sites than trace element analysis, but also clearly distinguished the genuine ceramics from the fakes. The geochemical separations between ancient and fake ceramics indicate that different raw materials were used in their production.

3. Description of samples and relevant background

Two types of glaze are involved in the present study—limestone glaze and ash glaze from South China. In terms of the limestone glaze, no other site is more representative than Jingdezhen, because arguably Jingdezhen is the place where the limestone glaze was first developed in South China and where it was applied for the longest time. Blue-and-white ware was the commonest Jingdezhen porcelain type which was covered with limestone glaze. Twelve blue-and-white shards from Jingdezhen were selected for this study, ten of them are Ming and Qing dynasty official kiln products from different reigns: XD1, XD3 (Xuande period: 1425–1435 AD), CH2, CH5 (Chenghua period: 1464–1487 AD), ZD5, ZD11 (Zhengde period: 1505–1521 AD), JJ1, JJ10 (Jiajing period: 1521–1567 AD), QL3, QL7 (Qianlong period: 1735–1795 AD), and the other two are high quality traditional 'folk kiln' export porcelain wares from the Ming dynasty Wanli period (1572–1620 AD): EP1, EP2.

Ash glaze was the dominant type of glaze used before limestone glaze was introduced. Arguably the Yue kiln produced one of the highest quality ash glazed ceramics of all time. At the peak of its production Yue kiln high quality products were used as court tribute and the colour of these wares was praised in poems as being mysterious. Eight samples from the Silongkou Yue kiln site near the Shanglin lake kiln complex, Cixi, Zhejiang Province, four dated to the Five Dynasties and Ten Kingdoms period (907–960 AD): Ya-1, Ya-2, Ya-3, Ya-5, and four dated to early Southern Song dynasty (1127–c.1150 AD): Yb-1, Yb-2, Yb-3, Yb-5, are included in our study.

Ancient Chinese glaze recipes are made up of two components—the flux and the siliceous portion. The siliceous materials for southern Chinese high fired ceramics were commonly weathered acid igneous rock, and they are commonly referred to as porcelain stone in many publications (Guo, 1987). Porcelain stone forms the major part of the glaze slip² as well as the body paste. The refinement process is crucial to porcelain stone, for it not only reduces the impurities in the original rock, but also turns porcelain stone from rock into a useable material. The refined porcelain stone in Jingdezhen is made in the form of *Petuntse* 白不 (little white brick). Seven porcelain stone samples from Jingdezhen are included in our study, and two of them from *Yao'li* (YL A, YL B) belong to a subtype—glaze stone. Although nearly all porcelain stone could be used to create glaze slip and body paste, glaze stone is a more suitable material for making glaze. Apart from being more fusible and

² Glaze slip is a suspension which is applied to the surface of ceramic biscuit. This layer turns into the glaze after being fired.

having a finer texture, there is no significant difference mineralogically between normal porcelain stone and glaze stone (Tite et al., 1984), so they are not treated separately in this study. The two Yao'li samples are in the form of *Petuntse*. The other five porcelain stone samples are two from Xiao'li (one in form of *Petuntse*, XL and the other in its original state, XL rock), two from San'bao'peng (one in the form of *Petuntse*, SBP and the other in its original rock state, SBP rock) and one from Chen'wan (CW) in form of *Petuntse*.

The flux for limestone glaze is glaze ash, which is a mixture of a major component of calcium carbonate powder and botanic ash. Traditional Jingdezhen glaze ash is made by first burning limestone to produce quicklime (CaO) in a lime kiln; then the quicklime is left for a period of time with some water poured on the surface of the heap. In the process some of the quicklime absorbs water and turns into slaked lime (Ca(OH)₂). The resulting substance is piled up with fern in alternate layers and the whole is burnt again. The last step is repeated several times until a proper powder is obtained. Finally the glaze ash is washed to remove the unburned fern residues and the unwanted alkali salts before being used (Liu and Xu, 1986). Since there are still potters in Jingdezhen today who make hand-made porcelain wares, either as high quality artefacts or fake antiques, glaze ash made according to the traditional way is still available to buy in Jingdezhen. Glaze ash is produced in a small village called Si'qian 30 km southeast of Jingdezhen town (Liu and Xu, 1986). During our sampling trip to Jingdezhen, Si'qian village was visited. Although a workshop making glaze ash was not found, a mine of limestone was found near the village. So a sample of limestone (LS) and several samples of local fern (FN1-3) were taken from there. Two glaze ash samples (GA1, GA2) bought from a Jingdezhen pottery craft shop are also included in this study, and the owners of the shops claimed their glaze ash was from Si'qian village. The glaze ash samples used in this study are unwashed raw glaze ash.

4. Methodology

Chemical analyses were carried out on our glaze samples to confirm their recipe type. Fragments of each ceramic shard were mounted in cross-section in epoxy resin blocks and polished to a 0.25 mm diamond paste finish so as to reveal a flat analytical area.

The blocks were carbon coated so as to prevent surface charging and the distortion of the electron beam during analysis.

A JEOL JXA-8200 electron microprobe in the Microanalysis Research Facility in the Archaeology department of Nottingham University was used for the chemical analysis of the samples. The system is equipped with four wavelength-dispersive X-ray spectrometers with LIF, TAP, PETJ and LIFH crystals, a single energy-dispersive X-ray spectrometer and both secondary and back-scattered detectors. A defocused electron beam with a diameter of 50 μm was used so as to prevent volatilisation of light elements such as sodium. The probe was run at an accelerating voltage of 20 kV and a beam current of 5 nA. The system was calibrated with a mixture of mineral and metal standards. A ZAF program was used to correct and quantify the results. The Corning B glass standard was routinely used as a secondary standard to check for accuracy and precision and to monitor any drift in the instrument. The analytical precision and accuracy achieved by using Corning B standard are listed in Table 1. The poor accuracy level for phosphorous oxide (over 20%) means that the original measured values for this oxide must be considered semi-quantitative. However, the relatively high precision found for this oxide allows datasets in this study to be compared.

For Sr isotope analysis, the glaze samples need to be separated from the ceramic body first. Because the glaze layer on the ceramic body is very thin (200–400 μm), the samples taken are even thinner. This separation was done by 'peeling' the glaze off the porcelain using a dental drill. First the top layer of ceramic shard was cut off with a flexible diamond edged rotary dental bit, then inner surfaces were mechanically cleaned with a tungsten carbide bur to remove the adhering ceramic body. The resulting samples were then transferred to a clean (class 100, laminar flow) working area for further preparation. In the clean laboratory, the samples were first cleaned ultrasonically in high purity water to remove dust, rinsed twice, dried in high purity acetone and then weighed into pre-cleaned Teflon beakers. The samples were spiked with ⁸⁴Sr tracer solution and dissolved in Teflon distilled 16 M HNO₃. Strontium was collected using Dowex resin columns.

Strontium was loaded onto a single Re Filament with TaF following the method of Birck (1986). The ⁸⁷Sr/⁸⁶Sr and Strontium elemental concentrations were determined by Thermal Ionisation Mass spectroscopy (TIMS) using a Thermo Triton multi-collector

Table 1
Chemical compositions of glaze samples.

		SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	FeO	MnO	MgO	P ₂ O ₅	Total
St. Dev. (n = 9)		0.89	0.08	0.16	0.01	0.07	0.01	0.01	0.03	0.06	
Error (%)		2.3	5.0	1.3	2.1	0.6	16.3	16.7	7.8	27.0	
Jingdezhen limestone glaze samples											
	XD1	70.82	16.93	3.42	3.79	4.46	0.52	0.09	0.39	0.05	100.49
	XD3	68.91	15.63	2.93	3.37	8.70	0.64	0.10	0.93	0.07	101.29
	CH2	68.46	17.44	1.84	5.67	5.35	0.77	0.33	0.35	0.07	100.29
	CH5	69.31	16.90	1.73	5.93	3.80	0.92	0.10	0.26	0.05	99.00
	ZD5	68.89	15.75	2.80	4.65	6.23	0.76	0.12	0.24	0.10	99.53
	ZD11	67.65	16.47	1.76	5.49	6.83	0.82	0.11	0.33	0.08	99.54
	JJ1	64.85	15.63	2.21	4.75	9.61	1.18	0.48	0.43	0.10	99.26
	JJ10	66.56	17.11	2.43	4.35	8.38	0.72	0.10	0.37	0.06	100.09
	EP1	63.72	16.04	1.80	3.22	13.32	0.71	0.41	0.27	0.08	99.57
	EP2	67.50	15.77	1.88	4.21	9.83	0.71	0.09	0.22	0.04	100.25
	QL3	70.55	16.47	1.81	3.87	4.92	0.86	0.11	0.25	0.03	98.87
	QL7	69.21	16.87	1.50	3.96	5.46	0.93	0.89	0.22	0.04	99.08
Yue Kiln ash glaze samples											
	Ya-1	57.58	12.28	0.87	1.58	17.16	1.44	0.36	2.74	1.07	95.08
	Ya-2	59.09	12.98	0.95	1.81	15.78	1.97	0.26	2.31	0.77	95.93
	Ya-3	57.23	11.81	0.83	1.68	17.92	1.42	0.37	2.75	0.95	94.96
	Ya-5	59.62	12.36	0.93	1.75	16.40	2.04	0.28	2.56	1.08	97.01
	Yb-1	53.96	11.72	0.77	1.29	20.34	1.86	0.57	3.99	1.43	95.94
	Yb-2	54.22	11.58	0.96	1.85	19.13	1.60	0.47	3.26	1.23	94.31
	Yb-3	54.65	12.38	0.82	1.60	18.20	2.15	0.51	3.60	1.33	95.25
	Yb-5	53.68	11.90	0.84	1.51	20.60	1.77	0.54	3.58	1.44	95.84

mass spectrometer at the NERC Isotope Geosciences Laboratory. The international standard for $^{87}\text{Sr}/^{86}\text{Sr}$, NBS987, gave a value of 0.710250 ± 0.000006 ($n = 8$, 2σ) during the analysis of these samples. Procedural blank values were in the region of 100 pg.

5. Results

5.1. Chemical compositions of glaze samples

The chemical compositions of our glaze samples are given in Table 1. The chemical compositions of the same types of glaze produced in the same sites have been reported in Hu et al. (2011) and Wu et al. (2009), and our results agree with these published results. Jingdezhen limestone glaze samples show high contents of alkali oxides, comparatively low contents of CaO and low contents of MgO and P_2O_5 . These chemical features are regarded as typical for the glazes made by mixing porcelain stone and glaze ash, and discussed in detail in Hu et al. (2011). The Yue kiln ash glaze samples have high contents of CaO, low contents of alkali oxides and high contents of MgO and P_2O_5 . These chemical features are regarded as typical for glazes made by mixing porcelain stone and botanic ash, and discussed in detail in Wu et al. (2009). These results confirm that our samples are typical of the suggested recipe types.

5.2. Sr isotopic compositions of glaze samples

The Sr isotopic compositions of our glaze samples are given in Table 2 and plotted as Sr ppm against $^{87}\text{Sr}/^{86}\text{Sr}$ in Fig. 1. The plot shows that Jingdezhen limestone glaze and Yue kiln ash glaze have completely different Sr isotopic composition patterns. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Jingdezhen limestone glaze samples cover a wide field

Table 2
Sr isotopic compositions of all tested samples.

Sample description	Label	Sr concentration (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	
Jingdezhen limestone glaze samples	XD1	71	0.737772	
	XD3	98	0.729991	
	CH2	64	0.748799	
	CH9	40	0.755702	
	ZD5	102	0.743484	
	ZD11	98	0.743235	
	JJ1	41	0.754651	
	JJ10	65	0.749738	
	EP1	68	0.743327	
	EP2	46	0.748450	
	QL3	38	0.757685	
	QL7	50	0.759138	
	Yue kiln ash glaze samples	Ya-1	252	0.712852
		Ya-2	549	0.712464
Ya-3		486	0.712394	
Ya-5		279	0.712813	
Yb-1		294	0.712469	
Yb-2		401	0.712838	
Yb-3		390	0.712650	
Yb-5		375	0.712097	
Petuntse samples	YL A	75	0.735331	
	YL B	62	0.730019	
	CW	79	0.735565	
	SBP	105	0.738851	
	XL	72	0.732985	
Row porcelain stone samples	SBP Rock	57	0.749616	
	XL Rock	38	0.759763	
Glaze ash samples, limestone samples and fern samples	GA1	207	0.708901	
	GA2	281	0.708554	
	LS	331	0.708123	
	FN1	43	0.711768	
	FN2	22	0.712811	
	FN3	29	0.713766	

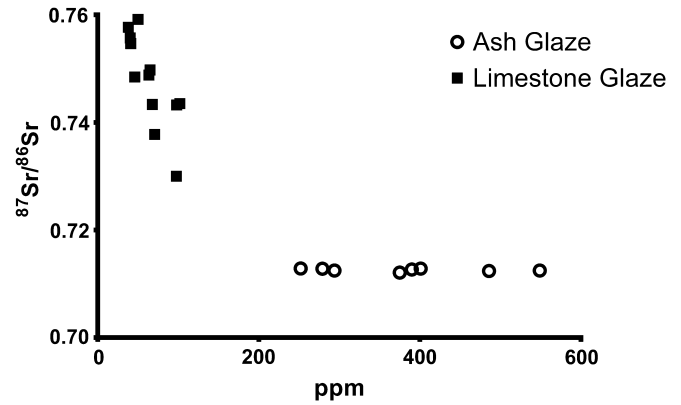


Fig. 1. Sr isotopic compositions of glaze samples.

while their Sr concentrations are restricted. A mixing line formed by the Sr isotopic compositions of Jingdezhen samples is clearly identifiable in the plot. On the other hand, Yue kiln ash glaze samples have a very consistent $^{87}\text{Sr}/^{86}\text{Sr}$ signature of between 0.7120 and 0.7128, and their Sr contents are high and have a wide variation. These two patterns clearly reflect differences in the two types of glaze recipe.

5.3. Sr isotopic compositions of Jingdezhen porcelain stone samples

The Sr isotopic compositions of 7 porcelain stone samples (5 in the form of *Petuntse* and 2 in original rock state) are given in Table 2 and plotted as $1/\text{Sr}$ ppm against $^{87}\text{Sr}/^{86}\text{Sr}$ in Fig. 2. Despite the similar chemical and mineralogical characteristics that these samples share, the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of these samples have a large range of variation. However, it can be seen from the data that the raw material refinement process tends to bring down this variation in the *Petuntse*. In the original rock state, the porcelain stone from the *San'bao'peng* mine has a $^{87}\text{Sr}/^{86}\text{Sr}$ signature of 0.7496 and the porcelain stone from *Xiao'li* mine has a $^{87}\text{Sr}/^{86}\text{Sr}$ signature of 0.7598; their difference is 0.0102. In the *Petuntse* samples, the $^{87}\text{Sr}/^{86}\text{Sr}$ of *San'bao'peng Petuntse* is 0.7389 and $^{87}\text{Sr}/^{86}\text{Sr}$ of *Xiao'li Petuntse* is 0.7330; their difference is 0.0059.

It is also noticeable in Fig. 2 that the Sr isotopic compositions of *Petuntse* samples form a straight line. According to geochemical theory, a line formed from a bi-plot of $1/\text{Sr}$ ppm against $^{87}\text{Sr}/^{86}\text{Sr}$ implies that the Sr isotopic compositions forming the line are mixtures of different proportion of the two end members (Dickin, 2005). Therefore expressed in terms of the Sr isotopic

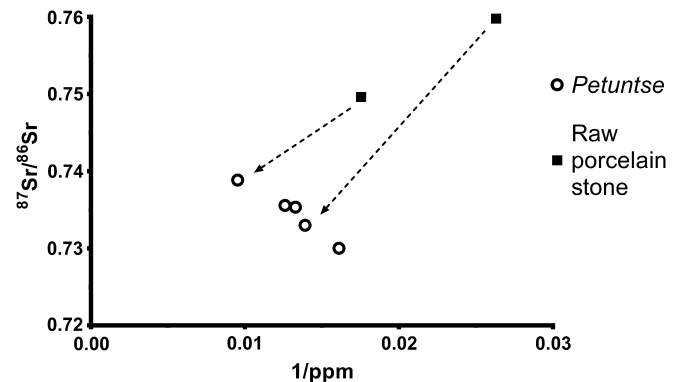


Fig. 2. Sr isotopic compositions of porcelain stone samples before and after refinement.

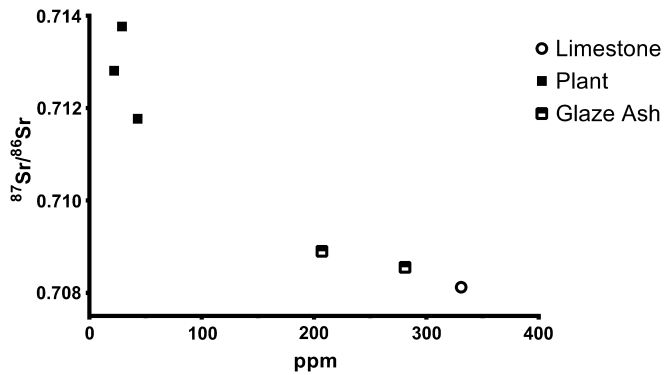


Fig. 3. Sr isotopic compositions of glaze ash, limestone and plant samples.

compositions, the porcelain stone refinement process turns a multiple component mixing system into a two component mixing line by removing the minerals that are unwanted in the final raw material. What minerals are removed in the refinement process and the Sr isotopic composition alteration caused by the removal are addressed in the third section of the discussion.

5.4. Sr isotopic compositions of Jingdezhen glaze ash samples

The Sr isotopic compositions of the two glaze ash samples, the limestone sample and the three fern samples are given in Table 2 and plotted as Sr ppm against $^{87}\text{Sr}/^{86}\text{Sr}$ in Fig. 3. Our fern samples were not ashed before being tested. Since the Sr concentrations in the ferns and the ashed ferns are not of the same magnitude, the Sr concentration of our fern samples are not relevant and should not be considered in this context. The three fern samples have much higher $^{87}\text{Sr}/^{86}\text{Sr}$ signatures than that of the limestone and glaze ash samples. The Sr isotopic compositions of the glaze ash samples are slightly more radiogenic than that of limestone and slightly lower in Sr level. This result shows that the Sr isotopic composition of glaze ash is mainly inherited from limestone and is slightly altered by the presence of botanic ash. However because the glaze ash samples used in this study were unwashed glaze ash, which contains a certain amount of unburned fern residue and higher content

of alkali salts than the washed glaze ash, the Sr isotopic composition of the washed glaze ash, especially the Sr concentration, should be slightly different from our result.

6. Discussion

6.1. The isotopic composition pattern of Yue kiln ash glaze

The consistency of the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of Yue kiln samples suggests that one raw material component with a high Sr concentration and consistent $^{87}\text{Sr}/^{86}\text{Sr}$ dominates the Sr contribution in the glaze. According to Wood (2009), the Yue kiln ash glaze recipe is composed of 30%–50% by weight of botanic ash with the remainder being porcelain stone. The average Sr concentration retrieved from our Yue kiln samples is 378 ppm, with a maximum value of 549 ppm in sample Ya-2. The question to be asked here is which raw material component is the one dominating the Sr contribution: Porcelain stone or botanic ash?

Yue kiln porcelain stone is weathered acid igneous rock (Wood et al., 2005). According to the 1:1,500,000 geological map of Zhejiang Province the rocky hill area south of Cixi city, where the most densely populated Yue kiln complex of over 100 kiln sites was distributed, has isolated strata formed largely from mid-late Jurassic acid igneous rock and surrounded by a much larger area of Quaternary sediments (Fig. 4). So it is highly likely that the weathered mid-late Jurassic acid igneous rock was the porcelain stone used for making Yue kiln ceramics by ancient Yue kiln potters and they chose this site deliberately for its convenient access to this type of rock. Although no porcelain stone from Yue kiln is included in this study, according to the geochemical study of Mesozoic igneous rocks in Zhejiang Province (Lapierre et al., 1997), the Sr contents of acid Mesozoic igneous rocks (SiO_2 of over 63 weight%; not all of the 11 samples are from the area of the Yue kiln) are quite low, ranging from 21.8 to 196 ppm and with an average of 84.5 ppm. So it is more than reasonable to assume that the porcelain stone used by Yue kiln contain 100 ppm Sr. 50%–70% by weight of porcelain stone provides 50–70 ppm of Sr in the final glaze. The remaining over 300 ppm of Sr, which is the major portion, must have come from the other raw material—the botanic ash. The consistent $^{87}\text{Sr}/^{86}\text{Sr}$ signature in the Yue kiln glaze is a reflection of the $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the ashed vegetation. This result is

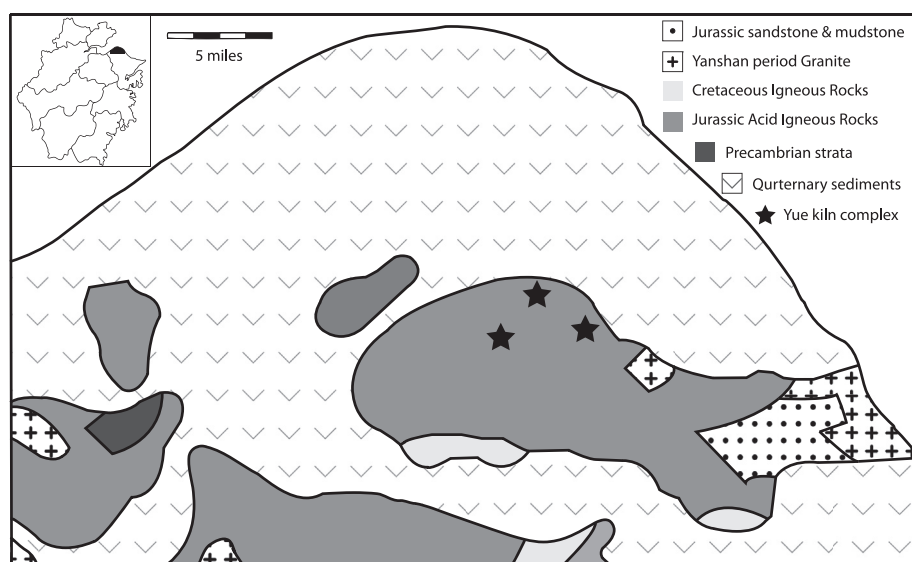


Fig. 4. The geology in the vicinity of Yue kiln complex (small map: the location of the mapped area in Zhejiang Province).

consistent with the results obtained from previous plant ash glass studies: botanic ash is capable of providing a high concentration of Sr in the glass. The $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the plant ash glass is inherited from the plant used to make it (Freestone et al., 2003; Henderson et al., 2005).

6.2. The Sr isotopic composition pattern of Jingdezhen limestone glaze

The mixing line shown in Fig. 1 for the Jingdezhen glaze samples suggests that two raw material components balance the Sr isotopic compositions of Jingdezhen limestone glaze. Porcelain stone and glaze ash were the raw materials used to make limestone glaze, so their isotopic compositions should be reflected in the isotopic end members respectively. The Sr isotopic compositions of Jingdezhen glaze samples, glaze ash samples and raw porcelain stone samples are plotted as $1/\text{Sr}$ ppm against $^{87}\text{Sr}/^{86}\text{Sr}$ in Fig. 5. In Fig. 5, the Sr isotopic compositions of Jingdezhen limestone glaze samples basically plot on the lines which have glaze ash and raw porcelain stone samples being the end members. This suggests the glaze ash samples and raw porcelain stone samples are proper analogues for the raw materials involved in the ancient production process.

6.3. What happens during the porcelain stone refinement process?

As shown in Fig. 2, as a result of the conversion of raw porcelain stone to *Petuntse* a significant alteration to the Sr isotopic composition of the raw material occurs. The mineralogical changes that caused the alteration in Sr isotopic compositions are described in this section.

Levigation, a refinement process for ceramic raw materials is used commonly in ceramic production centres. The traditional levigation procedure being used in the Jingdezhen *Petuntse* production workshop today is not very different from that used 300 years ago when the French missionary Père d'Entrecolles recorded it. In the first letter Père d'Entrecolles wrote back to France to report on the Jingdezhen porcelain making craft, he recorded the procedure in the following way³: 'This is what is first done to the rock. An iron hammer is used to break these pieces of stone, after which the broken pieces are put in some mortars; then using lever arms which have a head of stone armoured with iron, the stone is reduced to a very fine powder. These lever arms work incessantly powered either by men or by water wheels in much the same manner as the tilt hammers in our paper mills. This powder is then taken and is thrown into water where it is stirred vigorously with an iron paddle. After allowing it to stand for several moments, there will be a kind of cream on the top with a depth of 4–5 fingers. This is removed and put in another container of water. The water of the first tank is agitated several times, each time collecting the supernatant cream which is formed, until finally only large grains remain at the bottom of the first tank. The coarse sediment of the first tank is eventually re-pulverised. With regard to the fine slurry in the second tank, one merely waits until a kind of paste forms at the bottom. When the supernatant liquid is clear, it is decanted without disturbing the sediment, and one places this paste in some large moulds appropriate for drying. Before completely dry, it is divided into litter bricks which are sold by hundred.' Except for the man power being replaced by electricity in the dry season, the procedure being used today seems basically unchanged.

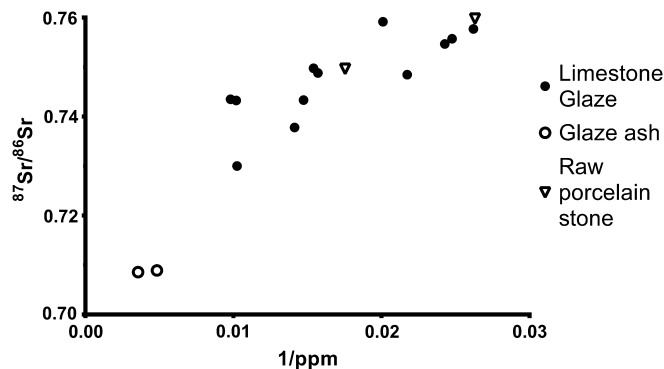


Fig. 5. Sr isotopic compositions of Jingdezhen porcelain glaze samples, glaze ash samples and raw porcelain stone samples.

Jingdezhen porcelain stone is developed from quartz-feldspar based acid igneous rock through weathering and sericitisation by hydrothermal fluids. The mineralogy of Jingdezhen porcelain stone rock is mainly quartz and sericite, albite and a small amount of large grain primary mica, calcite and heavy minerals (Vogt, 1900; Tite et al., 1984; Li, 1998).

After levigation the amount of fine-grained minerals, like fine-grained quartz and sericite, are further increased in *Petuntse*, but the coarse-grained minerals, like coarse-grained quartz, primary mica and heavy minerals are largely removed (Guo, 1987; Li, 1998). The Sr isotopic alteration that occurs during the refinement process reflects exactly these mineral changes.

Coarse grained quartz and heavy minerals such as rutile contain negligible Sr concentrations. So their removal or near removal explains the increase of strontium concentration in *Petuntse* because Sr becomes more concentrated. Calcite is still in *Petuntse*, but because its content is so low (CaO content of 1–2 wt%), its Sr contribution is negligible.

Primary mica is richer in rubidium than other co-magmatic minerals in the same rock. Since co-magmatic minerals have the same starting $^{87}\text{Sr}/^{86}\text{Sr}$, the ^{87}Rb decay ($^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + \beta^- + \bar{\nu} + Q$) gives the rubidium-richer minerals a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio according to their geological age. So primary mica has higher $^{87}\text{Sr}/^{86}\text{Sr}$ than other co-magmatic minerals (Dickin, 2005). Therefore the removal of primary, coarse-grained mica in the refinement process results in a drop in the $^{87}\text{Sr}/^{86}\text{Sr}$ in *Petuntse*. The fine-grained quartz is abundant in *Petuntse*, but because its Sr content is negligible (Henderson et al., 2005), it also doesn't contribute much to the Sr composition of *Petuntse*.

Therefore the two component mixing in *Petuntse* is probably a reflection of the Sr contributions from the other two major mineral components—sericite and albite.

6.4. Have we overestimated the porcelain stone refinement technique used by ancient Jingdezhen potters?

The same levigation procedure mentioned in the previous section could be traced back as early as the Jiajing reign in the Ming dynasty (1521–1566 AD) according to historical records⁴ and its actual starting point is likely to have been even earlier. For this reason and that the quality of the best porcelain wares made by Ming and Qing Jingdezhen potters is so high, it has been assumed by scholars of ancient Chinese ceramics that the raw materials used for making those wares were refined to a degree that is similar to their

³ The texts are quoted from Tichane (1983). Ching-Te-Chen: Views of a Porcelain City, New York State Inst. for Glaze Research. The letter was originally written in French, but Tichane translated them into English.

⁴ The Great Gazetteer of Jiangxi Province 江西省大志 compiles in the Jiajing reign recorded that the Jingdezhen porcelain stone was made into the form of *Petuntse*, but no details of how it was made was given in the texts.

modern counterparts. In the present study, the Sr isotopic composition of modern *Petuntse* samples were expected to be one of the end members of the limestone glaze Sr isotopic compositional mixing line when glaze ash is the other. However this is not the case.

The Sr isotopic compositions of Jingdezhen limestone glaze samples, glaze ash samples, *Petuntse* samples and raw porcelain stone samples are plotted as 1/ppm against $^{87}\text{Sr}/^{86}\text{Sr}$ in Fig. 6. As shown in the figure, the majority of Jingdezhen limestone glaze samples plot beyond the range defined by the Sr isotopic compositions of the modern *Petuntse* and the glaze ash samples. If our glaze samples had been made by mixing glaze ash with porcelain stone refined as thoroughly as modern *Petuntse*, their Sr isotopic compositions would have distributed within the range defined by the Sr isotopic compositions of *Petuntse* samples and glaze ash samples in Fig. 6. This result suggests the modern *Petuntse* samples do not appear to be a good analogue for ancient production processes.

Although the Sr isotopic compositions of Jingdezhen limestone glaze do not plot within the bracket defined by the Sr isotopic compositions of glaze ash and *Petuntse*, they do plot within the brackets defined by Sr isotopic compositions of glaze ash and raw porcelain stone. So the raw porcelain stone has turned out to be a better analogue for the siliceous raw material of the ancient glaze recipe than modern *Petuntse*. The differences between Sr isotopic compositions of raw porcelain stone and *Petuntse* have been discussed in the previous section, and the former has a higher $^{87}\text{Sr}/^{86}\text{Sr}$ signature and lower Sr concentration due to the inclusion of coarse-grain quartz, heavy minerals and primary mica. This result implies that the porcelain stone used by ancient potters was refined much less thoroughly than modern *Petuntse*: although the levigation procedure seems to have changed little over time, a smaller proportion of the unwanted minerals were removed in the ancient process.

Can these observations have a role to play in provenance work? They potentially could but at the moment it is only scientific speculation, and a number of glaze samples from modern fake porcelain need to be analysed to legitimate this speculation. If the Sr isotopic compositions of glaze samples from modern fake porcelain antiques do distribute within rather than beyond the bracket defined by the Sr isotopic compositions of modern *Petuntse* and glaze ashes, this method could be used as one of the practices to distinguish fakes from genuine Jingdezhen porcelain antiques.

6.5. The potential of applying Sr isotopic analysis to the study of Chinese high fired glazes

Since this is the first application of Sr isotopic analysis to Chinese glazes, one of the original aims was to explore the potential of the technique in this particular context. The first set of glaze Sr

isotopic compositions produced by our study shows that there is great potential for this technique.

Firstly, Sr isotopic compositions could be used as an effective way to identify high fired southern Chinese ceramic glaze recipes. Nearly all of South China high fired ceramic wares, no matter what they might look like, were coated with glaze based on a recipe of porcelain stone plus botanic ash or porcelain stone plus glaze ash. Since Jingdezhen limestone glaze and Yue kiln ash glaze are the original and typical examples of the glaze types in South China, the different Sr isotopic composition patterns of limestone glaze and ash glaze revealed in this study could be used as a fingerprinting method to provenance the glaze recipes used.

The conventional scientific approach to identify whether a glaze was fluxed by glaze ash or botanic ash is via the combined chemical composition of P_2O_5 and MgO in the glaze.⁵ If this value is high, the glaze is regarded as being fluxed by botanic ash; otherwise the glaze is regarded as being fluxed by glaze ash. However this approach is sometimes undermined by the difficulty of accurate P_2O_5 measurements using some analytical techniques. The semi-quantitative P_2O_5 results produced by some methods can prevent the cross-laboratory comparison of these data.

Secondly, Sr isotopic compositions could be used as a highly accurate fingerprinting method to provenance ceramics covered with ash glaze. As revealed in previous glass studies and in this study, botanic ash fluxed glass (or glaze) from a specific production site share a very consistent $^{87}\text{Sr}/^{86}\text{Sr}$ signatures with variations only from the fourth decimal digit. The $^{87}\text{Sr}/^{86}\text{Sr}$ signature of botanic ash glass (or glaze) is inherited from the plant used for burning the ash, and the $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the plant depends on the immediate geological and hydrological environment in which the plant grew. Once this ash glaze $^{87}\text{Sr}/^{86}\text{Sr}$ signature of a certain site is determined, it could be used as a fingerprint to identify if a ware is from that site. This method holds great potential of tackling academic issues which could not resolved by chemical analysis, like the longstanding debate over the provenance of the earliest Chinese stoneware (proto-porcelain: a high fired ceramic covered with ash glaze). The $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the ash glaze on proto-porcelain would help to identify whether this earliest Chinese stoneware was produced in the North or the South.

Using glaze Sr isotopic compositions to provenance limestone glazes may not be as straightforward as provenancing botanic ash glaze because the $^{87}\text{Sr}/^{86}\text{Sr}$ signature of limestone glaze falls into a range rather than being a specific value; the $^{87}\text{Sr}/^{86}\text{Sr}$ signature range for one kiln site could overlap with that of another. By identifying the mixing line from the Sr isotopic compositions of multiple samples, provenancing limestone glazes may also be possible.

7. Conclusion

1. Jingdezhen limestone glaze and Yue kiln ash glaze have completely different Sr isotopic composition patterns. The Sr isotopic pattern of Jingdezhen limestone glaze is a two component mixing model with low Sr concentration and high variant $^{87}\text{Sr}/^{86}\text{Sr}$, while the Sr isotopic pattern of Yue kiln ash glaze is characterised by having a highly consistent $^{87}\text{Sr}/^{86}\text{Sr}$ and high Sr concentrations with a large variation. The differences between the two patterns are largely due to the flux component involved in the recipes.

⁵ Sometimes the chemical content of MnO is also considered along with P_2O_5 and MgO in the combined chemical composition, but it is less frequent and least important.

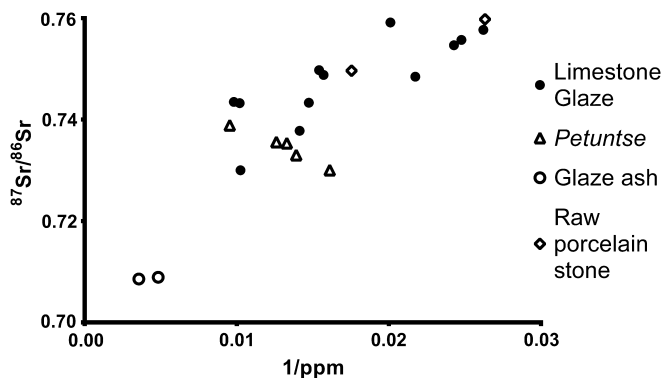


Fig. 6. Sr isotopic compositions of Jingdezhen porcelain glaze samples, glaze ash samples, *Petuntse* samples and raw porcelain stone samples.

2. The levigation refinement process lifts the Sr concentration and lowers the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the conversion of raw porcelain stone to *Petuntse*.
3. With the removal of coarse-grain quartz, primary mica and heavy minerals in the refinement process, the Sr isotopic compositions of sericite and albite control the Sr balance in *Petuntse*.
4. Jingdezhen glaze ash (a mixture of a major component of calcium carbonate and plant ash) has a Sr isotopic composition largely resembling that of Jingdezhen local limestone but just slightly altered by the presence of botanic ash.
5. Modern *Petuntse* samples do not appear to be a good analogue for ancient production processes.

Acknowledgement

Special gratitude is given to the NERC Isotope Geosciences Laboratory, British Geological Survey for funding the authors to carry out the TIMS analysis (IP-1185-0510) and special gratitude is also given the University of Nottingham for funding H. Ma and so that he has been able to fulfil his ambition to study Chinese ceramics as a PhD student. The authors are grateful for Department of History of Science and Archaeometry, Graduate University of Chinese Academy of Science for providing the Jingdezhen official kiln samples, and for the Institute of Cultural Relics and Archaeology of Zhejiang Province for providing Yue kiln samples.

References

- Birck, J.L., 1986. Precision K-RB-SR isotopic analysis-application to RB-SR chronology. *Chem. Geol.* 56 (1–2), 73–83.
- Degryse, P., Shortland, A., De Muynck, D., Van Heghe, L., Scott, R., Neyt, B., Vanhaecke, F., 2010. Considerations on the provenance determination of plant ash glasses using strontium isotopes. *J. Archaeol. Sci.* 37 (12), 3129–3135.
- Dickin, A.P., 2005. *Radiogenic Isotope Geology*. Cambridge University Press.
- Freestone, I.C., Leslie, K.A., Thirlwall, M., Gorin-Rosen, Y., 2003. Strontium isotopes in the investigation of early glass production: byzantine and early Islamic glass from the Near East. *Archaeometry* 45, 19–32.
- Guo, Y.Y., 1987. Raw materials for making porcelain and the characteristics of porcelain wares in North and South China in ancient times. *Archaeometry* 29, 3–19.
- Henderson, J., Evans, J.A., Sloane, H.J., Leng, M.J., Doherty, C., 2005. The use of oxygen, strontium and lead isotopes to provenance ancient glasses in the Middle East. *J. Archaeol. Sci.* 32 (5), 665–673.
- Hu, D., Zhang, H., Liu, S., 2011. Researches of Porcelain Wares Unearthed from Ming Dynasty Jingdezhen Imperial Factory Remains (景德镇明代御窑遗址出土瓷器研究). Science Press, Beijing.
- Kerr, R., Wood, N., 2004. Science and Civilisation in China. In: *Chemistry and Chemical Technology, Part 12, vol. 5. Ceramic Technology*, Cambridge University Press.
- Lapierre, H., Jahn, B., Charvet, J., Yu, Y., 1997. Mesozoic felsic arc magmatism and continental olivine tholeiites in Zhejiang Province and their relationship with the tectonic activity in southeastern China. *Tectonophysics* 274 (4), 321–338.
- Li, B.P., Zhao, J.X., Greig, A., Collerson, K.D., Feng, Y.X., Sun, X.M., Guo, M.S., Zhuo, Z.X., 2006. Characterisation of Chinese Tang sancai from Gongxian and Yaozhou kilns using ICP-MS trace element and TIMS Sr–Nd isotopic analysis. *J. Archaeol. Sci.* 33 (1), 56–62.
- Li, J., 1998. *History of Science and Technology of China: Ceramics Volume (中国科学技术史陶瓷卷)*. Science Press, Beijing.
- Liu, Z., Xu, C., 1986. The making method of traditional glaze ash and the science behind (传统釉灰的制法及其工艺原理). *J. Ceram. (陶瓷学报)* 1.
- Tichane, R., 1983. *Ching-Te-Chen: Views of a Porcelain City*. New York State Inst. for Glaze Research.
- Tite, M.S., Freestone, I.C., Bimson, M., 1984. A technological study of Chinese porcelain of the Yuan dynasty. *Archaeometry* 26 (2), 139–154.
- Vogt, G., 1900. Recherches sur les porcelaines Chinoises. *Bull. Soc. d'encourag. pour l'ind. natl.* 99, 560–612.
- Wedepohl, K.H., Baumann, A., 2000. The use of marine molluscan shells for Roman glass and local raw glass production in the Eifel area (Western Germany). *Naturwissenschaften* 87 (3), 129–132.
- Wood, N., 2009. Some implications of the use of wood ash in Chinese stoneware glazes of the 9th–12th Centuries. In: Shortland, A.J., Freestone, I., Rehren, T. (Eds.), *From Mine to Microscope: Advances in the Study of Ancient Technology*. Oxbow Books, Oxford, pp. 190–200.
- Wood, N., Doherty, C., Rastelli, S., 2005. Some aspects of Yue ware production at Shanglinhu in the late Tang dynasty. In: Guo, J. (Ed.), *Proceedings of International Symposium on Ancient Ceramics 2005*. Shanghai Scientific and Technological Literature Publishing House, Shanghai.
- Wu, J., Luo, H., Li, Q., Li, W., Wu, J., 2009. Composition model and microstructure characteristic of Yue ware, Longquan ware and Southern-Song Guan ware. *J. Chin. Ceram. Soc.* 38 (8), 1408–1414.