Applied Surface Science 351 (2015) 624–634

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Composition analysis of ancient celadon via femtosecond laser ionization time-of-flight mass spectrometry

Miaohong He, Yuanfang Xiao, Shudi Zhang, Rong Liu, Wei Hang*, Benli Huang

Department of Chemistry and the MOE Key Lab of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 10 February 2015
Received in revised form 30 April 2015
Accepted 29 May 2015
Available online 6 June 2015

Keywords:
fs-LI-TOFMS
Ancient porcelain
Elemental features
Elemental imaging

ABSTRACT

High irradiance femtosecond laser ionization time-of-flight mass spectrometry (fs-LI-TOFMS) has been applied to determine the elemental composition of the porcelain body as well as glaze from Yue kiln (in southern China) and Yaozhou kiln (in northern China) of different cultural eras. In addition, elemental mapping of a cross-section of Yaozhou porcelain is demonstrated. The results indicate that Ti and Fe of the porcelain body and Ca, Fe, P, Mn, Mg of the glaze from Yue kiln are considered as characteristic elements to classify porcelains among the different eras, even discriminate the contemporary counterfeits. The high concentration of P also reveals the usage of plant ash as the raw material for glaze at ancient times. The sudden rise in trace element concentrations of La, Ce, Nd, and Co in Ming Dynasty from Yaozhou porcelain body proves the historical record about the alteration of kiln site due to the warfare. With the comparison of glazes between the two kilns, their differences can be revealed in the aspects as raw material, structure of layers, and firing techniques, exhibiting the distinction of porcelain between southern and northern China. Via elemental mapping of a cross-section of Yaozhou porcelain, the elemental distribution in glaze-transition-body structure can be acquired, aiding the exploration of the formation mechanism of the transition layer. Overall, fs-LI-TOFMS is a versatile technique, which is capable of obtaining comprehensive information in porcelain analysis.

1. Introduction

China is considered as the earliest country inventing porcelain in the world [1]. Yue kiln in Zhejiang Province, which was the cradle of celadon (a type of porcelain with greyish-green glaze) and whose history could date back to the Eastern Han Dynasty (25–220AD), boomed in the Tang Dynasty (618–907AD), Five Dynasties (907–960AD) and Song Dynasty (960–1279AD) [1]. On the other hand, the development of Yaozhou kiln in Shanxi Province, whose period of producing celadon were from the Tang Dynasty to Ming Dynasty, was based on the technical groundwork of Yue kiln [2]. Among the history of Chinese porcelain, Yue kiln and Yaozhou kiln lay in the indispensable status in southern and northern China [1,3,4].

In archaeology, ancient porcelain study is always a field of great significance [5,6]. Presently, the customary method for identifying the age and the provenance of porcelain is the visual observation of the exterior characteristics. However, it is quite difficult to identify the specific date and provenance correctly in such a way, especially in the case of imitations with similar appearances [7]. Therefore, the aid of scientific techniques is particularly essential [8]. Since most ancient kilns adopted their local raw materials, porcelains of various localities might take on different geochemistry and mineralogical characteristics [9]. Additionally, the manufacturing technologies, such as grinding, elutriation, firing, etc. [10,11], would also have impact on the elemental features of resultant products [12,13], which varied with different historic periods [9]. Consequently the elemental analysis including major, minor, and trace elements via analytical techniques can be utilized for tracing the porcelain age, manufacturing technology as well as its provenance [14–17]. This knowledge can also contribute to the understanding of ancient civilization and trade, providing information about its conservation as well as restoration [18–22].

Varieties of techniques have been applied for analysis of porcelain, such as X-ray fluorescence spectroscopy (XRF) [16,23], proton-induced X-Ray emission spectroscopy (PIXE) [24,25], instrumental Neutron activation analysis (INAA) [15,19,26], laser induced breakdown spectroscopy (LIBS) [27–30], Raman spectroscopy (RM) [31–34], etc. and mass spectrometry (inductively coupled plasma mass spectrometry (ICPMS) [12,13], laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) [35,36] and thermal ionization mass spectrometry (TIMS) [13,37]).

* Corresponding author.
E-mail address: weihang@xmu.edu.cn (W. Hang).

http://dx.doi.org/10.1016/j.apsusc.2015.05.175

Table 1
Ion source parameters of fs-LI-TOFMS.

Type of laser	Femtosecond laser
Laser pulse frequency	10 Hz
Laser wavelength	1030 nm
Laser pulse duration	500 fs
Laser incident angle	0°
Laser pulse energy	0.9 mJ
Spot diameter	50 μm
Laser irradiance	9.1×10^{13} W/cm^2
Source pressure	1200 Pa

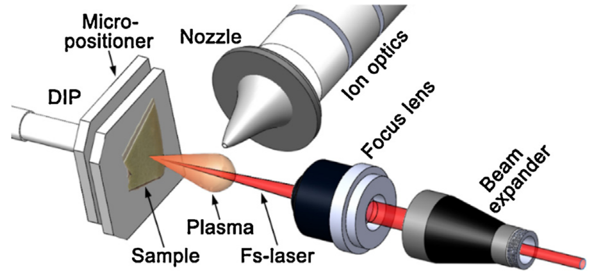

Fig. 1. Schematic diagram of the ion source in the fs-LI-TOFMS system.

For the assessment of these analytical techniques in archaeology, the involved time, destructiveness to the sample, sensitivity as well as multi-elemental analysis capability should be taken into consideration [38–40]. Although optical spectrometry techniques are simple, straightforward, and easy to operate, they generally determine limited elements, lack sensitivity, and suffer spectral interferences [41]. Among the mass spectrometry techniques, TIMS is a powerful technique to explore the provenance and age via tracing the change of the elemental isotopes, but its requirement of sample dissolution is a bottleneck in ancient porcelain analysis [13]. ICPMS can accurately provide the element content as well as isotope ratios; nevertheless, it is also a solution-based technique. LA-ICPMS is capable of direct solids analysis, but it is unable to provide element content without matrix-matched solid standards [13,36,42].

The buffer-gas assisted high irradiance laser ionization time-of-flight mass spectrometry (LI-TOFMS) is a potential candidate in the study of ancient porcelain. Some pioneering experiments have demonstrated its semi-quantitative capability in determining almost all elements simultaneously without standards, including non-metal elements [43,44]. With the introduction of high irradiance femtosecond laser, matrix effect can be reduced to a great extent [45], which further improves its quantitative capability. The assistance of buffer-gas efficiently decreases the interferences of oxides as well as multiply charged ions via collision and three-body recombination [41]. Moreover, it is a micro-damaging technique for its solid sampling via the focused laser beam of micrometers in diameter. Although this is less superior to nondestructive techniques such as PIXE and XRF, yet it does not suffer from large deviation for determining elements with low atomic numbers [23–25]. The high spatial resolution of LI-TOFMS ensures the acquisition of the information about the layer between the porcelain body and glaze, which is difficult to be achieved by most other techniques. Thus it could be a feasible technique for studying the ancient porcelain.

2. Experimental setup

2.1. Instrument

All experiments were carried out with an in-house-built buffer-gas-assisted high irradiance fs-LI-TOFMS system that has been described previously with a few modifications [44,45]. Briefly, a femtosecond laser (S-pulse HP, Amplitude System, France) with duration of 500 fs was employed with its parameters summarized in Table 1. Samples mounted on the direct insertion probe (DIP) were ablated and ionized by the laser pulses, as shown in Fig. 1. Ultrahigh purity helium (99.999%) acting as the buffer-gas was introduced into the ion source with 1200 Pa. The ions generated in ion source were sampled via the nozzle, passed through the transportation system, and were finally repelled orthogonally into the TOFMS. A digital storage oscilloscope (42Xs, Lecroy, USA) was employed to record the signal from the micro-channel plates (MCP). Elemental images were obtained via moving the micro-positioner (Physik Instrumente) with step distance of 50 μm, and the data was processed with a self-developed LabVIEW program.

2.2. Sample preparation

All the samples were provided by the Shanghai Museum. They include 8 typical celadon sherds from Yue kiln, which can be grouped into four cultural eras: the Tang Dynasty, Five Dynasties, Northern Song Dynasty and contemporary era. In addition, 5 typical celadon sherds from Yaozhou kiln, manufactured in the Tang, Five Dynasties, Northern Song, Jin, as well as Ming Dynasty were selected. The details are illustrated in Table 2 and the photographs of representative celadon sherds as well as the typical cross-sections of celadon are shown in Fig. 2.

For sample preparation, all sherds were sliced with a diamond blade cutter, and cleaned with ethanol solution in an ultrasonic bath, then mounted on an XY two-dimensional micro-positioner (Physik Instrumente) after drying. The surface of the sherd was used for analysis of the glaze, while the center of cross-section was used for the analysis of the porcelain body.

3. Results and discussion

Ancient porcelain was made of several raw ceramic clay materials following high temperature firing. The elemental distribution in porcelain is usually inhomogeneous [46]. In order to acquire the accurate composition, enlarging the size of sampling spot or multiple spots measurement has been used previously [46]. In this work, the method of averaging the information of 16 spots for each sample was adopted, as enlarging sampling spot size would decrease

Table 2
Archaeological information on the porcelain sherds from Yue kiln and Yaozhou kiln.

Production time	Yue kiln		Yaozhou kiln	
	Amount of sample	Location	Amount of sample	Location
Tang Dynasty	2	Cixi, Zhejiang	1	Huangbao, Shanxi
Five Dynasties	2	Cixi, Zhejiang	1	Huangbao, Shanxi
Northern Song Dynasty	2	Cixi, Zhejiang	1	Huangbao, Shanxi
Jin Dynasty			1	Huangbao, Shanxi
Ming Dynasty			1	Shanxi
Contemporary era	2	Modern kiln, Cixi		