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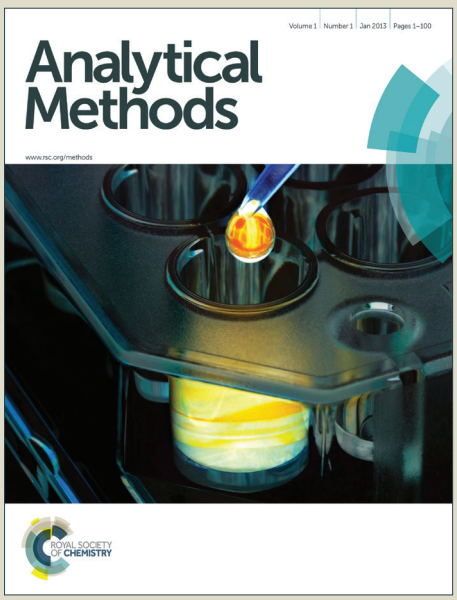

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The fast and direct characterization of blue-and-white porcelain glaze from Jingdezhen by laser ablation-inductively coupled plasma mass spectrometry

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Abstract: This study evaluated the classification of blue-and-white porcelains of Jingdezhen during the Ming Dynasties based on elemental concentrations measured by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). The blue-and-white porcelains of the Ming Dynasties are subdivided into three periods: Hongwu (HW), Xuande (XD) and Wanli (WL), representing to early Ming, middle Ming and late Ming Dynaties, according to Fe-Mn-Co distribution and Co contents. We propose ratios of Fe/Mn ratio and Co contents in light-blue areas as criterion to identify the classification of blue-and-white porcelains of Jingdezhen. The reference value of Fe/Mn of HW, XD and WL are 11.9±0.39, 2.31±0.54, and 7.09±2.07 μg/g, while the cobalt concentration of HW, XD and WL porcelains are <100 μg/g, 500-600 μg/g and >2500 μg/g, respectively. Other elements, including Li, B, Mn, Ni, Cr, Ho, Pb, Th, U and rare earth elements can also assist identification of the blue-and-white porcelain classification. Further measurements of more blue-and-white porcelains need to be analyzed using LA-ICP-MS to get more elemental concentration and obtain statistical database for blue-and-white porcelain identification.

Keywords: LA-ICP-MS; blue-and-white porcelain; Fe/Mn; Cobalt pigment; trace elements

Introduction

Blue-and-white porcelain was underglaze faience, which was painted on the body using cobalt pigment and presented dark blue, light blue and white after single firing. The Yuan (AD 1271-1368) and Ming (AD 1368-1644) Dynasties witnessed the development of the technique of blue-and-white porcelain: during the 80 years from the 1320s to the early 15th century, the blue-and-white porcelain made in Jingdezhen soon became the mainstream of Chinese porcelain production[1]. The Jingdezhen official kiln, also named the Guan kiln, was managed by the government. The production of the Jingdezhen Guan kiln represented the highest quality amongst the contemporaneous porcelain. The source of the pigment ore, the selection procedure and the machining process were subject to strict criteria and regulations, so the chemical composition of porcelain made in the Jingdezhen Guan kiln was uniform within one period and shows variations between different periods[2]. Cobalt pigment was imported from other countries to China in the Yuan and early Ming Dynasties[3-5], while domestic asbolane began to be used in the early Ming Dynasty. A mixed pigment composed by both imported and domestic origin was used in late Ming Dynasty.

The differences in cobalt ore sources, glaze components and manufacture techniques result in elemental concentration variations of porcelain, which provide the basis for authenticating the ancient ceramic origin, chronology, circulation and truth. Several analytical techniques has been applied in the major and trace elemental analysis of ceramics, including neutron activation analysis (NAA), energy dispersive X ray fluorescence (EDXRF), scanning electron microscopy (SEM), electron microprobe analysis (EMPA), time of flight mass spectrometer (TOF), thermal ionization mass spectrometer (TIMS), laser induced breakdown spectroscopy (LIBS), laser ablation/solution nebulization inductively coupled plasma mass spectrometry (LA/SN-ICP-MS), and SN-inductively coupled plasma atomic emission spectrometry (SN-ICP-AES)[3, 6-16]. SN-ICP-MS, TIMS, SN-ICP-AES and NAA techniques are rarely used in archaeological research due to chemical digestion of 50 mg to 5g sample powder during sample preparation prior to instrumental analyses. Although EDXRF and EMPA are an undamaged-analysis technique,

its high detection limits lead to the non-accurate trace element measurement. The LA-ICP-MS is an in-situ micro analytical technique for accurate multiple-elemental contents measurements with low detection limit and high spatial resolution, and can be applied in archeologist research based on trace element concentration analyses.

In this work, we used the LA-ICP-MS technique to analyze trace elemental concentrations of ancient Chinese blue-and-white porcelains from Guan kiln of the Yuan dynasty, the Ming dynasty and the Qing dynasty in Jingdezhen, Jiangxi province for the first time. The Ming Dynasty can be further divided into three periods, early Ming, middle Ming and late Ming Dynaties. The three subdivision of Ming dynasty were also named Hongwu (HW, Hongwu-Yongle, AD 1368-1424), Xuande (XD, Xuande-Hongzhi, AD 1426-1505) and Wangli (WL, Zhengde-Wanli, AD 1506-1620) periods, respectively. Three typical blue-and-white porcelains fragments (Fig 1) were manufactured in Hongwu, Xuande and Wangli periods, which were excavated from Jingdezhen Guan kiln site in 2002. They were selected to investigate the possibilities to clarify the blue-and-white porcelains based on trace elemental concentrations and ratios measured by LA-ICP-MS.

Methods and techniques

Instruments

In this work, micro in situ analysis of ceramic fragments was carried out by using laser ablation (GeoLas LA, Coherent, USA) coupled with a Quadrupole ICP-MS (Agilent 7700a ICP-MS, USA). In the LA system, the 193nm UV laser beam coming from the Compex102 laser unit (Lambda Physik, Germany) underwent homogenization, enabling flat-topped laser beam. The diameter of laser ablated spot sizes are varied from 5 to 120 μm with the homogeneous energy density distribution[17]. A home-made homogenizer is applied between the sample cell and ICP torch to obtain smooth signal. High purity helium gas (99.9995%) was used as the carrier gas. All LA-ICP-MS measurements were carried out using time resolved analysis (TRA) mode, which operated in a fast, peak jumping mode. Signal intensities were around 2M cps for 60 μm spot size in terms of uranium in NIST (National Institute of Standards and Technology, USA) Standard Reference Material 610. Each spot

analyses consisted of approximately 25s background, 3s of pre-ablation, and followed with 40s data acquisition. The pre-ablation step can remove any contamination on the sample surface. The ICP-MS instrument settings were optimized aiming at maximum and stable signal intensities, low oxide ratio and low double charge ratio for all analytes. Detailed instrumental parameters are summarized in Table 1. A scanning electron microscope (SEM, FEI Quanta FEG) was used for evaluating the laser ablated craters and the thickness of glaze.

Procedure for the characterization of different areas by LA-ICP-MS

Prior to analyses, the surface of the porcelain fragments was cleaned with high pure water (18.2MΩ·cm^{-1}, MilliQ-E) for about 5 min in ultrasonic bath. In order to obtain representative values for every ceramic fragment, several sampling positions were analyzed including dark-blue area (Co-enriched), light-blue area (Co-medial) and white glaze area (Co-least). Each ablation consisted of 200 laser pulses. At each spot, the sample surface was ablated for 3s to remove any contamination prior to real analyses. The signal of $^{59}Co^{+}$ was monitored to prevent from ablating the ceramic bodies (Fig 2), and the craters were examined finally by SEM with the acceleration voltage 20 kv, and the current 0.6 nA. NIST 610 was used for external calibration, while SiO_2 obtained by EDXRF was used as internal standard (IS). The LA-ICP-MS data was reduced by ICPMSDataCal software[18].

Results and Discussion

Characterization of laser ablated craters of porcelain

Fig 3 shows the section of porcelain and spot quality of laser ablated crater. The porcelain can be divided into two layers, the glaze layer and the body. The glazer layer is about 400 μm in thickness, while the top 280 μm part is free of hole (Fig 3A). The depth of the laser ablated crater is about 30 μm (Fig 3B) which can guarantee the crater is inside the hole-free glaze layer. The laser ablated carter shows round, deep and flat bottom characters, which reveals that the excimer laser can ablate the blue-and-while porcelain effectively (Fig 3B). Each crater consumed less than 1 μg sample with 60 μm spot sizes in diameter, which

is hardly observed with naked eye.

Comparison of Fe/Mn ratios and Co concentration in different areas of the blue-and-white porcelain

Fe/Mn ratio of light-blue areas of porcelain changed systematically of different periods and could be served as a criterion to identity the period of the blue-and-white porcelain since the blue area of the porcelain represents the original pigment, which can be used to trace the ore sources and the ore source is not changed during the same period[6, 13, 19]. The Mn, Fe and Co concentrations of white, light-blue and dark-blue areas of the three selected samples of HW, XD and WL periods measured in this work are listed in Table 2. The Mn concentration of both light-blue and dark-blue areas of HW is relatively lower than that of both XD and WL. The Mn contents of all blue areas of XD are higher than that of XL. The dark-blue and light-blue areas of XD porcelains show 20x and 5x higher Mn contents than that of HW porcelains, and 5.9x and 1.6x higher than that of WL porcelains. The Fe contents show different distribution among these blue-and-white porcelains comparing to Mn concentration. The Fe concentration of both white and light-blue areas of the blue-and-white porcelains of WL is almost 2x higher than others measured in this work which may indicate that the modification during late Ming Dynasty. The average Fe/Mn ratios of white areas of porcelains of HW and XD are close to 11 (10.8-11.4), which is lower than that of porcelains of WL ($Mean_{Fe/Mn}$=14.9±0.3). It is fairly difficult to distinguish the differences between different period of porcelain with only Fe/Mn ratios in white glaze areas. However, the Fe/Mn ratios in light-blue areas of HW, XD, WL, are 11.9±0.39, 2.31±0.54, and 7.09±2.07 μg/g, which is the same as Wen's conclusion[13] that the Fe/Mn values exceed 11 in the early Ming period, lower than 2.5 in the middle Ming period and 3~10 in the late Ming period.

Co is a candidate tracer besides Mn and Fe due to significant variations light-blue and white areas of porcelains of different periods. The light-blue areas of porcelains of HW, XD and WL periods have different Co concentration ranging from <100, 500-600 and >2500 ppm. The Co contents of white areas of the HW, XD and WL porcelains are <2, ~10,

and >20 μg/g which are much lower than that of both light-blue and dark-blue area of the blue-and-white porcelains of the three periods. The Co contents of light-blue area of porcelain of the three Dynasties are >40X of that of white areas of porcelains of the same sample, while the dark-blue areas show 100X higher than that of the white areas. The phenomenon could be caused by dark spots, which are the result of crystallization and enrichment of manganese and iron contained in cobalt blue pigment after high-temperature sintering.[20]

Analysis of the iron, manganese and cobalt correlation in light-blue areas allows us to identify the blue-and-white porcelains of the Ming Dynasties. In Figure 4 the triangular correlation plot of Fe, Mn and Co is displayed. These three elements in light-blue areas seem to have the ability to group the porcelains in three different clusters, while these elements in white areas are difficulty to identify the porcelains, as can be visualized in the ternary plot.

Trace elements in dark-Blue areas

One of the advantages of the LA-ICP-MS technique is that it can measure trace element concentrations with great accuracy and precision, as well as low detection limit (down to ppb level for most elements). The elemental concentration of the dark-blue areas of the blue-and-white porcelains of HW, XD and WL are more heterogeneous than that of light-blue and white areas due to some dark spots which concentrated in Co, Fe and REEs. The elemental concentration of the dark-blue areas of blue-and-white porcelains could be used to justify the source of the ore since these areas are more concentrated of pigments. Most elements (including Be, B, P, Mn, Fe, Ni, Cu, Zn, Ge, Sn, Ce, Ta, W, Pb, U and T_{REE} (total rare earth elements)) of dark-blue areas of porcelains of WL samples show middle concentration between the HW and XD, which indicates that the pigments of WL are the mixture of those used for HW and XD and this agrees with earlier results[13, 19] that the pigments of HW is imported while that of XD was local, and both imported and local pigments are mixed in WL period(Fig 5). All porcelain samples show similar chondrite normalized REE distribution (Fig 6) while the HW shows low REE contents and XD

samples show higher REE concentrations with positive Ce anomalies. The REEs concentrations of WL samples are between relative HW and XD samples which illustrate that the pigments applied in WL period are the mixture of imported pigments at HW period and local pigments at XD period.

The possible ore source used as the cobalt pigment in different periods

Some elements are taken into account to evaluate the possible ore source, including Fe, Mn and Co, as well as other elements which could be associated to cobalt, like Cu, Pb, As and Ni. Cu is characteristic of the HW samples for its high correlation coefficient (R^2=0.9353), but it seems to be poor correlated (R^2 value are 0.2862) in the XD samples but intermediate in WL samples (R^2=0.6004). Similarly, As becomes distinctive in the Hw samples for its high correlation (R^2=0.8797), while it is poor correlated (R^2 =0.0007) in XD samples and intermediate correlated (R^2=0.6532) in WL samples. Fe also has the similar behavior as Cu and As (R^2 values are 0.9926 in HW samples, 0.7638 in WL samples, and 0.3622 in XD samples). Pb is an element with high correlation with Co in the three samples (R^2 values are 0.6908 in HW, 0.8251 in XD and 0.3491 in WL). In XD samples, Mn have the highest correlation proportion (R^2=0.9715) apart from Ni (R^2=0.5255) and Li (R^2=0.4052). Based on the elemental correlations, cobalt pigments of each sample could be summarized as: Co-Fe-Cu-Zn-Pb (As) for HW samples, Co-Mn-Pb-Ni-Zn-Li for XD samples and Co-Fe-As-Cu-Pb for WL samples (elements in parentheses correlate to Co but low in the pigment; Fig.7 show the values of Mn, Pb, and Ni correlation coefficient with Co in XD samples).

Due to the high concentration and high correlation coefficient of Fe, Cu and Zn with Co in HW samples and cobalt production is usually linked to chalcopyrite ($CuFeS_2$) or pyrite (FeS_2), even sphalerite (Zn,Fe)S, cobalt source should be related to a cobalt-associated copper mineral or iron mineral, which could have been a probable source in the Yuan and early Ming periods. In the middle Ming dynasty, domestic asbolane ($(Co,Ni)OMnO_2 \cdot nH_2O$) is applied in the blue-and-white porcelain manufacture, which is composed of lithiophorite ($(Al,Li)MnO_2(OH)_2$), vernadite ($MnO_2 \cdot nH_2O$) and ebelmenite.

The combination of the ores explains high correlation coefficient for Mn, Ni and Li in XD. Some asbolane deposits were also exploited in Zhejiang, Jiangxi and Yunnan provinces, and began to be widely used in Middle Ming[13]. The correlation coefficient of Fe, Cu and As are intermediate between HW and XD samples, and the correlation coefficient of Li, Zn, Mn are lowest in WL samples, which proves again that the mixture of imported pigments and domestic asbolane were used in late Ming period.

Conclusions

Our study demonstrates that high-precise/accurate LA-ICP-MS trace element analysis is very powerful for charactering of blue-and-white porcelain by the Fe-Mn-Co and REEs concentration distributions of the pigment. The blue-and-white porcelains of Ming Dynasty can be divided into three phases: HW, XD and WL, based on the ratios of Fe/Mn ratio and cobalt concentrations in light-blue areas. The reference value of Fe/Mn of HW, XD and WL in light-blue areas are 11.9±0.39, 2.31±0.54, and 7.09±2.07 μg/g, respectively. The cobalt concentration of light-blue area of HW porcelains are lower than 100 μg/g, which is distinguished from that of XD porcelains (500-600 μg/g) and WL porcelains (>2500 μg/g). The LA-ICP-MS may be a very promising method for archaeological materials research due to its ability of measurement of more than 40 elements with low detection limit. Further work need to be done to analysis more blue-and-white porcelains to obtain statistical meaningful database for blue-and-white porcelain identification.

Acknowledgements

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Figure captions

Fig.1 three classical blue-and-white porcelains in Ming dynasty from Hongwu (HW), Xuande (XD) and Wangli (WL), which represent three phases: early Ming, middle Ming and late Ming . Each sample can be divided into three areas: dark blue area (-d), light blue area (-l) and white glaze (-w).

Fig.2 Signal intensity versus time profiles obtained upon ablation of the glazed layer of the XD sample. The cleaning period is not considered for quantification purposes.

Fig.3 SEM images of cobalt-decorated ceramics. A, image of the thickness of the vitreous layer. B, image of the crater produced by laser ablation

Fig.4 Triangle diagram relative to iron, manganese and cobalt in light-blue areas and white glaze.

Fig. 5 Comparison of LA-ICP-MS trace element contents (in μg/g) or ratio of dark blue area from Hw, Xd and Wl. Hollow rhombuses are the ratios of HW, while hollow squares are for XD and stuffed triangles are for WL. The error bars are 1*s*

Fig.6 Chondrite-normalized rare-earth-element (REE) patterns showing comparisons among HW, XD and WL. Black real lines are the ratios of HW, while gray lines are for XD and broken lines are for WL.

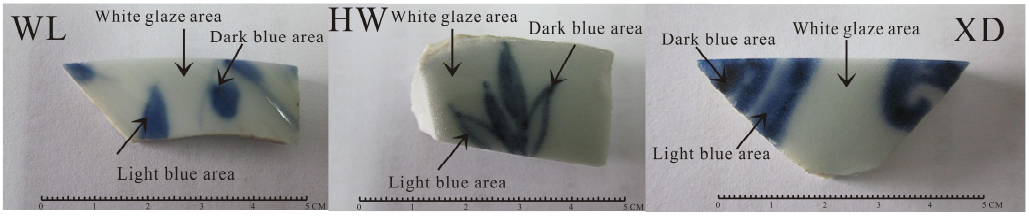
Fig.7 the values of Mn, Pb, Ni and Zn correlation coefficient with Co in XD sample.

Table 1 Instrument operating conditions and data acquisition parameters for the LA-ICP-MS measurements

Geolas laser ablation system					
Laserwave length	193 nm	Energy density	13 J cm^{-2}	Laser Frequency	5 Hz
Number of cleaning pulses	15 pulses	Spot size	60 μm	Number of pulses for analysis	200 pulses
Operating Parameters of ICP-MS					
RF power	1340 W	Carrier gas	1.0 L min^{-1}	He carrier gas	0.8 L min^{-1}
Omega lens	12.2 V	Omega bias	-110 V	Extraction 2	-200V
Extraction 1	0 V	Plate bias	-60 V	Deflect	14.2 V
Dwell time per acquisition point	20 ms	Scanning mode	Peak hopping	Sample depth	6.1 mm
Signal monitored	$^{7}Li^{+}$, $^{9}Be^{+}$, $^{11}B^{+}$, $^{23}Na^{+}$, $^{25}Mg^{+}$, $^{27}Al^{+}$, $^{29}Si^{+}$, $^{31}P^{+}$, $^{39}K^{+}$, $^{43}Ca^{+}$, $^{45}Sc^{+}$, $^{49}Ti^{+}$, $^{51}V^{+}$, $^{53}Cr^{+}$, $^{55}Mn^{+}$, $^{56}Fe^{+}$, $^{59}Co^{+}$, $^{60}Ni^{+}$, $^{63}Cu^{+}$, $^{66}Zn^{+}$, $^{69}Ga^{+}$, $^{72}Ge^{+}$,$^{75}As^{+}$, $^{85}Rb^{+}$, $^{88}Sr^{+}$, $^{89}Y^{+}$, $^{90}Zr^{+}$, $^{93}Nb^{+}$, $^{95}Mo^{+}$, $^{115}In^{+}$, $^{118}Sn^{+}$, $^{121}Sb^{+}$, $^{133}Cs^{+}$, $^{137}Ba^{+}$, $^{139}La^{+}$, $^{140}Ce^{+}$, $^{146}Nd^{+}$, $^{147}Sm^{+}$, $^{153}Eu^{+}$, $^{157}Gd^{+}$, $^{159}Tb^{+}$, $^{163}Dy^{+}$, $^{165}Ho^{+}$, $^{166}Er^{+}$, $^{169}Tm^{+}$, $^{172}Yb^{+}$, $^{175}Lu^{+}$, $^{178}Hf^{+}$, $^{181}Ta^{+}$, $^{182}W^{+}$, $^{205}Tl^{+}$, $^{208}Pb^{+}$, $^{209}Bi^{+}$, $^{232}Th^{+}$, $^{238}U^{+}$.				

Table 2 The Mn, Fe and Co concentrations of white, light-blue and dark-blue areas of the three selected samples of HW, XD and WL.

		Mn	Fe	Co	Fe/Mn
HW-white		591	6940	1.08	11.8
		593	6564	1.10	11.1
		590	6502	1.14	11.0
		608	7251	1.28	11.9
		576	6535	1.42	11.3
		648	7508	1.84	11.6
	Average±1s	601±25.2	6883±424	1.31±0.29	11.5±0.37
	RSD	4.19	6.15	22.1	3.26
HW-light		496	5675	41.5	11.4
		565	6720	81.5	11.9
		533	6692	105	12.5
		540	6477	111	12.0
		575	6823	112	11.9
	Average±1s	542±30.9	6477±466	90.2±29.9	11.9±0.39
	RSD	5.70	7.19	33.1	3.28
HW-dark		526	6369	130	12.1
		491	5886	135	12.0
		652	7440	164	11.4
		670	9143	418	13.6
		751	19867	1796	26.4
	Average±1s	618±107	9741±5707	529±719	618±107
	RSD	17.4	59.5	136	42.2
XD- white		562	6296	7.79	11.2
		427	4922	8.60	11.5
		633	6689	12.1	10.6
		541	6084	13.4	11.3
		633	6442	13.8	10.2
		537	5425	15.2	10.1
		521	5445	19.0	10.4
	Average±1s	551±70.9	5900±645	12.8±3.85	10.8±0.57
	RSD	12.9	10.9	30.0	5.3
XD-light		2762	6401	413	2.32
		2551	7589	420	2.97
		2330	6569	459	2.82
		3340	5680	549	1.70
		3789	8957	636	2.36
		4652	7905	732	1.70
	Average±1s	3237±876	7184±1190	535±129	2.31±0.54
	RSD	27.1	16.6	24.1	23.2
XD-dark		11545	11426	2124	0.99
		14158	13076	2870	0.92
		15559	15734	2892	1.01
		17240	15616	3079	0.91
		17276	15361	3183	0.89
		22299	14529	4696	0.65
		25545	16408	5563	0.64
	Average±1s	17660±4797	14593±1759	3487±1199	0.86±0.15
	RSD	27.2	12.1	34.4	17.7
WL-white		676	9776	19.1	14.5
		667	10080	29.2	15.1
		681	10081	33.3	14.8
		673	9924	37.1	14.7
		675	10298	47.2	15.3
		704	10596	67.4	15.0
	Average±1s	679±12.9	10126±289	38.9±16.7	14.9±0.29
	RSD	1.90	2.86	43.1	1.95
WL-light		2593	12330	2105	4.76
		1317	12900	2412	9.80
		1956	13252	2844	6.77
		1963	13781	3822	7.02
	Average±1s	1957±521	13066±610	2796±748	7.09±2.07
	RSD	26.6	4.67	26.8	29.2
WL-dark		4019	13191	2709	3.28
		2195	13870	3967	6.32
		5284	15625	5248	2.96
		1783	13716	3918	7.69
		1565	12730	3597	8.13
	Average±1s	2969±1615	13826±1102	3888±913	5.68±2.43
	RSD	54.4	7.97	23.5	42.8



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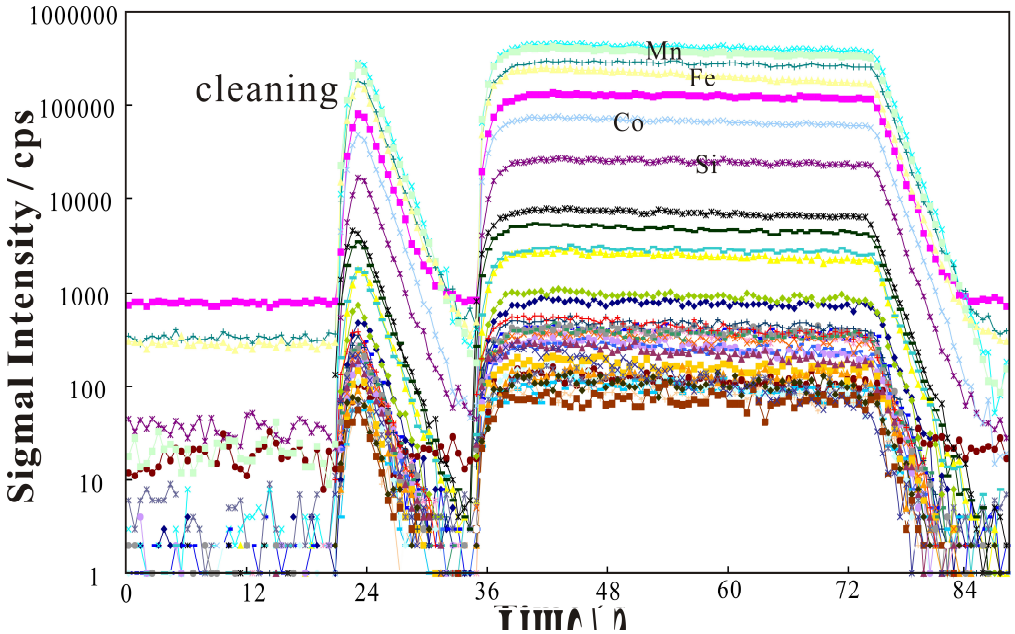

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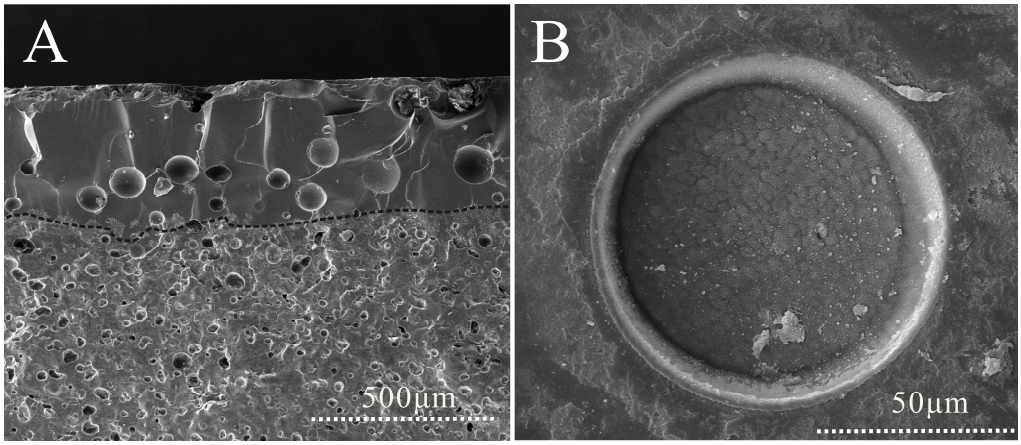

Fig.3 SEM images of cobalt-decorated ceramics. A, image of the thickness of the vitreous layer. B, image of the crater produced by laser ablation

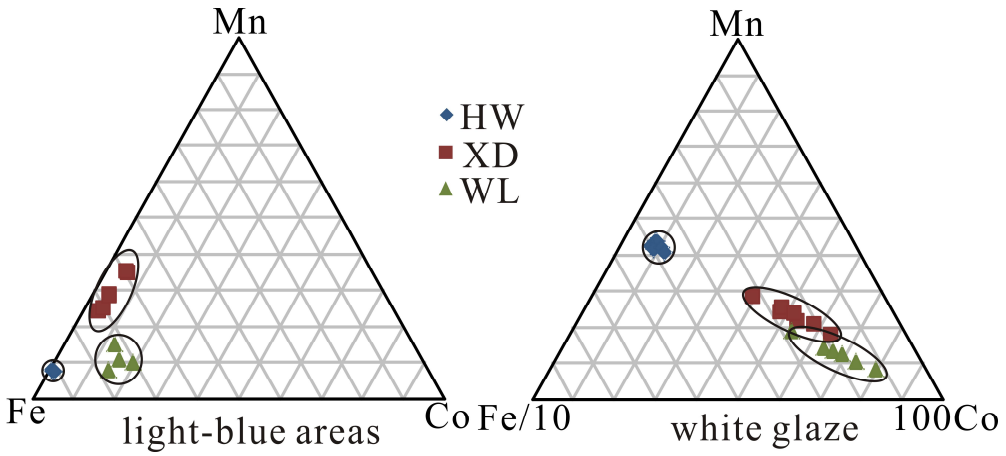

Fig.4 Triangle diagram relative to iron, manganese and cobalt in light-blue areas and white glaze.

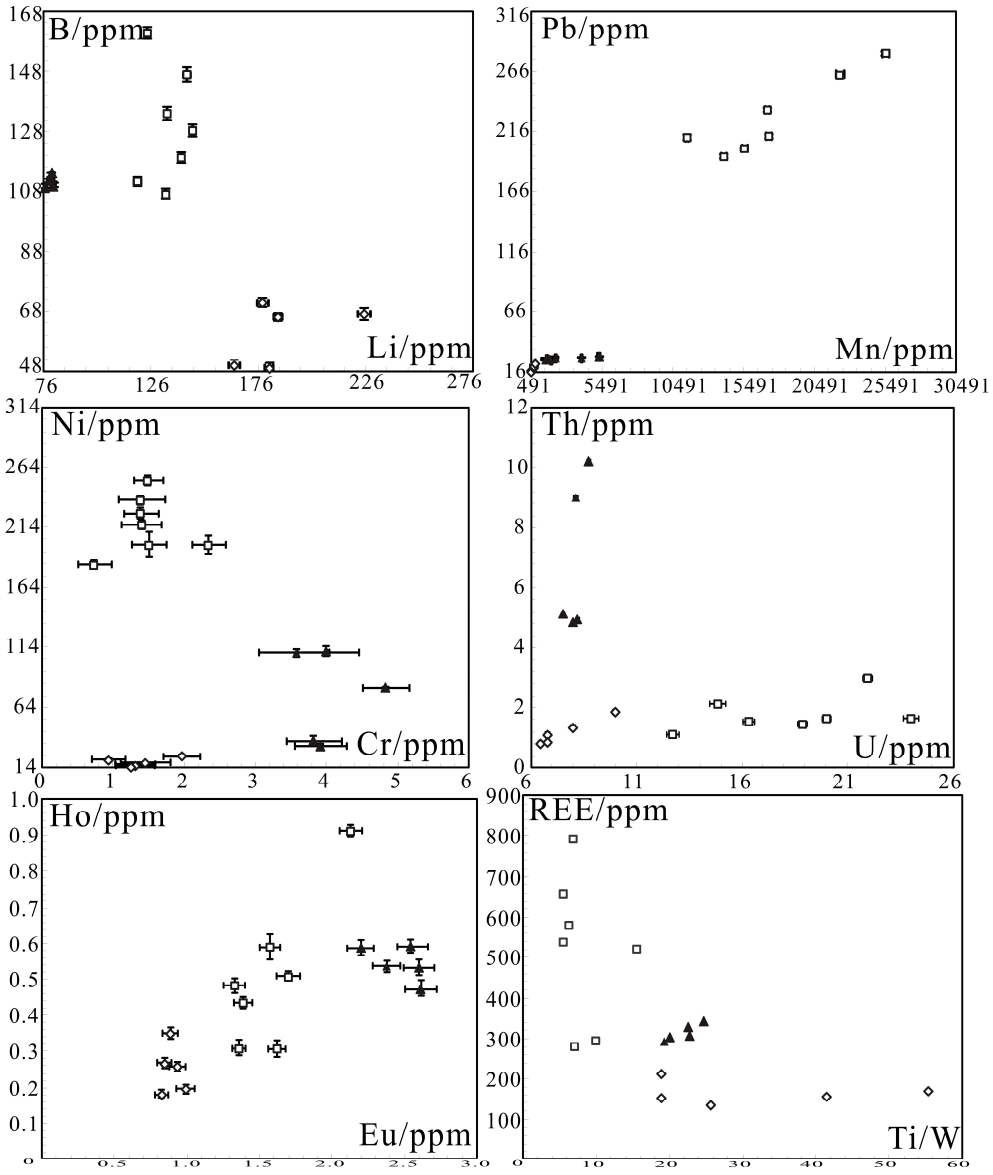

Fig. 5 Comparison of LA-ICP-MS trace element contents (in μg/g) or ratio of dark blue area from Hw, Xd and Wl. Hollow rhombuses are the ratios of HW, while hollow squares are for XD and stuffed triangles are for WL. The error bars are 1*s*

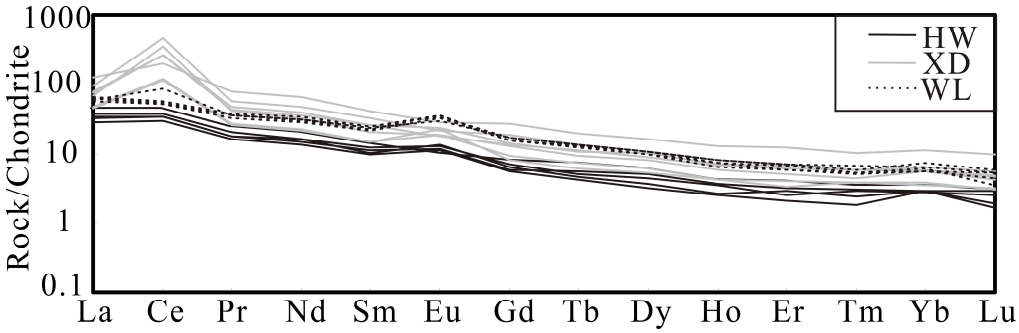

Fig.6 Chondrite-normalized rare-earth-element (REE) patterns showing comparisons among HW, XD and WL. Black real lines are the ratios of HW, while gray lines are for XD and broken lines are for WL.

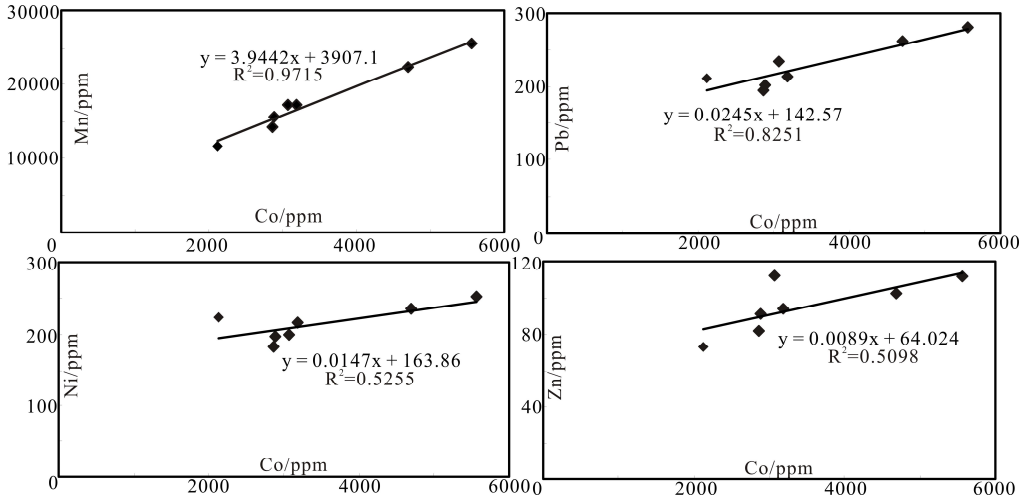

Fig.7 the values of Mn, Pb, Ni and Zn correlation coefficient with Co in XD sample.