The Blues of the Santa Cruz: A study of porcelain color and composition

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Abstract

For the study of ceramics found in a shipwreck, stylistic and provenance analysis are two approaches that can provide critical information about period and trade route of the vessel. In this paper, we investigate the characteristics of trade ceramics from the well-preserved Santa Cruz shipwreck, which sunk along the west coast of Luzon Island in the Philippines. Underwater excavation has brought to light more than 15,000 ceramics, mainly Chinese Jingdezhen blue-and-white porcelain and Longquan celadon of the Hongzhi period (1488-1505 CE) as well as other wares from Thailand, Vietnam, and Burma. Here, we have focused on the Jingdezhen blue-and-white porcelain and selected twelve dishes with similar decorative patterns, but showing different tones and shades of the blue color. The dishes were most likely produced in the same workshop or within a small region and the primary goal was to investigate production variability. The chemical composition of the ceramics and the characteristics of the blue pigment were studied non-invasively with portable X-ray fluorescence pXRF) and fiber optics reflectance spectroscopy (FORS). Results have shown that pXRF data are relatively homogeneous which reflects some constancy in term of raw materials procurement usage. On the other hand, although the blue pigment was as expected a cobalt-based material, FORS spectral profiles present significant differences which might be due to variations in the pigment composition and/or firing conditions, while for others, they could also be *related to weathering. From an archaeometry perspective, this research provides some insight on production standardization in Jingdezhen as well as on subsequent modifications that can affect ceramics found in an underwater archaeological context.*

Key words: Ceramics, shipwreck, Philippines, blue-and-white, pXRF

Introduction

Chinese blue-and-white porcelain was one of the most popular commodities during the pre-modern and early modern periods, and it was frequently found along the maritime trade routes. Because the decorative patterns of blue-and-white porcelain changed over time, the artistic style of this type of material is usually the primary research focus for clarifying dating issues. However, the chronology of Chinese blue-and-white porcelain was established based on fine wares made mostly for the court, and the variability of the production was relatively ignored. Regarding the color of the decoration observed with naked eyes, there is a broad range of "blues" on blue-and-white porcelain, ranging from blue, green, purple, gray, and sometimes even black.[1] In this research, we have used scientific analysis to investigate the causes of the color difference among a selected set of blue-and-white porcelain from a shipwreck. This archaeological context provides a particular opportunity for this research: loaded in the same boat as merchandise, a same kind of mass-produced cargo was most likely made around the same time and was even from the same or nearby workshops.

The artifacts were selected from the cargo of the Santa Cruz shipwreck that sunk about ten nautical miles off the northern Zambales coast on Luzon Island. This shipwreck is one of the representative fifteenth-century vessels in maritime Asia (Fig. 1). The underwater excavation was conducted in 2001 by the National Museum of the Philippines in collaboration with the Far Eastern Foundation for Nautical Archaeology. The vessel was about twenty-five meters long and six meters wide and was built following the so-called South China Sea Tradition of shipbuilding. The structure itself is well preserved as 80 percent of the lower hull was discovered and the cargo was still loaded in the 16 transverse bulkheads. A variety of materials were found in the Santa Cruz including ceramics, metal products, glassware, wooden and stone materials. Among these artifacts, more than 15,000 ceramics were recovered during the campaign, including Chinese and Vietnamese blue-and-white porcelain, Chinese celadon, as well as Thai and Burmese stoneware (Orillaneda, 2008, 2016). Mainly based on the style analysis of the ceramics, the Santa Cruz shipwreck could be dated to the Hongzhi period in Ming China (1488~1505 CE). The discovery of the Santa Cruz shipwreck and its cargo is an important piece of evidence for the so-called *Dongyang* (Eastern Sea, from the Chinese perspective) trade route during the "Age of Commerce" in Southeast Asia (Reid, 1988, 1993). Additionally, the vast amount of late fifteen-century CE Jingdezhen blue-and-white porcelain on board marked the end of the "Ming Gap" (Brown, 2009) and the revival of the trade of Chinese ceramics in Southeast Asia. This research therefore, not only contributes to the general issue of color variation among blue-and-white porcelain but also sheds light on the production process and trade of Chinese porcelain during this particular period.

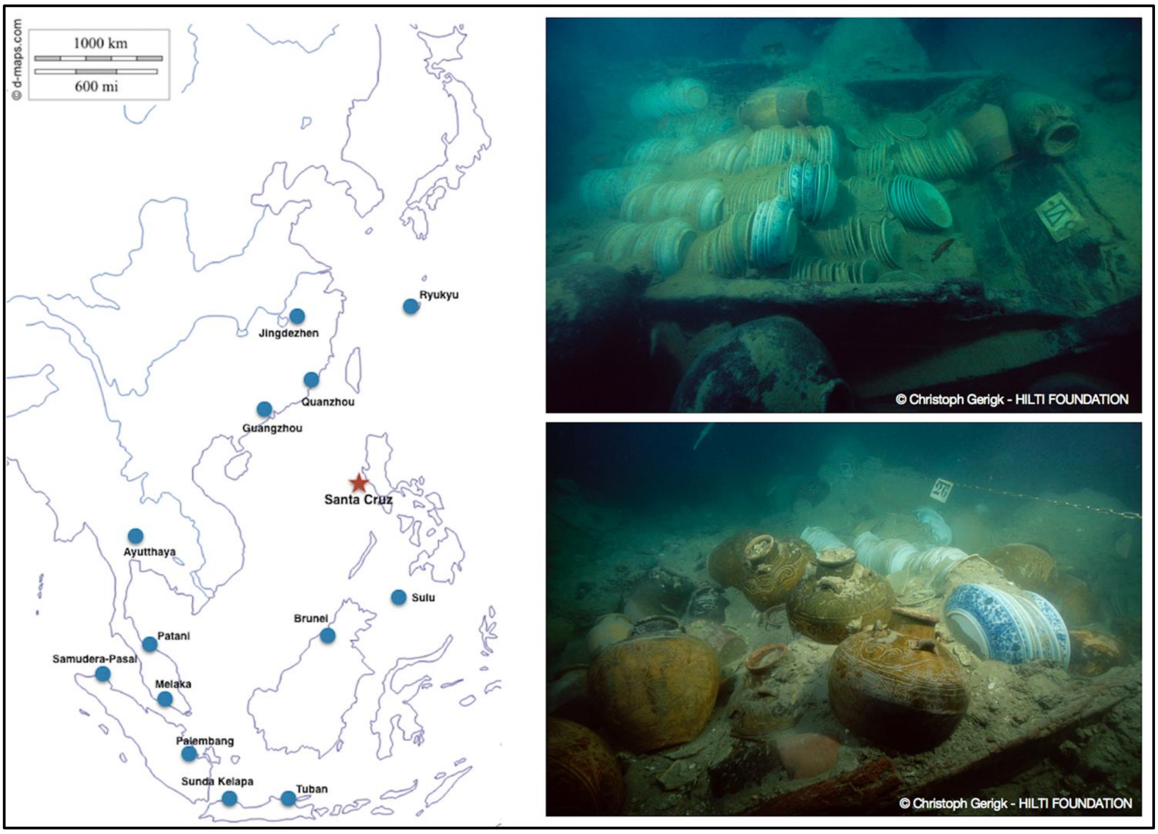

Fig. 1: Map of East and Southeast Asia with the location of the Santa Cruz Wreck (left) and images taken during the excavation (right).

Materials and methods

Blue-and-white porcelain

Twelve blue-and-white dishes were analyzed with a particular focus on the different tones and shades of the blue color (Tab.1; Fig. 2). The porcelain ware was loaded in piles mostly at the port side of the boat, and the dishes were distributed in bulkhead 1, 3, 5, 7, and 9 (Orillaneda, 2008). The locations of these samples show that those from the same bulkhead did not necessarily share similar appearance or quality (e.g. III-2001-Z-2963 and III-2001-Z-3245). The selected dishes are all saucer-shaped and of similar size: diameter of the mouth rims is about 26cm, height is about 4cm, and the diameter of the foot rim is about 13cm. Most of them are entirely decorated with the same kind of casual-style patterns (e.g., flora and rock, deer and pine tree). The blue decoration was applied on both the interior and exterior of the dishes. To leave the foot rim unglazed, the transparent glaze was applied separately at the bottom of the dishes. In many cases, the glaze applied on the bottom looks different from the glaze in the other parts. While all dishes have been cleaned and desalinated after the excavation, some still show shell encrustations.

Methods

Two non-invasive technologies were used in this study: portable X-ray fluorescence (pXRF) and fiber optics reflectance spectroscopy (FORS). Previous research has shown that these two techniques are suitable for the compositional analysis of blue-and-white porcelain and details of the settings used here for the two instruments can be found in the corresponding paper (Fischer and Hsieh, 2017). For pXRF, soil mode was used to acquire data on minor and trace elements from both the blue and white areas while mining mode was used for major elements from the transparent glaze. Measurements on the blue areas (glaze + blue pigment) were all taken on the main decoration at the center of the plate. As to the white area, due to the difference of the glaze application mentioned above, measurements were taken on two locations: one on the area next to the blue decoration and another one at the bottom. Depending on the size of the 'white' areas, the location of the first measurement was sometimes on the external side of the dishes. Compositional data of the body was collected on the only dish with a bare bottom (i.e. III-2001-Z-7026). Regarding FORS, measurements were taken on the blue decorated areas and on the 'white' at the bottom because there was not enough space for the measuring probe in between the blue decor.

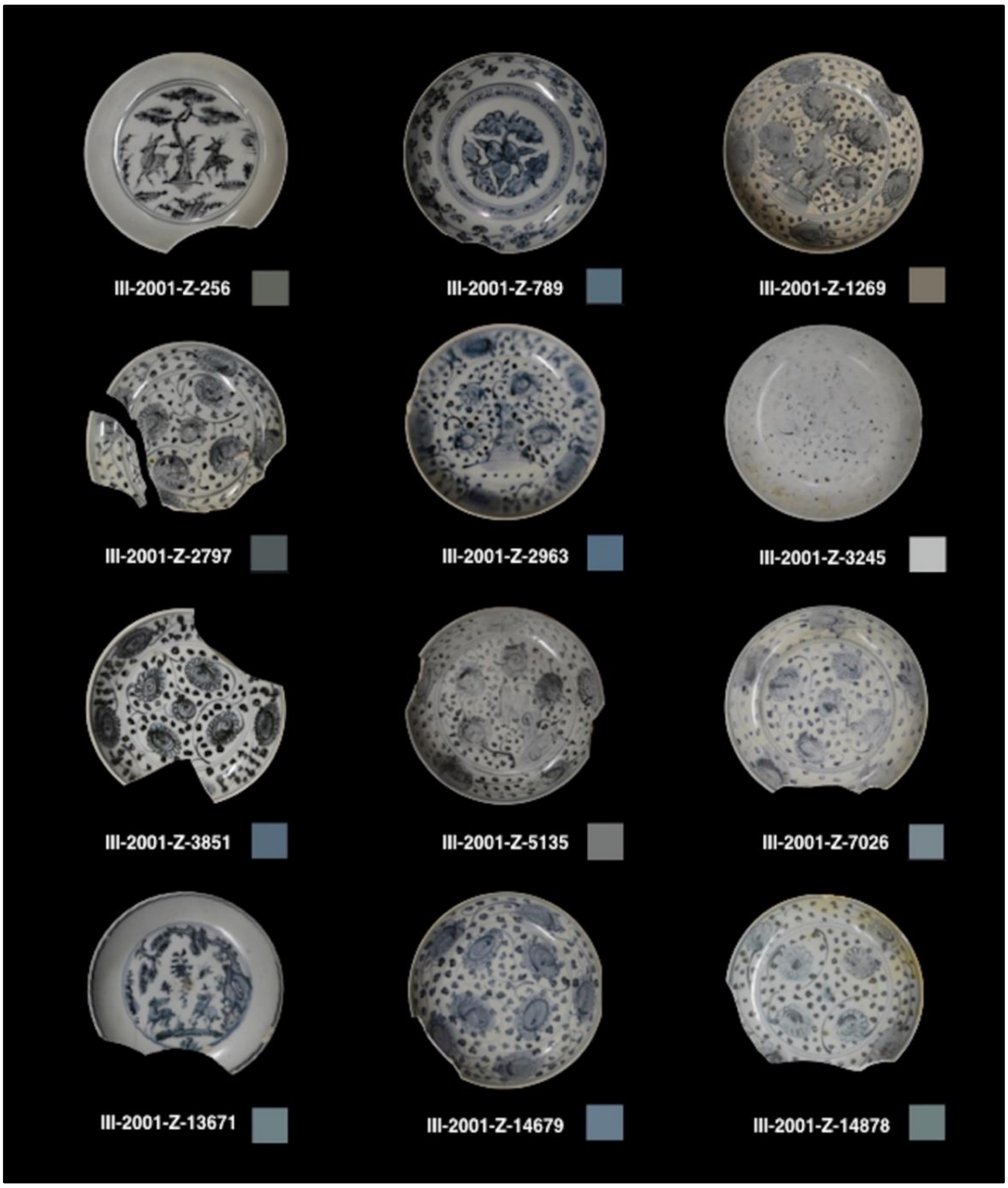

Fig. 2: The dishes selected and analyzed in this study, with the color references of the decorations.

Table 1. Characteristics of the selected blue-and-white porcelain dishes

Reference	Grid location	Motif	Aspect of the glaze	Color	Colorimetric data*		
					X	Y	Z
III-2001-Z-256	N22W5	deer and pine tree	transparent; a bit shrinkage at the bottom	brownish gray	13.5	12.4	3.9
III-2001-Z-789	N19W7	fruit and vine	transparent; a bit shrinkage at the bottom	blue	14.5	14.0	6.6
III-2001-Z-1269	N19W8	flora and rock	some opacity, crack concentrate on one side	greenish brown	20.3	17.9	5.1
III-2001-Z-2797	N27W5	flora	semi-transparent; shrinkage at the bottom	gray	10.6	10.0	3.7
III-2001-Z-2963	N29W5	flora and rock	transparent and crazed on the decorated area; shrinkage and milky at the bottom	blue	14.6	14.3	7.4
III-2001-Z-3245	N29W5	flora and rock	opaque; milky; shrinkage	light gray	56.2	51.0	17.9
III-2001-Z-3851	N30W7	flora	transparent at the decorative area; milky and shrinkage at the bottom	gray	14.0	13.5	6.5
III-2001-Z-5135	N25W10	flora and rock	some opacity, shrinkage and cracks	gray	20.3	18.5	6.5
III-2001-Z-7026	N31W7	flora	opacity, shrinkage	gray	24.3	22.9	9.3
III-2001-Z-13671	N36W7	deer and pine tree	transparent	blue	21.4	20.4	8.3
III-2001-Z-14679	N34W10	flora	semi-transparant; cracks	blue	19.5	18.8	8.7
III-2001-Z-14878	N34W5	flora	some opacity	gray	20.5	19.7	7.6
*Data type: 1964 CIE 10° XYZ standard colorimetric data							

Results and discussion

Visual observations

The selected blue-and-white dishes share general characteristics regarding size, form and decoration styles. The shape of the foot rims and the way of applying the glaze show that the manufacturing process might be similar. In general, the glaze is quite transparent though a bit grayish, but for a few dishes, it shows a milky and opaque appearance that influence the visibility of the blue pigment beneath. Cracks and dewetting features related to shrinkage are also commonly observed. In some cases, these characteristics are only visible on one side of the dish, suggesting that the variations of glaze might be mainly due to firing conditions, such as the temperature of the kilns and where the plates were loaded in kilns. The surfaces of the glaze are weathered to various degrees after staying hundreds of years under the sea. In some cases, it is however hard to tell whether the opaque aspect of the plates is due to their inferior quality or weathering at first glance. The blue areas are generally dull and look greenish or grayish with the naked eye. The primary motifs are outlined and filled with light colors, whereas the small leave patterns were drawn directly with thicker pigments favoring the formation of darker spots after firing. Sometimes, a brownish material can be observed on the top of those dark blue areas, which is most likely due to weathering.

Chemical composition and production kilns

Chemical composition data obtained with pXRF on the transparent glaze indicate that the blue-and-white plates were produced in Jingdezhen based on the concentrations of some discriminative elements such as zirconium, thorium and titanium (Tab. 2), a result consistent with the stylistic analysis and historical context. Values for these elements are close to the ones measured in previous studies despite the different time periods (Fischer and Hsieh, 2017; Ma, et al. 2012) and such compositional similarities could correspond to a relative constancy in the procurement of raw materials and processing technologies from the middle to late-Ming period. However, variations in rubidium levels, i.e. the higher values reported in the present study, also found for the Guanyinge and other unspecified late-Ming kiln sites (Rb: 428±78 ppm, Zhu et al. 2016; Rb: 436±84 ppm, Ma et al. 2012) compared to the lower averages measured on Jingdezhen blue-and-white ware from the Nan'ao One shipwreck in China (Rb: ~270 ppm, Zhu et al. 2016) and sherds from the Philippines and Indonesia (315±40 ppm, Fischer and Hsieh 2017) dated to the late-Ming and early-Qing periods, might reflect some intra-site variability among the numerous kilns in Jingdezhen.

Based on the analyzed elements[2], the chemistry of the glaze measured in the 'white' area, corresponds to an alumino-silicate glassy network containing calcium and potassium added as fluxing agents and network modifiers. The composition of the glaze is relatively homogeneous, independently of its degree of transparency, making it difficult to identify the origin of the opacity which could be linked to the firing process, underwater weathering, or both. For some dishes, calcium levels are low and such levels, associated with lower firing temperatures in some areas of the kiln, could indeed contribute to opacify the glaze. On the other hand, almost invisible defects in the glaze induced by composition and firing conditions could favor the weathering in an underwater environment as well, and explain the lack of transparency for the glaze of some dishes. Also noticeable are some differences in the composition of the glaze applied to the base which shows lower calcium and higher iron and titanium in comparison to the ‘white’ and decorated areas. Although this trend is not systematic (see e.g. III-2001-Z-3245), it could suggest usage of a slightly different recipe for the glaze applied to the bottom. Finally, it can be mentioned that the desalination process was rather effective as the levels of chlorine and sulfur, not reported here, are generally low, apart may be for the dish with reference III-2001-Z-14679.

Table 2. Compositional data from pXRF and FORS analysis.

Accession N°	Spot	Selected Elements from pXRF Analysis												FORS Analysis					
		Major (% oxides)		Minor and Trace (ppm)										Spectral absorptions (nm)*					
		CaO	K_2O	Fe	Ti	Mn	Rb	Sr	Zr	Co	Cu	Th	Ni	Mn(II)	Mn(III)	Co (II)			H_2O
III-2001-Z-256	blue			2546	--	7265	408	87	46	1276	47	11	341	421w	491vw	519w	583s	678s	
	white	4.4	5.2	2104	116	340	412	95	45	--	28	8	--						
	base	3.9	5.1		84	495	403	71	58	--	28	17	71						
III-2001-Z-789	blue			4019	128	3035	385	99	44	279	37	10	244	422m	491w	517m	582s	673m	
	white	6.1	4.0	3585	125	348	411	97	50	--	27	10	--						
	base	5.5	4.0		139	391	406	101	48	--	19	9	--						
III-2001-Z-1269	blue			2996	103	3038	385	82	57	442	54	11	206	420m	489vw	521vw	584m	679s	+++
	white	5.4	5.0	2553	251	326	392	87	53	--	33	11	83						
	base	3.4	5.0		187	254	395	62	63	--	28	12	57						
III-2001-Z-2797	blue			3375	115	1796	448	109	45	275	51	9	115	424w	493w	520m	585s	676s	
	white	6.9	4.2	2697	116	295	408	136	40	--	32	--	67						
	base	5.8	4.3		228	371	475	122	56	--	37	15	77						
III-2001-Z-2963	blue			4678	--	3840	307	100	45	611	45	9	415	422w	491w	517m	583s	677m	
	white	6.6	3.9	4591	--	440	318	95	53	--	37	10	107						
	base	5.7	4.0		95	464	326	72	59	--	26	14	83						
III-2001-Z-3245	blue			3484	--	2150	322	111	48	343	58	9	281	423w	491w	521m	581s	665br	++
	white	5.4	4.2	2997	156	262	335	97	54	--	33	12	--						
	base	5.5	4.3		133	233	334	73	63	--	29	14	54						
III-2001-Z-3851	blue			3408	--	8910	333	94	50	1047	112	12	237	423w	491w	520m	583s	677s	
	white	8.1	4.1	3194	148	602	331	112	49	--	52	12	87						
	base	6.6	4.1		229	439	361	78	62	--	32	16	82						
III-2001-Z-5135	blue			3376	285	2011	417	106	49	186	113	9	164	426w	491vw	522m	585s	675s	++
	white	5.6	4.2	3131	81	229	457	84	53	--	47	10	--						
	base	5.0	4.7		151	327	492	71	58	--	37	10	86						
III-2001-Z-7026	blue			2925	105	1305	573	88	39	133	48	8	218	421m	491w	519m	583s	670s	++
	white	5.9	4.2	2835	202	240	601	92	48	--	24	--	--						
	base**	4.1	3.5		266	310	669	42	57	--	19	18	--						
III-2001-Z-13671	blue			3884	133	3543	392	92	50	355	56	12	465	421m	492w	520m	581s	672m	
	white	5.9	4.8	3061	191	428	394	91	52	--	49	10	111						
	base	4.4	4.6		117	398	414	66	55	--	29	13	64						
III-2001-Z-14679	blue			3416	103	2516	400	54	52	356	34	10	351	421w	490w	518m	584s	671m	+
	white	5.9	4.3	2561	214	438	391	71	50	--	35	8	88						
	base	4.9	4.5		172	528	415	49	61	--	27	14	--						
III-2001-Z-14878	blue			4335	129	3169	539	84	45	166	71	21	701	422m	492w	522m	586s	655br	
	white	5.9	4.6	3752	142	347	567	85	54	--	66	10	93						
	base	4.9	4.1		255	607	655	57	66	--	43	13	56						

* Absorptions: vw: very weak, w: weak, m:medium, s: strong, br: broad
** body

Composition and color variations of the blue decorations

The pXRF analysis of the blue decorated areas has shown that the cobalt-based pigment contains high levels of manganese, low iron and significant amounts of nickel as well as traces of copper. After subtraction of the manganese and iron contribution from the transparent glaze (white area), normalized percentages of Mn, Co and Fe are similar to the blue pigment analyzed on other export blue-and-white porcelain produced in Jingdezhen (Fig. 3). This compositional profile is consistent with the results of previous studies (Chen et al., 1978; Cheng et al., 2005; Fischer and Hsieh, 2017; Wen et al., 2007) and also supports the use of Mn-rich asbolite ores in folk kilns during the Hongzhi period of the Ming dynasty.

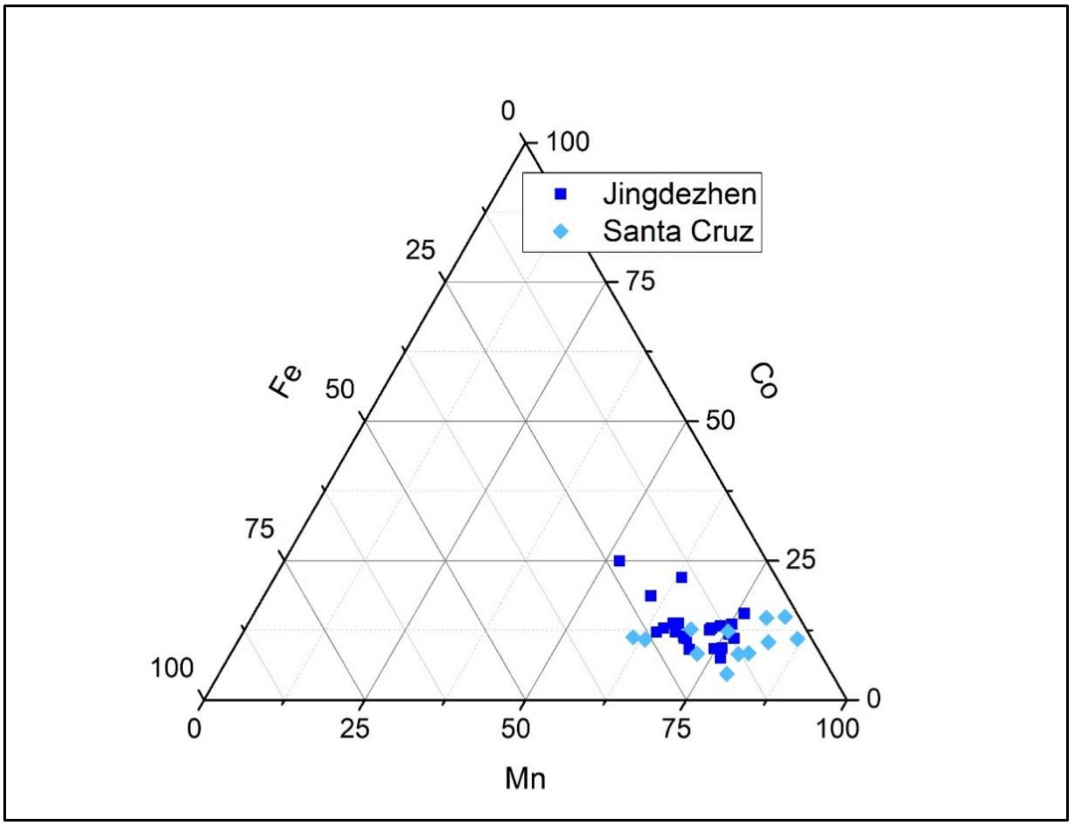

Fig. 3: Ternary plot showing the blue pigment composition based on the relative proportions of Co, Mn and Fe.

FORS analysis provided colorimetric data using the 1964 CIE 10° XYZ standard which were converted to visible references, confirming the variability of the blues based on visual observations (Fig. 2). Spectral profiles obtained with FORS on the blue decorated areas (Fig. 4, left) show the characteristic absorptions of Co^{2+} in tetrahedral coordination with the triplet located around 520, 580 and 670 nm (Ceglia et al., 2012; Fischer and Hsieh, 2017). For some plates, darker colors translate in an overall lower spectral reflectance in the visible, but the cobalt absorptions are always present though with variable intensities (Tab. 2). However, in these darker areas obvious signs of weathering are often visible (Fig. 4, right) and the associated brownish color is most likely due to an oxidation of Mn and Fe phases. Moreover, the grayish or blackish hue of the decoration might be correlated with high levels of manganese in the composition of the pigment, combined with redox firing conditions favoring the crystallization of Mn-rich oxide phases (Wen et al., 2007). Some analogy can be made with ‘black’ glasses containing several percent of MnO making the glass appear black to the human eyes (Möncke et al., 2014). Similar dark colors were also found on blue-and-white from the Chenghua period (1465 ~1487 CE) though the amount of manganese in the blue pigment was not analyzed (Qu et al., 2014). In the FORS spectra, the presence of Mn-rich phases might be associated with the absorption of Mn(II) at 420 nm and a broad but weak Mn(III) absorption around 490 nm (Tab. 2), although the latter attribution would need to be confirmed by further research on reference materials. Finally, in the near infrared spectral range, some plates show a strong and asymmetrical combination band around 1910 nm which seems to be correlated to the degree of opacity and can be attributed to the presence of water adsorbed in the glaze and/or in the body that might result from the weathering and/or indirectly reflect a more porous body and lower firing temperatures.

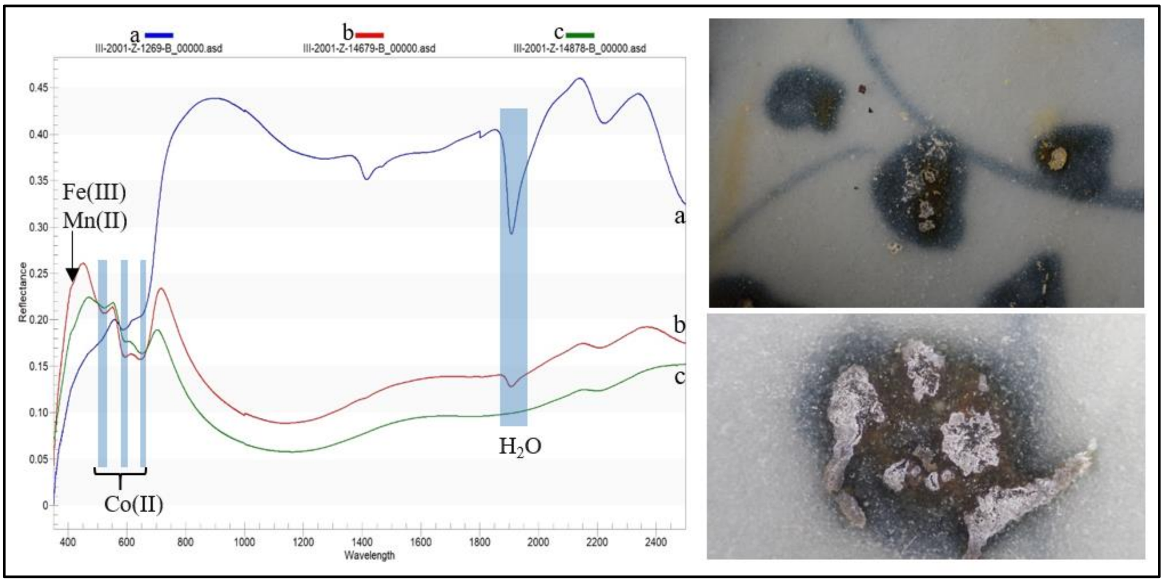

Fig. 4: FORS spectra of the blue decorated area from selected dishes (left) and weathering features of the glaze and dark spots concentrated in blue pigment. (III-2001-Z-14878, right)

In this preliminary study, the variability of the blue colors of blue-and-white porcelain from Santa Cruz shipwreck was explored by using pXRF and FORS. Factors associated with composition, recipe and production process as well as underwater conditions can all affect the appearance of the excavated ware, the most critical ones being the recipe of the glaze, the firing conditions and the weathering induced by water. The results of the pXRF data have shown that regardless of the appearance variability, the chemical composition of the selected dishes share the characteristics of middle and late Ming blue-and-white porcelain produced in Jingdezhen. The pXRF data also shed light on some aspects of production processes of the dishes. FORS provided colorimetric data which are well correlated with the visual perception and variability of the 'blue' colors. Also, the spectral profiles and related absorptions have given some insight on the potential causes for the darker colors. To further examine the variability of the blue-and-white porcelain loaded in the Santa Cruz, it would be necessary to investigate a larger set of dishes and if possible, compare dishes from the same pile.

Endnotes

[1]It is worth noting that the Chinese name of blue-and-white porcelain is "Qinghua," meaning "patterns with qing color." And qing can refer to colors ranging from green, blue and black.

[2]For major elements, values for Si and Al are considered qualitative and not reported in Table 2.

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Bios

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Dr. Christian Fischer received a PhD in Geochemistry and Physical Chemistry from the Louis Pasteur University in Strasbourg. After years of scientific research in the private sector in France and China, he returned to academia in 2001. At UCLA since 2005, he has been teaching on various topics including archaeometry, conservation science and stone conservation as well as spectroscopy for the analysis of archaeological materials. He conducts research on raw materials sourcing and conservation of cultural artifacts, particularly of stone in Cambodia and neighboring countries in collaboration with the École Française d'Extrême-Orient (EFEO), Chinese export blue and white ceramics in Southeast Asia, and is involved in other projects in Cyprus, Chile and Mexico. Dr. Fischer is also the co-director of the Archaeomaterials group and the Molecular and Nano Archaeology Laboratory at UCLA as well as a scientific consultant for UNESCO on the preservation of cultural heritage.

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