Tang Dynasty (618-907) bowl measured with PIXE

M. Laitinen[a,b], M. Käyhkö[a], G. Hahn[c],

N. von Uexküll-Güldenband[c], T. Sajavaara [a,b]

[a] University of Jyvaskyla, Department of Physics, P.O. Box 35, 40014 University of Jyvaskyla, Finland

[b] RECENART – Research Center for Art, Jyväskylä, Finland

[c] Documents + Documentaries, Pte. Ltd. 51, Waterloo Street, #02-01, 187969 Singapore

Abstract

Brownish bowl originating from an underwater shipwreck located near Belitung island in the Java Sea, some 600 km south-east from Singapore, has been measured with particle induced X-ray emission. This study was a pilot project for the – now a spin-off company – Recenart research team where one target was to evaluate the authenticity of the different type of art objects. PIXE measurements were done from three different material positions from a single bowl received from a customer. These locations were categorized as a bluish/greenish pigment (under glaze), thick glaze and the body clay. When the obtained data was compared to the other references from different dynasties and kiln sites, the closest match was indeed the Tang dynasty, Tongguan/Ghangsha kiln-site potsherds – from where the bowl in question was also suspected to originate.

Keywords: PIXE, Tang dynasty, Ghangsha kiln ware, Belitung shipwreck

1. Introduction

Art forgeries are a major problem in the art market which was about €51 Billion in 2015 [1] [2]. Depending of the source, the estimate of the number of forgeries in the art market range wildly, from 2 % to more than 70 % [3] [4]. Here, the lower figure comes from the traditional gallerist/art dealer, the higher from the art research institute in Switzerland.

The problem of authenticity does not only apply to the paintings but also to the ceramics. For the ceramics, however, it is possible to estimate the manufacturing time of the object by thermoluminescence dating (TL) [5], but this method always requires physical sampling. Small sample of few hundred mg for the TL dating is not a problem for an already broken shard but for an intact ancient object of an unknown value, it can be a limiting factor. To estimate the authenticity of this type of objects the elemental composition data can already rule out fake products in many cases, without the need of a physical sampling.

In this study, a clay based bowl with bluish/greenish colors and bright glaze was received from the customer (see Fig. 1). For this type of ceramic objects, particle induced X-ray emission (PIXE) measurement is one option to gain the elemental data of the pigments and materials of the object. Second option for the elemental data could have been the X-ray fluorescence (XRF) measurement, but ultimately the PIXE is better choice because of its smaller minimum detection limit (MDL) at wider elemental range [6] [7]. Another traditional method to evaluate the authenticity of the object is to compare the theme, style and shapes of the object against the known artefacts of the time period (or the specific artist) in question – a technique used by the connoisseurs. When these two complementary approaches – materials analysis and art historical study – are combined, a more accurate understanding can be formed from the object.

To form a deeper understanding of the origin of the bowl was also something that this pilot study of the Recenart-project [8] was focused of. The received and now studied bowl (Fig. 1) originated, according to the customer, from the Belitung shipwreck [9]. The objects at the

shipwreck site are mostly different type of Changsha ware from Tongguan kiln site originating from the Tang dynasty (618−907) during which time the cobalt containing blue pigments appeared in Chinese ceramics for the first time [10]. Two research questions link together in this matter: Is it possible that the bowl in question originated from the Tongguan/Ghangsha kiln site from the Tang period and does the blue pigment of the bowl contain cobalt?

Figure 1. a) PIXE setup of the bowl, b) bluish/greenish measurement positions (1-2) from the front side and c) body clay (3) and thick glaze (4) positions from the back side of the bowl.

2. Measurement setup and methods

PIXE analysis was performed using a 3 MeV proton beam from the 5SDH-2 Pelletron accelerator at the Accelerator Laboratory of the University of the Jyväskylä. The measurements were done with an ion beam that was brought to the atmosphere through a 200 nm thick, 2×2 mm^2 SiN window from Silson [11]. Prior to the SiN window, the beam was collimated to ∅1.5 mm. Single X-ray detector, X-123SDD spectrometer from Amptek [12] was used with the ~110 µm thick polyimide foil in front of the detector to filter the low-energy X-rays and to stop the backscattering protons from entering the Si crystal. Due to the polyimide filter practical data from the elements lighter than potassium could not be obtained.

The beam and the X-rays from the sample had to travel 19 mm and 32 mm in the air before hitting the sample or the detector, respectively. Detector angle was 36 degrees from the beam direction. The measurement positions were selected so that the millimeter-sized beam spot fitted

inside the area in question, creating X-ray emission from the relatively uniform colored positions.

Analysis software was Gupix v2.3 [13] where iterated matrix solution was used to calculate the elemental concentrations. Chemical compositions in the analysis were assumed to be oxides with nominal valence "-2" for the oxygen, which was absorbed in the air and was not seen in the detector. During the Gupix analysis multiple trials were made using initially more elements in the fits than at the end. Results shown in the next section are directly extracted from the Gupix results. Standard reference materials SRM 611 (trace elements in glass) and SRM 1633C (coal fly ash) were used to calibrate the analysis. The exact ion beam current was not measured but it was monitored from the argon of the air (also during no sample). The current did not change between the 20 second measurements from different sample positions (4 in total) and the reference samples, which were measured both after and before the sample spots. Count rate at the detector was in the order of 1000 counts/s.

Prior to the bowl in question, test measurements were made from a glaze in another bowl and the beam damage was evaluated (flux vs. time). Based on these test measurements, the 20 second measurement time was selected to be sufficiently short to prevent any visible beam damage to the glaze of the studied bowl. The only actual pretreatment of the measured bowl is thought to be de-salting after the recovery from the wreck and the PIXE analysis will thus include the possible elemental changes due to long period in the sea-water.

3. Results

The elemental data from the Gupix analysis for bluish/greenish position, thick glaze and body clay sample spots (see Fig. 1 and Table 1) were compared against the ancient Tongguan kiln site / Ghangsha ware (shard) measurements from the Tang dynasty period [14] [15] (see also Fig. 2). In addition, a selection of other measurements from different [16] [17] [18] Chinese kilns and dynasties from different time periods were included to the comparison. These reference data-sets

from other kiln sites and time periods gave some normalization for the better understanding of the possible scatter between the measured bowl and the known Ghangsha ware data. To clarify our interpretation about the color/pigment and the glaze: this particular bowl had transparent glaze and the colors seemed to exist underneath the glaze.

Table 2. Gupix analysis results from the four measurement spots (see Fig 1.). Values for each element represent mass composition in ppm and the uncertainty of the result is given in % of the value e.g. [result in µg/g and the statistical+fit uncertainty in %]. Cells colored in red have resulted "not present" and cells in yellow "user decides" in the Gupix analysis.
Note: the smallest, most uncertain(red+yellow), values are given only for reference purposes.

	K		Ca		Ti		V		Mn		Fe		Co		Ni		Cu		Zn		As		Rb		Pb	
Thick Glazing	26079	6	147493	2	3760	9	76	218	2776	11	10786	5	154	128	153	63	166	62	136	92	0	0	389	211	0	0
Body Clay	23607	6	1602	15	4033	9	184	90	75	121	16431	4	0	0	87	92	57	164	51	218	0	0	520	183	279	260
Blue 1	12181	12	52395	3	3438	11	148	131	869	29	67190	2	314	83	189	84	72995	2	781	53	1400	49	458	214	3052	76
Blue 2	9861	11	87508	2	4672	11	296	79	2929	11	11237	5	0	0	105	101	46296	3	256	140	399	109	0	0	455	399

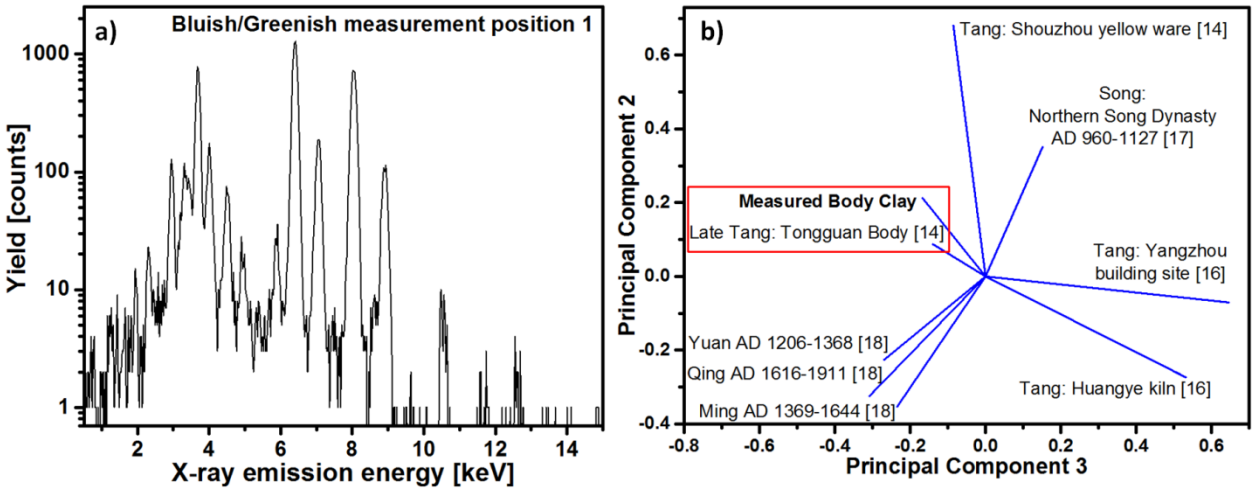

Figure 2. a) PIXE spectra of bluish/greenish measurement position, b) principal component analysis of body clay. Principal components of 2 and 3 are presented on the axis as the body clay analysis didn't have as good spread/separation with the principal component 1 and 2 selected.

For the measurement position of "blue 1" and "blue 2", seen at the Table 1 it is possible that the "blue 1" had more deeper (possibly also more pure) color. Due to the relatively small statistics, some of the uncertainties (given in % at the Table 1) are very large and for example in the case of V, Co, Ni, Zn, As and Rb the Gupix analysis result did not yield any certain concentrations for these elements - which needs to be taken into account if the numbers are used

somewhere else. However, despite the relatively large uncertainties for some of the elements, we can try to match these results as a group of body clay, glaze and bluish/greenish composition, and to compare how these correlate to other data available. This comparison can be made from the data given in Figures 3–5.

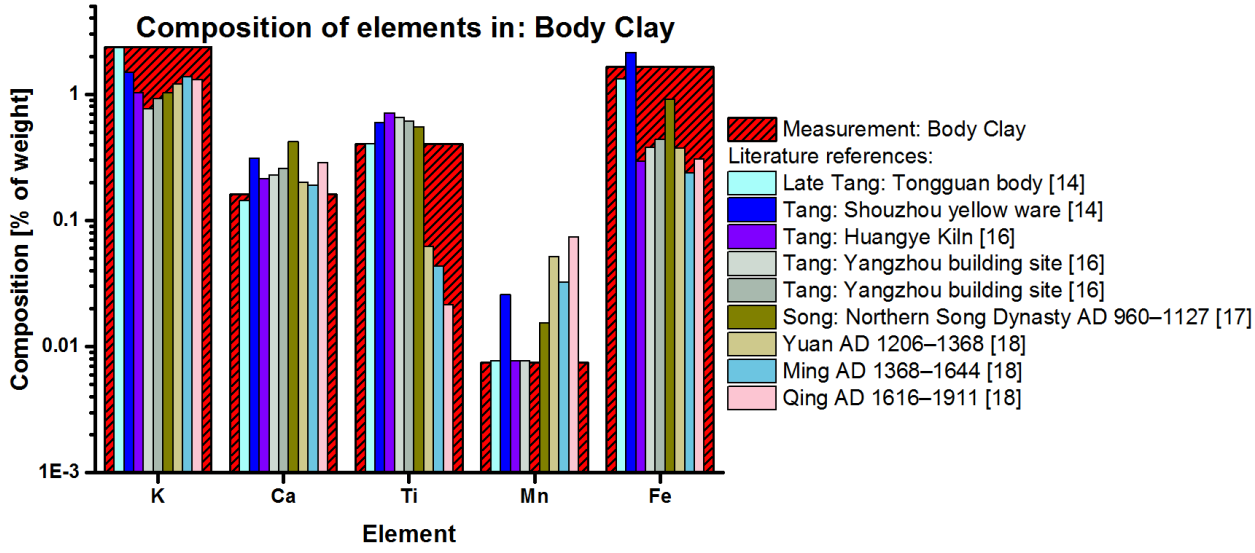

Figure 3. Measurement result of body clay compared to other data in the literature.

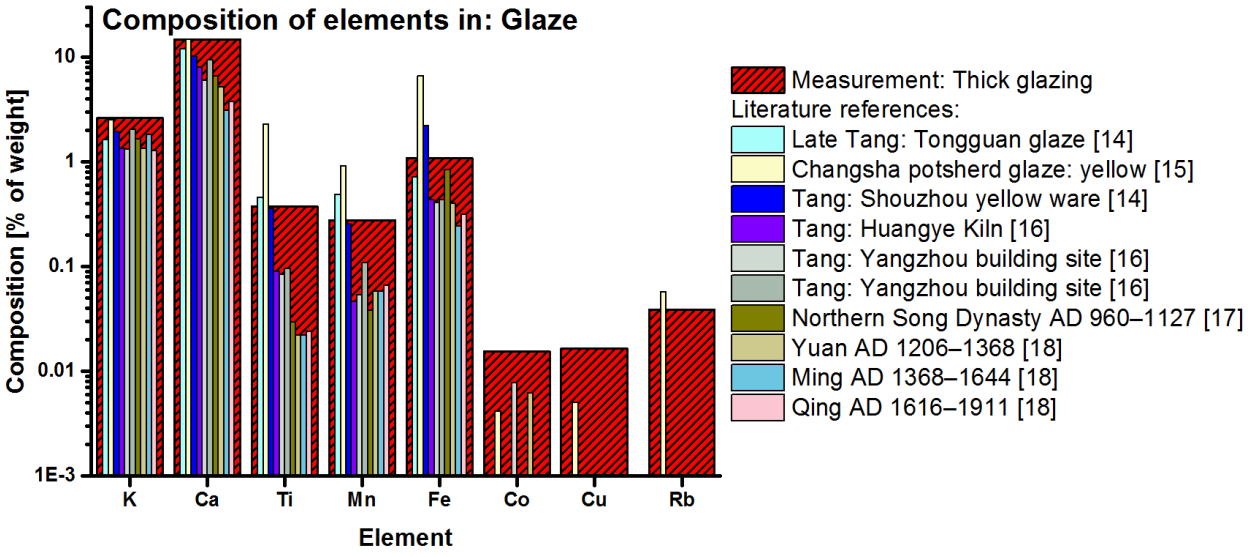

Figure 4. Measurement result of thick, transparent, yellowish glaze compared to other data in the literature.

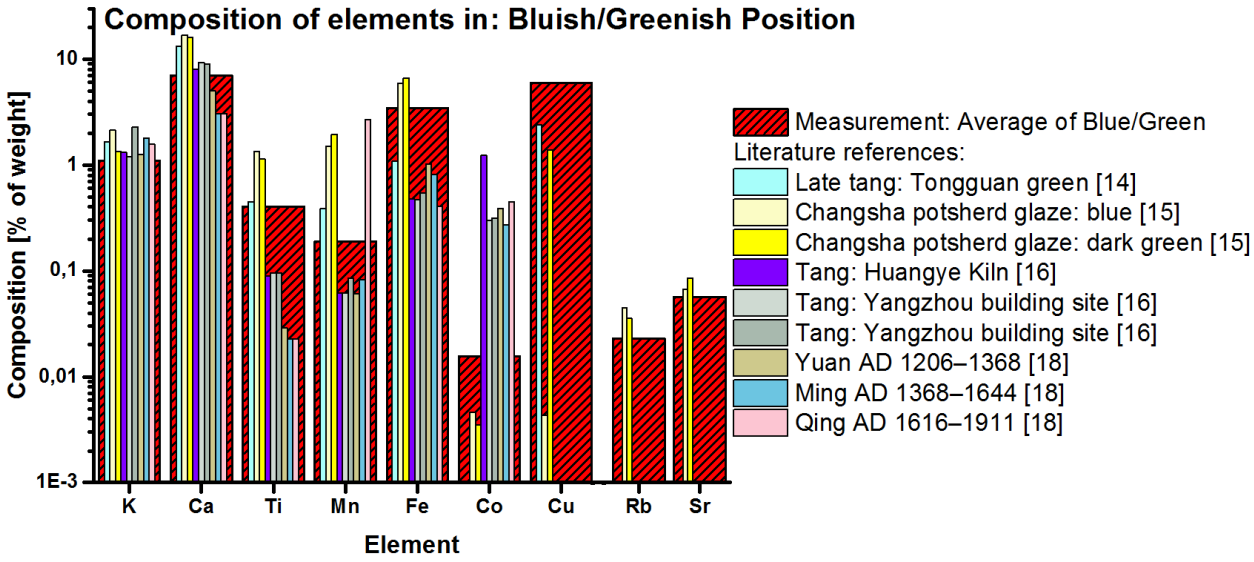

Figure 5. Measurement result of the bluish/greenish positions compared to other data in the literature.

In the Figures 3−5 the analysis results from the bowl are mainly compared to those of the Tongguan kiln site [14], in the vicinity of Changsha [15]. In addition, other (non-similar) references from the same period ceramics (Tang: 618-907, Late Tang: 923-936) [15,16] are given as references, together with the official Guan kilns of the later periods [18]. The similar data (e.g. all 'blue' colored positions) from the Refs. [14] and [15] were averaged and values from the Refs. [15−17] were used as such, as some were already averages of up to 50 measurements. For the two bluish/greenish measured data spots, which had slightly different hue of blue/green, possibly also the thickness of glaze, an average was used for the Fig. 5.

4. Discussion

From the Figure 3, the comparison of the body clay compositions, results cannot be said to differ crucially from the references, although the two reference data sets from [14] and especially the one from the Tongguan kiln do have the closest match. The match to the Tongguan body clay is also supported by the principal component analysis (PCA) presented in the Fig 2 b).

The thick transparent glaze measured from the backside of the bowl have again a close match in Fig. 4 to the Tang references from [14] and especially to the Tongguan/Changsha [15] area. In

average, the best matching reference for the glaze seems to be the Late Tang: Tongguan glaze, which agrees with the PCA analysis (not shown).

When first time going through the results for the bluish/greenish measurement spots, the amount of copper and the lack of cobalt, was evident from the data (Table 1 and Fig. 5). However, when comparing data to other references, the originally assumed more blue color seemed actually more similar to the green labeled data in the Refs. [14] and [15]. When comparing the bluish/greenish measurements to the references, it seems like the green Ghangsha potsherds [15] and Late Tang: Tongguan dark green [15] are the closest match for the measured data. PCA analysis of the bluish/greenish color confirms this observation (not shown).

The old blue pigments with strong copper component are the *egyptian blue* (used from Egyptian times to Roman times) and from the later period the *azurite* (from 1300 to ~1600 AD) [19]. For the green color option the most probable pigments could be the *malachite* (Egyptian times to 16th century), verdigris (Greek times to 19th century) and the *copper resinate* (15th century to 17th century) [20]. Now, if this bowl dates back to the (late) Tang dynasty period, the known [19] [20] copper containing blue and green pigments gives only one option: the measured bluish/greenish color positions were actually a greenish color from copper containing pigment.

5. Conclusions

It can be concluded that the now measured bowl has a high probability that it is originally from the Tongguan kiln site at the vicinity of Changsha, and dates to the (late) Tang period. This judgement is based on the elemental composition analysis of the body clay, thick glaze and bluish/greenish color measurement position, which turned out to be most likely a green colored (under)paint or glaze. These three analyses have very close elemental fingerprints to the actual shards unearthed from the Tongguan kiln site and from its vicinity. Although it is possible that there is also cobalt element present in the bluish/greenish measurement position, the pigment itself is not a cobalt containing blue pigment – but a copper containing green pigment instead.

This is also the answer to the second research question requested by the customer, who wanted to study that could this bowl belong to the first generation of cobalt blue pigments used in ancient China.

Acknowledgements

This study was supported by the Finnish TEKES TUTL funding under the RECENART – Research Center for Art – program and under the auspices of Finnish Centre of Excellence Programme (Project number 251353 Nuclear and Accelerator Based Physics).

References

[1] http://www.bloomberg.com/news/articles/2015-05-21/here-s-how-to-make-millions-as-an-art-forger (cited 13.6.2016).
[2] TEFAF art market report 2015 (www.tefaf.com).
[3] http://www.thedailybeast.com/articles/2014/10/17/are-over-half-the-works-on-the-art-market-fakes.html (cited 13.6.2016).
[4] http://www.independent.co.uk/arts-entertainment/art/news/the-big-question-how-many-of-the-paintings-in-our-public-museums-are-fakes-1946264.html (cited 13.6.2016).
[5] Aitken, M.J., *Thermoluminescence Dating*, Academic Press, London (1985).
[6] G.Calzolai, M. Chiari, F. Lucarelli, F. Mazzei, S. Nava, P. Prati, G. Valli, R. Vecchi, Nucl. Instr. and Meth. in Phys. Res. B 266, (2008), p. 2401-2404.
[7] F. Bnyaïch, A. Makhtari, L. Torrisi, G. Foti, Nucl. Instr. and Meth. in Phys. Res. B 132, (1997), p. 481-488.
[8] RECENART - Research Centre for Art (www.recenart.fi)
[9] https://en.wikipedia.org/wiki/Belitung_shipwreck (cited 13.16.2016).
[10] Rui Wen, D.Phil. thesis, *The Cobalt Blue Pigment Used on Islamic Ceramics and Chinese Blue-and-white Porcelains*, Oxford University (2012).
[11] Silson Ltd, www.silson.com
[12] Amptek Ltd, www.amptek.com
[13] J. L. Campbell, N. I. Boyd, N. Grassi, P. Bonnick, J. A. Maxwell. , Nucl. Instr. and Meth. in Phys. Res. B 268 (2010), p. 3356-3363.
[14] Nigel Wood, *Chinese Glazes: Their Origins, Chemistry, and Recreation*, A&C Black Limited, 35 Bedford Row, London (1999) p. 40-43.
[15] E.K. Lin , Y.C. Yu, C.W. Wang, T.Y. Liu, C.M. Wu, K.M. Chen, S.S. Lin, Nucl. Instr. and Meth. in Phys. Res. B 150 (1999), p. 581-585.
[16] "H.S. Cheng, B. Zhang, D. Zhu, F.J. Yang, X.M. Sun, M.S. Guo, Nucl. Instr. and Meth. in Phys. Res. B 240 (2005), p. 527–531.
[17] D. Zhu, H.S. Cheng, J.W. Lin, F.J. Yang, Nucl. Instr. and Meth. in Phys. Res. B 249 (2006),

p. 633–637.
[18]H.S. Cheng , Z.Q. Zhang, H.N. Xia, J.C. Jiang, F.J. Yang, Nucl. Instr. and Meth. in Phys. Res. B 190 (2002), p. 488–491.
[19] http://www.webexhibits.org/pigments/intro/blues.html (cited 17.6.2016).
[20] http://www.webexhibits.org/pigments/intro/greens.html (cited 17.6.2016)