Chemical Fingerprinting

TRACING THE ORIGINS OF THE GREEN-SPLASHED WHITE WARE

Li Baoping, Chen Yuh-shiow, and Nigel Wood

Among the ceramics found on the Belitung shipwreck, the green-splashed white ware represents both the most interesting and the most puzzling group.[1] These pieces feature large areas of low-fired green splashes lavishly applied over a white glaze, and a few are incised with a lozenge design with palmette projections (fig. 125), a motif that originated and was popular in Iraq.[2] They also are surrounded by controversy, namely, a heated debate among researchers regarding their manufacturing place in China.

Ceramics of a similar style were found in recent decades in Yangzhou, the trade port in China's Jiangsu province, and in early twentieth-century Samarra, a capital north of Baghdad founded in 836 by the Islamic Abbasid caliph al-Mu'tasim. But nearly a century after the find in Samarra, researchers still do not agree on where the green-splashed white ware was made. As Hsieh Ming-liang summarized in 2002, the places of production proposed by various researchers include Yaozhou in Shaanxi province, Gongxian in Henan, Changsha in Hunan, Yangzhou in Jiangsu, or the general area of Henan or Shaanxi provinces. Hsieh proposed Hebei province, particularly the Xing and Jingxing kilns, for priority consideration.[3] That so many possible sources have been proposed for one type of Chinese ceramics is extraordinary, particularly because, prior to 2002, no green-splashed white ware identical to the Belitung wreck finds had been found at any kiln site in China, including the main excavations of the Gongxian kilns that were discovered in 1957.[4] (Some Tang dynasty kilns in China did produce green-splashed wares but at higher temperatures and, as a result, they have more regimented designs than those found on the Belitung wreck.)

In 2002–2004, soon after Hsieh's survey, new excavations at the Gongxian kilns yielded green-splashed white ware similar to that found in the Belitung cargo (fig. 123).[5] This new find shed significant light on the debate and appeared to support the view that the Belitung ceramics had been made at Gongxian. Liu Lanhua, one of the chief archaeologists conducting the excavations, pointed out that some visual differences exist in terms of form, body, glaze, and color between the cups with appliquéd straws found at the kilns and those pieces found in the wreck, implying that the Belitung finds may not have been made in Gongxian.[6] Regina Krahl proposes, however, that most of the Belitung green-splashed white ware looks like the Gongxian products, although some pieces might be from the Xing kilns.[7] Krahl's view is supported by Qin Dashu, who reports seeing green-splashed white ware at the Xing kilns that is "basically identical" to items from the Gongxian kilns. Qin believes that the Belitung cargo includes green-splashed ceramics from both the Gongxian and the Xing kilns and proposes still another possible producer, namely, the recently discovered Xiangzhou kilns in Anyang, Henan.[8]

Clearly, determining ceramic sources is a complex issue that requires more than a visual comparison of objects or fragments. There are two primary reasons for this. First, archaeological research reveals only a fragmentary picture of ancient ceramic production. By necessity, archaeological surveys and excavations are performed on limited areas of a ceramics center, and thus they can uncover only a partial view of its operations at any given time. The very recent finds of green-splashed white ware at Gongxian, after fifty years of work had taken place there, is a good case in point. In addition, there are ancient kiln sites that are unknown to modern scholars; some eventually are discovered as fieldwork goes on, while others may remain lost to history forever. Second, wares of similar or identical styles often were manufactured in more than one known production center. Ceramics scholars, who may have different personal perspectives and emphases, rarely have the chance to examine carefully and compare all the relevant ceramics from several find sites—shipwrecks, kiln locations, etc. This can lead to divergent views on whether two groups of ceramics can be regarded as identical or not and therefore (by inference) represent the same or a different production center. It also leads to difficulties in sourcing traded wares with great certainty. Thus, while archaeologists can identify origins for traded wares based on current knowledge, they must be prepared to adjust their views in light of new information or discoveries, both at known production centers and at newly found kiln sites.

PAGE 176

Fig. 122 Detail, Ewer with lugs, dragon-head spout, and feline-shaped handle. (See also fig. 124.) Cat. 222.

The ICP-MS Technique

Given the many uncertainties that surround stylistic comparison, the chemical compositions of ceramic fragments from particular production centers can be considered useful and independent criteria for sourcing purposes. This is because different places used different types and sources of raw materials and technology (methods of refining and mixing, etc.), which may have left distinct chemical traces in the finished products. This essay compares the elemental compositions of eight green-splashed white-ware shards from the Belitung ship with ceramics, including *sancai* (tri-color glazed) and white ware, from the Gongxian, Xing, and Yaozhou kilns using the analytical technique ICP-MS (inductively coupled plasma mass spectrometry). Compared with other more conventional techniques, such as INAA (instrumental neutron activation analysis) and XRF (X-ray fluorescence), ICP-MS is relatively new and is predicted by some archaeological scientists[9] to herald a revolution in archaeometry due to its numerous advantages.

At the University of Queensland and the University of Melbourne, we developed an acid-digestion ICP-MS technique for ceramic analysis, which achieved an analytical reproducibility of 0.5–3 percent for most of the approximately forty trace elements that were routinely measured. While silicone (Si) and aluminum (Al) are the primary mineral components in ceramic raw materials, the trace elements in clay and ceramics have less than 1,000 ppm (parts per million) in concentration and are partially dependent on the compositions and geological histories of the original source rocks. For this reason, trace elements can be very useful for differentiating and identifying sources of the raw materials.

The large number of trace elements that ICP-MS can analyze and its high accuracy and precision make it an ideal technique for chemically differentiating the various origins of ceramics.

The ceramic shards were prepared for ICP-MS analysis using the following procedures. The glaze was completely removed by grinding the shards on a tool called a diamond lap. The bodies were cleaned with 18.2 megohm water in an ultrasonic bath and then dried. Approximately 50 to 100 milligrams of each sample were weighed and dissolved in distilled hydrogen fluoride and nitric acids (HNO_3). We used high-pressure Teflon bombs in an oven at 180 degrees Celsius for 60 hours to ensure the dissolution of all minerals, particularly refractory minerals such as zircon. The samples then were dried and redissolved in distilled hydrochloric acid (HCl) placed overnight in an oven at 180 degrees Celsius. The solutions were transferred to a polystyrene tube and centrifuged. Any remaining solids were transferred back to the bombs and once again dissolved in HCl overnight in the oven. Once the dissolution was complete, we combined and dried the samples and converted them to nitrates by adding HNO_3 twice and drying the mixture again. We then analyzed the samples with the ICP-MS, which combines an inductively coupled plasma as an ion source with a mass spectrometer as a means of detecting the ions. More details about ICP-MS's analytical methods, precision, and accuracy have been described in previous papers.[10]

Chemical Differentiation among the Gongxian, Xing, and Yaozhou Kilns

The fragments we compared included seven *sancai* pieces and four white-ware shards from Gongxian; seven *sancai* shards from Yaozhou[11]; and five white-ware shards from the Xing kilns. Earlier research on the chemical sourcing of Chinese ceramics found outside China had been hampered by the lack of accredited control samples.[12] Studies on ancient Chinese ceramics demonstrate that a single production center often made a variety of wares using the same material for the body but different glazes or decorations. The kilns under discussion are no exception in this regard[13]; therefore, it is reasonable to compare the bodies of *sancai* and white-ware shards from the Gongxian, Yaozhou, and Xing ceramic centers with bodies of green-splashed white ware from the Belitung shipwreck.

Figure 126 demonstrates that the Gongxian *sancai* and white ware have only small variations in the concentrations of most of the approximately forty trace elements routinely analyzed by the ICP-MS and cluster closely together, while the Xing white ware and Yaozhou *sancai* shards show a greater variability. Samples from the three ceramic centers vary in composition for many of the approximately forty elements and fall in two or three distinct fields on many of the binary plots: in particular, titanium-lithium (Ti-Li), yttrium-cesium (Y-Cs), tantalum-tungsten (Ta-W), vanadium-scandium (V-Sc), uranium-thorium (U-Th). These differences clearly distinguish products from one place from those of another area. It is also noteworthy that products from Xing and Yaozhou have an identical or overlapping range of composition for many of the analyzed elements—i.e., W, Ta, Y, beryllium (Be), tin (Sn), niobium (Nb), barium (Ba), cobalt (Co), gallium (Ga)—so these elements cannot be used to differentiate those two places. In this regard, the large number of elements that ICP-MS is capable of analyzing also greatly improves the potential for distinguishing different places of production.

Similarity between the Belitung Samples and Gongxian Products

The eight green-splashed white-ware shards from the Belitung cargo define a restricted field on nearly all the binary plots of the trace elements. They are aligned very closely to the Gongxian products but are remarkably different from the Xing and/or Yaozhou products (i.e., Ti-Li, Y-Cs, W-Ta, V-Sc; see fig. 126).

As mentioned earlier, because the trace elements in clay and ceramics are partially dependent on the compositions and geological histories of the original source rocks, they can be very useful for identifying sources of the raw materials. The same trace-element compositions in the Belitung green-splashed white ware and the Gongxian *sancai* and white ware indicate that the products were made with similar or identical raw materials. Thus, it is almost certain that the Belitung objects were made in Gongxian rather than at the Xing, Yaozhou, or other kilns. This fits well with the latest finds at Gongxian that establish it as a manufacturer of green-splashed white wares. In hindsight, this conclusion—based on the chemical comparison among associated ceramic types and kilns—could have been reached without the prior knowledge that green-splashed white ware had recently been found at the Gongxian kilns. In view of this, chemical fingerprinting may be an effective tool for connecting a ceramic type to its manufacturing site

RIGHT

Fig. 123 Fragment of green-splashed white ware ewer from the 2002–2004 excavation of the Gongxian kilns; extant height 12 cm.

Fig. 124 Ewer with dragon-head spout and feline-shaped handle. Cat. 222.

LEFT

Fig. 125 Four-lobed dish with incised floral lozenge. The lozenge motif originated in 8th- or early 9th-century Iraqi wares in cobalt blue; it was copied by Chinese potters as a way to appeal to foreign markets. Cat. 229.

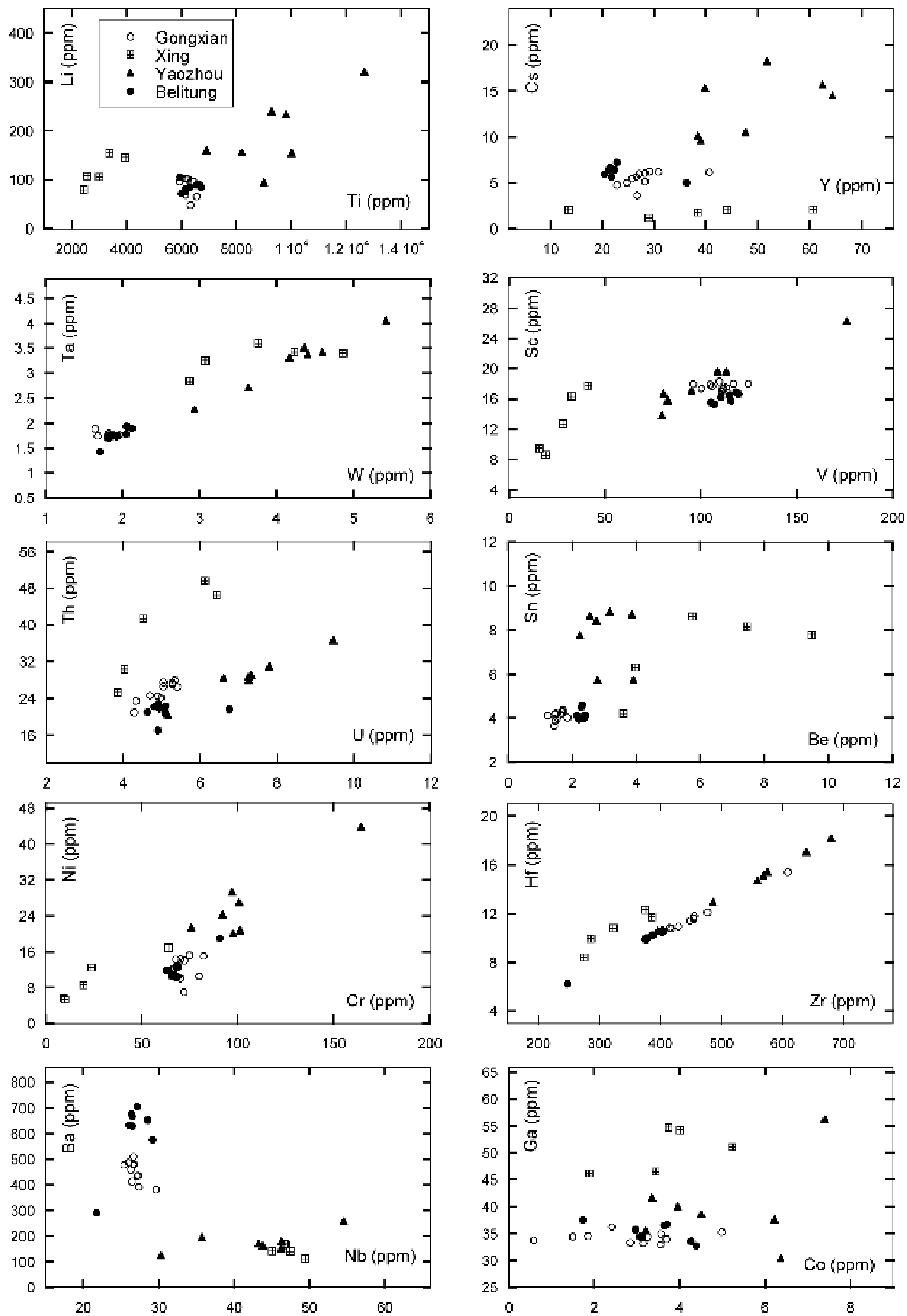
even before such objects have been found in the kilns. It also may help archaeologists predict what types of ceramics will be excavated at a particular production center.

It is noteworthy that while the eight Belitung samples can be included in the same group as the Gongxian products—unlike the Xing and Yaozhou products—seven of these cluster more closely and tend to form an independent subgroup separate from the Gongxian *sancai* and white ware (as demonstrated in the plots of Y-Cs, V-Sc, U-Th, Be-Sn, chromium-nickel [Cr-Ni], zirconium-hafnium [Zr-Hf], and Nb-Ba). Two tentative explanations may account for this additional clustering. One is that the Belitung samples may have been made in Gongxian but at different workshop(s) from the one(s) manufacturing the *sancai* and white-ware samples and using slightly different raw materials and/or technology. The other is that, after soaking in seawater for more than a millennium, the Belitung samples might have undergone slight changes in their elemental composition. It is hard to confirm or rule out either of these possibilities or decide which factor contributed more to the observed chemical differences. Nonetheless, the fact that ICP-MS detects such subtle differences demonstrates that it may help to identify even ceramics made in different workshops at a single production center. This is important for the type of in-depth, microscopic study of ancient ceramics that may be hard to achieve with field archaeology alone.

Fig. 126 Differentiation of ceramic bodies from the Gongxian (11), Xing (5), and Yaozhou (7) kilns and attribution of eight green-splashed white ware samples from the Belitung shipwreck to Gongxian using trace elemental contents (in ppm: parts per million) analyzed by ICP-MS. (Numbers in parentheses refer to the number of pieces tested.)

Conclusion

Comparison of the trace elements of eight green-splashed white-ware pieces from the shipwreck with ceramics from the Gongxian, Xing, and Yaozhou kilns demonstrates that the Belitung ceramics are chemically different from Xing and Yaozhou wares but similar to products from Gongxian kilns. This indicates that these samples almost certainly were made in Gongxian and that chemical sourcing can be a tremendous boost to traditional archaeology. On the other hand, it should be pointed out that not all of the nearly 200 green-splashed white-ware items salvaged from the Belitung wreck look identical in their bodies, glazes, and decorations. Likewise, only a few shards from each of the three production centers have been analyzed for comparison, although over the centuries each center has produced a wide variety of ceramics. Therefore, this research should not be regarded as representing the entire Belitung cargo or all of the centers at Gongxian, Xing, and Yaozhou until a larger number of samples covering a wide range of body textures and decorations (and hopefully representing multiple workshops) has been analyzed. It is clear that a firm archaeological context—including intense field surveys and excavations (both within individual ceramic centers and at relevant kiln sites across the country) and subsequent comprehensive sampling—remains the cornerstone of archaeometry studies. An approach closely integrating archaeology and chemical sourcing is important for the final determination of the origins of green-splashed white ware from the Belitung cargo and elsewhere.


Gongxian
Xing
Yaozhou
Belitung
Li (ppm)
Ti (ppm)
Cs (ppm)
Y (ppm)
Ta (ppm)
W (ppm)
Sc (ppm)
V (ppm)
Th (ppm)
U (ppm)
Sn (ppm)
Be (ppm)
Ni (ppm)
Cr (ppm)
Hf (ppm)
Zr (ppm)
Ba (ppm)
Nb (ppm)
Ga (ppm)
Co (ppm)

SHIPWRECKED

TANG TREASURES AND MONSOON WINDS

HOW TO ORDER

Cloth edition

328 pages | 9"x 12" | $65.00 US / $74.00 Can
220 color and 235 B&W illustrations
ISBN 978-1-58834-305-5
Distributed worldwide by Smithsonian Books via Random House
Available from Amazon.com, Barnes & Noble.com, and fine bookstores everywhere.

Paperback edition

328 pages | 9"x 12" | $40.00 US/$52.00 Sing
220 color and 235 B&W illustrations
ISBN 978-0-934686-18-1
Available in Singapore from:
ArtScience Museum, Marina Bay Sands
Asian Civilisations Museum and other National Heritage Board museum shops:
www.museumshop.com.sg

ABOUT THIS BOOK

Twelve centuries ago, a merchant ship—an Arab dhow—foundered on a reef just off the coast of Belitung, a small island in the Java Sea. The cargo was a remarkable assemblage of lead ingots, bronze mirrors, spice-filled jars, intricately worked vessels of silver and gold, and more than 60,000 glazed bowls, ewers, and other ceramics. The ship remained buried at sea for more than a millennium, its contents protected from erosion by their packing and the conditions of the silty sea floor. *Shipwrecked: Tang Treasures and Monsoon Winds* explores the story of both the sailors and the ship's precious cargo through more than 400 gorgeous photographs and essays by international experts in Arab ship-building methods, pan-Asian maritime trade, ceramics, precious metalwork, and more.

Edited by

Regina Krahl, John Guy, J. Keith Wilson, and Julian Raby

With contributions from

Alison Effeny | Michael Flecker | John Guy | Jessica Hallett | Hsieh Ming-liang | Regina Krahl
Li Baoping with Chen Yuh-shiow and Nigel Wood | Liu Yang | François Louis | Qi Dongfang
Tom Vosmer | Wang Gungwu | J. Keith Wilson

Published by

Arthur M. Sackler Gallery, Smithsonian Institution, Washington, DC
National Heritage Board, Singapore | Singapore Tourism Board