Journal of Archaeological Science: Reports xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: http://ees.elsevier.com/jasrep

PXRF analysis of pigments in decorations on ceramics in the East Mediterranean: A test-case on Cypro-Geometric and Cypro-Archaic Bichrome ceramics at Tel Dor, Israel

Shlomo Shoval [a,b,*,1], Ayelet Gilboa [c]

[a] Geology Group, Department of Natural Sciences, The Open University of Israel, The Dorothy de Rothschild Campus, 1 University Road, Raanana 43537, Israel
[b] The Freddy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of Jerusalem, Edmund J. Safra Campus, Jerusalem 91904, Israel
[c] Zinman Institute of Archaeology and the Department of Archaeology, University of Haifa, Mount Carmel, Haifa 3498838, Israel

ARTICLE INFO

Article history:
Received 31 October 2014
Received in revised form 2 April 2015
Accepted 13 August 2015
Available online xxxx

Keywords:
Cypriot pottery
East-Mediterranean pottery
Iron Age
Iron-based pigment
Manganese-based pigment
Ochre ore
Paint pigment
Umber ore

ABSTRACT

As part of an attempt to identify the provenances and technology of pottery in Cypro-Geometric and Cypro-Archaic Bichrome styles at Tel Dor, Israel, the black and the red paint pigments and the ceramic body were analysed chemically by using a pXRF apparatus in a handheld configuration. This method enables analysis of the thin painted decoration directly on the surface of the vessels. As a comparison, we also analysed the fabric of the vessels, as well as comparative potential Cypriot pigment ores. The analyses reveal that the black paints consist of manganese-based pigments comprising manganese and iron. The red paints consist of iron-based pigments rich in iron and poor in manganese. In contrast, the ceramic body of the vessels is rich in silica and alumina and contains lesser concentrations of iron and only traces of manganese. The results demonstrate the utilization of Cypriot pigment ores (black umber and red ochre) for the painted decoration on these ceramics. Beyond the specific Tel Dor case, the results are intended to initiate a compositional data-base of pigments on East Mediterranean ceramics in the Bronze and Iron Ages. We argue that to serve this end the chemical data should be presented in detail, in order to enable future comparative studies.

1. Introduction

1.1. Cypriot and Cypriot-style pottery at Dor

Dor is situated on the East Mediterranean seaboard, on Israel's Carmel coast, about 30 km south of Haifa (Gilboa and Sharon, 2008). It was one of the main port sites along the southern Levantine littoral and its material culture through most of the late 2nd and 1st millennia BC can be defined as Phoenician (Gilboa, 2005; Nitschke et al., 2011; Sharon and Gilboa, 2013). Among other commodities, imported Cypriot pottery, especially in the early Iron Age, occurs there more than in any other site outside Cyprus (preliminarily for the Iron Age, Gilboa, 1989, 1999).

Most of the Cypriot-style pottery at Dor dates to the Iron Age 1b–Iron 2a chronological range of Phoenicia, paralleling the Cypro-Geometric (CG) I–III periods in Cyprus, the 11th–9th centuries BC. These vessels belong mostly to Cypriot White Painted (I–III) and Cypriot Bichrome (I–III) wares. Respectively, these are vessels where the designs are painted only in shades of black (grey and brown as well) on a light background, or with the addition of paint in various shades of red (Gjerstad, 1948). In this period, there is also evidence for local production of pottery in Cypriot style (e.g., Gilboa, 1999: Fig. 5:7; Yellin, 1989; A. Georgiadou, personal communication), but currently it is unclear how extensive this phenomenon might have been. Lesser quantities of Cypriot pottery imports at Dor, of Types IV–V, belong mainly to the Iron Age 2c (7th century BC), paralleling part of the Cypro-Archaic (CA) I period, and even smaller numbers originate from contexts of the Persian period (5th/4th centuries BC), equaling *grosso modo* late Cypro-Archaic II and the beginning of the Cypro-Classic (CC) period.

1.2. XRF analysis of pottery

X-ray Fluorescence Spectroscopy (XRF) is one of the methods used for chemical analysis of archaeological ceramics and other cultural heritage artefacts (Liritzis and Zacharias, 2011; Goren et al., 2011; Frahm and Doonan, 2013). It provides quantitative chemical data regarding major elements, as well as regarding several trace elements in the composition of ceramics (Speakman et al., 2011), slips (Scarpelli et al., 2014) and paints (Stos-Fertner et al., 1979; Hochleitner et al., 2003; Centeno et al., 2012; Attaelmanan and Yousif, 2012; Kaplan et al., 2014). However, this method does not detect several 'light' major elements and the detection of Al, Si, S and P, for example, requires analysis under

* Corresponding author at: Geology Group, Department of Natural Sciences, The Open University of Israel, The Dorothy de Rothschild Campus, 1 University Road, Raanana 43537, Israel.
E-mail address: shovals@openu.ac.il (S. Shoval).
[1] Sabbatical Year status at The Freddy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of Jerusalem, Edmund J. Safra Campus, Jerusalem 91904, Israel.

http://dx.doi.org/10.1016/j.jasrep.2015.08.011
2352-409X/

Table 1
List of Dor's Bichrome pottery studied. CG = Cypro-Geometric; CA = Cypro-Archaic; Ir = Iron Age.

Sample no.	Vessel type	Area/locus	Reg. no.	Cypriot classification	Horizon
CD-64	Bichrome deep bowl	B/7746	77481	CG; Bichr III	Unstratified
CD-153	Bichrome jug	B/3341	33377	CG; Bichr III?	Ir2a
CD-121	Bichrome deep bowl	B/7189	71899	CG- CA; Bichr III–IV	Unstratified
CD-223 (CYI-14)	Bichrome plate	D2/5251	52195	CG- CA; Bichr III–IV	Ir2a?
CD-272 (CYI-45)	Bichrome jar	D2/surface find	150957/1	CA; Bichr IV	Unstratified
CD 273 (CYI-5)	Bichrome jar?	D2/06D2-040	06D2-0369	CA; Bichr IV	Ir2a late?
CD-274 (CYI-44)	Bichrome- red amphora?	D2/unstratified	104837	CA; Bichr IV–V	Unstratified
CD-275 (CYI-48)	Bichrome amphora	D2/15213	151563	CA; Bichr IV–V	Ir2b–Ir2c
CD-178 (CYI-27)	Bichrome-red amphora	D5/10D5-219	10D5-2603	CA; Bichr IV–V?	Ir2c
CD-183 (CYI-41)	Bichrome amphora	D4/11D4-791	11D4-8276	CA; Bichr IV–V?	Ir2c?
CD-177 (CYI-1)	Bichrome barrel jug?	D5/09D5-456	09D5-8709/2	CA; Bichr IV–V?	Ir2c–Hellenistic
CD-182 (CYI-47)	Bichrome amphora	D4/04D4-510	09D4-5197	CA; Bichr IV–V?	Persian
CD-185 (CYI-43)	Bichrome trefoil jug	D1/16664	168648/1	CA; Bichr V	Ir2c–Persian
CD-157 (CYI-8)	Bichrome amphora	D5/09D5-409	09D5-8743/1	CA; Bichr V	Persian–Hellenistic

vacuum. As well, trace elements can be measured by this method in good accuracy (in ppm) only when they appear in sufficient concentrations.

Another obstacle when employing on-surface pXRF specifically for the study of decoration on pottery lies in the thinness of the painted bands/lines. The penetration-depth of the radiation, and concomitantly the contributions from the ceramic body substrate to the analysis depend on the thickness and contiguousness of the paint bands, as well as on the atomic number Z of the detected element (Aloupi et al., 2001). For some ways to overcome this problem, at least partially, see below.

In the study presented here we used a portable X-ray Fluorescence apparatus (pXRF) in a handheld configuration. The major advantage of pXRF for ancient artefacts is that the method is cheap, rapid, and non-destructive and therefore can be used on a large scale. The equipment is easily movable and thus is instrumental in investigating artefacts that cannot be moved, such as in museums (Karydas et al., 2005).

1.3. PXRF analysis of paint on decorated pottery in the East Mediterranean

XRF analyses of paint pigment on ceramics of the ancient East Mediterranean are still a rarity (but see, for example, Kaplan et al., 2014). Especially relevant for the study presented here are *in situ* XRF analyses of various Cypriot archaeological media, including ceramics (reported in Aloupi, 2001; Aloupi et al., 2000, 2001). In Aloupi et al. (2000, 2001), this method was used for analysing the black and red paint pigments on Cypriot decorated pottery in the Cyprus Museum (Nicosia), from a very long time-span. Interestingly, Aloupi and her co-investigators concluded that from ca. 5000 BC to the Middle Bronze Age, the dark ('black') painted decoration was essentially based on iron-rich minerals. Only from the end of the Late Bronze Age onwards (ca. 1050–325 BC;

Fig. 1. Examples of Dor's Cypro-Geometric and Cypro-Archaic Bichrome pottery studied: (a) bichrome barrel jug (CD-177); (b) bichrome bowl (CDI-223); (c) bichrome amphora (CD-157; two views).

Please cite this article as: Shoval, S., Gilboa, A., PXRF analysis of pigments in decorations on ceramics in the East Mediterranean: A test-case on Cypro-Geometric and Cypro-Archaic B..., Journal of Archaeological Science: Reports (2015), http://dx.doi.org/10.1016/j.jasrep.2015.08.011