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TECHNOLOGICAL AND COMPOSITIONAL CHARACTERIZATION OF RED POLISHED WARE FROM THE BRONZE AGE KOURIS VALLEY (CYPRUS)

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ABSTRACT

In order to perform a physico-chemical multitechnique characterization, 26 fragments of Red Polished ware from the archaeological survey in the Kouris river valley (Limassol district, Cyprus) have been analyzed. Despite the gloss-like macroscopic aspect of the potsherd surfaces, Scanning Electron Microscopy (SEM) morphological observation revealed traces of mechanical polishing on the surfaces and the lack of a slip. Energy Dispersive X-ray (EDX) elemental analyses in both scan and map modes confirmed the absence of differentiation between body and surface composition. Chemometric evaluation on EDX bodies data showed a lack of sub-classification. Mineralogical patterns, obtained by X-Ray Powder Diffraction (XRPD) analysis revealed great variability among samples and the presence of amphiboles in 14 sherds, whose identification as hornblende and riebeckite was confirmed by petrographic examination. The unusual presence of these minerals in a ceramic ware fits with the Kouris valley geology, in agreement with traditional models of local raw materials exploitation for protohistoric societies. XRPD data, together with SEM images evaluation, pointed to firing temperatures ranging from 800 to 1050°C, suggesting the use of kilns instead of open fires or pits; on the other hand the colour heterogeneity testified to limited control of the kiln atmosphere.

KEYWORDS: Ceramic, SEM-EDX, XRPD, Surface Finish, Firing Technology
1. INTRODUCTION

The Kouris River Valley Project (KVP) started in 2007 as an archaeological survey in the middle valley of the river, between the village of Erimi and the modern dam; the project was carried out by the Università degli Studi di Firenze and the Università degli Studi “G. D’Annunzio” di Chieti e Pescara, in collaboration with the Università di Torino (Bombardieri et al. 2009; Jasink et al. 2008). The Bronze Age occupation of the valley seems to be mainly located on the eastern bank, where ten sites have been identified; their sequence of occupation ranges from the end of the Early Bronze Age to the Late Bronze Age. Sites located on the western bank, on the other hand, are dated to the Hellenistic and Roman periods (Bombardieri et al. 2009, 119). Within the investigation of the settlement pattern and landscape use of the Bronze Age eastern bank of the river, a specific research has been undertaken on the ceramic assemblage collected during survey activities.

Figure 1: Map of the whole island of Cyprus and the inset of the surveyed Kouris Valley.
In Cypriot ceramic tradition Red Polished (henceforth RP) ware is the characteristic pottery of the Early and Middle Bronze Ages (2400 – 1700 B.C.). Following the early literature by the Swedish Cyprus Expedition (RP IV in Åström 1972, 122; RP I-III in Dikaios and Stewart 1962, 225-229), RP ware could be briefly described as an hand-made production characterized by a glossy and shiny red polished surface. While the first phase of the research on RP already stressed “a variety of fabrics, of which only the commonest can be mentioned” (Dikaios and Stewart 1962, 228), both the acquisition of materials on a large scale and the development of specifically pottery-oriented researches (Barlow 1996; Barlow and Iđiak 1989; Barlow and Vaughan 1991; 1999; Dikomitou 2010; Frankel 1994; Frankel and Webb 2012; Martinon-Torres and Dikomitou 2012; Stephen 1998; Weisman 1996) has greatly expanded our understanding of Prehistoric Cypriot pottery, allowing for example the identification of specific north coast and south coast style types (Herscher 1976; 1981; 1991), even up to the definition of local sub-wares (Swiny 1979).

Pottery production in the Early and Middle (henceforth MC) Bronze Ages is traditional part of the wider phenomenon of regionalism which strongly characterized the island of Cyprus in prehistoric periods (Hein 2009; Webb and Frankel 2013). On the basis of differences in ceramic production, different traditions within wares have been identified (Frankel 1974; Herscher 1976; MacLaurin 1980) instead of an island-wide tradition. Marki Alonia and Alambra Mouttes, two very important Early and Middle Bronze Age sites in central Cyprus, have provided interesting new stratified data improving knowledge of pottery production in MC, pointing to a RP manufacture processing two types of clay according to the function and use of pots (Barlow 1991, 52-53; Barlow and Iđiak 1989; Barlow and Vaughan 1992). Both the sites are however located in the northern igneous foothills of the Troodos Mountains; the sedimentary areas of South-Western Cyprus have been less investigated in terms of RP manufacture, even if a south coast style has been identified (Herscher 1976; 1981). The RP ware from the Bronze Age Kouris valley is to date unexplored; the present paper reports a general characterization of a set of sherds from the survey, conducted in order to obtain a multidisciplinary overview on the pottery production in the valley in MC. The small surveyed area (2 sq km ca.) and the limited sample set is inadequate to represent this pottery production as a whole. In so far, however, as this research does not aim to provide universal and holistic hypotheses, a small sample may serve as “[…] a starting point for identifying technological similarities or differences and attempting to define some basic compositional characteristics of local ceramic production” (Dikomitou 2007, 107).

First of all, morphological evaluation and compositional analyses were carried out by using Scanning Electron Microscopy coupled with the Energy Dispersive X-ray microanalysis (SEM-EDX). SEM-EDX is the most suitable technique in the study of archaeological pottery in order to simultaneously perform a morphological study and to obtain information on the elemental composition both on surface layers and on bodies (Froh 2004; Gulmini et al. 2006; Mirti 2000; Mirti et al. 2004; Pace et al. 2008). EDX bodies data were processed through several chemometric algorithms in order to check for a possible sub-classification.

Firing technology was also explored. A classical method for evaluating the original firing temperature is the mineralogical pattern determination by means of X-Ray Powder Diffraction (XRPD) analysis, but several studies pointed out that the development of mineralogical phases pending firing is strongly affected by other conditions, like composition of raw materials and firing atmosphere (Iordanidis et al. 2009; Maritan et al. 2006; Papachristodoulou et al. 2006). Therefore, a multi-technique approach is required (Bertolino and Fabra 2003). The SEM examination of the fresh fractures of the frag-
ments allowed the evaluation of the micro-
morphology and of the degree of vitrifica-
tion of the ceramic paste, thereby contrib-
uting to an estimation of the firing temper-
ature (Belfiore et al. 2007; Maniatis and Tite

2. METHODS

2.1 Sampling

Working with assemblages collected through survey activities implies several preliminary problems in terms of sampling strategy and features of the material as-
semblage itself (Given 2004; Mattingly 2000; Millett 2000; Webb and Frankel 2004; 2009). The project adopted an intensive field survey methodology employing a 40% sampling strategy (Jasink et al. 2008); on the eastern bank more than 6000 arte-
facts has been collected, 640 of which are RP ware sherds. The most common ware is RP III Mottled with a small percentage of RP III and RP IV (RP IV was not included in the samples selected for the present study). Red Polished III Mottled ware is charac-
terized by a very lustrous polished surface that is normally mottled with well-
defined grey or black spots. Traditionally this ware dominates the ceramic record of the whole Middle Bronze Age in South Cyprus (Swiny 1979, 227-228).

The main classification used the traditional parameters for pottery fabrics characteriza-
tion (Orton et al. 1993); a methodological discriminating factor was the distinc-
tion between commonly used vessels (closed vessels, such as jugs, juglets and jars, and open vessels, such as bowls and basins) and storage vessels (pithoi) because of the specific function of the latters. The macroscopic analysis of the selected as-
semblage produced a complex of 11 fabrics (RPW01-11) in commonly used vessels and 4 fabrics (RPWPy01-04) in storage vessels. Fabrics were defined considering the traditional morphological and petrologic features: paste typology and hardness, fracture type, percentage and dimension of grits and tempers, colour range and type of firing (some of which are reported in Table 1) (Chelazzi and Davit 2010, 137-138). Given the fragmentary state of preservation of the finds collected during the survey and the purely technological and compositional aim of this study, parameters such as incised decorative motifs and plastic decora-
tions were not included in the analysis.

<table>
<thead>
<tr>
<th>Table 1: Macroscopic classification of the collected samples.</th>
</tr>
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<tbody>
<tr>
<td>Paste type</td>
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<tr>
<td>------------</td>
</tr>
<tr>
<td>Common Fabric 1</td>
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<td>Common Fabric 2</td>
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<tr>
<td>Common Fabric 3</td>
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<tr>
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<td>Common Fabric 9</td>
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<tr>
<td>Common Fabric 10</td>
</tr>
<tr>
<td>Common Fabric 11</td>
</tr>
<tr>
<td>Pithos Fabric 1</td>
</tr>
<tr>
<td>Pithos Fabric 2</td>
</tr>
<tr>
<td>Pithos Fabric 3</td>
</tr>
<tr>
<td>Pithos Fabric 4</td>
</tr>
</tbody>
</table>

* L is limestone, Q is quartz, O means organic fibres (marks) and I indicates igneous rocks as gabbro and diabase.
2.2 The chemical and physical analysis of the samples

Scanning electron microscopy (SEM) observations and energy dispersive X-ray microanalyses (EDX) were carried out with a SEM-VP EVO50 (Carl Zeiss AG, Deutschland) microscope coupled with INCA x-sight model 7636 (Oxford Instruments, Concorde, MA, USA) microprobe, at operating conditions of 20 kV and 200 pA. The morphological examination was carried out on fresh fracture samples obtained by cutting the original sherd with the aid of a diamond disk using a Dremel 400 digital grinder on the not-to-be-analysed side and then breaking a cubic sample (from 5 mm to 1 cm of edge) with the aid of a pair of steel tweezers. The polished samples for the chemical analyses were obtained with the same procedure. They were then encompassed in an epoxidic resin and the obtained sections were subjected to an abrasive treatment on silicon carbide papers with a 500 and 1000 grit size and polished with a 1 µm granulometry diamond paste on special clothes. Surface alterations were removed from the sherds with the aid of a grinding wheel. The fresh fractures and the polished sections were then mounted on aluminium stubs using carbon tape and they were covered with a coating of Au–Pd and graphite, respectively, approximately 10 nm thick using a coating unit SCD 050 Sputter Coater (Bal-Tec, Scotia, NY, USA).

EDX analyses were submitted to a statistical treatment by multivariate chemometric techniques. Unsupervised pattern recognition methods as agglomerative Hierarchical Cluster Analysis (HCA) using different linkage methods (group average, complete linkage and Ward’s method) (El-Hamdouchi and Willett 1989) for building up dendrograms and Principal Component Analysis (PCA) using the Non-linear Iterative PArtial Least Squares (NIPALS) method to compute principal components were used. Analytical data were first subjected to a pre-processing procedure by autoscaling. The statistical treatment was performed using the Pirouette 4.0 statistical package by Infometrix Inc. (Woodinville, USA).

As to the mineralogical analysis, X-Ray Powder Diffraction (XRPD) patterns were collected using an Analytical X’Pert Pro (PANalytical B.V., Almelo, The Netherlands) equipped with X’Celerator detector powder diffractometer using Cu Kα radiation generated at 40 kV and 40 mA. The 2θ range was from 5 to 90°. The appropriate amount of grinded sample was placed in a quartz sample holder and compressed with a glass slide.

Petrographic examinations were carried out by using an Olympus BX-41 optical microscope, equipped with a digital Jenoptik camera. 30 µm-thick sections were prepared and observed under polarized transmitted light, images were acquired by ProGres capture pro 2.6.

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Raman spectra were performed by means of a Vertex 70 FTIR spectrophotometer equipped with the LABRAM II accessory. A 1064 nm laser excitation was employed and 1000 scans at 4 cm⁻¹ resolution were collected. The spectra have been recorded on finely grinded specimen held on a sample holder; the laser spot was about 1 mm.

3. RESULTS AND DISCUSSION

3.1 Morphology: SEM analysis of fracture sections and surfaces

In the case of RP, both the presence of a clay slip and a simple surface polishing treatment are known (Barlow 1996, 249-250 and 252-253; Weisman 1996, 457). The macroscopic observation of our sherds showed smooth and quite shiny surfaces, referable to the typical aspect of the glossy coatings of some later ceramic classes, i.e. Campana A and B (Mirti and Davit 2001), and Terra Sigillata (Mirti et al. 1999), where the microscopic evaluation evidenced a significant discontinuity due to the vitrification of the surface slip. Figure 2 shows the SEM backscattered (BS) electron images (200X magnification) of the fracture sections of 2 (RPW10A and RPW11) out of the 26 analysed samples.

BS images showed neither discontinuity between the ceramic body and the surface nor evidence of vitrification. Therefore the microscopic examination seemed to point to the absence of a slip in RP from Kouris valley suggesting the use of a simple pottery burnisher to smooth and burnish the vessel exterior. Modified trapezoidal sherds with smoothed ends have been interpreted as pottery burnishers at Marki Alonia (Frankel and Webb 1996, 203; 2006, 177-178) while in Sanida Moutti tou Ayiou Serakou (Todd and Pilides 1992, 104-107) and in Alambra Mouttes (Palmer 1996, 221) stone burnishers have been identified.

In order to identify possible marks of polishing on the surface at a microscopic level, perpendicular views onto the surfaces were also acquired. Figure 3 shows SEM images of the surface of samples RPW06, RPW11, RPW02D and RPW02E at 500X magnification.

Three out of the four samples showed traces of polishing: RPW06 revealed a flat
surface, scratched by regular lines plainly visible, RPW11 showed a more irregular surface with few and less regular polishing scratches and RPW02D showed a very smooth surface, with traces similar to RPW11 and round cracks, probably due to burying. Finally, some of the samples, like RPW02E, presented an uneven surface, with no traces of polishing at microscopic level. Two are the possible explanations of this variability of the microscopic features: the first one points to a dissimilarity in the polishing treatment before the firing phase while the second one points to a different degree of post-depositional degradation of the surface. Actually these two explanations can be easily and logically reconciled if we consider that it is likely that a different accuracy in the polishing treatment could have influenced the resistance of the external surfaces to the burial environment.

3.2 Elemental composition

Elemental composition data were obtained by EDX analysis. In the case of all the 26 analysed sherds, surface layer EDX data (not reported) did not show any variation in the mean chemical composition with respect to the ceramic bodies, thus confirming the lack of a slip. This homogeneity is illustrated by the elemental map distribution (Figure 4), which revealed the complete absence of the typical elemental trend characterizing RP ware slip coatings with respect to the ceramic bodies, i.e. lower Ca and higher Fe contents as in Alambra Mouttes (Barlow and Idjiak 1989) and Marki Alonia (Martinon-Torres and Dikomitou 2012) and higher Si, K and Fe and lower Ca contents as in Deneia (Dikomitou 2007).

Table 2 illustrates the complete set of bodies compositional data, expressed as mean weight percentage of the corresponding oxide for each of the seven detected elements (Si, Al, Fe, Ca, Mg, K and Na) and their standard deviation (STD) values.

The data screening showed relatively slight values for standard deviations, with few exceptions, indicating a pretty good uniformity in composition among the five areas analysed for each sample. The observation of the wt% values deserves some comments. The most remarkable spread was in the CaO abundance, starting from the 2,10 wt% of the samples RPW04A and reaching 51,7 wt% for the sample RPW02B and 53,5 wt% for RPWP03. Nevertheless, CaO values exceeding 50 wt% strongly suggest post depositional alterations, then samples RPW02B and RPW03 were not taken into account in successive considerations. As for Na2O, sample RPW04A showed relatively higher values (3,54 wt% ) compared to the other sherds, while sample RPW02D had the lowest detected value (0,80 wt%) and for several samples sodium was not detectable. MgO ranged from 1,90 wt% of sample RPWP04B to 7,01 wt% of sample RPW02D and K2O varied from 0,69 wt% of sample RPW06 to 3,77 wt% of sample RPW04B. Al2O3 and SiO2 contents extended from 13,1 wt% (RPW01B) to 23,9 wt% (RPW09B) and from 48,8 wt% (RPWP01B) to 65,5 wt% (RPW11), respectively. FeO ranged from the 5,60 wt% (RPW02E) to 14,0 wt% (RPW10B), and 7 samples out of 24 showed FeO higher than 10 wt%. Indeed, values cited in the literature for Fe oxides wt% detected on the same (Frankel and Webb 2012) or other wares of the Late Bronze Age, from other districts of Cyprus (Renson et al. 2011;
Tschegg et al. 2009) and from other sites in Greece (Hein et al. 1999) and Middle East (Erb-Satullo et al. 2011) are typically 1-10 wt%. A similar range is reported in other studies on red pottery from different areas and different periods (Fermo et al. 2008; Mangone et al. 2012; Mirti et al. 2004). Unusually high levels of iron seemed to suggest a second way of introducing this element in the pottery, other than the clay.

Chemometric evaluation was performed on the compositional dataset of the 24 samples. HCA (not showed) underlined both the lack of grouping between samples identified as belonging to the same fabric (i.e. samples RPW02A, RPW02C, RPW02D, RPW02E) and the absence of compositional differentiation between commonly used vessels and pithoi. PCA diagram (Figure 5) showed a strict correlation of Si and Al, as expected when raw materials are not subjected to any particular treatment (e.g. sedimentation) during the manufacturing process. Ca and Mg showed only a limited correlation and Na and K appeared to be almost anti-correlated, suggesting multiple different sources (raw materials). The Fe variable turned out to be anti-correlated with respect to Al and Si, confirming that the iron origin in the studied sherds can not be only ascribed to the clay used for the manufacturing process.

Table 2: EDX data (mean value of five measurements on each sample and the corresponding standard deviation, STD) for the analysed pottery assemblage, reported as weight % (wt %) of the corresponding oxides of the seven detected elements (Si, Al, Fe, Ca, Mg, K and Na).

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
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<td>62.5</td>
<td>8.1</td>
<td>16.1</td>
<td>3.0</td>
<td>7.88</td>
<td>1.55</td>
<td>6.24</td>
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<tr>
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<td>65.2</td>
<td>8.6</td>
<td>18.3</td>
<td>2.0</td>
<td>7.51</td>
<td>1.39</td>
<td>17.4</td>
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<td>0.44</td>
<td>4.59</td>
<td>0.24</td>
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<td>8.22</td>
<td>0.30</td>
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<td>1.39</td>
<td>17.4</td>
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3.3 Qualitative mineralogical composition

As to the mineralogical (XRPD) analysis, the main identified minerals were feldspars of the plagioclase series (albite (NaSi₃AlO₈) and anorthite (CaAl₂Si₂O₆)), calcite (CaCO₃), hematite (α-Fe₂O₃), an amphibole (identified as riebeckite (Na₂[Mg,Fe(II)]₃Fe(III)₂Si₈O₂₂(OH)₂) or hornblende (Ca₂[Mg,Fe(II)]₄[Al,Fe(III)]Si₇AlO₂₂(OH)₂) by the XRPD software), montmorillonite (Na₀.₃(Al,Mg)₂Si₄O₁₀(OH)₂), micas and quartz (SiO₂), while other phases occur in few sherds.

Table 3 illustrates the qualitative mineralogical composition of 22 sherds expressed as the main mineralogical phases detected in each sample.

Quartz and feldspars of the plagioclase series were the most abundant phases, found in 22 and 19 out of the 22 samples, respectively, and some samples presented montmorillonite and micas. Hematite was detected in 7 out of the 22 samples, while an almost complete absence of Fe(II) oxides, except for the presence of wustite in the sample RPW02B, has to be taken into account. These observations were quite unexpected on the basis of the chemical composition results which pointed to a quite high iron content in our samples. Moreover, the development of hematite was not directly connected to the FeO wt% (see Table 2 and 3), indicating that iron abundance is neither due to an intentional procedure adopted by the potters in order to obtain the red colour of the ceramic body nor due to the natural (unintentional) development of hematite from the iron present in the clay, pending firing. The relatively high iron content together with the anti-correlation between FeO and SiO₂/Al₂O₃ variables and the scarce presence of iron oxides can be easily explained by the occurrence of amphiboles. Petrographic analyses confirm that the amphibole revealed by XRPD is hornblende in some samples, as shown by the yellow-reddish pleochroism, and riebeckite in others, with a greenish-violet pleochroism. Figure 6 shows an hornblende fragment in sample RPW08A. In all the examined samples the amount of amphibole could be evaluated around 15-20% of the total volume.
Amphiboles occurrence in ceramics has hardly been reported before (Bertolino and Fabra, 2003, 25), nevertheless our finding fits in every respect with the Kouris valley geology and orography and with the accepted model of raw materials exploitation for small agricultural communities. Several studies report the presence of amphiboles (Cameron 1985; Laurent et al. 1991) in the Troodos Ophiolite, a complex constituting the geological core of Cyprus and appearing in the Limassol district.

The distance between the Troodos Ophiolite complex and the survey area is less than 6 km as the crow flies and they are connected by the Kouris river, which could drag ophiolitic detritus in the area. In fact, the river bed is located within the 1 hour-by-foot buffer area around all the sites recorded by the survey, which is traditionally considered the site exploitation territory for small agricultural communities as those in the Kouris valley (Kipfer 2000, 517, Martinon-Torres and Dikomitou 2012, 6). This assumption well fits within a model of local landscape exploitation, supported by several archaeometric researches in other Cypriote Bronze Age contexts (e.g. for Alambra Mouttes see Barlow 1996, 240; Barlow and Idjiak 1989, 74-75; Barlow and Vaughan 1992; for Denia see Dikomitou 2007; for Marki Alonia see Dikomitou 2010, 2-4 and Martinon-Torres and Dikomitou 2012; for Ambelikou Aletri see Frankel and Webb 2012). Notwithstanding it is not our intention to provide a provenance investigation comparing our samples with clays and raw materials, the model of the local

Table 3: Mineralogical phases, detected by XRPD, firing temperature estimated by XRPD and SEM results and colours evaluated under macroscopic observation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogical pattern</th>
<th>Estimated firing T (°C)</th>
<th>Colour range</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPW01A</td>
<td>Al, Am, (An), Q</td>
<td>850-950</td>
<td>Buff</td>
</tr>
<tr>
<td>RPW02A</td>
<td>(An), (At), G, Q</td>
<td>850-950</td>
<td>Grey/green</td>
</tr>
<tr>
<td>RPW02B</td>
<td>C, Q, (W)</td>
<td>≥ 800</td>
<td>Grey</td>
</tr>
<tr>
<td>RPW02C</td>
<td>(Al), An, (C), (D), Q</td>
<td>950-1050</td>
<td>Grey</td>
</tr>
<tr>
<td>RPW02D</td>
<td>(Am), An, C, Q</td>
<td>850-1050</td>
<td>Sandwich</td>
</tr>
<tr>
<td>RPW02E</td>
<td>Al, (Am), An, He, Mi, Q</td>
<td>850-950</td>
<td>Red</td>
</tr>
<tr>
<td>RPW03B</td>
<td>Al, Am, He, Mi, Q</td>
<td>800-900</td>
<td>Red</td>
</tr>
<tr>
<td>RPW03C</td>
<td>Al, (Am), (An), (He), Q</td>
<td>80-950</td>
<td>Red</td>
</tr>
<tr>
<td>RPW04A</td>
<td>Al, An, He, Q</td>
<td>850-1050</td>
<td>Red</td>
</tr>
<tr>
<td>RPW04B</td>
<td>(An), G, Q</td>
<td>850-950</td>
<td>Orange/grey</td>
</tr>
<tr>
<td>RPW05</td>
<td>(Al), (Am), (Mo), Q</td>
<td>850-950</td>
<td>Orange/grey</td>
</tr>
<tr>
<td>RPW06</td>
<td>Al, Am, (An), Q</td>
<td>850-950</td>
<td>Black</td>
</tr>
<tr>
<td>RPW07</td>
<td>Al, C, (Mi), Q</td>
<td>≥800</td>
<td>Buff</td>
</tr>
<tr>
<td>RPW08A</td>
<td>(Al), Am, An, (He), Q</td>
<td>≥850</td>
<td>Red</td>
</tr>
<tr>
<td>RPW08B</td>
<td>G, (Mo), Q</td>
<td>≥900</td>
<td>Sandwich</td>
</tr>
<tr>
<td>RPW09A</td>
<td>Al, (Am), (An), Mi, Mo, Q</td>
<td>850-900</td>
<td>Red/grey</td>
</tr>
<tr>
<td>RPW09B</td>
<td>(Al), (Am), He, Mo, Q</td>
<td>850-900</td>
<td>Red</td>
</tr>
<tr>
<td>RPW10A</td>
<td>Al, Am, (An), Q</td>
<td>850-950</td>
<td>Black</td>
</tr>
<tr>
<td>RPW10B</td>
<td>Al, Am, (An), Mi, Q</td>
<td>850-900</td>
<td>Red/grey</td>
</tr>
<tr>
<td>RPW11</td>
<td>G, He, (Mi), Q</td>
<td>900-950</td>
<td>Orange</td>
</tr>
<tr>
<td>RPWP01A</td>
<td>Al, Am, (An), Mi, Q</td>
<td>800-850</td>
<td>Dark grey</td>
</tr>
<tr>
<td>RPWP02</td>
<td>Al, Am, (An), (D), Q</td>
<td>950-1050</td>
<td>Red/grey</td>
</tr>
</tbody>
</table>

*Al=Albite, Am=Amphibole, An=Anorthite, At=Anorthoclase, C=Calcite, D=Diopside, G=Graphite, He=Hematite, Mi=Mica, Mo=Montmorillonite, Q=Quartz, W=Wustite. (Symbol)=weakly detected.
landscape exploitation would be appropriate for the Kouris valley as well, as Garzanti et al. (2000, 207) refer that sands from Troodos, containing hornblende, are deposited in the southeast of the island, from Larnaca to the Episkopi gulf.

3.4 Firing technology

The macroscopic observation of the sherds revealed colours ranging from red to brown/grey and in some cases a sandwich structure was present, with a brown/grey or grey core and red surfaces (Table 3) revealing an evident lack of control of the firing atmosphere. Hematite was detected in 7 samples, in agreement with the red/reddish colour, as expected. On the contrary, the almost complete absence of the typical iron (II) compounds left the question open on the grey/black colour. This can be explained by the presence of carbon from the decomposition of organic matter, eventually present in the raw materials or intentionally added during the manufacturing step, pending the firing process. As reported above, XRPD patterns of some of these samples revealed crystalline graphite while in other cases the presence of more amorphous carbon is reasonable (Holclajtner-Antunović et al. 2012). In the samples RPW02A, RPW04B and RPW08B the presence of carbon was confirmed by Raman analyses (not reported), showing two broad signals around 1600 and 1300 cm⁻¹, usually attributed to modes of graphitized carbon and less crystalline carbonaceous materials (Smith et al. 1999, Goodall et al. 2009).

The mineralogical pattern can also be used to estimate the maximum temperature reached by the ceramic materials during the firing process, due to the different thermal stability of the various mineral phases (Heimann 1982). However, mineralogical composition is also related to the composition of raw materials, reducing or oxidizing conditions and residence time in the furnace (Iordanidis et al. 2009; Maritan et al. 2006; Papachristodoulou et al. 2006). Thus, SEM observations of the morphological features of the ceramic paste, were also performed in order to make an integrated assessment of the firing temperature. The SEM examination of the fresh fractures provided information on the degree of vitrification and on the characteristics and distribution of the pores developed during the original firing step.

Figure 7: Secondary electron microphotographs of the fracture sections of RPW02A (1000X magnification), RPW02E (5000X magnification) and RPW07 (1000X magnification) samples.

SEM microphotographies of three samples (RPW02A and RPW07 at 1000X magnification and RPW02E at 5000X magnifica-
tion) are reported in Figure 7. Crossing the data, firing temperature can be inferred with good accuracy. For instance, sample RPW02A contained incipient anorthite, whose formation is assigned by many authors around 950 °C (Belfiore et al. 2007; Papachristodoulou et al. 2006). In our samples the presence of anorthite could also be due to raw materials, but its formation pending the firing step is in accordance with the firing temperatures estimated by SEM observations in all the examined sherds. For example, in the case of sample RPW02A the 850 and 950°C range was confirmed observing the SEM microphotography (Figure 7) which showed Continuous Vitrification with Fine Bloating pores (CV(FB)) according to Maniatis and Tite (Maniatis and Tite 1981) classification for not calcareous pottery fired in a reducing atmosphere (the sample is grey).

Microscopic observation of sample RPW02E revealed the presence of pores classifiable as CV(FB) (Figure 7) in the case of non calcareous samples fired under reducing conditions. However, sample RPW02E is red, indicating an oxidant atmosphere. A possible explication is a firing process conducted in reducing condition until incipient bloating with a following step in oxidant atmosphere (probably due to the kiln opening) until the maximum firing temperature (850-950°C) with the subsequent bloating completion and development of the final colour. RPW07 is classifiable as calcareous (11.5 wt% of CaO, calcite clearly detected in XRPD pattern). The mineralogical pattern of this sample was not indicative of the original firing temperature, since the detected phases are stable in a wide range of temperatures (Riccardi et al. 1999; Schomburg and Zwahr 1997). The microscopic features of the not vitrified ceramic paste (Figure 7) pointed to a maximum firing temperature around 800°C. All the other samples were similarly examined and the estimated temperature ranges are reported in Table 3. In conclusion, the overall original firing temperatures could be assumed between 800 and at least 1050°C.

The relatively high temperatures observed in the analysed samples differ from the 750-815° temperature that has been previously recorded in some samples from Alambra Mouttes (Barlow 1996, 243-244) and Marki Alonia (Webb 1994, 17), where the open fire technique had been suggested. On the contrary, the observed estimated temperature range (from 800 to at least 1050°C) of our samples seemed to point to the use of kilns instead of pits or open fires. It is assumed that open pits achieve relatively low temperatures (800-900°C), while higher temperatures are reachable only in carefully constructed kilns (Henderson 2000, 135-140; Rye 1981, 96-103). Advanced skills in pyrotechnology and the possible use of pottery kilns in MC in Cyprus has been suggested also by Barlow and Idziak (1989, 74-75), even if no MC kilns and productive structures have been identified in the sites excavated so far. Specific pottery production structures in Cyprus are dated to the Late Bronze Age at Morphou Tounta Tou Skourou (Vermeule and Wolsky 1990) and Sanida (Todd and Pilides 2001). However, it is possible that pottery production in the Middle Bronze Age Cyprus was carried out away from the villages, probably close to clay and water sources (Barlow 1996, 243-244; Crewe 2007, 30-31). The reaching of high firing temperatures and the increase of the pyrotechnic skills have been claimed (Steel 2004, 135) as an indication of an early and progressive step towards pottery specialisation on the island. At last, the capability of reaching high firing temperatures in MC is not surprising at all, bearing in mind the extent and importance of the metallurgical Cypriot industry, the first evidence of which seems to date back even to the Late Chalcolithic (Knapp 2008, 74-75).

4. CONCLUSIONS

The physico-chemical study of the RP samples collected by KVP underlined several points.

A first remark regarded the surface treatment: SEM observation did not reveal discontinuities between bodies and surface...
layers and EDX analysis showed, for each potsherd, uniformity of elemental composition between body and surface, indicating a simple mechanical treatment of the surface without any slip application.

The chemometric evaluation of the EDX compositional data showed a general lack of clustering, even on the basis of the pottery function/use (commonly used ware vs. pithoi).

XRPD analysis revealed the presence of amphiboles (hardly reported before in a ceramic paste) in the majority of our samples. This is a signal of the presence of ophiolitic detritus in the raw materials utilized by potters and these remarks are in agreement with the topographical and geological framework of the Kouris valley. Moreover, the occurrence of amphiboles explained the absence of correlation between FeO wt% content, the presence/absence of Fe₃O₄ and colours.

As for the colouring mechanisms, the presence of hematite accounted for red/reddish sherds, while the lack of iron (II) compounds required an alternative colouring agent for grey/black samples, which could be identified as carbon both in the crystalline graphite and in more amorphous forms.

Firing temperatures were estimated by using a multi-technique approach, particularly appropriate for heterogeneous samples, as in our case. Temperatures were assigned crossing mineralogical (XRPD) and morphological (SEM) data, leading to a firing temperature range from 800 to at least 1050°C, and these quite high temperatures could be seen as an indication of the use of kilns. Nevertheless, the high variability in the colour range inter and intra-scherds, involved a scarce control of the firing atmosphere and revealed an overall ‘poor’ mastery, or at least a small interest in pyrotechnic processes except for the final result.

The absence of a distinction surface/body and the identification of relatively high firing temperatures seemed to differentiate the RP manufacture in the Kouris valley from the same ware production in the northern igneous foothills of the Troodos Mountains (Alambra Mouttes and Marki Alonia). This was not surprising at all within the wider regionalism of the Middle Bronze Age Cyprus and, furthermore, if we consider the great adaptability that Cypriot potters reveal even now.

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REFERENCES


