Post-depositional surface whitening of ceramic artifacts: alteration mechanisms and consequences

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Abstract
Surfaces on ceramic artifacts that are paler than the main sherd body are commonly interpreted as slips that were intentionally applied by the potter during the manufacturing process. However, due to post-depositional alteration, sherds that were not originally coated with a slip may macroscopically appear with deceptively similar pale surfaces. This paper presents a comparison of two sherds, both with pale to white surfaces, one of which is a real slip and the other a surficial corrosion that occurred during the burial stage. Observations using optical and scanning electron microscopy, as well as electron-probe image- and microanalysis, clearly illustrate the features of the two surfaces, as well as demonstrating their causes and effects. The superimposed slip is clearly delimited from the sherd body by a denser and much finer-grained fabric, in which clay minerals predominate and porosity is reduced by about 20% compared to the body. In the other sample, surface corrosion, due to invading fluids, has led to leaching of calcareous constituents and results in a remarkable increase in porosity close to the rim (ca. 25%). Sometimes called the “espresso crema effect” (Tschegg et al., 2009b), the surface becomes considerably brighter than the core and can easily be confused with intentional slips. This, as a consequence can lead to significant misinterpretations, to erroneous sherd characterizations and classifications, as well as to incorrect assignments to specific ware groups.

1. Introduction

It is known in ceramic research that ancient sherds with all their geochemical and mineralogical attributes as well as their physical properties, upon excavation, reflect a final result of countless natural and anthropogenic processes. These processes a priori define, influence, and diversify the physico-chemical characteristics of the findings. Before a sherd gets analyzed, raw material was removed from natural outcrops, conditioned and prepared, eventually mixed with other materials, formed to a vessel, dried, smoothed, textured, slipped, fired, burnished, decorated, etc. and finally, it was buried in a soil or sediment until being excavated. The burial stage is not only the last but also the longest and therefore holds great potential to modify the initial physico-chemical properties of archaeological artifacts. Depending mainly on the chemical composition of the sherd, its mineralogical constituents, fabric and experienced firing temperature as well as local environmental parameters (chemistry and mineralogy of sediment, availability of invading fluids, fluid chemistry, climate, etc.) and duration of the burial, ceramics may lose original constituents (dissolution), gain new material (cementation) or replace primary minerals by secondary phases (Maggetti, 1982). Processes that potentially modify bulk physico-chemical attributes of whole ceramic materials, and corrosion processes affecting the sherd surfaces have to be distinguished.

Effects of burial alteration and contamination on ancient ceramics, and the resulting problems for analytical and successive evaluation of data, were studied by several authors (recently by Buxeda I Garrigós et al., 2002 and ref. therein, Schwedt et al., 2006 and ref. therein and Zacharias et al., 2007 and ref. therein). These studies discussed alteration as a result of post-depositional processes that affected variations in geochemistry, mineral dissolution phenomena and mineral growth, and perturbations in dating along with several methods for identifying and resolving these problems. Furthermore, causes and effects of alkaline metals that leached out due to alteration of glassy phases and crystallization of analcime, both processes that may change the chemical composition and mineralogy of whole sherds, were addressed. Thus, post-depositional alterations can not only lead to surface corrosion, but also cause originally homogenous groups of vessels to show strong compositional variations (Schwedt et al., 2006).

Ca profile formation (decreasing Ca contents from the core towards the edge of sherds), which occurs unrelated to
heterogeneities of the original fabric were studied by Schwedt et al. (2004, 2006). They showed that many ceramic artifacts with corroded surfaces exhibited a reduction of Ca, and also alkalis (Na, K, Rb, Cs), towards the surface, in part due to the leaching of Ca from calcareous temper phases (mainly calcite).

Molera et al. (1998) studied alternative processes that are unrelated to intentional slipping and burial corrosion, which are also capable to modify the color of calcareous sherd surfaces though and showed how complete decomposition of calcite at high temperatures (950 °C), blastesis of pyroxenes and low presence of iron oxides lead to creamy surface colors. Buff ware pottery that also exhibits lighter appearance after manufacturing was studied by Abbott (2008). The author realized how the reaction of additive Ca-carbonate and salt in a defined clay matrix causes bleaching effects under strictly controlled atmospheres and temperatures.

The present study highlights a common kind of surface alteration that occurs during burial of ceramic materials. It not only affects the physico-chemical properties of the sherds but much more than this, easily can lead to wrong pottery classifications and false ware group assignments. Detailed microstructural investigations of vessel surfaces revealed that leaching of calcareous constituents considerably increases porosity on the surface of ceramics. This, besides changing the chemical composition of the surface layer with respect to the core area (investigated by Schwedt et al., 2004), results in an appearance of the sherd-exterior that is deceptive similar to intentional superimposed slips. A slip sensu stricto is a layer of fine clay-rich material which is intentionally applied to a dried ceramic body. It reflects a commonly used pottery manufacturing technique, as irregularities and defects on the paste-surfaces can easily be covered (Velde and Druc, 1999). Consequently, it is of supreme importance to determine whether sherds have a deliberate slip or not, since this is a documentation of the level of technology used at that time in that pottery workshop. Slips are in general very fine-grained containing fusing agents or easier fusible alkali-rich clay mineral assemblages to strengthen and protect the vessel surfaces (Velde and Druc, 1999). Because of esthetic reasons, kaolinite rich, innately light-colored clays are often used for slip preparation. This implies a strong brightening of the external surface with respect to the core seems to be obvious though. Fig. 2b illustrates the surface section of the Cypriot sample 2191-5 in transmitted light. The pale, typically 200–300 μm thick rim is visibly distinguishable from the core section and indicates the difference in color and the obvious higher porosity, identical mineralogical features.

Secondary electron (SE) images in Fig. 3 again illustrate the difference of ceramic body and surface of both, the slipped and the corroded sample. Fig. 3a shows a section of 8106GK, in which the transition from the coarse-grained core fabric to the approx. 400 μm thick, finer-grained slip is clearly identifiable. Within this superficial surface, refinement of material with hardly any temper grains results in a durable and smooth crust. In contrast, sample 2191-5 shows no difference between core and rim section concerning paste-matrix and included temper material (Fig. 3b). The detail of Fig. 3b which is shown in Fig. 3d though indicates an approx. 200 μm thick surface zone that appears more uneven than the core area. The observed roughness is caused by the quite abruptly increased porosity, showing up best in Fig. 3c, in which the same section as in Fig. 3b is presented, pictured with the back-scattered electron detector. The rim appears clearly darker because of first, higher porosity and second, decreased contents of elements with higher atomic number (e.g. Ca).

BSE images of the slipped Egyptian sample 8106GK and surface corroded Cypriot sample 2191-5 are presented in Figs. 4 and 5. They impressively illustrate the two different types of surface layers. Fig. 4 shows the highly dense, fine-grained superimposed slip that in contrast to the body indicates a much higher grade of levigation and/or an innately finer-grained nature, as larger temper grains are hardly existent. The pale color of the slip in general can be ascribed to...
higher amounts of clay minerals per area and resulting higher potential of electrons to be excited and backscattered. Fig. 5 in contrast clearly visualizes the highly increased porosity of the corroded surface zone with respect to the ceramic body section of sample 2191-5. Despite the massive increase of voids, the mineralogical assemblage of the rim is identical to one in the body section.

In the 256 × 192 μm large details that are outlined in the BSE images (Fig. 4a, b and Fig. 5a, b), wavelength-dispersive element maps for Al, K and Ca were performed to illustrate their distribution within the paste. Higher detected intensities result in brighter appearing spots on the map, alternatively, no intensities result in black shading. Looking at the three element mappings of Fig. 4, a direct comparison of the Al, K and Ca distribution in the core section (Fig. 4a) as well as in the rim section (Fig. 4b) is possible for sample 8106GK. Al and K indicate higher abundances in the slip than in the core area, due first to the denser and finer-grained paste in the slip and second, to higher amounts of clay minerals per defined area, which contain these elements. Ca remains more or less at the same level. The exact opposite effect is observable in Fig. 5, in which the same arrangement is given for sample 2191-5. Due to higher porosity in the surface area, the measured element abundances per area are reduced as demonstrated by darker shadings in the mappings of Fig. 5b with respect to element maps of the core (Fig. 5a). This is true for both, Al and K; the calcium mapping makes this observation evident with highest significance though.

Multiple modal analyses on 1000 × 200 μm BSE images were assessed in order to gain the percentage of porosity in the core as well as in the surface areas. For sample 8106GK, the measurements reveal a core porosity of 25%, while in the slip the porosity decreases more than 20% to less than 5%. For 2191-5, measurements yield the opposite trend – 20% porosity in the core section and 45% in the surface section, an increase in porosity of 25% – slightly depending in which position the images were acquired. The size of the newly formed voids ranges between 10 and 100 μm, just sporadically larger ones can be found.

Several EPMA line measurements were performed from the core to rim of both samples in order to gain geochemical profiles and to provide quantitative estimations of body and surface composition. Results are presented in Table 1 and illustrated in Fig. 6. For sample 8106GK, the profile concerning mean composition reveals an increase in measured total intensities in the slip of about 10% with respect to the core section. Summing up the analyses to 100% and taking the mean values of the 250 μm long lines into account, an abrupt increase of SiO₂ (+3 wt.%), Al₂O₃ (+2.8 wt.%) and K₂O (+1 wt.%) is obvious from the core to the rim section, with a decrease of mainly FeO (−5 wt.%), MgO (−0.7 wt.%) and Na₂O₃
(−1.5 wt.%), while CaO remains ± the same. As was already shown in the element maps, the clay mineral constituents Si, Al and K indicate raised contents in the slip compared to the body. For sample 2191-5, the assessed mean composition of body and corroded surface, besides SiO₂ and CaO, shows hardly any difference. The CaO values indicate a decrease of more than 10 wt.% that is chemically balanced by SiO₂ (±10 wt.%) and Al₂O₃ (±0.9 wt.%) when normalized to 100% total (Table 1 and Fig. 6b). The loss of

![Fig. 3. Secondary electron images of surface areas of (a) sample 8106GK and (b) 2191-5 at 100× magnification; (d) detail of the surface of 2191-5 at 500× magnification. (c) Backscattered electron image of the section showed in (b).](image)

![Fig. 4. EPMA backscattered electron image of a surface section of sample 8106GK. (a) and (b) illustrate element mappings for Al, K and Ca for body and rim sections that were assessed exactly at the positions indicated in this figure.](image)
non-normalized total intensities when crossing the transition is around 30%, indicating the distinct increase in porosity and the caused loss of excited electrons. It is interesting to mention that with EPMA, which normally is not the appropriate method to assess geochemical bulk compositions of such porous and inhomogeneous composite materials, very good results were achieved. Good correlations were observed between the bulk major element chemistry of the two sherds analyzed with X-ray fluorescence (Tschegg et al., 2008, 2009b) and the mean results of the core section measured with EPMA (Table 1).

### 4. Discussion

Alteration mechanisms of ceramic surfaces during burial and their potential to influence the bulk geochemical composition and/or the bulk mineralogical assemblage are known problems in pottery analyzing studies (see citations in the Introduction). Most researchers dealing with the question of provenance and technology of ancient ceramics remove corroded surfaces before analysis. This is appropriate and necessary for their intentions, although essential information of mainly archaeological interest can consequently not be evaluated.

Sherds, which are embedded in soil and sediment layers for 1000s of years, do variably react with invading fluids. The intensity and result of this interaction depends on the mineralogy, bulk geochemistry, the manufacturing procedure and the firing conditions of the sherds. However, these issues often remain elusive to scientific analysis. Good correlations were obtained between the major element chemistry of the body and the rim sections for both sherds, which were measured through EPMA line measurements from the core into the surface areas. Standard deviations for the analyses are also given.

**Table 1**  
 EPMA core and surface major element analyses.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
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<tr>
<td>8106GK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mean core</td>
<td>52.22</td>
<td>17.90</td>
<td>7.06</td>
<td>2.52</td>
<td>15.79</td>
<td>3.35</td>
<td>1.16</td>
</tr>
<tr>
<td>St. dev.</td>
<td>5.69</td>
<td>2.56</td>
<td>4.32</td>
<td>1.95</td>
<td>5.06</td>
<td>0.86</td>
<td>0.64</td>
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<tr>
<td>Mean surface</td>
<td>55.25</td>
<td>20.73</td>
<td>2.11</td>
<td>1.79</td>
<td>16.07</td>
<td>1.89</td>
<td>2.17</td>
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<tr>
<td>St. dev.</td>
<td>3.57</td>
<td>2.02</td>
<td>1.01</td>
<td>1.34</td>
<td>3.81</td>
<td>0.41</td>
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</tr>
<tr>
<td>Bulk (XRF)</td>
<td>50.90</td>
<td>15.50</td>
<td>8.36</td>
<td>3.77</td>
<td>13.90</td>
<td>1.78</td>
<td>1.83</td>
</tr>
<tr>
<td>2191-5</td>
<td></td>
<td></td>
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<tr>
<td>Mean core</td>
<td>51.15</td>
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<td>6.91</td>
<td>13.79</td>
<td>0.62</td>
<td>2.30</td>
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<td>2.14</td>
<td>0.68</td>
<td>1.47</td>
<td>2.00</td>
<td>0.15</td>
<td>0.97</td>
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<tr>
<td>Mean surface</td>
<td>61.16</td>
<td>17.75</td>
<td>8.30</td>
<td>6.40</td>
<td>3.56</td>
<td>0.53</td>
<td>2.28</td>
</tr>
<tr>
<td>St. dev.</td>
<td>3.86</td>
<td>1.77</td>
<td>1.77</td>
<td>1.45</td>
<td>0.71</td>
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<tr>
<td>Bulk (XRF)</td>
<td>51.20</td>
<td>13.00</td>
<td>6.76</td>
<td>7.73</td>
<td>15.90</td>
<td>1.68</td>
<td>2.13</td>
</tr>
</tbody>
</table>

St. dev. – standard deviation.
temperatures of the sherd (Maggetti, 1982; Buxeda I Garrigós et al., 2002), the duration of burial, the chemistry of fluid and environment, predominant pH, etc. The ceramic samples presented in this study have similar age and similar bulk geochemical major element composition (Table 1). However, they reflect different types of surface treatment techniques. In the Egyptian sherd 8106GK an intentional slip was superimposed whereas in the Cypriot sherd 2191-5 this was not the case. Macroscopically also 2191-5 appears having a pale surface, which indeed can be confused with a slip, but actually is related to surface corrosion during burial and can definitively not be a deliberate part of the manufacturing process.

Observations via optical microscopy and scanning electron microscopy as well as analytical results from the microrope confirm this statement. The Egyptian Bichrome ware sherd 8106GK indicates a surface that results from a commonly used, comprehensible intentional manufacturing technique. No natural process could define such an effect. A very fine-grained, dense, 200–500 μm thick outer layer was applied on the sherd surface (Figs. 2–4), in all probability to first, cover the rather “simple” manufactured ceramic body (Tscheegg et al., 2008) and secondly, to smooth and prepare the surface for the final decoration, for bichromic painting. BSE images substantiate the differences of ceramic body and rim sections and therefore it was archaeologically categorized and described as strongly being levigated.

Because of its pale appearance, the Cypriot sherd 2191-5 macroscopically looks as having a deliberate manufactured slip, and therefore it was archaeologically categorized and described as being slipped (Crewe, 2004). It is assigned to the Plain White ware group, which in general summarizes sherds with a variety of vessel types, but typical fabric colors and a slip (Crewe, 2004). Detailed investigation though revealed that not a slip is responsible for the pale appearance of many Plain White Wheelmade ware ceramics, but a drastic increase in porosity at inner and outer sherd surfaces. This higher porosity at the surface of the sherd is confirmed by observations with all applied methods of this study. SEM imaging demonstrates the rough and porous nature of the surface (Fig. 3), BSE images make a quantification of the leap of porosity of about 25% possible. Profile EPMA measurements confirm the higher degree of porosity in the surface sections by the severe and abrupt loss of total detected intensities. Together with the BSE images and the element maps it furthermore turns out that mainly CaO is lost in the rim section compared to the ceramic body (Figs. 5, 6 and Table 1). Therefore, it is obvious that calcareous inclusions that were initially included in the paste were affected by infiltrating fluids and as a consequence leached out of the zone close to the surface. This resulted in the observed decrease of Ca and at the same time lead to the immense modal increase of remained voids. Since the profiles in core section of the sherd show homogeneous calcium contents, the possibility of natural heterogeneities in the fabric that resulted in the observed surface modification can be excluded (also stated by Schwedt et al., 2006).

Deliberate manufacturing techniques of the potter yielding the present surface properties can be excluded, since the observed decreased amounts of calcareous phases in the surface areas and the connected increase in porosity can not be achieved by any pottery production technique.

The reason why the surface appears brighter due to increased superficial high porosity can simplest be explained using the analogue of the espresso crema. The crema (coffee foam) has differing physico-chemical properties compared to the subjacent coffee, in terms of a much higher degree of included vesicles and varying molecular compounds (Illy and Viani, 1995; Perkowitz, 2000). The gas phase is stabilized against coalescence and collapse by liquid films consisting of natural compounds (Piazza et al., 2008). Although the processes of vesicle generation are different, just as in the ceramic exterior, sparsely increased areas of gas–liquid/gas–solid interactions cause advanced light reflection and refraction, enhanced light scattering respectively, what in the end results in a bright opaque appearance (Vera et al., 2001). The increased amount of voids on the ceramic surface causes a higher potential of light scattering, making these materials appear brighter than the medium beneath. This physical process brings on the pale appearing surface not only of sherd 2191-5 but many other specimens of the studied PWW ware group.

5. Conclusion

This paper demonstrates how easily corroded surfaces of ancient ceramics, which form as a result of post-depositional alteration processes, can be confused with superimposed slips (sensu stricto), which intentionally were made by the potter during the manufacturing process. For this reason, a representative example for both, a slipped and a corroded ceramic sample, were compared to each other and investigated in detail to learn the causes and effects of their specific surface distinctiveness, their microstructural build-up as well as their geochemical characteristics. The increased porosity of the corroded ceramic surfaces causes them to appear whitish, and leaves the macroscopic impression of being deliberate and man-made. The significant process behind this effect is the surface dissolution and erosion of calcareous inclusions through sediment invading fluids and the resulting immense increase of porosity.

Many archaeological ware groups are classified on the basis of their attributes of surface finish (Shepard, 1956). That’s why the studied corrosion effect may lead to erroneous groupnotations and descriptions as well as wrong group assignments. Since several pottery families have been partly or mainly classified by means of their whitish appearing surfaces (some examples from the Mediterranean region: White Painted ware, White Lustrous Wheelmade ware, White Shaved ware, Plain White ware, White Painted Wheelmade ware; Åström, 1972), the importance of sherd surface corrosion urgently needs to be considered in their definition.

For future excavations and macroscopic pottery group assignments, one should be aware when dealing with sherds that have a brighter surface relative to the ceramic body, that this could be the result of burial alteration and not of pottery manufacturing.

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