Technology and Provenance of Ceramics (Including Ceramic Pigments) and Glass

Topic: Post-depositional Alteration of Ceramics

070 The Role of Chemical, Micromorphological and Archaeological Evidence in Determining Site-specific Production Provenance of Archaeological Ceramics, and Post-depositional Alteration of their Composition

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With the goal of tracing intraregional and interregional contacts and mobility in and around Roman Galilee (first century BC - fourth century AD) based on the production and distribution of common household pottery, the members of one of the two main pottery provenance groups in use in this period and region have been determined rigorously, employing instrumental neutron activation and high-precision X-ray fluorescence analyses, and several multivariate statistical tests. The site specific provenance of this group was located at Shikhin (production dates: ca. late first century BC - fourth century AD), a large village about 1.5km from the city of Sepphoris, based on chemical, micromorphological, and literary evidence. The Shikhin provenance group (N=151) was subsequently compared, using chemical, micromorphological and statistical analysis, with 4 other pottery groups, of first and fourth century AD date, each well defined on archaeological criteria. Using chemical compositional data and archaeological evidence, we were able to conclude that two of these groups were not produced at Shikhin, but evidently in the near vicinity of Shikhin and Sepphoris, while the other two groups were probably made at Sepphoris.

The analytical study of the Shikhin provenance group, the four groups made nearby, and other pottery provenance groups made during the Roman period at Galilean settlements ca. 7 to 22km from Shikhin, has shed light on the extent of compositional variation that can be encountered in pottery made at different locations very close to one another, that can be compared to differences in composition characterizing the pottery of more distant producers. It has also provided evidence on production technology and settlement patterns in Roman Galilee. These insights have been achieved as a result of a lengthy study of the measurement precisions of each chemical element, and careful attention to post-depositional effects on various elements, as determined by chemical and micromorphological analyses.

The paper will present the study of the Shikhin and nearby groups, and a comparison with other contemporaneous Galilean provenance groups. We will also demonstrate the effect of post-depositional alteration on alkaline earth elements, and their apparent effect on alkali elements, as shown by chemical and micromorphological analysis. Such compositional alteration needs to be taken into account to enable high-resolution differentiation of pottery provenance groups.

References
Roman Amphorae from the Iulia Felix Shipwreck: Alteration and Provenance

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The Iulia Felix Shipwreck was found near Grado (Italy), and it can be dated about the middle of the 2nd century AD. The cargo is composed of a great variety of amphorae (Dressel 22, Forlimpopoli A, Cnidia, Ostia LIX, Africana IA, Tripolitana I, Pseudo-coe and Dressel 19), mainly devoted to the transportation of fish products. The Dressel 19 amphora is a not very well known type, and it has been sparsely documented. The amphorae found in this shipwreck cannot be attributed to the Dressel 19 type without problems, even if they present several morphological similarities. Its provenance is suspected to be the southern part of the Iberian Peninsula.

In order to further investigate this possibility, several individuals, as well as two other individuals of eastern amphorae, have been sampled and have been characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy by thin-section (OM) and scanning electron microscopy (SEM). The results show the existence of severe alteration and contamination processes, which mainly affects Mg and Ca contents, as well as the alteration of hematite. As a result of these processes the investigation of provenance is dramatically affected.

Experimental Pottery Alteration Using Autoclave Treatment

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Ceramic artefacts can lie in archaeological deposits for several centuries or millennia before they are studied by archaeologists or subjected to physical-chemical analysis. Whilst they lie in the ground the potsherds are affected by a variety of factors which attack them both mechanically and chemically. It is of fundamental importance to establish, as far as is possible, how the ‘post-depositional effect’ affects the results of laboratory analysis.

Does the chemical composition of the potsherd undergo any crucial changes, does its phase composition change, will it be possible to accurately gauge the temperature at which the vessel was
originally fired? Is the ‘post-depositional effect’ so strong that, for example, the provenance groups established on the basis of chemical composition analysis results, in truth relate only to the variety of post-depositional factors?

Experimental analysis was carried out on marly-clay from Wadi Qubur in Palmyra. Chemical analysis results indicate that this raw material was used in the production of Roman pottery of the common ware type. In laboratory conditions, however, it proved impossible to make a stable ceramic product—the pottery produced fell apart several days after refiring because of its very high CaO content (c. 45%). A stable ceramic product was not achieved until the ceramic body was prepared with a make-up water to which salt (NaCl) was added. This fact inspired further analysis. As part of an experiment samples were produced using make-up water with various salt contents. These samples were fired at different temperatures ranging from 600°C to 1200°C and then divided into three groups (each group comprised samples which had been fired at the same temperature). The first group was kept in air-dried conditions, the second was placed in an exsiccator immediately after firing, whilst the third group was subjected to autoclave treatment, in which water vapour, temperature and pressure are used to accelerate the ageing process of the pottery. The following analyses were then carried out on all three groups of samples: chemical analysis, X-ray diffraction, TG-DTG-DTA analysis, dilatometric analysis and thin-section studies. This type of procedure made it possible to describe the physical-chemical changes induced in the ceramic sherds by the firing temperature, as well as facilitating a description of the changes induced in the sherds by their storage conditions in correlation to their original firing temperature.

073 Scraping the Surface: Investigations into the Alteration and Contamination of the Decorative Pigments on Ceramics

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While the investigation of post-depositional alteration or contamination of the clay body of archaeological pottery is becoming standard practice in archaeometric ceramic studies, rarely has it been explicitly considered during the examination of the pigments used for decorating the same vessels. Even though care is taken to reduce the possibility of contamination when studying the clay paste (e.g. by mechanical cleaning), in some instances such care is not taken during the study of the decoration. The recent move towards the use of non-destructive techniques of analysis in pigment studies raises the possibility of the analysis of contaminated surfaces. While the problem of surface contamination may be overcome, to some extent, by the examination of fresh fractures or polished sections, these would not overcome the effect of alteration or contamination that has been leached into the clay body.

Studies of clay bodies have suggested that the identification of alteration products and contamination may cause confusion in such interpretations of analytical results. The main secondary phase formed is that of calcite, whose presence obscures the microstructure of the pigments or can be mistaken for the original pigment in the case of white colour. The present paper concerns a case study based on the analysis of polychrome and bichrome Middle Bronze Age pottery from Crete, Greece, in which the presence of secondary calcite is demonstrated by thin section petrography. Using SEM-EDAX as our prime analytical tool, we address the problem of the post-depositional alteration and contamination of decorative pigments and discuss the implications of this for technological and provenance studies.
074 An Examination of the Relationship between Firing Temperature, Soil Type and Post-depositional Alteration in Fine Wares

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The chemical characterization of ceramics has become an increasingly important aid to the investigation of manufacture and trade. A range of analytical techniques have been used in attempts to provenance ceramics to pottery types, manufacturing sites and clay sources. However, this type of investigation is of uncertain value if the possible post-depositional composition change in ceramics is not taken into account. The statistical treatment of the results of this type of investigation would be invalid if the degree of post-depositional was significant and varied with burial environment. Thus the derived conclusions relating to manufacture and trade may be incorrect.

This project examined the relationship between firing temperature and compositional alteration of fine wares buried in four different soil types. Unglazed fine ware discs were made from the same clay and fired at a range of temperatures. Discs of each firing temperature were buried in each of the soil types, at the same depth, in leaching columns. The columns were then subjected to an acid-leaching regime intended to represent accelerated natural chemical weathering. Discs of each firing temperature type were recovered from each of the soil types at five-day intervals for five weeks. Unleached discs and those recovered from the leaching columns were dried and crushed and samples of each were subjected to acid digestion. Each sample was analysed for a range of elements by AAS and UV/Vis. Homogenised samples of each soil type were also analysed in the same manner.

Results showed a correlation between firing temperature and post-depositional elemental concentration change for each soil type. The concentrations of elements under test increased in three of the depositional environments and decreased in one. Compositional changes were sufficient to cause discriminant analysis and principal component analysis to classify discs, which all had the same initial composition, to a range of different groups. Had the discs been archaeologically recovered sherds their provenance would have been inaccurate, highlighting the need for further investigation of post-depositional alteration in ceramics.

075 Bone Ash Coatings on Late Bronze Age Pottery from Ipsach-Räberain (Kt. Bern, Switzerland)

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The use of calcined bones as white fillings of incrustations is a common ceramic decoration technique in Europe since the Neolithic and up to the Hallstatt period (e.g. Geilmann & Gebauer 1954, Rychner-Faraggi & Wolf 2001). Contrasting, there was only one record until now of the use of a thin bone ash coating on the inner surfaces of store jars from Onnens VD-Le Motti from the Hallstatt period (Ha C/Ha D = 800-650 BC), detected by X-ray diffraction (Rychner-Faraggi & Wolf 2001).

During the excavations at Ipsach-Räberain in the year 1997, Late Bronze Age (end of the 12th/first half of the 11th century BC) fragments of coarse grained (diameter of the a-plastic inclusions > 3mm) pottery were found showing a red outer layer and a white, partially bluish-grey thin layer on the internal surface. Scanning electron microscopy evidences the extremely fine grained nature of both layers and EDS as well as X-ray fluorescence analyses reveal high amounts of calcium and phosphor, pointing to a CaP-phase for both layers. By X-ray diffraction analysis the white pigment was identified as hydroxy-apatite Ca₁₀(PO₄)₆(OH) and the bluish-grey as vivianite Fe₃(PO₄)₂·8H₂O. The latter must be a secondary, post-depositional decomposition product of former bone ash particles. This
interpretation is supported by microscopic observations, indicating that the bluish-grey layer lies on top of the white one. The red outer layer consists of hematite. Microscopical results rule out the hypothesis that the white layer was deposited by accident during burial processes, but point to an application of calcined bones before the ceramic firing. The reason for using this specific kind of internal coating is puzzling (Increase of the sealing in order to store liquids or to avoid moisture penetration from outside? Protection layer against insects or fungi?). The new occurrence indicate that bone ash internal coating was used during late Bronze Age also and it can be hypothesized that this specific technique was employed for Neolithic ceramics too.

References

076 Chemical Alteration of Ceramics Made from Calcareous and Non-calcareous Clays

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Chemical data of pottery collected in a databank of some 20,000 analyses of major and trace elements by WD-XRF offer a possibility to discussing a statistical evaluation of the problems arising with post-depositional changes. There are not too many but, in some rare cases, they could prevent any useful analysis in terms of provenance determination. The most common effect is the absorption of phosphorus in the sherds, described and discussed by many scholars. More than 10% P$_2$O$_5$ may be found in sherds from certain burial conditions. These contents are not correlated with calcium and must be from organic phases. At the same time, ignition losses, barium and strontium contents may be elevated. Another effect, often connected with the absorption of phosphorus, is the leaching of certain elements in acid burial conditions (alkali elements, calcium). Also, besides secondary calcite from recarbonatisation, calcite could be a secondary contamination increasing the original calcium content, an effect which only could be controlled by thin section analysis. Washing of sherds using HCl is often used to clean painted pottery in the field. This, like burial in acid soils, could cause leaching of calcium in calcareous pottery or in pottery tempered with calcite. This can be seen in thin sections but rarely in the chemical analysis. Examples will demonstrate how post-depositional alterations are related to finding places and to the differing ceramic properties of the sherds. Another type of secondary changes of chemical compositions could be contamination of sherds by copper, lead or tin or, in dry climates, by salt or gypsum.

077 Direct Evidence of Alterations in Pottery During Burial by Neutron Activation Analyses of Surface Samples

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Since chemical provenancing of ceramics is used in archaeometry, the question whether and in which way the chemical composition of archaeological pottery is affected by several hundreds or thousands of years of burial has been investigated mainly by two different approaches. Either burial conditions were simulated using various experimental conditions or the compositions of different sherds were compared, for which the use of the same clay paste was assumed by archaeological reasons. Both approaches rely on assumptions, on the validity of which there is still no common agreement.
In order to analyse alteration and/or contamination effects directly, i.e. without needing these assumptions, two samples were taken at the same position for a group of sherds with corroded looking surface, one from the surface and one from the core lying below the first sample. All of them were analysed using Neutron Activation Analysis. The aim of these analyses was to observe possible differences in the trace element pattern due to the corrosion, which should be stronger at the surface of the sherd. Additionally for some samples XRD was performed to estimate the firing temperature of the sherds. Mainly samples of Greek pottery from the Mycenaean time, but also some examples of Rhenish and Saxon (post)medieval pottery have been available for these comparisons.

The results show various differences in the trace elements, most striking for the alkalines, esp. Rb and Cs, for which in about one third of the cases reduced values at the surface were found. According to the diffractograms of these sherds a high firing temperature can be assumed. Most of these samples are calcareous, but not all.

Finally the influence of these changes on the Bonn grouping procedure is studied to see in how far these elements have to be handled with greater care during the formation of groups on the basis of trace element data.

ARCHON - Netherlands School of Archaeological Research

ARCHON is a national research institute and graduate school, comprising the archaeology departments of five universities (University of Amsterdam, Free University Amsterdam, University of Groningen, Leiden University, University of Nijmegen) and the National Service for Archaeological Heritage (ROB) at Amersfoort.

The researchers participating in ARCHON represent a very broad spectrum. In chronological terms they cover all archaeological periods, from the earliest Palaeolithic up to the complex societies of the Old and New World. Geographically the focus is on northwestern Europe and the Mediterranean, but ARCHON members also work in the Americas, South-eastern Asia and Africa.

In terms of research perspectives the diversity is likewise large, with approaches rooted in various disciplines such as the natural sciences, geography, cultural anthropology and philosophy.

Currently, the school has 62 senior members and 36 associates. A total of about 30 PhD-students with an official research contract is registered.

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