Chemical Analyses of Ancient Ceramics: What for?

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Abstract: Several examples of the use of chemical methods to solve questions such as the effects of soil contamination, the use, the provenance, and the manufacturing of clay-based ceramics are presented. Assisted by the element phosphorus, it is possible for chemical components to migrate into and out of a broken pot during the burial stage. The analysis of food residues, such as crusts on or organic substances in the ceramic piece shows that the medieval population in England ate mainly cabbage, whereas the Indians of Manitoba (Canada) relied on a diet of fish and animal fats during the 10th–16th centuries. The chemical analysis of the unusually large bricks produced by Cistercian monks in Switzerland during the 13th century gives evidence of the existence of other manufacturing places, such as Fraubrunnen and Friesenberg, in addition to the main factory located at the monastery of St. Urban. Some 18th to 19th century Swiss faience from the Matzendorf and Kilchberg-Schooren production sites are not easy to attribute to a specific center based on stylistic arguments alone, but they can be clearly differentiated in their chemical composition. Furthermore, scientific evidence suggests that artisans moved from Kilchberg-Schooren to Matzendorf, and vice versa. As exemplified by the so-called 'glossy clay layer', surprising results show that not only the mineralogical and chemical composition of the clay layer, but also the CaO content of the ceramic body, has a significant influence on the gloss – a fact that was well known to ancient Roman potters.

Keywords: Analysis · Ancient ceramics · Contamination · Function · Provenance

1. Introduction

From a historical point of view, fired earthenware was not widely used until the Neolithic period (in Switzerland from the end of 5th/beginning of 4th millennium BC), due to the fact that the properties of such a fragile material with limited shock resistance were more valuable for settled farming communities than nomadic hunters and gatherers. A vast amount of broken pots is usually collected during archaeological digs. These ceramic fragments are subsequently analyzed using an archaeological or art-historical approach, but recently also by scientific methods to answer the following questions:

- a) when (date of manufacture),
- b) where (place of manufacture),
- c) how (technique) and
- d) for what purpose (function) was the ceramic object produced?

At the Institute of Mineralogy and Petrography in Freiburg/Switzerland, a working group has been studying the mineralogical, petrographical, chemical and technological aspects of such objects since 1974.

1.1. Ceramics = Artificial Rocks

The manufacture of ceramics, especially the clay-based ceramics discussed here, follows three steps: (1) processing of the raw materials (in the case of clay-based ceramics, these consist of clays and loams); (2) forming and (3) firing. Clay and loam contain an association of fine-grained (smaller than 0.002 mm) clay minerals, responsible for the plastic behavior of the clay and coarser components, the so-called a-plastics, both characteristic of the particular type of raw material. Processing of the clay makes the material suitable for its subsequent use. This treatment consists of reducing the clay to small pieces, the extraction of coarse impurities, soaking the clay with water and possibly the addition of a temper (sand or crushed rocks), as well as mixing and depositing of the clay mixture.

Subsequent water extraction makes the material malleable, and through kneading, the desired homogeneity can be obtained. The resulting plasticity of the material now allows manual molding, with or without a potter's wheel. Before firing, the object has to be air-dried. During firing, clay minerals release their chemically bound water at temperatures above approximately 500 °C. The microscopic, fine-grained decomposition products have a disordered crystalline structure. They react easily with partial melts formed in the temperature range of 700–1000 °C. At this stage, the decomposition of hydroxides, sulphates, carbonates, etc. generates oxides, which dissolve in the melts or form new silicates. All these reactions result in a chemically quite resistant, but water-absorbing material, whose utility can be increased by coatings (e.g. glossy clay layers or glazes).

Ancient and modern ceramic products can be studied from different perspectives. To the petrologist, they are artifi-
cial rocks which have been subjected to relatively high temperatures and have recrystallized to become thermomorphologic products, analogue to those naturally formed through metamorphism. In contrast to natural rock-forming processes, pressure is insignificant in the genesis of such objects, because the kiln can be considered as a technical system. In such open systems, neither pore solutions, present before firing, nor gaseous reaction products, which may have been produced during the high temperature process, have an influence on the transformation, because they can leave the system at any time.

Similar to natural rocks, ceramic objects consist of an assembly of crystalline and amorphous phases, which can be analyzed with the same petrographical, mineralogical and chemical methods as micaschists which are formed from clay during metamorphism.

### 1.2. Ceramics – A 'Book' with a Great Deal of Information

Any ceramic fragment, however insignificant it may appear, can be compared to a potential ‘book’, because it contains, as if stored on pages, a wealth of information about its history [1]. As shown in Fig. 1, the lifespan of a piece of pottery can be divided into five steps: (1) extraction of the clay from the pit; (2) manufacture of the object (processing of the clay, firing); (3) use, with subsequent breakdown; (4) burial; (5) excavation, cleaning, treatment and analysis.

During all these steps, the sherd has stored information, and this ‘memory’ can be activated by a variety of chemical and physical methods. Considering the chemical composition of a sherd, it is obvious that it will reflect the composition of the original clay, its processing (the extraction of coarse, a-plastic particles or the addition of temper fragments can change the chemistry), the use of the object (e.g. the chemical composition of a cooking pot can be affected by reaction processes between the pot itself and the food), the burial stage (infiltration of foreign matter into the ceramic body or extraction of sherd matter caused by solvents from invading solutions) and the post-extraction treatment (e.g. cleaning with acids can lead to dissolution of carbonates).

Chemical analysis is extremely useful in the study of historic ceramics. Considering the individual constituents of a ceramic object (Fig. 2), two basic questions need to be looked at: (1) qualitative or quantitative determination of the composition of homogeneous microdomains (spot analysis of glazes, paintings and a-plastic fragments) by electron microanalysis (microprobe) or by energy-dispersive X-ray spectrometry using a scanning electron microscope (SEM-EDX) for the identification of the material; (2) quantitative analysis of sample series by X-ray fluorescence analysis (XRF), instrumental neutron activation (INA) or inductively coupled plasma mass spectrometry (ICP-MS) to establish chemical groupings and identify the provenance of the pottery. Furthermore, the organic matter, present either as charred residues on the inner or outer surface of a vessel or as non-visible deposits absorbed into the porous ceramic body, can be analyzed by gas chromatography–mass spectrometry (GC-MS) or isotope ratio monitoring GC-MS in order to interpret a vessel’s use.

The following examples illustrate how chemical methods can be applied to solve cultural-historical problems involving ceramics. It is obvious that chemical methods alone cannot solve all problems, e.g. dating, but need to be combined with physical methods (i.e. achemagnetism, Mössbauer spectrometry, termoluminescence, microscopy, X-ray diffraction, porosity analysis).

### 2. Phosphorous Contamination During the Burial Stage

A ceramic body reacts sensitively to post-firing environmental influences. Due to the high porosity of the sherd (often more than 30 vol.%), circulating soil solutions can easily access a ceramic fragment and react with its phases. Such an interaction is exemplified by the element phosphorous. The $P_2O_5$ content of clays and soils on our planet rarely exceed 0.2–0.5 wt.% [2]. As a consequence, one would expect to find similar concentrations in ceramics, despite the fact that...
These values increase slightly during firing due to loss of volatiles (H₂O, CO₂, etc.). However, several authors have measured much higher concentrations, ranging up to 14 wt.% P₂O₅ (see quotations in Collomb and Maggetti [3]). These observations can be explained by: (1) treatment of the clay with a substance rich in phosphorus, such as urine or fecal material, before firing, in order to increase the plastic behavior of the material [4]; (2) contamination of the ceramic vessel after firing caused by either its content, e.g. a substance rich in phosphorus, such as milk, wine, eggs [5], or due to the use as a funeral urn (dissolution of the bones and precipitation of the solvents into the ceramic [6]) and (3) post-use enrichment during burial in a phosphorus-rich soil [7][8].

The latter is evidenced by the case of exported ceramics [9]. The so-called Terra Sigillata, a type of fine ceramics manufactured amongst other places in Pisa (Italy) by Roman potters during the 1st century AD, was exported to the military camp of Neuss (Germany). As shown in Fig. 3, only a few of the pieces excavated in Pisa exceed P₂O₅ values of 1 wt.% in contrast to those found in Neuss, which reach significantly higher levels. Since the origin of the ceramic ware is undoubtedly identical, this unusually high P₂O₅ content cannot be linked to a particular treatment of the clay. If this was the case, the same variation would be found in the sherds excavated in Pisa. Also, it is unlikely that the eating and drinking habits of those days differed greatly between the regions of Pisa and Neuss, which could explain differential uptake of phosphorus in the ceramic body by diet contamination. Therefore, the increased phosphorus content can only be the result of secondary burial effects.

A series of samples taken from an amphora’s profile shows a decrease in phosphorus towards the core of the sherd (Fig. 4, [10]). This observation supports the argument of soil contamination outlined above. However, it also emphasizes the complexity of this kind of process, because along with phosphorus, an enrichment of barium and manganese, as well as a decrease of calcium could be observed in this object. It could be argued that the water used for the preparation of the clay was responsible for transporting these elements from the core towards the periphery during the drying process. However, the low water solubility of common salts formed by these elements excludes this possibility.

Fig. 3. P₂O₅ contents of Terra Sigillata produced in Pisa and exported to Neuss. Left histogram: 30 fragments, excavated in Pisa. Right Histogram: 82 fragments found in Neuss [9].

Fig. 4. Profile of a massiliotic amphora and variation of the P₂O₅-, MnO-, CaO- and Ba-contents [10].

(All these various contaminations need to be considered very carefully before each analysis, as well as during the interpretation of the results. This can be achieved by either cutting down a few millimeters of the possibly contaminated surface of the object before the analysis, or by identifying and ignoring the mobile components that apply to the particular case.)

3. Use of Ancient Pottery Vessels

According to Rice [11], a ceramic vessel can be used for three purposes: (1) storage of dry substances; (2) carrying liquids and (3) heating liquid or solid substances over a fire. Culinary activities (3) involving repeated heating of animal or plant foodstuffs can leave organic residues, present either as visible surface deposits or as absorbed residues in the porous ceramic body. In the latter case, lipid extracts produced by solvent extraction of sherds, are analyzed (Heron and Evershed and references therein [12]). Theoretically, the absorbed material could originate from three different sources: (1) as a result of vessel use, (2) from the burial environment and (3) from organic material present in the clay before firing. The firing temperatures attained during the pottery making are high enough to carbonize such originally present organic matter, ruling out the third source. As
shown by Charters et al. [13], post-burial contamination due to lipid migration in and out of the ceramic body is minimal, because of the hydrophobic nature of lipids, which limits their solubility in soil solutions. Compositional alterations through post-depositional microbial activity are also minimal. Hence, chemical analysis of organic residues associated with cooking vessels can be used to gain evidence for the preparation and consumption of food, as shown by Charters et al. [14] on vessels from late Saxon and Medieval settlements (AD 1000–1150) from England. The ceramic samples were subjected to lipid extraction, derivatization, and GC and GC/MS analysis. The authors detected cabbage (Brassica oleracea) leaf wax components (Fig. 5), confirming documentary evidence that cabbage was a staple food in this period. Experimental cooking of the brassica vegetable in replica vessels showed that epicuticular waxes from the surface of the leaves were mobilized and absorbed into the porous ceramic body. Also, wax accumulation was much higher in the rim than at the base of the experimental vessels, an observation that is consistent with the flotation of lipids released from the brassica on the surface of the water. It should, however, not be dismissed that the intense heat of approximately 800 °C applied to the base of the cooking pot would be sufficient to degrade any organic component absorbed in the lower parts! Due to the fact that an analogue higher lipid concentration in the upper parts of the ancient jars was observed, the authors reached the conclusion that this type of pottery was used in a similar way to the replica vessels, i.e., boiling cabbage.

Sheriff et al. [15] studied carbonized coatings on pottery from Indian settlements (10th–16th century) of Northern Manitoba (Canada), in order to reconstruct their prehistoric diet. They analyzed the major organic components of food, i.e., lipids (fats), proteins and carbohydrates by 13C cross-polarization magic-angle spinning nuclear magnetic resonance spectroscopy (CPMAS NMR). Variations in the 13C/12C ratio of terrestrial foods are caused by differing photosyntheses of plants. C4 plants are normally found in hot, dry climates and show higher 13C as C3 plants. Corn (maize) is an example of such a C4 plant and was known to be imported to southern Ontario about AD 700. Herbivores have a 13C/12C ratio very close to that of the plants eaten. Charred food residues preserve the 13C/12C and 15N/14N ratios (δ13C resp. δ15N) of the food cooked in the pots [16], and these ratios remain virtually unchanged during burial [17]. In Fig. 6 the range of compositions of foods available to the native population of Manitoba are presented [15]. The analyzed food residues have a very low δ13C indicative of the absence of corn. Some plots account for a prevailing fish diet or a mixture of C3-herbivore flesh and fish. The formation of residues with depleted δ13C can be explained by mixtures of fish flesh with a large proportion of animal fats, known to be 13C depleted. This fits well with the interpretation of the aliphatic region of the CPMAS NMR spectra that no significant amount of plant material can be observed in the residues. In conclusion, the results are consistent with the use of the pots to cook fish stew with meat and animal fat from both aquatic and terrestrial sources, a likely high-calorie diet for people living in subarctic to arctic climates.

**Fig. 5.** Partial gas chromatograms of the lipid extracts from (a) modern brassica leaves; and (b) an ancient jar. In each case, the peaks represent brassica leaf wax components: 1 = n-nonacosane; 2 = n-hexacosanol; 3 = n-heptacosanol; 4 = nonacosan-15-one; 5 = nonacosan-15-ol; 6 = n-hentriacontane; and 7 = n-octacosanol. i.s. = the internal standard n-tetraatriacontane. The internal standard was not added to the leaf wax extract (a) [14].

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4. **Provenance Analysis**

When faced with the question where a particular ceramic object was manufactured, it is not sufficient to determine its quantitative elementary composition only. If its potential place of origin was, for instance, either Rome or Florence, it would be necessary to compare the single analysis with material from those cities. In other words, a comparison with so-called reference groups would be required. These are a series of analyses of ceramic fragments (n = at least 20–30) whose place of origin has been clearly determined as local (criteria: archaeological arguments or a chemical and petrographic correspondence with wasters, kiln findings and local raw material.) The chemical composition of a reference group should have little variation and should be significantly different from others. If reference groups are known and if a single analysis
Fig. 6. Plot of $\delta^{15}$N (nitrogen isotope ratio) versus $\delta^{13}$C (carbon isotope ratio) values of residues from Indian pots (stars). Boxes define the fields of measured compositions of whole flesh, of aquatic fish and C$_4$ plant-consuming herbivores, and of whole tissues of C$_3$ (e.g. wild rice) and C$_4$ plants [15]. Isotope ratios by CPMAS NMR.

Fig. 7. Schematic map of Switzerland showing the sites mentioned in the text.

The following two examples gives evidence of this. The first case, the bricks of St. Urban, can be used to illustrate group definitions. The Cistercian monastery of St. Urban (Fig. 7), founded in AD 1194–95, is well known for its unusually large (54x30x22 cm) and richly decorated bricks, produced between AD 1255 and AD 1285 [18] (Fig. 8). These products were exported on demand to neighboring monasteries, castles, and cities. However, in interpreting the varying decoration themes, Schnyder [18] came to propose the existence of at least two other Cistercian monastery production sites (Fraubrunnen and Frienisberg). This idea is strongly supported by multivariate discriminate analysis (Fig. 9), showing quite distinct chemical compositions of the three groups [19].

The Swiss 18th and 19th century Fayence products are very popular collectables. Unfortunately, stylistic features are often insufficient to clearly identify the manufacturing place of a piece. This applies to the Matzendorf production [20][21], whose differentiation from other centers, especially Kilchberg-Schooren [22], is a controversial issue. A study of a selection of representative samples from several museums shows that both productions differ in their chemical composition and can be separated relatively well by binary variation diagrams (Fig. 10 [23]). In addition, a detailed analysis of this figure illustrates: (1) the presence of outliers such as Mz 18, which was found in the Aare river close to Solothurn. Its lower CaO content can be explained by the hypothesis that portlandite Ca(OH)$_2$, normally formed after the firing process, has been washed out by river water; (2) the subdivision of both productions into two subgroups each and (3) the discrepancy in the stylistic and chemical classification of some pieces. This is evidenced by Mz 55, 59 and 60. These pieces show a typical 'Schooren' decoration, but their chemical composition belongs to the Matzendorf reference group. This applies not only to the CaO content, but
also to all other elements and oxides measured. Nevertheless, it could be argued that these pieces were manufactured in Schooren, using raw material from Matzendorf. However, there is no historical evidence of material being transported from one location to another. On the other hand, it is known that artisans from Schooren moved to Matzendorf, where they decorated pieces in the Kilchberg-Schooren style, or vice versa [21], a fact that easily explains the stylistic-chemical discrepancies found in some pieces. Similarly, Mz 41 shows the characteristic Matzendorf decoration, but its chemical 'fingerprint' indicates clearly a Kilchberg-Schooren provenance. Mz 27 and Mz 44 do not match the reference group, neither stylistically with their decoration of blue roses, nor chemically with a Sr content above 500 ppm. Also, they cannot be attributed to any known Fayence manufacturing place.

5. Technical Properties of the Glossy 'Clay Layer'

The reason for the high glossy appearance of the black Attic ware and the red Roman Terra Sigillata (Fig. 11) has been studied, amongst others, by Le Chatelier [24] and Verneuil [25]. The contrast in chemical composition between the gloss and the sherd matrix is pronounced. The body differs markedly in its major elemental chemistry, especially its CaO content, which is virtually absent in the gloss, but high in the sherd (gloss: CaO: 0.2–0.8 wt.%, K₂O: 6–7 wt.%, Fe total as FeO: 15–16 wt.%, sherd: CaO: 9–10 wt.%, K₂O: approx. 3 wt.%, Fe total as FeO: 6–7 wt.%, [26]).

The glossy coating corresponds to a fine-grained CaO-poor clay-rich slip or engobe, which sintered during the one-step firing process (900–1000 °C) due to the high amount of fluxes. This is in contrast with the CaO-rich sherd body, which still shows a high level of porosity due to its differing chemical composition, i.e. low levels of fluxes (Fig. 12).

Fig. 9. Factor 2 vs. Factor 1 diagram using 19 elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Cr, Cu, Ni, Rb, Sr, Y, V, Zn, Zr) [19]. The bricks from Fraubrunnen (n = 19), Frienisberg (n = 13) and St. Urban (n = 51) are clearly distinguished. Only the latter group has enough specimens to be considered a reference group from a pure statistical point of view. For clarity, three outliers are not shown.

Fig. 10. Sr-CaO correlation diagram of Fayence pieces from Matzendorf and Kilchberg-Schooren. Classification according to stylistic arguments. Mz 55, Mz 59 and Mz 60 represent pieces whose style indicates a Schooren provenance, while their chemical composition belongs to the Matzendorf group. Mz 41 has a typical Matzendorf decoration but from a chemical point of view it is a Schooren product [23].
6. Conclusion

The aim of this paper was to give a short introduction in archaeometric research applied to the field of ancient ceramics. Chemical and other scientific methods are currently becoming more widely used in interdisciplinary archaeological studies. By analyzing the ceramic material unearthed in archaeological digs, the place of manufacture, the technique used by the potters and the nature and function of these objects through the ages can be explained, resulting in a better understanding of technology, trade and socio-cultural behavior of our ancestors.

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Fig. 11. Roman Terra Sigillata (Dressel 38) from Eastern Gaul with the characteristic high gloss. Late 2nd century AD. British Museum.

Attempts to reconstruct the gloss of the Terra Sigillata carried out by Michel et al. [27], have shown that the best results are obtained with coatings rich in illite (a mica-type clay mineral). The gloss increases strongly from 950 °C onwards, with a maximum between 1000-1050 °C. Surprisingly, it turns out that the gloss not only depends on the mineral composition of the coating, but also on the CaO content of the body [28]. If the same coating is applied on a CaO-poor clay body and if a gradual increase in CaO of this body is performed by adding finely ground, pure Carrara marble, the gloss intensifies with the increase of CaO in the substrate (Fig. 13). This can be observed up to a maximum of approximately 15 wt.% CaO. Beyond this level, the reflectance drops. The Roman potters were well aware of these connections, for the glossiest Terra Sigillata belongs to manufacturing centers where the CaO content of the clay for the ceramic body lies between 10–15 wt.% (Fig. 14).

Fig. 13. Correlation between the reflectivity of a glossy clay layer and the increasing CaO content of the sherd body [28].

Fig. 14. Maxima, minima and average (white dot) of CaO for Terra Sigillata from different manufacturing places. 1 = Schwabegg, 2 = Westerdorf, 3 = Lezoux, 4 = Paffenhofen, 5 = Chémery-Faulquemont, 6 = Blickweiler, 7 = Rheinzabern, 8 = Rozié, 9 = Banassac, 10 = La Graufesenque, 11 = Lezoux 2/3rd century AD, 12 = Terre Franche, 13 = Arezzo, 14 = Montans, 15 = La Péniche, 16 = La Muette A, 17 = Loyasse, 18 = La Muette B.