

Effects of Acid Treatment on Ceramics from Kaman-Kalehöyük

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ABSTRACT

Acid treatment is a common conservation treatment for ceramics at archaeological sites; however, the effects of different acids on ceramic composition are not entirely understood. In this study, the composition of several types of ceramic fabrics found at Kaman-Kalehöyük were determined by energy dispersive x-ray fluorescence (ED-XRF). Sherd samples were then exposed to HCl, HNO₃, and acetic acid using standard treatment protocols. The treated sherds were re-analyzed by ED-XRF and the after treatment results compared with those before treatment. Results reveal significant changes in the elemental composition of all ceramic types following acid treatment. Both the type of acid and type of ceramic fabric were shown to influence the changes that occur.

INTRODUCTION

Ceramic analysis is an essential component of the research performed on materials from Kaman-Kalehöyük, Turkey (Omura 2006). While ceramics may be sampled immediately after excavation for analysis, much of the material recovered goes into storage on-site or to the conservation laboratory where treatment and vessel reconstruction are undertaken. Treated ceramics may then be placed in storage where they are available for research purposes. Consequently, any ceramic in storage at Kaman-Kalehöyük may have undergone a number of conservation treatments that could have fundamentally altered the ceramic fabric and may potentially interfere with further technical analysis. It is therefore essential to understand the effects of conservation treatments on these ceramics in order to avoid problems with their analysis and to direct future treatment choices.

The application of acids to remove otherwise insoluble encrustations is a conservation treatment known to affect changes in some ceramics and has

been used on a variety of ceramic materials excavated at Kaman-Kalehöyük. A search of the conservation database at Kaman-Kalehöyük has confirmed over 100 ceramic items on-site that have been treated with acids. The database, however, is relatively new and does not include a vast number of ceramics treated before the adoption of computerized documentation methods. The treatment reports from the database indicate that a variety of acids have been used in the past, including HNO₃, HCl, and acetic acid. This study examines the compositional changes caused by these three acids on several different types of ceramic fabrics found at Kaman-Kalehöyük to determine what effect current or past acid treatments may have on the elemental analysis of local ceramics.

BACKGROUND

In dry climates, mineral salts in the burial environment may accumulate on the surface of ceramic artifacts. These salts, including carbonates, sulfates,

sulphides, phosphates, and silicates, usually form hard crusts that are minimally soluble in water and are therefore referred to as insoluble salts (National Park Service 1998). Insoluble salt encrustations do not cause physical damage to the ceramics but can be disfiguring and bulky, preventing proper reconstruction of broken pieces. The removal of these accretions may therefore be necessary to gain an adequate understanding of the ceramic artifact.

Acids are commonly used on archaeological ceramics in order to remove encrustations of calcium carbonate, calcium sulfate, and silicates. For an overview of the effects of acid treatment on ceramics see Buys and Oakley (1993) and Johnson (1999). The potential danger to the ceramic from acid treatment is well known. Dissolution of calcareous components in the temper and slip can occur, iron oxides can be leached out, and lead glazes may be damaged by the application of nitric acid.

The removal of these ceramic constituents by acid treatment can affect subsequent analysis of the ceramic composition. The results from past research have indicated that contamination by chlorides and formation of chromophoric species may occur in earthenware ceramics from treatment with HCl (Johnson *et al.* 1994). Acid induced dissolution of inclusions, slip deterioration, and friability has been confirmed through physical testing as well as visual and microscopic examination (Johnson *et al.* 1994; Leskard 1982). XRD analysis of ceramics treated with hydrochloric and oxalic acids has also revealed a loss of iron oxides occurring from iron rich ceramic glazes (Olive and Pearson 1975).

EXPERIMENTAL

SAMPLING

Three different types of ceramic ware common to Kaman-Kalehöyük were chosen for testing. A variety of fabric types were selected in order to examine a range of ceramics that could be utilized for ceramic analysis. Upon searching through the ceramic context material from the 2007 excavation, three types of ware were found to be most abundant and easily identifiable. The three ceramic types sampled include: Early Bronze Age coarse ware, Iron Age gray ware, and red-slipped



Photo 1 The nine sample sherds: Bronze Age sherds (top row), reduction ware sherds (middle row), red-slipped sherds (bottom row)

ware from the Assyrian Colonial Period. A total of nine samples, three for each type of ware, were created from six sherds selected from the ceramic context material (Photo 1).

A large coarse ware sherd from the Early Bronze Age was identified in a box of material from North trench, sector IV. The visible inclusions, high porosity, wall thickness, and coarse surface texture are characteristic of this type of ceramic. The sherd was cut with a diamond saw into three samples of roughly equivalent sizes. In addition, a small piece was kept as a control that did not undergo acid treatment.

Two Iron Age (Stratum IIa) gray-ware sherds were chosen from amongst the context material in a box from South trench, sector LI-XXIX. This type of reduction ware, as the name implies, was fired in a reducing atmosphere, producing a distinctive dark gray to black coloring (Matsumura 2000). Reduction ware ceramics generally have lower porosity and fewer visible inclusions than the Bronze Age coarse ware, and was therefore considered to be a useful variation in the sample breadth. The two sherds selected were very

similar in appearance, however, it is unknown if they belong to the same vessel. The larger of the two sherds was cut in half using a diamond saw to produce two samples of roughly equivalent sizes.

For the last group of samples, three red-slipped sherds from the Assyrian Colonial Period were selected from a box of context material from North trench, sector VII. These sherds have an iron rich slip, fired in an oxidizing atmosphere to produce a deep red surface color. The dark gray to black interior of these ceramics, however, is in a reduced state, resulting from incomplete oxidation during the firing process. Although all three sherds appear to be alike, it is not certain that they originated from the same vessel.

PROCEDURE

After the sherds were chosen and cut to provide three groups of three, all of the samples were washed in deionized water. The sample numbers were etched into the sherds to allow for easy identification. Each sherd was then photographed and weighed. Before the sherds underwent acid treatment they were first analyzed by energy dispersive x-ray fluorescence (ED-XRF).

XRF analysis was performed using a Seiko instruments SEA2010 ED-XRF with a Rh target and Si(Li) detector. Sixteen elements were chosen for detection (Al, As, Ca, Cl, Fe, K, Mn, Ni, P, Rh, S, Si, Ti, V, Zn and Zr). At least three measurements were taken at different locations on each of the nine sample sherds. The running time for each measurement was 300 sec at 3 μ A current and 50kV in a vacuum. The aperture was set to 10mm, however the exact location of the test area is uncertain as the location of the aperture is not marked on the instrument.

While XRF is non-destructive, it is considered a surface or sub-surface technique when used on whole samples. Penetration of x-rays will vary depending on the density of the sample material and energy of the x-ray source. The compositional information obtained from XRF is therefore assumed to be indicative of the surface of the sample and not the bulk composition. For the current study, analysis of surface composition is adequate as the goal is to determine how acid treatment may affect

subsequent analysis by XRF and similar surface level techniques. Any change in the composition of the surface is therefore assumed to be a significant alteration to the ceramic itself.

ACID TREATMENT

A sherd of each fabric type was treated with one of three different types of acids: HCl, HNO₃, and acetic acid. Treatment reports and the conservation manual of the Kaman-Kalehöyük conservation laboratory were consulted in order to determine the concentrations and procedure for the acid treatments in this study (Wharton 2001). Following the laboratory manual, 4% HCl, 4% HNO₃, and 10% acetic acid were used.

The treatment was altered in some aspects to account for typical deviations from lab procedure. The treatment manual recommends repeated immersion and brushing of sherds until the insoluble encrustations are removed but warns against immersing sherds for longer than a couple minutes at a time. The sherds in this study, however, were immersed for 10 minutes without brushing to provide a reproducible treatment process. While most of the treatment reports in the conservation database indicate an immersion time of five minutes, it is assumed that actual contact with the acid may vary from this standard by at least several minutes in the case of more tenacious encrustations.

After immersion in acid, the sherds were rinsed for three days and monitored by conductivity meter and pH strips following the suggested procedure in the treatment manual. Individual beakers were used for each sherd to avoid cross-contamination. The circumstances of the water supply at Kaman-Kalehöyük have led to a standard desalination and washing procedure specific to the site (Tsu 1994). Deionized water is only used for final rinses as it is bought and transported in relatively small quantities from the nearest town. Spring water, which is readily available at Kaman and less saline than the tap water, is usually used for initial rinses. For the purposes of this study, however, it was decided to rinse the sherds entirely with deionized water to avoid any contamination from the spring water.

The sherds were then air dried and analyzed again

by XRF using identical parameters to those of the initial analysis of the ceramics before acid treatment. Analysis was performed at three different locations on each sherd. Additionally, analysis of the standard glass sample SRM 621 was carried out by Mr. Willy Bong using the same experimental parameters.

RESULTS

The results from ED-XRF analysis, initially reported in counts per second, were normalized to Si (Table 1). The normalization to Si is justified by its major element nature in silicates (*i.e.*, fixed as an essential structural constituent of silicate minerals rather than a potential trace contaminant). If the sherds contain variations in the abundance of modal phases such as quartz, mica, feldspar etc., then potentially significant variations in SiO₂ content could exist within the sherds thus influencing the interpretation of variations in minor elements such as Ca, Na, K, etc.

To assess whether immersion in HCl, HNO₃, and acetic acid results in changes in the chemical composition of ceramic sherds we need to know: (1) the intrinsic detection reproducibility of an element using the Seiko SEA2010 ED-XRF; (2) the measurement uncertainty of an unknown, both before and after treatment; and (3) the variability within a sample. Calculation of error is essential for this study as the low sensitivity of the instrument and small number of measurements could limit the detection of relatively small changes in element intensities.

We can assess (1) by repeated analysis of a homogeneous and well-characterized standard material, in our case, SRM 621. For example, three replicate measurements of SRM 621 (Table 2) yield an average Ca/Si count rate ratio of 0.659±0.76% (1σ). Given that the true Ca/Si = 0.222±0.5% (Uriano 1982), our measurement yields a relative sensitivity coefficient of 0.337 that we can then use to correct apparent count rate ratios of unknowns. While the uncertainty in our Ca/Si measurement exceeds that of the certified values, it is within 2σ of that reported by Uriano (1982).

Table 2 SRM 621 measured values at three points and normalized to Si

x	x/Si	x/Si	x/Si	x/Si _{AVE} (±1σ)
Si	1	1	1	1
Ca	0.662	0.653	0.662	0.659±0.005
K	0.148	0.145	0.138	0.144±0.005
As	0.465	0.495	0.528	0.496±0.031
Ba	0.544	0.606	0.577	0.576±0.031
Fe	0.720	0.602	0.708	0.677±0.065
Na	0.420	0.383	0.341	0.381±0.040
Ti	0.519	0.610	0.683	0.604±0.082
Al	8.007	7.135	6.502	7.215±0.756
S	0.597	0.748	0.675	0.674±0.076
Zr	2.074	1.795	1.806	1.892±0.158

We can assess (2) by repeated XRF measurements of individual sherds. Each of the three pottery fragments were analyzed three times before acid treatment, each analysis in a different position. For sherd 1, for example, the three results yield an average Ca/Si value of 0.374±7% (Table 1). Note that individual counting statistics suggest a significantly higher level of precision (~1%) than indicated by this level of reproducibility suggesting a systematic source of error. We will return to this issue in the following section where intra-sample variability is specifically addressed.

We can assess (3) by measuring several fragments from the same sample. For example, once corrected for relative sensitivity, sherds 1, 2 and 3 *before* treatment yields an average Ca/Si = 0.41±4.3%. Note that this uncertainty is significantly greater than that observed in SRM 621, reflecting either sample variability or reduced counting statistics. We can assess the former possibility by examining the internal statistical systematics using a reduced χ^2 distribution, or mean square of weighted deviates (*MSWD*) test (McIntyre *et al.* 1966). An *MSWD* that greatly exceeds unity indicates sample heterogeneity. For example, the three Ca/Si analyses of sherd 1 *before* treatment yield a weighted mean of 0.39±5.9% with an *MSWD* of ~1, consistent with a single population (Table 3). An implication of this result is that we can assume that intra-herd variability is also below the level of ~6%. Results of the three Ca/Si analyses of sherd 1 *after* treatment are treated in the discussion section.

Table 3 MSWD values for the three groups of sherds before and after treatment

Sherds		MSWD (BT)	MSWD (AT)
1,2,3	Ca/Si	0.48	11.64
	K/Si	0.24	9.27
	P/Si	0.24	5.82
	S/Si	12.45	6.34
	Cl/Si	0.14	6.75
	As/Si	6.28	57.04
	Fe/Si	0.88	20.82
	Ti/Si	0.46	0.01
4,5,6	Mn/Si	3.44	3.18
	Ca/Si	50.37	1.91
	K/Si	406.20	138.34
	P/Si	615.95	2.88
	S/Si	41.19	13.75
	Cl/Si	195.87	19.99
	As/Si	1.71	6.90
	Fe/Si	17.53	1.33
7,8,9	Ti/Si	3.27	6.26
	Mn/Si	0.61	3.24
	Ca/Si	3.43	2.83
	K/Si	14.72	22.52
	P/Si	0.29	1.26
	S/Si	0.28	7.84
	Cl/Si	50.19	25.29
	As/Si	0.14	0.68
	Fe/Si	43.20	42.44
	Ti/Si	91.74	34.80
	Mn/Si	0.40	0.27

DISCUSSION

The results indicate a change in the composition of each of the nine sherds. The specific effects of the acid treatment, however, were found to be dependant upon the type of acid used and the type of ceramic fabric. Based on the XRF analysis in this study, which measured 16 different elements, sherds treated with acetic acid exhibited the least elemental changes. Similarly, while the changes in elemental composition of the first two groups of ceramics followed the same pattern, the last group of sherds, the red-slipped Assyrian ceramic, was affected differently.

A reduction in weight occurred in every sherd,

indicating a loss of material and change in composition. A loss of between 0.38% and 2.6% of the original sherd mass resulted from acid treatment (Table 4). While each sherd experienced a reduction in mass, there was little to no correlation between degree of loss and the ceramic fabric, or type of acid used. The largest weight change, in fact, occurred in the sherds treated with acetic acid, the group of ceramics that underwent the least amount of elemental change in XRF analysis. The weight changes can therefore be taken to indicate that material was lost in the process, while the data from XRF will suggest more specifically what changes took place.

Table 4 Weight measurements of sherds before and after acid treatment

Sample	Ceramic Type	Acid	Before (g)	After (g)	Change (g)	% of sherd
1	Early bronze age	HCl	37.04	36.66	0.38	1.03
2	Early bronze age	HNO ₃	36.64	35.98	0.66	1.80
3	Early bronze age	Acetic	42.12	41.02	1.10	2.61
4	Iron age (IIa)	HCl	36.56	36.42	0.14	0.38
5	Iron age (IIa)	HNO ₃	36.04	35.86	0.18	0.50
6	Iron age (IIa)	Acetic	30.38	30.22	0.16	0.53
7	Assyrian	HCl	25.24	25.10	0.14	0.55
8	Assyrian	HNO ₃	18.69	18.52	0.17	0.91
9	Assyrian	Acetic	18.16	17.96	0.20	1.10

While the Ca/Si MSWD values for the Bronze Age sherds 1, 2, and 3 before treatment confirm that the three sherds are from the same sample populations (*i.e.* the three samples are of the same ceramic fabric type), the Ca/Si MSWD values from after treatment indicate a distinct divergence from the original fabric composition. This increased heterogeneity is due to the differential effects of the acids, which vary in strength and elemental affinities. The gray-ware sherds, however, are initially far more heterogeneous than the other groups of sherds. The high χ^2 value of sherd 6 before treatment appears to be responsible for the large Ca/Si MSWD. This variability is understandable as sherds 4 and 5 were cut from the same ceramic piece, while 6 was a separate sherd found in the same box of context material.

While many of the MSWD values for the other elements follow a pattern similar to that of Ca/Si, there

is some divergence and occasionally high values (Table 3). These numbers indicate relative homogeneity of the ceramic types with some inherent variability. Ceramics are not completely homogeneous materials and mineral inclusions will naturally result in a wider range of measured elemental concentrations. Some heterogeneity is therefore expected due to intra-vessel variability. In addition, the samples in two of the ceramic groups originated from different sherds of the same type, which may have come from multiple vessels. Compositional variability between different vessels may therefore have also had an influence on the *MSWD* values in these cases.

Ca/Si

The most significant change in all of the acid treated sherds was the loss of Ca. The Ca/Si values decreased after acid treatment beyond the margin of error in almost every sherd. While Ca/Si diminished significantly in sherds 1 and 2, the change in Ca/Si for sherd 3, which was treated with acetic acid, was much less, falling within the margin of error. Similarly, the gray-ware sherd treated with acetic acid was found to decrease less in Ca/Si than the same type of ceramic fabric (sherds 4 and 5) treated with HCl and HNO₃. Clearly the organic acid produced less of an effect on the first two groups of ceramic types than the mineral acids.

The data also indicates that the ceramic fabric type plays a role in the loss of Ca. The largest losses of Ca were from the Iron Age gray-ware, which had the highest Ca/Si values before treatment as well. The red-slipped ceramics, which initially had the second highest Ca/Si values, also presented the second largest decrease in Ca/Si. The first group of ceramics, the Bronze Age sherds, began with the lowest Ca/Si values and also exhibited the least amount of change in Ca overall.

P/Si, K/Si, S/Si, and As/Si

The response of P, K, S, and As to acid treatment appears similar as the values for each of these elements, normalized for Si, follow the same pattern. The most substantial decrease in P/Si, K/Si, S/Si, and As/Si values was observed in sherds 1, 2, 4, and 5, which belong to the first two groups of sherds, the Bronze Age coarse ware and the Iron Age gray-ware, which were treated with the mineral acids HCl and HNO₃. Although the sherds treated

with acetic acid underwent a decrease in K/Si, the degree of change was smaller than in the sherds treated with HCl and HNO₃. The change in P/Si and As/Si in the sherds treated with acetic acid was within 1 σ , as were the S/Si values, except in one instance, where the S/Si slightly increased in sherd 6. Treatment with acetic acid was therefore found to cause the least loss of P, K, S, and As from the coarse-ware and reduction ware ceramics.

The Assyrian colonial red-slipped ware behaved differently from the other ceramic fabric types. None of these sherds underwent substantial decrease in P/Si, K/Si, S/Si, or As/Si values; however, the K/Si values did decrease slightly, on the same scale as occurred in the acetic acid treated sherds of the other groups. The change in P/Si and As/Si values were all within the margin of error, indicating no significant changes. The change in the S/Si values for the Assyrian sherds, however, behaved similarly to the sherds treated with acetic acid as one of the sherds appears to have slightly increased in S/Si, while the change detected in the other two sherds is within 1 σ .

Fe/Si, Ti/Si, and Mn/Si

The effects of acid treatment on the Fe, Ti, and Mn content of the sherds were relatively erratic. Four sherds exhibited an increase in Fe/Si values, while three sherds underwent a decrease and two sherds underwent no significant changes. The only significant pattern that emerged was the increase of Fe/Si and Ti/Si values in all of the red-slipped sherds after acid treatment.

Cl/Si

The only sherd that exhibited an increase in Cl/Si was sherd 7, the red-slipped ceramic treated with HCl. The slight increase of Cl/Si may be due to the formation of FeCl₃ upon exposure of the iron rich sherds to HCl. Previous studies have tentatively identified iron(III) chloride hexahydrate in sherds treated with HCl, degrading in an alkaline induced reaction to iron(III) oxide monohydrate (Johnson *et al.* 1994). The selective enrichment of sherd 7 is most likely due to the much higher Fe content of the red slip.

CONCLUSION

The XRF data illustrates several key factors influencing the changes that occur in acid treated ceramics. The acid type and ceramic type both affect the degree and form of compositional alterations. Treatment with 10% acetic acid was found to induce the fewest changes in the ceramics, while 4% HCl and 4% HNO₃ resulted in greater losses of Ca, P, K, S, and As. Also, the behavior of the Assyrian red-slipped sherds indicates the importance of ceramic fabric type on the outcome of acid-treatment. These red-slipped sherds all underwent similar changes on exposure to different acids, while displaying a pattern different from the other sherd types. Clearly the surface composition and morphology, in this case an iron-rich slip, can be considered a significant factor in the behavior of the ceramic on exposure to acid. The data also indicates that Cl from HCl treatment is more likely to form contaminating complexes with iron rich ceramics, such as the red-slipped sherds.

At present it is not standard procedure at Kaman-Kalehöyük to retain an untreated sherd from artifacts that undergo acid treatment. It is therefore possible that the original information contained in every acid treated ceramic object may be irretrievably lost. While the types of changes the ceramics undergo may require further elaboration, an alteration in the composition of ceramics from Kaman-Kalehöyük due to acid treatment has nevertheless been shown to occur. These changes are of a magnitude that even an analytical instrument of relatively low sensitivity can clearly detect them. Conservation ethics require that we do not hinder further study of an artifact by altering the original materials (American Institute for Conservation 1980). While acid treatments alter the ceramic composition, it may be the best treatment option in some cases where other factors are considered more important than the potential analytical data. Whether the corruption of some ceramic data is an acceptable loss is therefore a question that should be considered by those who regularly do analysis on these ceramics. A simple solution, however, to satisfy conservators and archaeologists alike, is to establish a procedure for saving an untreated sample from every acid treated ceramic.

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