CONSERVAR PATRIMÓNIO

ARTICLE / ARTIGO

Preliminary studies for the removal of carbonate deposits from painted ceramics using chemical solutions

Estudos preliminares para remover depósitos de carbonato de cerâmicas pintadas utilizando soluções químicas

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Abstract

This study analyzes the changes that painted archaeological ceramics undergo after direct and indirect cleaning treatments applied to remove carbonate deposits. Nine Iberian decontextualized sherds from the *Los Villares de Andújar* site (Jaén, Spain) were documented: macroscopic examination, digital photography, optical microscopy and scanning electron microscopy – energy dispersive X-ray spectroscopy. Lime putty was then applied to the ceramic surfaces to generate the deposits and several cleaning treatments were pursued. Finally, the changes resulting from the cleaning treatments were documented using the same techniques and procedures. The porosity of the sherds had a major influence on the suitability of the cleaning treatments. Nevertheless, treatments with ethylenediaminetetraacetic acid (EDTA) disodium salt applied by cellulose pulp poultice were more respectful to painted areas compared to immersion, whereas nitric acid solutions altered both polychromies and ceramic surfaces regardless of the application method. The ion-exchange resin, directly applied, presented promising results in uncolored areas.

KEYWORDS
Cleaning treatments
Archaeological ceramics
Iberian painted decoration
SEM-EDS
Conservation Science

Resumo

Este estudo analisa as alterações que ocorrem nas cerâmicas arqueológicas pintadas após tratamentos de limpeza, diretos e indiretos, usados para remover depósitos de carbonato. Nove cacos ibéricos descontextualizados de *Los Villares de Andújar* (Jaén, Espanha) foram documentados por: exame macroscópico, fotografia digital, microscopia ótica e SEM-EDS. Foi aplicada massa de cal [$Ca(OH)_2$] nas superfícies cerâmicas para gerar os depósitos; posteriormente foram efetuados vários tratamentos de limpeza e finalmente, documentaram-se as alterações resultantes dos tratamentos de limpeza, utilizando as mesmas técnicas e procedimentos. A porosidade dos fragmentos teve grande influência no ajuste dos tratamentos de limpeza. Os tratamentos com EDTA aplicados por cataplasma de pasta de celulose foram mais eficientes nas zonas pintadas do que por imersão, enquanto que as soluções de ácido nítrico alteraram tanto as policromias como as superfícies cerâmicas, independentemente do método de aplicação. A resina de permuta iónica, aplicada diretamente, apresentou resultados promissores nas zonas não coloridas.

PALAVRAS-CHAVE
Tratamentos de limpeza
Cerâmicas arqueológicas
Decoração Ibérica pintada
SEM-EDS
Ciências da conservação

Introduction

Ceramics are often the most abundant materials recovered from archaeological sites. This occurs due to their superior physical and chemical durability, which preserves this material for longer periods and in better conditions than metal, glass or organic ones. However, pottery objects do not remain entirely unaltered over time or throughout changes in the ambient conditions, as they can present abrasions, cracks, material loss, stains and salts. Both soluble and insoluble salts (understanding insoluble salts as having very low solubility in water) [1], are the most common and challenging alterations, as they appear in many pottery fragments and can cause severe conservation problems [2].

Salts may appear as deposits on the surface of the ceramics, known as accretions. The salts' deposits located inside the pore system of the ceramics are known as crypto-efflorescence, and if they are located just beneath the surface, as sub-efflorescence [3]. The penetration will vary according to the state of preservation of the sherds, the concentration and volume of the solution, the diameter of the pores, the type of salt and the environmental conditions [2]. The most common salts found in archaeological ceramics are sodium and potassium chlorides; sodium, potassium and magnesium sulfates; carbonates; nitrates and phosphates in burial environments [1]. The materials used to make the salts (clay, mineral tempers), their manufacturing process, the temperature and atmosphere during burning, and the surface decoration all have an impact on how the salts appear on the ceramics. The modifications produced by the presence of salts on ceramics also vary according on the salts' level of penetration, the thickness, age, size, and condition of preservation of the ceramics. The presence of salts covering ceramic objects can increase the surface pressure in the affected areas, which can lead to cracking, deformation and material loss [1]. Besides, these encrustations can also obscure important information that may reduce the artistic, symbolic, historical and archaeological values of such ceramics [4]. For this reason, their removal becomes commonly essential for the correct legibility of the objects [5-6].

Nevertheless, the removal of insoluble salt deposits, particularly calcium carbonates and sulfates, can become a complicated treatment, due to their hardness and strong adherence to ceramic surfaces. For this reason, the treatments for their removal are riskier than those designed for the removal of soluble salts. Indeed, one of the most common solutions is to combine chemical and mechanical methods: once the chemical products have successfully softened the deposits, they are removed by mechanical means. Among the latter are scalpels, gravers and micro drillers [2], which can produce surface damage during treatments, especially when the deposits are harder than the treated objects, or they are more firmly adhered to the decorative elements than to the ceramic surfaces [1]. In contrast, chemical methods applied to remove insoluble salts are based on the application of products that react chemically with the insoluble deposits to form soluble or volatile compounds, including acids, complex agents and ion-exchange resins. These products can change the ceramic objects' composition, which could have an impact on how they are understood.

The use of acids, such as nitric, hydrochloric, acetic or formic acids, in concentrations that vary from 10 to 20 % v/v applied both by immersion or locally (poultices) has been the most common solutions among conservators from the 1950s onward [1-2, 7-8]. Other type of products are complexing agents that can form bonds with metallic ions, such as calcium, magnesium, aluminum and iron, to produce soluble salts. Some complexing agents are sodic salts that derive from ethylenediaminetetraacetic acid (EDTA) [1-2, 6, 9-10]. According to Jover (1998), sodium hexametaphosphate (commercial name Calgon) and quaternary ammonium are also widely used [2]. Also trisodium phosphate and sodium citrate have been described in the literature [7]. As it occurs with acids, they are applied by immersion and poultices in solutions with concentrations between 5 and 10 % w/v. More recently, ion-exchange resins have been used for the same purpose [3, 11]. According to Osca Pons and other authors, these are very effective for the removal of deposits and calcium patinas [2-3, 12], even at higher temperatures (30-60 °C) and at 100 % relative humidity. Although they may be too acidic or alkaline for sensitive surface materials [4]. Moreover, the AB-57 poultice, originally designed for wall paintings, has been applied to ceramics [1]. As Mora et al. [13] state, "poultices composed of water, ammonium bicarbonate, sodium bicarbonate, EDTA disodium salt and carboxymethyl cellulose, offers a highly-controlled treatment due to its slow, non-aggressive reaction". This makes it more suitable for the removal of carbonate patinas rather than thick deposits [2].

Although it has been proved that some of these substances can cause irreversible damage to ceramics [7], many are still in use, even in academic studies and archaeological museums (unpublished survey, on file with authors). Surface damages and alterations of the chemical and mineralogical composition of ceramics have been reported, including the lixiviation of compounds, such as calcium or iron compounds, which can lead to color changes [2, 13-18].

As alternative and safer application methods, gels and thickening agents were explored by Richard Wolbers in the 1980s. Since then, studies by several universities and conservation institutes have been carried out to determine their properties and advantages when used in cleaning treatments [19-21]. However, they remain little used in archaeological conservation.

To sum up, the presence of insoluble salts on pottery objects may imply a decrease in their stability. Furthermore, artistic and historical information may be lost due to these deposits. For these reasons, salt-removal treatments are widespread among conservator-restorers of archaeological materials. However, such treatments can pose serious risks for the archaeological ceramic objects due to the removal or damage of the original materials. Hence, it is essential to evaluate any alterations that can occur during the treatment to apply the most effective and safe treatments. Despite that many studies have been carried out on ceramic conservation generally [5], specific reviews of salt-removal cleaning techniques for ceramic objects have not been undertaken by many experts [3, 14, 17-18, 22-23].

Given all these factors, and as the treatments for the removal of insoluble salts are still in use, the present study aims to evaluate the suitability of some of the most common products used, taking into account their concentrations, application methods and consequences for painted ceramic objects. The selected products included acids, for being the most common ones and ion exchange resins, for their newness in the field, as well as immersion, cellulose pulp poultices and agar physical gels used as application methods.

Materials and methods

Ceramic materials

The pieces studied were nine decontextualized sherds from the Iberian strata from the *Los Villares de Andújar* site, in Jaén (Spain), which is well known for its Roman remains (7 BCE-5 CE). These fragments came from two vessels with similar production characteristics in terms of porosity, thickness, color and decorative motifs, which production is restricted to the first phase of the aforementioned site, between 50-75 CE [24].

Firstly, an exhaustive study of the sherds was carried out to determine their principal morphological features, including dimensions, ceramic matrix, elaboration method, surface treatment, color and state of preservation. For this purpose, several techniques were employed, including macro and microscopic observations and photography (Leica EZ4 D, Nikon SMZ1000, Nikon D5000), as well as scanning electron microscopy with energy-dispersive X-ray microanalysis spectroscopy (SEM-EDX) (Gemini Leo 1500 FESEM/EDS/EBDS Carl Zeiss). This equipment is provided with Schottky type field emission electron source (hot cathode) and BSE (chemical) and X-ray energy dispersive analysis (elemental distribution maps) imaging with EDX Chemical Analysis System (Oxford Instruments). The accelerating voltage of the electron beam was set between 15 and 20 kV, depending on the sample, with a sampling size of 3 mm.

Regarding the technological characteristics and archaeological information, the sherds were organized into two groups: Aj.4643, comprising four sherds and Aj.4645, comprising five sherds (Figure 1), including one decontextualized fragment labelled as Aj.4615.

These sherds presented average dimensions of 5×5×1 cm. Their ceramic matrix was compact with low or medium porosity (Aj.4643 and Aj.4645, respectively). The modelling had been carried out on a potter's wheel in all cases, as was evident from the characteristic traces observed on the inner side of the sherds. Regarding the mineral tempers, quartz, feldspar and mica were common to almost all the sherds, although iron oxides and ceramic particles (grog) were detected in some cases (Aj.4643-1). The distribution of the mineral tempers was between 10 and 20 %, according to the inclusion estimation graph [25]. The inclusion distribution was uniform and presented a fine or medium size (0.5-2.0 mm). However, in some sherds, inclusions of greater width (2.0-3.0 mm) stood out from the ceramic matrix (Aj.4645-4). To a greater or lesser degree, all the sherds presented painted decoration based on a mixture of clay and a red pigment applied by brush [26] to different decorative motifs. In all cases, the polychromies presented high cohesion and adherence to the ceramic surfaces.

All the sherds presented a high consistency of the ceramic matrix. Most of them showed post-depositional elements, both muddy and calcareous surface deposits. Some of them also presented surface stains and abrasions.

The coloring particles were identified as iron oxides by means of elemental microanalysis. Earth pigments have been widely used since prehistoric times. The similarities between the painted decoration and the ceramic matrix, in terms of stability and durability, ensured a high degree of adherence to the ceramic surfaces. However, the decorated areas also presented abrasions and material loss. Solubility tests were carried out with cotton-tipped 20 cm wooden sticks moistened with deionized water and ethanol (96 % vol.), and gently applied onto the tested surfaces (both the ceramic matrix and the decorated areas). The results revealed that the paintings were not powdery. In all cases, the solubility was low or non-existent in both solvents, which allowed aqueous cleaning methods to be applied without protection. These solubility tests were also performed after the cleaning treatments, in order to identify possible changes due to the products and application methods employed.

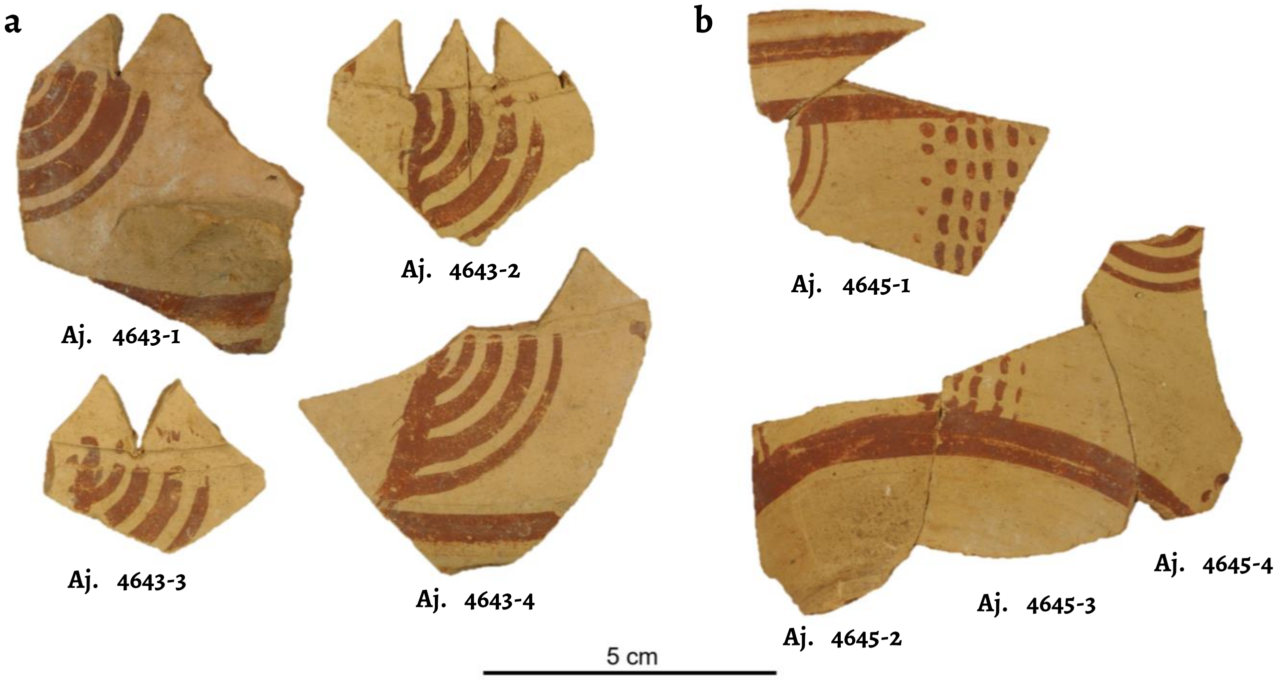


Figure 1. Ceramic groups selected for the research: *a)* Aj.4643 and *b)* Aj.4645.

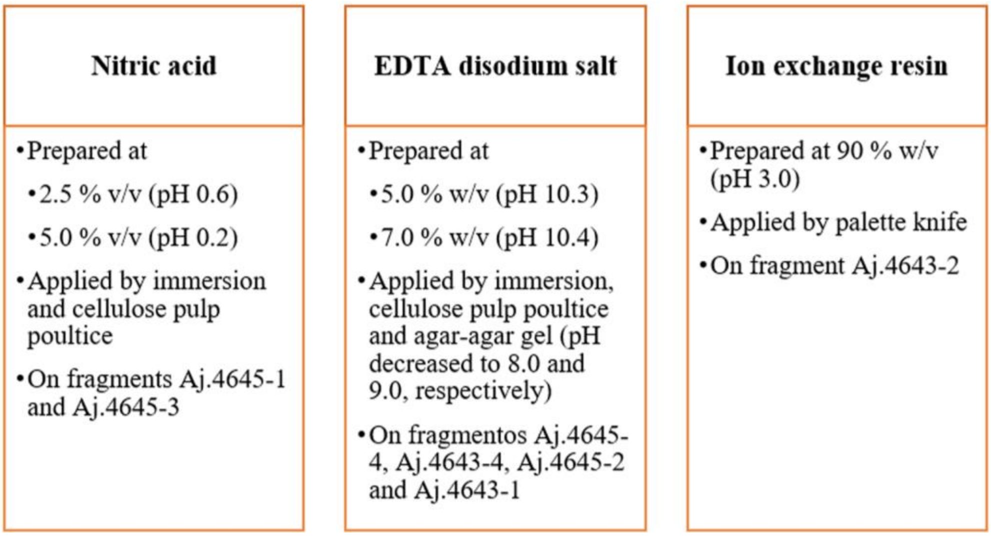
Carbonate deposits growth

Although the sherds presented natural concretions, these were insufficient for testing the cleaning treatments and obtaining representative results. For this reason, it was decided to apply thin coats of lime putty (CTS) on the ceramic surface to enable the formation of carbonate deposits. Before applying this product, the ceramic sherds needed to be humidified by at least three consecutive brush applications of deionized water. Two coats of the lime putty paste were brushed on the surface, first vertically and then horizontally, to avoid physical stress. Once the deposits had appeared, the different removal treatments were applied.

Cleaning treatments

The tests pursued consisted of three solutions at different concentrations (nitric acid, EDTA disodium salt, and strong cation-exchange resin), and three application methods (immersion, poultice and agar gel) applied on limited areas of the ceramic fragments (Figure 2). Each of the chemical treatments triggered different physicochemical reactions to the carbonate during the removal of the deposits. Firstly, the nitric acid solution turns the calcium carbonate salts, which are insoluble, into calcium nitrate salts, which are soluble. Secondly, the EDTA disodium salt creates a very stable and soluble chelating complex with Ca^{2+} ions. Thirdly, the strong cation-exchange resin, exchanges its ions with those of Ca^{2+}, resulting in a soluble compound. Four different application methods were used: two direct methods –immersion and application, depending on the product used–, and two indirect –cellulose pulp poultice and agar-agar rigid gel. The products used for the indirect applications were selected for being natural and neutral. They would therefore leave deposits that could affect the ceramics state of conservation. The poultice was made of cellulose fibres that swell in solutions without dissolving; thus, it turns into a homogenous paste that is easily applied. The rigid gel was made of agar-agar, a natural hydrocolloid with thickening properties extracted from red algae (*Rodoficee, Gelidium*). Both products can be used for punctual treatments and offer greater control over humidity, given its slow and gradual transfer to the piece being treated. As water diffusion is slower than in treatments performed by immersion, the application time can be better controlled. Not all the methods were used with the three selected products, due to some physical incompatibilities. It was not possible to apply the nitric acid using the agar-agar rigid gel, as the low pH did not fulfil the conditions for the gel to form. Furthermore, as the ion-exchange resin is solid when prepared, it cannot be applied using either the pulp poultice or the rigid gel. The nitric acid (HNO_3) was applied by immersion (AI1; AI2) and by cellulose pulp poultice (AP1; AP2). In line with the literature reviewed [2, 13, 27-28], two solutions diluted in deionized water were prepared, one at 2.5 % v/v and the other at 5.0 % v/v. For the immersion, both concentration tests were carried out on the same ceramic sherd (Aj.4645-1). 50 mL of each solution was poured into two beakers, and the sherd was introduced up to the pre-established level. The first treatment (AI1) was performed with the solution prepared at 2.5 % v/v on one half of the ceramic fragment, whereas the other half was treated with the solution at 5 % v/v (AI2). The first treatment (AI1) lasted 1 minute and the second one lasted longer, up to 6 minutes. In both cases, they implied major effervescence as well as a rise in temperature. As expected, the pH was acidic, between 0.2 and 0.6 (Table 1).

In the case of the pulp poultice application, 10 mL of each solution was mixed with the cellulose pulp, and each mixture was applied to each of the two halves of the selected sherd (Aj.4645-3). Once applied, it was covered with plastic film to slow the evaporation process, and the hardness of the deposits' remains of the two application areas were checked every ten minutes with wooden sticks until the treatment was finished. In both cases, the treatments lasted more than one hour (Table 1).



Nitric acid

- Prepared at
  - 2.5 % v/v (pH 0.6)
  - 5.0 % v/v (pH 0.2)
- Applied by immersion and cellulose pulp poultice
- On fragments Aj.4645-1 and Aj.4645-3

EDTA disodium salt

- Prepared at
  - 5.0 % w/v (pH 10.3)
  - 7.0 % w/v (pH 10.4)
- Applied by immersion, cellulose pulp poultice and agar-agar gel (pH decreased to 8.0 and 9.0, respectively)
- On fragmentos Aj.4645-4, Aj.4643-4, Aj.4645-2 and Aj.4643-1

Ion exchange resin

- Prepared at 90 % w/v (pH 3.0)
- Applied by palette knife
- On fragment Aj.4643-2

Figure 2. Cleaning treatments performed, based on three products and three application methods.

The EDTA disodium salt was applied by immersion (EI1; EI2), with cellulose pulp poultice (EP1; EP2), and with agar-agar rigid gel (EG1; EG2). Again, two solutions diluted in deionized water were prepared at 5.0 and 7.0 % w/v, in line with the recommendations of the literature [1-2, 27-28]. The procedures followed for immersion and the poultice were the same as those used for the nitric acid tests. However, the rigid gel needed to be prepared before its use with the EDTA disodium salt, in accordance with current protocols [10, 16, 21, 27]. The gel was prepared at 1.5 % w/v so that it presented a neutral pH (6.0-7.5) which would increase with the addition of the EDTA solution, reaching optimum values for the formation of the complex with the Ca^{2+} ions (pH > 8) [29]. While the agar-agar solution was still liquid, the EDTA solutions were added before it cooled down and turned into gel form. Once in gel form, it was cut into 5 mm-thick sheets and directly applied onto the deposits' surfaces and covered with plastic film. It was initially checked every hour, but subsequently less frequently. The pH values were basic, in the range of 8.0-10.4, and the duration of the treatments extended from four to sixty hours (Table 1).

The strong cation-exchange resin (IONEX H CTS) was directly applied with a palette knife. A mixture was prepared at 90 % w/v in deionized water. The low pH values measured prior to its application confirmed its acidity. Two tests were performed, with the application method changing only slightly. In the first case (RP1), the paste was applied and covered with plastic film. After 30 minutes, when the deposits were soft enough to be mechanically removed with wooden sticks, the paste was removed.

Table 1. Cleaning tests performed, with nitric acid, the EDTA disodium salt and the ion exchange resin.

Test	Reference	Application method	Inventory number	Concentration %	pH	Treatment duration
Nitric acid	AI1	Immersion	Aj.4645-1	2.5	0.6	6 min
	AI2			5.0	0.2	< 1 min
	AP1	Poultice	Aj.4645-3	2.5	0.6	1h 20 min
	AP2			5.0	0.2	1h 10 min
EDTA disodium salt	EI1	Immersion	Aj.4645-4	5.0	10.3	12 h 30 min
	EI2		Aj.4643-4	7.0	10.4	12 h
	EP1	Poultice	Aj.4645-2	5.0	10.3	4 h
	EP2			7.0	10.4	
	EG1	Gel	Aj.4643-1	5.0	8.0	60 h
	EG2			7.0	9.0	
Ion exchange resin	RP1	Palette knife	Aj.4643-2	90	3.0	30 min
	RP2					20 min

A second test was performed by applying the paste and stirring it, this time without using plastic film (RP2) and with a shorter treatment duration of 20 minutes (Table 1). It is important to bear in mind that the effectiveness of the paste decreases while the deposits are being removed. For this reason, the paste needs to be continually renewed throughout the process.

Once all the chemical tests had been performed, the remaining deposits were removed by mechanical methods (pointed 20 cm wooden sticks and scalpel). The treatments were then neutralized in a deionized static water bath for 24 hours. In all cases, the pH of the products was measured with a hand-held pH meter (Hanna Instruments HI-98107).

Results and discussion

This section includes the observations made, following the evaluation of the results obtained by different techniques: macroscopic examination, optical microscopy and SEM-EDX. The results are described by cleaning agent and application method.

Nitric acid tests

Immersion

To the naked eye, the nitric acid treatments applied by immersion appeared to be very effective, as the carbonate deposits were almost invisible. However, microscopic observation showed that the painted decorative areas had decreased because of the treatment. The matrix was also affected, as evidenced by the small (< 2 mm) rounded holes that had appeared on the ceramic surface (Figure 3a-b). Besides, a thin white deposit could also be observed on the ceramic surface following the treatments. This may be a residue of the calcium carbonate deposits or of the calcium nitrate salt resulting from the cleaning treatment. The SEM observation confirmed the aforementioned surface alterations: cracks, increased roughness and loose particles (Figure 3c). Therefore, the general stability of the ceramic matrix had decreased. The painted decoration was also affected, as proved by the solubility tests performed after the treatment, as cotton swabs shown powdery residues form painted surfaces. Similar results were observed for all tested nitric acid concentrations (2.5 and 5 % v/v).

Cellulose pulp poultice

Again, the treatment had clearly been effective to the naked eye, as the carbonate deposits had been removed. However, it could be observed that the painted decoration had suffered major losses (Figure 4a). In the microscopy images, several holes were detected in the ceramic matrix, as well as, thin white layers, probably of calcium carbonate remains or calcium nitrates, as a result of the cleaning treatments applied (Figure 4b). Consequently, the stability of the matrix had decreased. The solubility tests, performed in the same way as prior to the cleaning treatments, exhibited alterations in painted areas, in opposition to their previous stability, already mentioned. The SEM images showed the surface to be altered, presenting signs of detachment and loose particles (Figure 4c), but less then in case of immersion. As in the immersion tests, no meaningful differences were observed varying the concentration of the nitric acid solution.

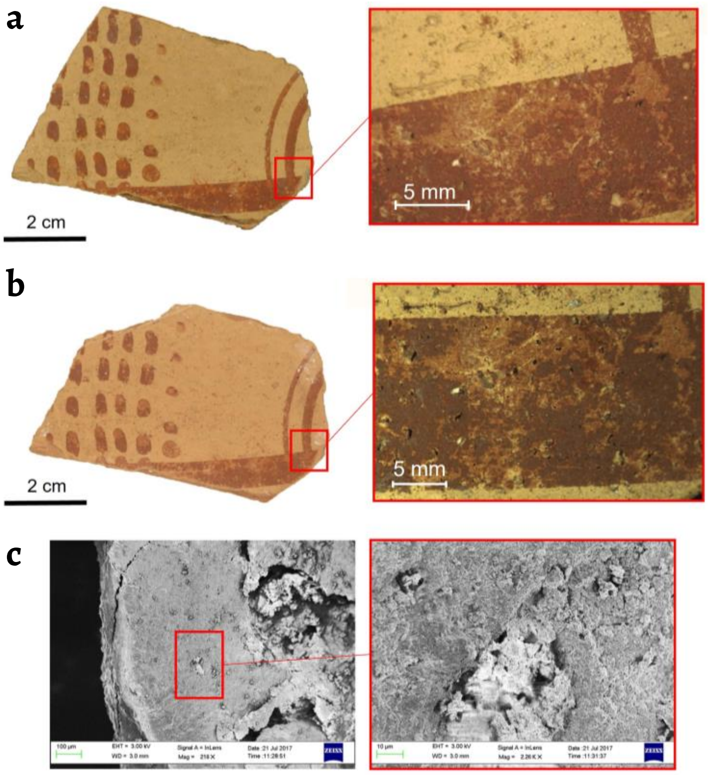


Figure 3. Differences observed on sherd surface Aj.4645-1, at naked eye and detail of the surface under optical microscope: *a)* before and *b)* after the treatment with nitric acid applied by immersion; *c)* SEM image of the surface at two magnifications.

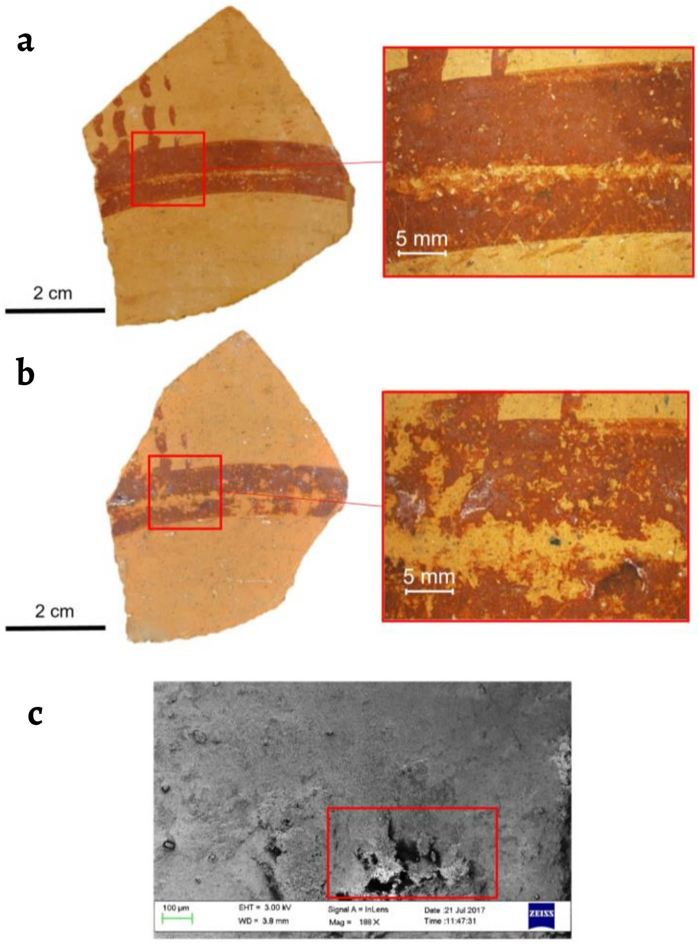


Figure 4. Changes observed on Aj.4645-3 surface, at naked eye and detail of the surface under optical microscope: *a)* before and *b)* after the treatment with nitric acid applied with cellulose pulp poultice; *c)* SEM image of the surface with mechanical alterations (squared).

EDTA disodium salt

Immersion

The treatment can be considered effective, as almost all the deposits had been removed despite some incrustations in porous areas, both at 5.0 and 7.0 % w/v. To the naked eye, no damage was observed at either concentration (Figure 5a-b and Figure 6a-b).

However, in the case of 5.0 % w/v (sherd Aj.4645-4), SEM analysis detected severe surface alterations such as cracks, loose particles and increased roughness (Figure 6c). All these factors led to a decrease in the stability of the ceramic matrix. Solubility tests showed that the painted decoration was also affected. By contrast, in the case of 7.0 % w/v (Aj.4643-4), no alterations were detected (via either SEM or solubility tests). This is due to the difference in porosity between the two pieces. Aj.4645-4 presented slightly higher porosity under microscopic observation, which implies that this piece was more vulnerable to the effects of the treatments.

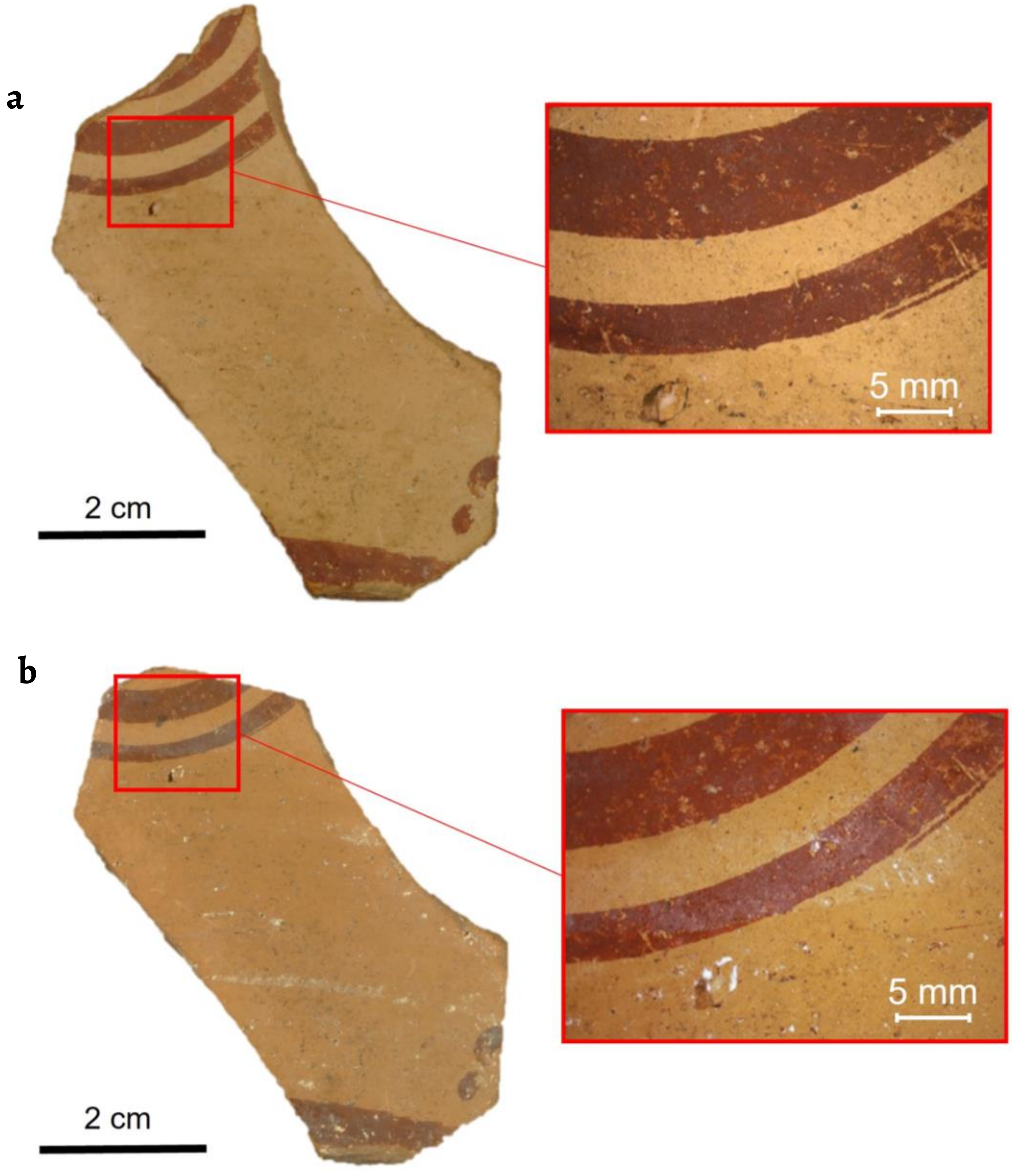


Figure 5. Aj.4645-4 surface, at naked eye and detail of the surface under optical microscope: *a)* before and *b)* after the treatment with EDTA disodium salt 5.0 % w/v by immersion.

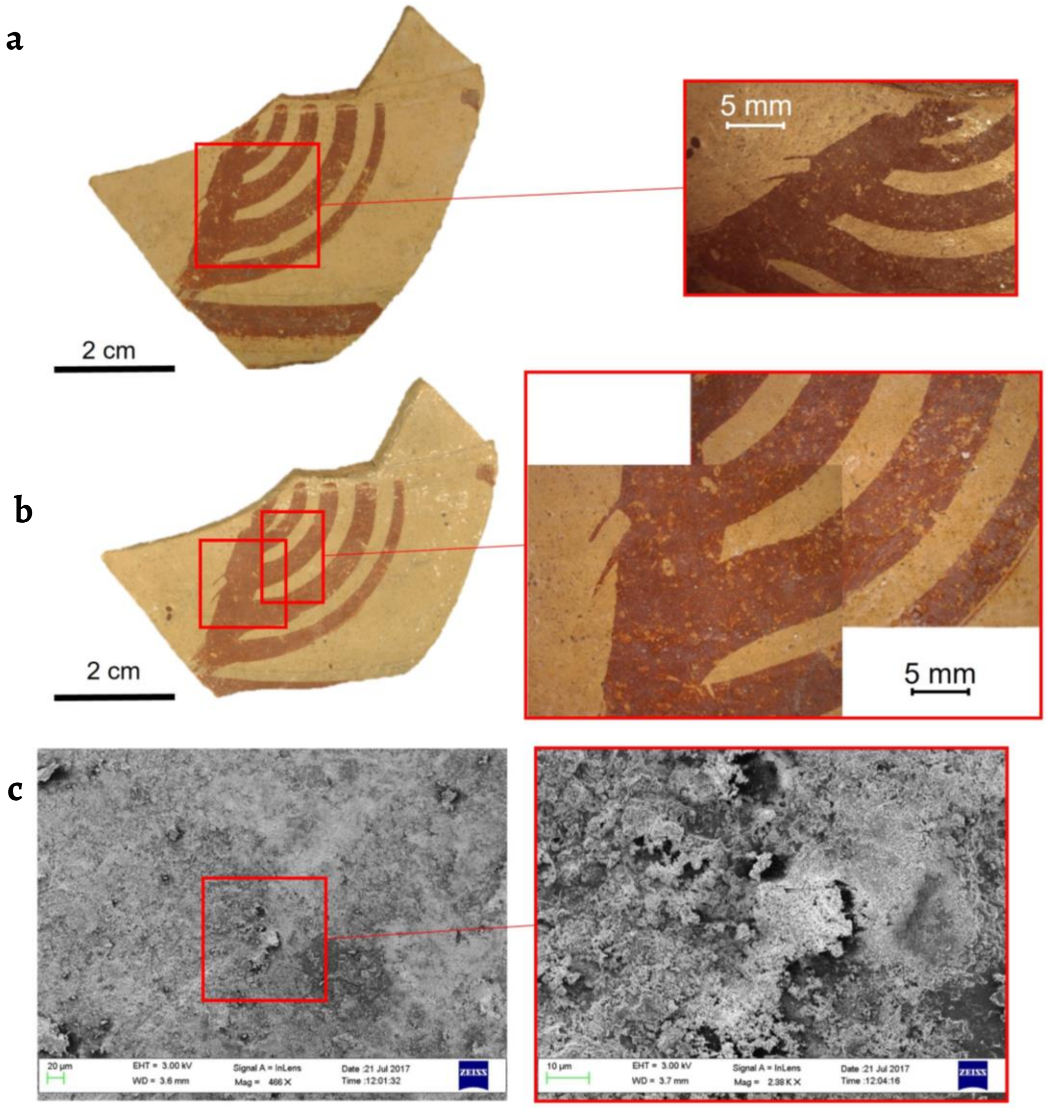


Figure 6. Aj.4643-4 surface, at naked eye and detail of the surface under optical microscope: *a)* before and *b)* after the treatment with EDTA disodium salt 7.0 % w/v by immersion; *c)* SEM image of the surface at two magnifications.

Cellulose pulp poultice

The results of these tests were very similar to the immersion ones. The carbonate deposits had been removed almost completely. With the naked eye, no surface alterations were observed, whether on the painted surface or ceramic body. Microphotography showed that neither the sherd nor the polychromy had been altered, and the solubility tests were negative for both solvents, meaning that the products tested did not alter painted areas (Figure 7a-b). However, SEM images revealed surface alterations, such as cracks and loose particles (Figure 7c). Just as in the nitric acid tests, results were similar with tested EDTA concentrations.

Agar-agar rigid gel

At first sight, and via microscopy observation, the treatment appeared to have been effective and did not alter the ceramic sherd (Figure 8a-b). SEM images revealed only some loose particles (Figure 8c), which were identified by EDX analyses as rigid gel remains. Solubility tests confirmed that the painted decoration was not altered. As before, there were no meaningful differences in the results in relation to the concentration of the solution.

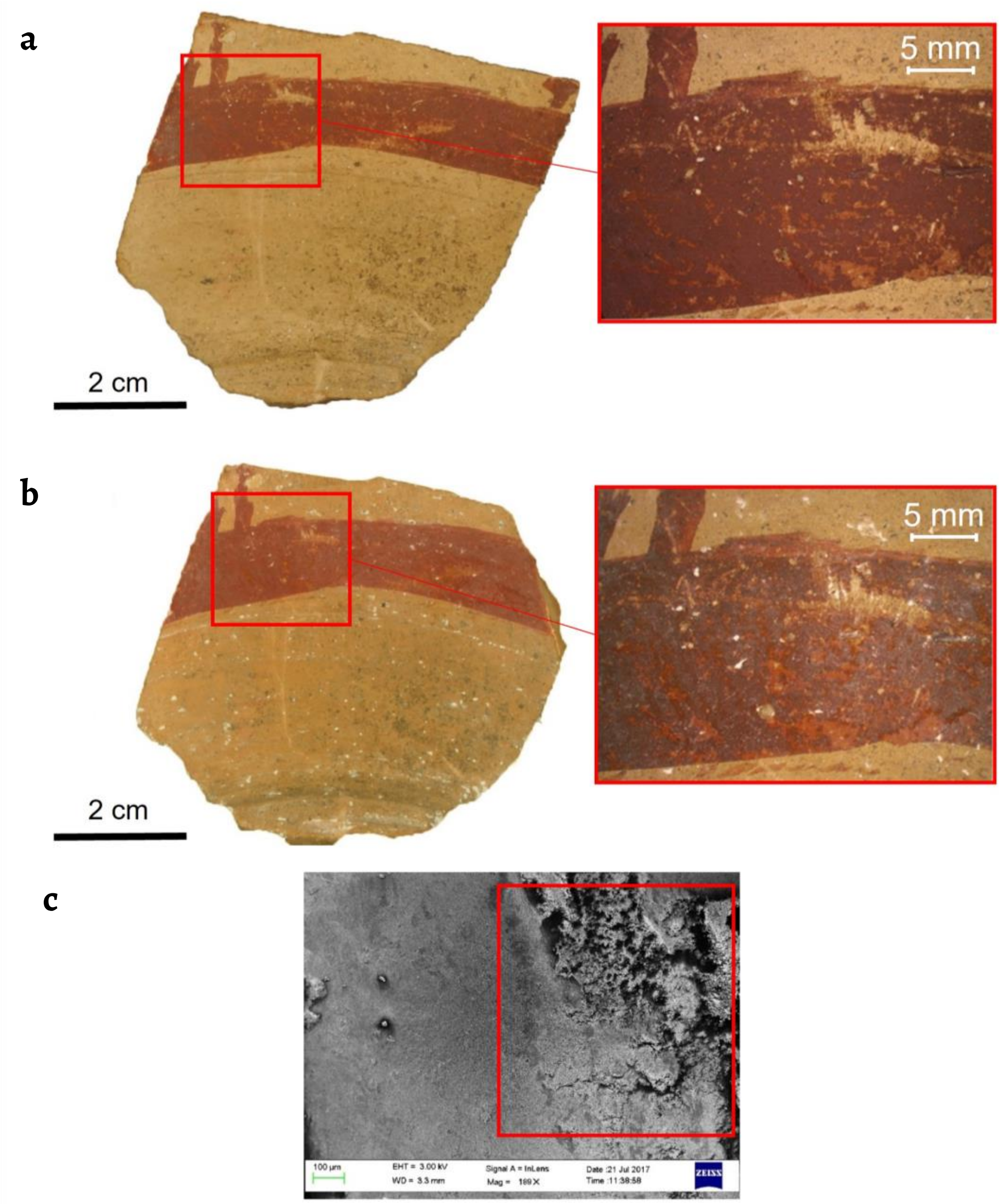


Figure 7. Aj.4645-2 surface, at naked eye and detail of the surface under optical microscope (0.8 ×): *a)* before and *b)* after the EDTA disodium salt treatments applied with cellulose pulp poultice; *c)* SEM image of the surface by SEM.

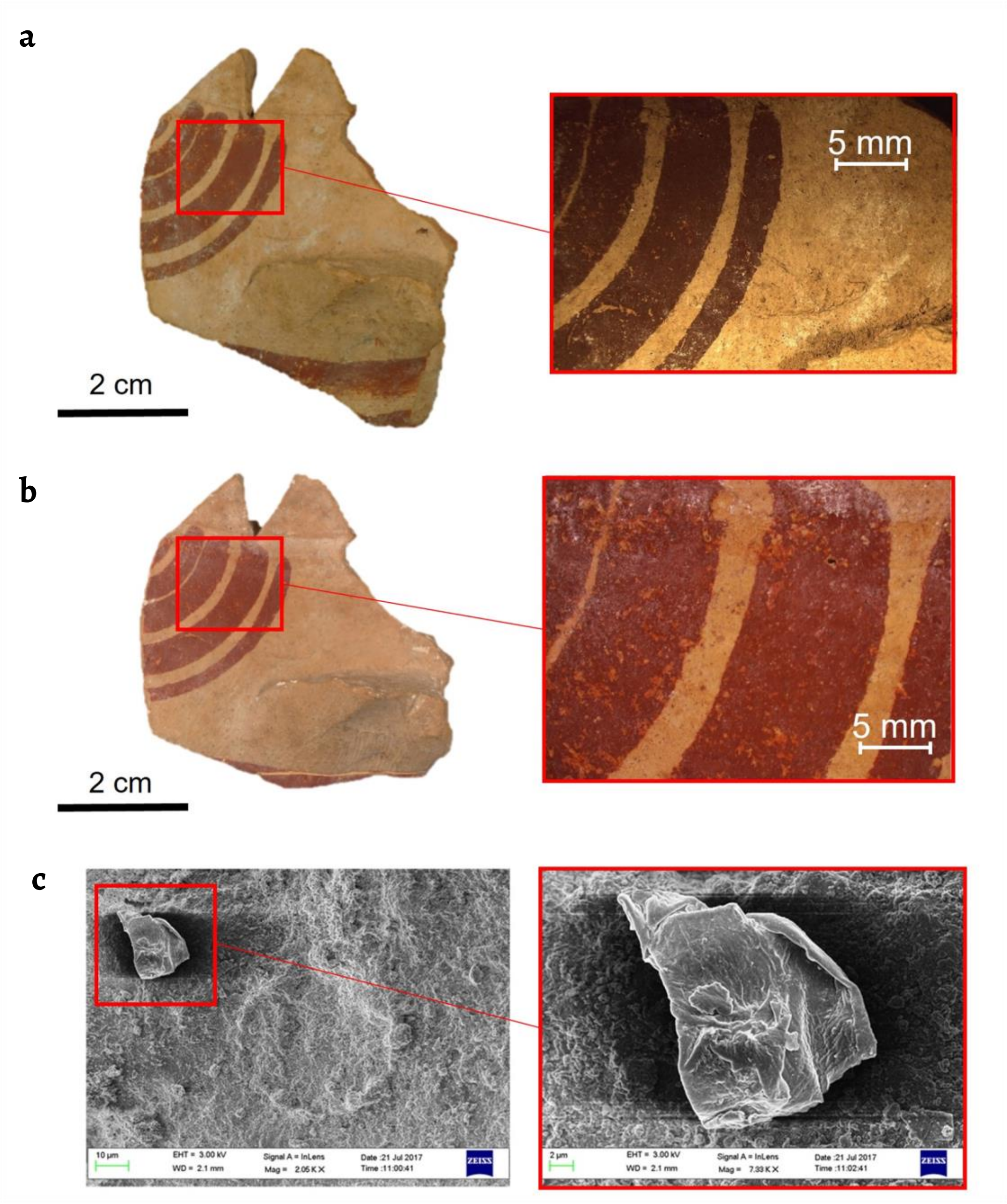


Figure 8. Aj.4643-1 surface, at naked eye and detail of the surface under optical microscope: *a)* before and *b)* after the EDTA disodium salt treatments by agar-agar rigid gel; *c)* SEM image of the surface at two magnifications.

Strong cation-exchange resin (IONEX H CTS)

Palette knife

To the naked eye, the treatment appeared to have been effective, as the deposits had been removed. Nevertheless, the painted decoration had clearly been damaged (Figure 9a-b). This was also confirmed by the SEM images, which detected cracks and increased roughness in decorated areas (Figure 9c). The solubility tests also demonstrated that the polychromed areas had undergone alterations. However, there was no evidence of damage to the ceramic surface.

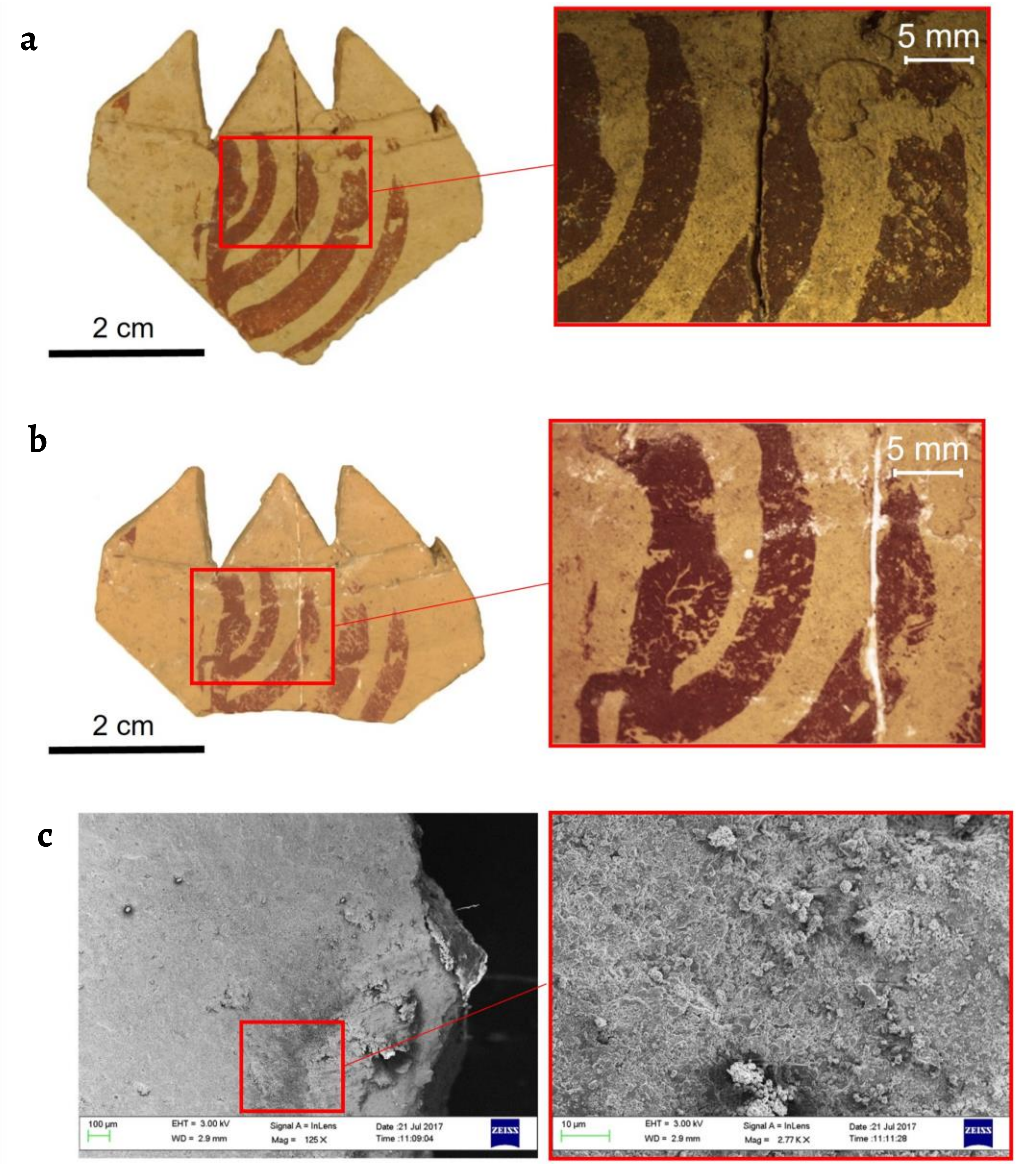


Figure 9. Aj.4643-2 surface, at naked eye and detail of the surface under optical microscope: *a)* before and *b)* after the application of the strong cation-exchange resin; *c)* SEM image of the surface at two magnifications.

Conclusions

According to these results, the porosity of ceramics is an important variable in the restoration process. In general, the treatments that were tested on low-porosity sherds (Aj. 4643) caused less alterations on the ceramic body, while some of those tested on medium-porosity sherds (Aj. 4645) caused severe alterations.

Regarding the painted areas, most of them showed alterations after the cleaning treatments, by optical observation corroborated by solubility tests performed with deionized water and ethanol (96 % vol.). However, the polychrome areas treated with EDTA disodium salt applied by cellulose pulp poultice remained unaltered.

Treatments based on nitric acid, regardless of its concentration and application method (immersion and poultice), damaged both the ceramic and the painted surfaces, as proved by solubility tests and optical observation. Alterations were visible at microscopic and macroscopic level of observation and in SEM images. Within the cleaning treatments based on the EDTA disodium salt, there were differences linked to the porosity of the fragments. Low-porosity sherds (Aj. 4643) did not present alterations, regardless of the application method and product concentration (immersion and agar-agar gel). Whereas medium-porosity fragments (Aj. 4645), treated by immersion and cellulose pulp poultice, suffered damages in polychromies and ceramic surfaces, despite the application methods. Therefore, in further research it would be interesting to test agar-agar gel application onto a medium-porosity fragment, in order to compare the results obtained so far by immersion and cellulose pulp poultice. Following macro and microscopy observation, the cation-exchange resin appears to damage only the painted surfaces.

Furthermore, the pH of the solutions used to remove the calcium carbonate deposits was shown to influence the treatment time needed. For more basic pH values (EDTA disodium salt solutions), more time was needed in order to be effective. Whereas for acidic pH values (nitric acid solutions and ion-exchange resin mixture), treatment times were lower. However, no meaningful differences were identified between the two solutions prepared for each product. So that, it would be interesting for further studies to test lower concentrations, controlling the pH values.

Additionally, in future research, further tests should be carried out with agar-agar gel isolated, to assess its effectiveness and any possible damages. The same testing process should be successively applied to cellulose paper poultices and deionized water. In this way, the role of each product in the removal of the calcium carbonate deposits would be proved. Moreover, it would be important to systematically extend the tests to low and medium porosity ceramic matrix ceramics.

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