Archaeological ceramic amphorae from underwater marine environments: influence of firing temperature on salt crystallization decay

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Abstract

Non-desalinated and desalinated fragments of Iberian, Italic and Tarraconensian amphorae sherds, found in different underwater marine environments, were compared to determine both their state of conservation and the decay caused by salt crystallization. Polarizing light and fluorescence optical microscopy, scanning electron microscopy coupled to energy dispersive X-ray spectroscopy, X-ray diffraction, ion chromatography and mercury intrusion porosimetry tests were conducted on the samples. Non-desalinated samples or samples in which desalination was not wholly effective exhibit a variety of signs of degradation, especially in those samples fired at lower firing temperature. Sherds fired at higher temperatures have lower surface area and less connected porosity, which entail a lower absorption of soluble salts containing water and eventually less decay. The composition and texture reached with the firing temperature is a key factor on salt crystallization decay and hence on the durability of these artifacts. This should be taken into account during desalination procedures that have to be optimized in order to be successful.

Keywords: Underwater ceramics; amphorae; salt crystallization; decay; firing temperature.

1. Introduction

The recover of archaeological artifacts allows studying their provenance, technologies of manufacture and understanding the lack of connection of some parts of the history of the human being. In the conservation of waterlogged artifacts, due to the large amount of material and lack of scientific knowledge on their physico-chemical properties, the efficiency of methods and products for desalination and consolidation is still unclear. Accurate methods for each specific object depend on composition and texture and these must be taken into account in order to select the most effective procedures.

Archaeological objects made of stone or fired clay are exposed to a number of processes, mechanisms and causes of decay; some are closely related to the intrinsic properties and nature of the materials, such as their mineralogy and texture (pores and cracks), while others are induced by outside agents such as microclimate, environmental pollution or the anthropogenic or natural surrounding environment (air, water, soil). Salt crystallization in porous materials is one of the primary causes of stone and ceramic decay, especially in marine environments.[1-4] While salt crystallization-mediated decay in stone materials has been extensively studied,[5-9] this type of decay has been less thoroughly analysed in archaeological ceramics, despite the abundance and variety of such materials found at archaeological sites.[10] Studies conducted on salt crystallization-induced decay in ceramics[11] show that the surface finishes and the presence or absence of temper or degreasing components, barely affect salt crystallization. These components are added to the clay mainly to provide the paste a better resistance, to support the temperature changes during firing, to accelerate drying, to decrease the retraction suffered during the drying of the paste or to reduce excess of plasticity or shrinkage.[12,13] Temper or degreasing components could be quartz, plagioclase, potassium feldspar, rock fragments, sand, powder or fragments of ceramics (grog), straw, feathers, shales, granulated slags or crushed shells. O´Brien, 1990, concluded that firing temperature is the main determinant in decay, since ceramics fired at high temperatures are less porous and consequently less permeable and more durable. However, after conducting his

2

experimental study on accelerated ageing induced by salt crystallization, the question of whether the long-term effects would be the same for ceramics fired at low or high temperatures was left unanswered.

In another vein, the conservation and decay of archaeological objects vary widely depending on environmental conditions. Marine environments are characterised by physical (abrasion, transport, deposition), chemical (dissolution-precipitation, oxidation-reduction) and biological (bacterial or benthic organism growth) processes. In addition to the prevailing environmental conditions (degree of salinity and acidity, temperature and thermal variations, type and concentration of soluble salts, eroding fluid movement, microorganisms, fauna and flora), archaeological remains are affected by the characteristics of the underlying substrate (soft or hard, type of sediment or rock and the associated organisms).[14] Seawater contains different types of salts, most prominently sodium, magnesium, calcium, potassium and strontium cations and chloride, sulfate, bromide and bicarbonate anions. These soluble salts in the sea water are absorbed through the pores of the ceramic artifacts. After centuries immersed in this salty underwater environment, these artifacts pass to the aerial environment with totally different physico-chemical conditions when are extracted from the water. Fluctuations of relative humidity and temperature mobilize the absorbed soluble salts, modify the composition and texture and eventually the salt crystallization process accelerates weathering[15,16] endangering durability of these ceramics.

The main objective of this research is to show the influence of firing temperature on decay caused by salt crystallization in non-desalinated and desalinated archaeological ceramic amphorae from underwater marine environments.

2. Materials and methods

2.1. Samples

The underwater marine ceramic amphorae fragments analysed in this study varied in origin and some of them were subjected to post-extraction desalination process. Samples A-Ibe-1, A-Ita-15 and A-Tar-24 were taken from the Cala de Aiguablava classic era anchorage ground at Begur, in the Spanish region of Catalonia (Fig. 1). All the samples from this site have been subjected to a desalination process after their extraction from the archaeological site. The desalination process was carried out in the laboratory of the Centre d'Arqueologia Subaquàtica of Catalunya in Girona, by submerging them in tap water and measuring the conductivity of the water with a conductivity meter until the readings stabilized.[17] By other hand, samples A-Ibe-31, A-Ita-33 and A-Tar-32 are non desalinated underwater sherds, with an unknown location since these were extracted in the 1970s by fishermen and divers. In this case, these fragments of amphorae have the same historical provenance than the former mentioned desalinated samples, and these were used in this research in order to carry out comparative studies. All the samples were exposed to the environmental room conditions of the lab warehouse where these were stored until the current research.

The approximate age and provenance of the sherds were studied by archaeologists using historic and archaeological sources.[17-19] The sherds denominated samples A-Ibe-1 and A-Ibe-31 were made by Iberian potters, whose production sites were located primarily on the east and south of what is now Catalonia (Fig. 1). They date from the second or first century BC and were possibly used to store wine or beer. Their main features are the red color, fine texture and the very thin walls of the vessels (Fig. 2a) and hence their fragility and the importance of the ratio between capacity and weight of the container. The no desalinated sample A-Ibe-31 displays thin flakes on the outer surface due to salt crystallization decay/processes.

Samples A-Ita-15 and A-Ita-33 are sherds of Italic origin. These were made in or around the Italian region of Campania and date from the mid-second to the mid-first centuries BC (Fig. 1). These display pale red color and plenty of calcareous concretions on the surface (Fig. 2b). The main characteristic of these vessels manufactured in the south of Italy was their strength due to their thick walls able to resist important tractions. Their main problem is the container-content ratio, since

4

some shapes could be 1:1, e.g. same weight for the container and same for the content. This ratio in the world of transport and commerce is very undesiderable.[18]

Samples A-Tar-24 and A-Tar-32 are an example of Tarraconensian amphorae. This type of pottery was made primarily on the Catalonian coast, with the most active production sites located in the Maresme region near Barcelone (Fig. 1). These fragments date from the mid-first century BC to the mid-first century AD. The shape is a copy of the Italic amphorae that precede them. The non desalinated sample A-Tar-32 displays thick flakes on the surface due to salt crystallization (Fig. 2c). These types of amphorae still had thick walls with large dimensions and high weight.[18]

Both Italic and Tarraconensian amphorae were used for wine transport. One important aspect is the the use of waterproofing materials to cover the internal surfaces of the amphorae to provide an impermeable inner surface, as can be observed in Fig.2b by the presence of a black color product on the inner surface of the sherd. The use of waterproofing materials was necessary because the high porosity of the pottery made them permeable and unsuitable to transport liquids, thus providing information about the pottery manufacture and the transported materials like wine or oil due to the remains found in the coatings.[20-23]

2.2. Analytical techniques

Polarizing light optical microscopy (PLOM) was carried out mainly to the study of main mineralogical constituents, physico-chemical weathering patterns and ratio aggregates:paste of the samples. A digital Micrograph software™ Gatan Inc. was used to measure grain sizes of the aggregates. Fluorescence light optical microscopy (FLOM) was carried out on the same microscope and the same samples to observe the porosity on the same areas pictured with PLOM. The samples were impregned with epoxy resin mixed with flouresceine and the porosity was filled with it. Then, thirty-micron thin sections of the samples were prepared and dyed with alizarin red to distinguish calcite from dolomite. These thin sections were studied with an Olympus BX51 polarized light

microscope fitted with an Olympus DP 12 (6V/2.5Å) digital camera and a fluorescence illumination system.

The mineralogical composition of the ceramic samples and the type of salts were determined, and their firing temperature estimated from mineral paragenesis obtained by X-ray diffraction (XRD), conducted on a Phillips PW-1710 CuKα radiation powder diffractometer. The scanning conditions were 2θ angles of 2º to 68º, scan step size 0.02º, scanning rate 2º/min, continuous mode, and beam intensity of 40 kV and 30 mA.

Ion chromatography (IC) was performed to identify soluble salts in all the samples by determining some anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+} and Ca^{2+}). The method used for extracting soluble salts was based on an alternative to the method described in the NORMAL standard[24] with some additional modifications. Approximately 0.1 g samples were dissolved in 10 ml of Milli-Q ultrapure water and placed for 45 min in an ultrasonic bath at room temperature. They were subsequently centrifuged for 5 min. at 3,500 rpm and a centrifugal force of 3,400 rfc. The soluble salts (anions and cations) in the extracted sample were quantified on a Metrohm 761 Compact IC ion chromatograph.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to identify the possible existence of salt subefflorescences under the surface flakes on some of the samples. The SEM microscope was a JEOL JSM 6400 and the analyses conditions were 0.2-40 kV accelerating voltage, $6x10^{-10}$ A current, 10^{-5} Torr vacuum, 35 Å resolution, 8 mm and 35 kV working distance and 20 kV accelerating voltage for image acquisition. The spectrometer was a microanalyser Oxford instruments analytical Inca with a 133 eV-5.39 kV nominal resolution. Graphite-sputtered flakes taken from the samples were studied in secondary electrons mode. The elemental composition of some selected components was qualitatively determined by means of EDS microanalyses.

Mercury intrusion porosimetry (MIP) was used to assess sample pore structure, i.e., total porosity (P), pore size distribution (PSD) and tortuosity. Readings were taken at pore diameters of 0.005 to 400 µm under measuring conditions ranging from atmospheric pressure to 60,000 psia (228 MPa) on a Micromeritics Autopore IV 9500 MIP.

3. Results and discussion

3.1. Polarizing light and fluorescence optical microscopy

There are clear differences among the studied thin sections from the three types of amphorae. The Iberian samples display the smallest size of aggregates and much more quantity of these compared to the other samples, being the aggregate:paste ratio 3:1 approximately. The main component of the aggregates is quartz with a fine (min. size 23 µm and max. size 185 µm approx.) and a monomodal clast grain size (Fig. 3a). As it has been already noted, this may indicate its adition and mixture with the clay to improve the mechanical properties of the paste.[12,13] Fine veins fill with calcite and sulfates are observed close to the outer surface of the amphorae. The matrix displays a brown-reddish color, probably due to the hematite developed during the firing of the pastes[25] from both iron oxides and oxyhydroxides present in the clayey raw material.[26] In sample Ibe-1, this reddish color is masking the paste and part of the aggregates. The contact between aggregates and paste is quite blurred, which may denote a high firing temperature. Some gehlenite crystals can be observed surrounding the plagioclase crystals in sample A-Ibe-1 and this denotes firing temperatures above 800ºC. Both Iberian samples display a foliation or penetrative planar fabric notably marked in A-Ibe-31 (Fig. 3a) where the aggregates and the matrix are oriented in alignment. By other hand, sample A-Ibe-31 displays calcite and phyllosilicates, besides quartz, feldspar, hematite and limonite gels. The contacts between aggregates and the paste are sharper and the color of the matrix or paste is more golden brown compared with the blurry contacts and dark red brown matrix of sample A-Ibe-1, which denotes lower firing temperature in the former and higher in the latter.[27] At lower firing temperatures (800ºC) the individual mineral temper grains are easily distinguishable from the

clay matrix; at higher firing temperatures (1000º-1050ºC) the sintering process produces an increase in the interconnection among these grains and the matrix and the porosity decrease.[28,29]

The clast grain size distribution is mainly bimodal in Italic and Tarraconensian samples (Fig. 3b and 3c, respectively) with prevalence of both larger and smaller quartz aggregates. This indicates the presence of clasts deriving from the original clay, the smaller ones, and from the added temper, the larger ones,[30] added to improve the mechanical properties of the pastes. The bimodal grain size distribution may also indicates the variable crystal nucleation and growth rates, affected by the temperature, fluids interactions and critical activation energy that needs to be overcome for nucleation and growth to ocurr.[31]

In the Italic samples some of the aggregates come from rocks with a basic igneous geological source (basaltic and andesitic) and calcium plagioclases. The presence of diopside crystals is quite common, and comes from the raw materials. It is not formed during firing as is also common in other cases from the transformation of dolomite and silicates.[27] However, the diopsides display coronitic reaction rims due to its amphibolization (hornblende) (Fig. 3b) with their cleavage planes parallel to the foliation, indicating that these have been affected by the firing temperature. The amphibolitization of the pyroxene could be produced by changes in oxygen fugacity and changes in temperature,[32] producing pseudomorphing. Furthermore, it could be associated to disequilibrium by retrograde reactions.[31] In this case, not in all the cases, the reaction rims could be identified, however, this reflects the variable degree of fluid infiltration and illustrates the important role that fluids play in promoting reactions.[31] Associated to diopside, agregates of columnar crystals of wollastonite are ocassionally identified. They display the cleavage planes parallel to new orientated diopside crystals, suggesting that a reaction process has taken place during firing.[32] The wollastonite is the result of the reaction $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$, where the silica from the matrix is reacting with oxides and hydrous gels and calcium carbonates which break down on heating to yield wollastonite.[33] Locally, gehlenite crystals and pyrite sulfides are also identified. The

presence of gehlenite associated to wollastonite is also common. The size of the aggregates ranges from min. 82 μm up to 500 μm in sample A-Ita-33 and up to 800 μm in A-Ita-15.

There is a bimodal distribution especially clear in the Tarraconensian amphorae (Fig. 3c) which could mean another level of manufacture technology. Also the shape of the degreasing agents has a significant effect on some physical properties, such as the ceramic toughness or impact resistance, especially if the objects had been fired at high temperatures;[34] higher firing temperatures and finer fabrics containing less temper material (as the sample A-Ibe-1) would be advantageous as well as platy-shape temper preferable over bulky one. Toughness was a particularly important physical property in amphorae, which were generally stacked during shipping and thus had to withstand both the load exerted by the rest of the crocks in the pile and the pressure generated by the content during transport.[34]

The Tarraconensian samples have largest grain size of aggregates compare to the other samples, with minimum sizes of 53 μm and 25 μm and maximum sizes of 80 μm and 1390 μm for A-Tar-24 and A-Tar-32, respectively. The presence of preserved (fresh) biotite can be observed in the dark brown color paste of these tarraconensian amphorae together with calcite. The sample A-Tar-24 display quartz, Na-K feldspars and Na-Ca plagioclases inside a matrix rich in iron oxides and oxyhydroxides. Two preferential orientations can be observed in the thin sections; one where there is an alignment of mica minerals and sulfates filling veins parallel to this foliation. A second orientation of the minerals can be observed overimposed to the first one, where the mica minerals cut to the first alignment direction. Sample A-Tar-32 displays potassium and sodium (K-Na) feldspars, anorthite and quartz with crystallographically controlled embayments caused by corrosion effects[35] (Fig. 3c). Pre-heating textures are preserved from the geological source area such as the presence of potassium feldspar twinned crystals which are not redirected by the flow direction. Illite-muscovite inclusions as a product of serizitation are present in the anorthite aggregates. Gehlenite is developed by nucleation and progressive aggregation to the grain boundaries of calcite. Occasional fibrolite needles of gypsum forming elongated segregations along

the foliation are present. Iron sulphurs are present as disseminated crystals along the matrix. Besides, an epidotization process is locally affecting the calcium plagioclases. Epidote is one of the most frequent alteration mineral occurring in processes implying thermal activity. Among them, factors controlling the chemical composition such as temperature, CO_2 and O_2 fugacities act modifying the Fe, Al, Ca and H ratio in water by changes in partial pressure of CO_2 gas or temperature.[36] Moreover, it is associated to changes in chemistry of aqueous solutions and mineralogy during sea water/ceramic interaction, similar to the interaction sea water/ rock.[37] It is very common to find the association epidote-hematite coexisting with iron sulphides as pyrite, generating enrichments in iron oxides, which have been explained as a result of differences in oxygen fugacity.[36]

The presence of different preferential orientations reveals different stages of mineralization. The first one is associated to the early compactation stage, including compositional bedding due to different mineralogical associations or different grain sizes. After that, several stages are observed, such as slight deformation pressure during compactation or crystallographic re-arrangements associated to heating producing earlier or contemporaneous mineralogical segregations. These processes act modifying the foliation, such in the case of phyllosilicates developing preferential orientations.[32] Moreover, the presence of new mineralizing fluids (for instance sulphides and other mineral salts) are implied in local deformation processes, mechanical rotation of pre existing grains, dissolution and new mineral growth.[31]

The images obtained with fluorescence light on these samples show the porosity of the samples in green (bright) colour (Fig. 3d-f). It can be seen the difference in the pore size and shape that differ among the samples and also between samples fired at different firing temperatures. In Ibe-1 and Ibe-31, some big and elongated pores that are left by the decomposition of carbonates can be observed (Fig. 3d). The Italic samples display more differences compared to the other samples, they show a skin serpert shape as a sign of beginning of sinterization (Fig. 3e) whereas tarraconensian samples still show the evidence of phyllosilicates in their matrix (Fig. 3f). The components of

ceramic materials are the "fingerprints" of the stable/or metastable solid phase formed during firing and the production processes of antique ceramics and pottery can be derived from their assemblage.[38]

3.2. X-ray diffraction (XRD)

Minerals such as quartz, K-Na feldspard and plagioclase are present in almost all the samples (Fig. 4). By other hand, the identification of hematite in all the samples indicates the presence of iron oxides in the clay used as raw material. Iron-rich minerals could also be generated during firing of clay pastes in an oxidising atmosphere, since iron oxides from the raw material may generate in turn hematite crystals.[25] However, it must be taken into account that calcareous lumps in calcium-rich clay prevent iron fixation in the network of neoformed calcareous silicate and aluminosilicate lattices and, consequently, inhibit the nucleation of new hematite crystals.[39]

The main difference between the two Iberian amphorae samples (Fig. 4a-b) lays in the absence in sample A-Ibe-1 of illite, biotite and calcite and the presence of the gehlenite ($Ca_2Al_2SiO_7$)-akermanite (Ca_2MgSiO_7) series of minerals, along with a higher hematite content (Fig. 4a). These findings may be indicative of a firing temperature of over 900ºC.[27,40-42] The presence of micas (biotite and muscovite), illite and some calcite in A-Ibe-31 (Fig. 4b), in turn, would denote much lower firing temperatures, under 800ºC[5,27,43]. The Italic amphorae (Fig. 4c-d) exhibit high diopside content (Fig. 4c) which may denote firing temperatures above 900ºC.[27,29,44-46] However, as was mentioned before, in this case diopside seems to come from the raw material and not developed during firing. The absence of illite and the presence of gehlenite, wollastonite and, in a lower extent, anorthite and diopside in the samples is a consequence of the reactions occurring when calcium or magnesium-rich clays are fired above 900ºC.[27,42,43,45,47] Because gehlenite starts to be developed from 800ºC,[48] its coexistence with illite, micas and calcite on both Tarraconensian sherds (Fig. 4e-f), suggests firing temperatures of around 800ºC.

Traces of gypsum ($CaSO_4 \cdot 2H_2O$) for both the desalinated and the non-desalinated Tarraconensian amphora sherds (Fig. 4ef) were identified. Salts such as, sodium-potassium chloride was also detected (also called, potassium halite, $K_{0.2}Na_{0.8}Cl$) in the non desalinated Italic amphorae (A-Ita-33, Fig. 4d). Presence of other salts could not be disregarded since the detection limit of this equipment only detects amounts of compounds above 5%. However, taking into account that the main soluble salts in seawater are chlorides followed by sulfates, as anions, and sodium followed by magnesium and calcium and potassium, as cations,[49] the gypsum and halite detected in these samples are some of the main salts that might precipitate from calcium sufate and sodium chloride dissolved in the seawater and absorbed by the sherds during centuries. Due to the lower solubility of gypsum compared to others salts,[50] its presence may indicate that it has not been totally removed during the desalination process in the case of the Tarraconensian sherds.

The presence of rozenite ($FeSO_4 \cdot 4(H_2O)$) has been detected in both tarraconensian samples (Fig. 4e) but mainly in the non desalinated sample A-Tar-32 and in the Iberian A-Ibe-31 (Figs. 4e-f and 4b). Is relatively frequent the presence of sulfate salts found on the artifacts from shipwrecks, like the in the Vasa, where gypsum ($CaSO_4 \cdot 2H_2O$), natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and melanterite ($FeSO_4 \cdot 7H_2O$) were identified; or in the Mary Rose, with oxides like magnetite (Fe_3O_4) or iron sulfates like jarosite ($KFe_3(SO_4)2(OH)_6$).[51] Ferrous sulfates (such as melanterite and rozenite) are common weathering products formed during abiotic chemical pyrite oxidation and their precipitation is dependent on relative humidity and time.[52]

3.2. Ion chromatography (IC)

The IC findings showed that the total soluble salt content in all the samples ranged from 0.16 to 2.35 wt% (Table 1 and Fig. 5). As a rule, the desalinated samples had lower total soluble salt contents than the non desalinated ones. The sole exception was the Tarraconensian sherds, in which sample A-Tar-24 had a marginally higher content (0.74%) than the respective non-desalinated sample, A-Tar-32 (0.65%) and these exhibit very similar percentages of sulfates: 0.42 and 0.38%,

respectively. The greatest difference between desalinated and non-desalinated samples was exhibited by the two Iberian sherds. The former (A-Ibe-1), with a firing temperature of above 900ºC, had 0.53% salt content, while the percentage in its non-desalinated counterpart, with a firing temperature below 800ºC, was 2.35%. Desalination-based differences were likewise observed for the Italic materials, with A-Ita-15, which was desalinated, containing just 0.16%, compared to 0.83% in the non-desalinated A-Ita-33. The highest percentage of chloride ions (Cl^-) was determined in the Italic amphora sample A-Ita-33 (0.30%). The high Na^+ cation content in this sample (0.20%) would appear to indicate the presence of sodium chloride (NaCl), identified by XRD as halite (Fig. 4d). This sample also contained a low but nonetheless higher level (0.02%) of nitrates (NO_3^-) than the others, whereas it, along with its desalinated counterpart, A-Ita-15, had the lowest sulfate (SO_4^{2-}) contents (0.04%). The non-desalinated Iberian sample, A-Ibe-31, had a very high sulfate content (1.95%), which declined substantially (0.29%) in desalinated sherd A-Ibe-1. This can correspond to calcium sulfate but also to magnesium sulfate due to the high amount of Mg^{2+} (0.19%). The high sulfate content in almost all the samples is not totally balanced with the Ca^{2+} and Mg^{2+} content. Other cations might be present in the samples, such as soluble Fe^{2+}, which would require a special detector coupled to the ion chromatographer in order to be identified, or the use of other techniques such as the tritation method.

The low firing temperature estimated for samples A-Ibe-31 (<800ºC), A-Tar-24 (800ºC) and A-Tar-32 (800ºC), may have played a role in the greater absorption of soluble salts and the less elimination of these ions during desalination. The higher firing temperature (>900ºC), estimated for both Italic amphorae and desalinated sample A-Ibe-1, seems to have led to a lower salt content.

3.3. Scanning electron microscopy (SEM-EDS)

The only two samples with flakes were A-Ibe-31 and A-Tar-32 (both non desalinated). So, some flakes from these samples were chosen to study their inner surfaces by SEM-EDS. The SEM images and EDS analyses of sample A-Ibe-31 revealed the presence of gypsum crystals (Fig. 6a-c), as well

as incrusted ceramic particles that were pulled off during the crystal growth of gypsum subefflorescences underneath the flakes (Fig. 6b).

In the sample A-Tar-32 signs of crystallization processes can be observed (Fig. 7a) and the EDS analyses show the presence of sulfur (S) and iron (Fe) (Fig. 7b), indicating the precipitation of pyrite (FeS_2). Analyses of marine archaeological wood from shipwrecks in the Baltic Sea area also show accumulation of sulfur compounds, pyrite and Fe^{2+} sulfides, together with elemental sulfur, which easily oxidise in aerobic conditions with high humidity.[53]

Further indications of dissolution-re-crystallization appear in some areas; the analyses of which revealed the presence of S, Fe and oxygen (Fig. 7c-d), a possible sign of the existence of iron sulfates. In other areas where these components were less altered, only the presence of S and Fe was identified in the EDS spectrums (Fig. 7a-b). Based on their morphology and EDS analyses, such components seem to have been pyrite (FeS_2), whose alteration may have given rise to the formation of iron sulfate salts. As it was mentioned before, ferrous sulfates (melanterite and rozenite) are common weathering products formed during abiotic chemical pyrite oxidation.[52]

Rozenite ($FeSO_4 \cdot 4H_2O$) is the main sulfate salt detected by XRD in A-Tar-24 and A-Tar-32 and A-Ibe-31 amphorae samples (Fig. 4b-e-f) and seem to be those morphologies observed under SEM (Fig. 7c) and analyzed with EDS (Fig. 7d). Sulfate-reducing bacteria, metabolising organic matter under anaerobic conditions, transform sulfate ions in seawater to dissolved sulfidric acid (H_2S). Wrecked ships contain iron from corroded iron bolts, nails and other metallic archaeological objects. On the seabed, soluble Fe^{2+} may react with hydrogen sulfide (H_2S) to form iron sulphides ($Fe_2O_3 + 4H_2S \rightarrow 2FeS_2 + 3H_2O + H_2$, such as as pyrrhotite (FeS) and pyrite (FeS_2).[54]

Pyrite is unstable with moisture and oxygen and produces sulfuric acid together with sulfates ($FeS_2(s) + 7/2O_2 + (n+1) H_2O \rightarrow FeSO_4 \cdot n(H_2O)(s) + H_2SO_4(aq)$ or oxyhydroxides ($FeS_2(s) + 15/4O_2 + 5/2H_2O \rightarrow FeOOH(s) + 2H_2SO_4(aq)$). [55-57]

3.5. Mercury intrusion porosimetry (MIP)

The pore size distribution (PSD) is polymodal and very similar in amphorae samples of the same type but very different from one type to another (Fig. 8). These differences are mainly due to the different composition, aggregate:paste ratio, grain size of the aggregates and firing temperatures.[45,58 -60] Most of the porosity observed in the sherds above 800ºC depends on the type of clays, the size and concentration of temper minerals, and the presence of carbonates, organic matter and volatils.[46] Even though, Iberian samples display a similar polymodal PSD (Fig. 8a), one sample (A-Ibe-1) has most of their pores in the range 0.1-3 µm and the other (A-Ibe-31) most of their pores are in the range 0.1-1 µm. In this case, A-Ibe-31 is no desalinated and was fired at much lower temperature (<800ºC) compared to the other sample (A-Ibe-1), desalinated but fired at higher temperature (>900ºC). The PSD of the other samples are quite similar comparing between desalinated and non-desalinated specimens. The Italic samples, which were fired at temperatures higher than 900ºC, display most of their pores between 10 and 50 µm (Fig. 8b), while the Tarraconensian samples, fired at lower temperatures (800ºC), show most of their pores in the range 0.01 and 1 µm, but mainly between 0.1 and 1 µm (Fig. 8c), like the Iberian sample also fired at ca. 800ºC (A-Ibe-31).

As a result of salt precipitation and crystal growth, the non-desalinated samples exhibit lower total porosity accessible to Hg than the desalinated sherds (Table 2), in part maybe because the salt crystals are blocking the pores. The non-desalinated samples had a lower bulk density than the desalinated fragments, perhaps due to the degradation induced by salt crystallization in the interiors of the former. The two Tarraconensian fragments and the non-desalinated Iberian sherd (samples A-Ibe-31, A-Tar-24 and A-Tar-32), whose firing temperatures were estimated to be the lowest, have lower total porosity accessible to Hg (between 23 and 26%), the greatest specific surface area (SSA) (9 and circa 20 m^2/g) and smaller pore mean diameter (between 0.02 and 0.06 µm). These samples also display the largest desalination / non-desalination differences. This may indicate more intense alteration, inferred by the lower firing temperature (800 or <800ºC) and higher clay detected by

XRD (Fig.4) and sulfate content detected by IC (Table 1). The higher SSA the greater the area exposed to weathering agents and more condensation can take place inside the pores of the materials. SSA may be used as a durability estimator because high SSA values mean that a greater surface area of the material will be decayed.[61]

The non-desalinated sherds exhibit greater tortuosity than the desalinated fragments, except in desalinated sample A-Tar-24 whose tortuosity is intense. The tortuosity value of this sample is ca.15 (Table 2) meaning that pores are not straight following longer lengths with irregular paths compared to the other samples with lower values and hence straighter pores. As the results achieved in A-Ibe-31 and A-Ita-33, the pores in the non-desalinated samples are consequently curvier than the pores in the desalinated fragments. This may have been due to salt crystallization-induced pore narrowing and rupture, which would lead to a more tortuous and complex pore network.

4. Conclusions

This study show that both soluble salts absorption and their elimination after the desalination procedure is closely related to ceramic firing temperature and, hence, to the surface area and porosity generated during firing. Therefore, ceramics fired at temperatures over 900ºC show small amounts of soluble salts (anions and cations characteristic of marine environments), while the materials fired at 800ºC or lower have more soluble salts and gypsum sub-efflorescences, even in the desalinated samples. Sherds fired at higher temperatures have lower surface area and less connected porosity, which entail a lower absorption of soluble salts. The amphorae fired at lower temperatures display lower total porosity but higher surface area, smaller pore mean diameter and more connected pores, so these are more prone to decay and less durable against weather.

The composition and texture reached with the firing temperature is a key factor on salt crystallization decay and hence on the durability of these artifacts. Therefore in order to optimize a desalination procedure is necessary to previously know the intrinsic characteristics of the artifacts, since their pore network can make difficult the desalination. The use and effectiveness of

desalination treatments are keys to the future conservation of ceramics artifacts. The environmental control, keeping constant temperature and relative humidity in suitcases can be an alternative conservation method if desalination treatment can not be done or if this was not successful.

Acknowledgments

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Figure captions

Figure 1. Location of samples of archaeological ceramic amphorae and the areas where these were manufactured.

Figure 2. Pictures of amphora fragments. a) Iberian sample A-Ibe-31 (non-desalinated); b) Italic sample A-Ita-15 (desalinated), showing the interior wall of the amphora where calcareous concretions and rests of waterproofing material (black color) can be observed; c) Tarraconensian sample A-Tar-32 (non-desalinated).

Figure 3. Polarizing light microscopy (PLOM) and Fluorescence optical microscopy (FLOM) of ceramic amphorae. a) PLOM image (crossed nicols, XN) of thin section of Italic amphora A-Ibe-31 fired <800ºC; b) same image under FLOM; c) PLOM image (XN) of thin section of Italic amphora A-Ita-15 fired >900ºC; d) same image under FLOM. e) PLOM image (XN) of thin section of Tarraconensian amphora A-Tar-32 fired 800ºC; f) same image under FLOM. Qtz: quartz; An: anorthite; Di: diopside; Hb: hornblende; Fd: K-Na feldspar

Figure 4. X-ray diffraction patterns (XRD) of the archaeological ceramic amphorae. Iberian amphorae a) desalinated; b) Non desalinated; Italic amphorae: c) desalinated; d) non desalinated; Tarraconensian amphorae: e) desalinated; f) Non desalinated.

Figure 5. Concentration of soluble salts (%) obtained with ion chromatography. a) sal concentration (%) in desalinated and non desalinated amphorae. b) Concentration of chlorides, sulfates and nitrates (mg/l) in desalinated and non desalinated amphorae.

Figure 6. SEM-EDS analyses of the inner side of the flakes over the ceramic amphorae: a) SEM image of gypsum crystals on sample A-Ibe-31; non desalinated Iberian amphora; b) SEM image of gypsum crystals with fragments of ceramic on the tips of the crystals in sample A-Ibe-31; (c) EDS analyses of calcium, sulphur and oxygen (gypsum).

Figure 7. SEM-EDS analyses of the inner side of the flakes over the ceramic amphorae: a) signs of crystallization processes on sample A-Tar-32; b) EDS analyses of iron and sulphur (pyrites); c) signs of dissolution processes on sample A-Tar-32; non desalinated Tarraconensian sample; d) EDS analyses of iron, sulphur and oxygen (iron sulfates).

Figure 8. Pore size distribution curves obtained with mercury intrusion porosimetry in the Iberian (a); Italic (b) and Tarraconensian (c) ceramic amphorae fragments.