



A review of available analytical methods to detect ancient salt production

L. Alessandri ^{a,b,*}, G. Sottili ^c, C. Belardelli ^d

^a Sapienza Università di Roma, Dipartimento di Scienze dell'Antichità, Italy

^b University of Groningen, Groningen Institute of Archaeology, the Netherlands

^c Sapienza Università di Roma, Dipartimento di Scienze della Terra, Italy

^d Istituto Italiano di Preistoria e Protostoria, Italy

ARTICLE INFO

Handling editor: I Hendy

1. Introduction

In ancient historical records, the significance of salt (NaCl) has consistently held considerable prominence. Consider, for instance, its pivotal role in the genesis and evolution of the city of Rome (Giovannini, 1985). According to Dionysius of Halicarnassus (*Roman Antiquities*, 2.53–55), one of the first wars undertaken by Romulus was against Veii, also for control of the saltworks located at the mouth of the Tiber River, which were then controlled by that city. Venice owes a substantial portion of its early growth to the trade in salt, an essential commodity sourced from diverse corners of the Mediterranean (Hocquet, 1979, 2022). Unfortunately, salt is also highly soluble in water; therefore, its presence is difficult to prove. Research on the methods of salt production, trade, and consumption in antiquity has long suffered from enforced oblivion due to the difficulty of identifying its traces in the archaeological record. In the past two decades, the field of archaeology has witnessed a proliferation of sophisticated methodologies derived from the so-called hard sciences. Physics and chemistry have offered the possibility, if not to directly identify salt crystals, at least to identify their proxies, understood as the physicochemical consequences of their presence. Various tools and methods have been applied to case studies, with differing degrees of success. The primary aim of this contribution is to present a state-of-the-art review (Booth et al., 2022; Efron and Ravid, 2018) of these methods, elucidating the strengths and shortcomings inherent to each approach. The intention is to provide an overview of the subject to facilitate the choice of the appropriate analytical method for researchers who need it and to suggest some new methodological approaches to the scientific community that could advance the field of study.

1.1. The briquetage and saltern salt production techniques

Since prehistory, inland salt lakes, seawater and salt exploitation from water-soluble mineral deposits (evaporites) were the main sources of salt (NaCl). Overall, the development of salt production techniques by either solar (saltern technique) or artificial (briquetage technique) seawater evaporation changed over the centuries and from location to location, as these were controlled by several factors. Although a full review of the complex interaction between climate conditions and the evolution over time of salt exploitation techniques is beyond the aim of the present review, we remark that for specific chronological and geographical contexts (Europe), previous works (e.g. Harding, 2014) hypothesized the existence of “salt production zones” sharing relatively homogeneous climatic conditions and a predominant technology (saltern or briquetage).

1.1.1. The saltern technique

In particular, salt production by solar seawater evaporation was a seasonal activity, just like agricultural productions, as it depends on climatic conditions such as solar intensity (radiation), atmosphere and water temperatures, wind velocity and direction, relative humidity and rainfall regime (Vyas et al., 2022). In fact, seawater evaporation is negligible when air temperature is below 10 °C, while the salt productivity, which can be expressed as the mass of salt per unit of free water surface, increases significantly at air temperatures from 20 °C to 45 °C (Vyas et al., 2022). Also, the direction and speed of the wind is a crucial factor as winds blowing from the sea are vapour-saturated and, thus, unable to absorb water vapour from brines (Vyas et al., 2022).

* Corresponding author. Sapienza Università di Roma, Dipartimento di Scienze dell'Antichità, Italy.

E-mail addresses: luca.alessandri@uniroma1.it, l.alessandri@rug.nl (L. Alessandri).

<https://doi.org/10.1016/j.quascirev.2024.108809>

Received 27 March 2024; Received in revised form 18 June 2024; Accepted 29 June 2024

Available online 9 July 2024

0277-3791/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1.1.2. The briquetage technique

Artificial evaporation of salt water by the briquetage method (Cassen and Weller, 2013; Harding, 2013, 2021), although quite laborious, was far less hampered by such unfavourable climatic conditions. The briquetage method essentially involves artificially evaporating brine using fire. However, even in this scenario, it is probable that initial evaporation occurred using solar radiation. This allowed, on one hand, to reduce the subsequently required energy for artificially heating the obtained brine; on the other hand, it enabled in some cases the removal of some chemical substances (such as calcium carbonate and calcium sulfate, among others) that precipitated before sodium chloride. Enrichment could be achieved through several methods. Some of the most common practices included evaporating saltwater in specialized basins or increasing the salt content of sandy soils by seawater irrigation. The sandy soil was then placed in raised containers equipped with filters and made of plant substances. In certain instances, items originally designed for alternative functions were adapted for this role, as seen with the repurposing of a canoe at the Maya site of Paynes Creek National Park (McKillop et al., 2014). Afterwards, additional water, either salted or fresh, was poured over the sand, and this water was subsequently collected after becoming enriched with salt as it passed through the sand (Antonites, 2016; Cassen and Weller, 2013; Reina and Monaghan, 1981).

2. Methods

The bibliographic research progressed through five stages.

Phase 1. : Bibliographic searches were conducted using the query string:

(salt OR NaCl OR halite) and (ancient OR prehistory OR Bronze Age OR Iron Age OR protohistory OR Roman OR medieval) on three search engines: Scopus, Web of Science, and Google Scholar.

The results from Scopus were filtered by narrowing the searches to the field of Arts and Humanities. The results from Web of Science were filtered using the Citation Topics Micro algorithm and the query string Archaeometry. As for Google Scholar, the first 200 results were extracted.

Subsequently, duplicates were removed (Table 1), resulting in a total of 383 contributions (Table S1).

Phase 2. After having removed the duplicates, all the abstracts were analysed. The manuscript which did not present archaeometry approaches to the detection of ancient salt presence were eliminated. The total number of remaining manuscripts was 11 (Table S2).

Phase 3. In the subsequent phase, the reference lists of each of the 11 surviving manuscripts were examined, aiming to identify additional manuscripts possessing the sought-after characteristics. We added 19 more manuscripts whose abstracts matched the characteristics we were looking for (Table S3).

Phase 4. In this phase we checked the papers that cited the ones found in phases 2 and 3 using Google Scholar search engine. Again, we added 9 more manuscripts whose abstracts matched the characteristics we were looking for (Table S4).

Phase 5. We added 2 manuscripts from our personal knowledge (Table S5).

3. Synthesis of the selected papers

Here, we provide a synthesis of the methods and results from the 41 identified contributions (Table S6, Fig. 1), classifying them into categories concerning ceramics, soils, and organic/inorganic residues.

Table 1

Summary of the results from the five phases of bibliographic research.

Search parameters	Where	Scopus	Web of Science	Google Scholar
(salt OR NaCl OR halite) and (ancient OR prehistory OR Bronze Age OR Iron Age OR protohistory OR Roman OR medieval)	Article title, Abstract, Author Keywords	413	2137	1,190,000
Search filter				
Limited to Arts and Humanities subject area		108		
Citation Topics Meso: Archaeometry			259	
Citation Topics Micro: Archaeometry			104	
First 200 results				200
Subtotal without duplicates (end of Phase 1)		383		
Appraisal				
Subtotal after abstract appraisal (Phase 2)		11 (A)		
Bibliographical research on A (with abstract appraisal) (Phase 3)		19 (B)		
Manuscripts that cite A and/or B (Google S., with abstract appraisal) (Phase 4)		9 (C)		
Personal knowledge (Phase 5)		2 (D)		
TOTAL (A-D)		41		

3.1. Analyses on ceramic

Many articles are dedicated to demonstrating the presence of salt in ceramic containers, mainly by identifying the molecules of chlorine and/or sodium that might have potentially become trapped within the ceramic fabric but also by utilizing other chemical elements found in salt deposits as proxies.

In the 1970s, some of the pioneering chemical analyses on containers for salt production were carried out at specific Polish archaeological sites. At the Barycz site (Lengyel culture, 5000-3400 BCE), analyses revealed a NaCl percentage of 1.25% in briquetage containers, compared to 0.55% in common ceramics and 0.01% in the surrounding sediments. The chemical analyses of some artifacts from Biskupice and Kraków-Kurdwanów (Lausitz culture, 1400-400 BCE) show a slightly higher content of sodium compounds in their composition compared to the common ceramics from the same site. The Biskupice briquetage contains 0.90% Na₂O, and the fragment of the common vessel from the same location only 0.70%. The common ceramics from Kraków-Kurdwanów contained 0.45% Na₂O, and the briquetage 0.48, 0.50, and 0.60%. Finally, the briquetage ceramics from Wieliczka's XI site exhibit an average NaCl content of 0.8%, in contrast to common ceramics that do not exceed 0.26% (Jodłowski, 1977).

At the 31st International Symposium on Archaeometry, Aloupi et al. presented a poster suggesting the utilization of Bromine (Br) as an indicator for the interaction between seawater, sea-salt, and ceramic or lithic artifacts or structures. This choice stems from the significantly higher concentration of Bromine in seawater (around 65–70 ppm) compared to its levels in the Earth's crust and rivers (only 4.0 and 0.02 ppm, respectively). In salt and brine, Bromine concentrations can exceed 2500 ppm. The efficacy of this approach was assessed through X-Ray Fluorescence (XRF) analysis on ceramics from the Greek site of Eleftherna, yielding promising results, as reported by the authors. However, detailed data from this study were not available in the abstract (Aloupi et al., 1998).

The method was subsequently elaborated upon in more detail in a later article. In this paper, in addition to reiterating the motivations

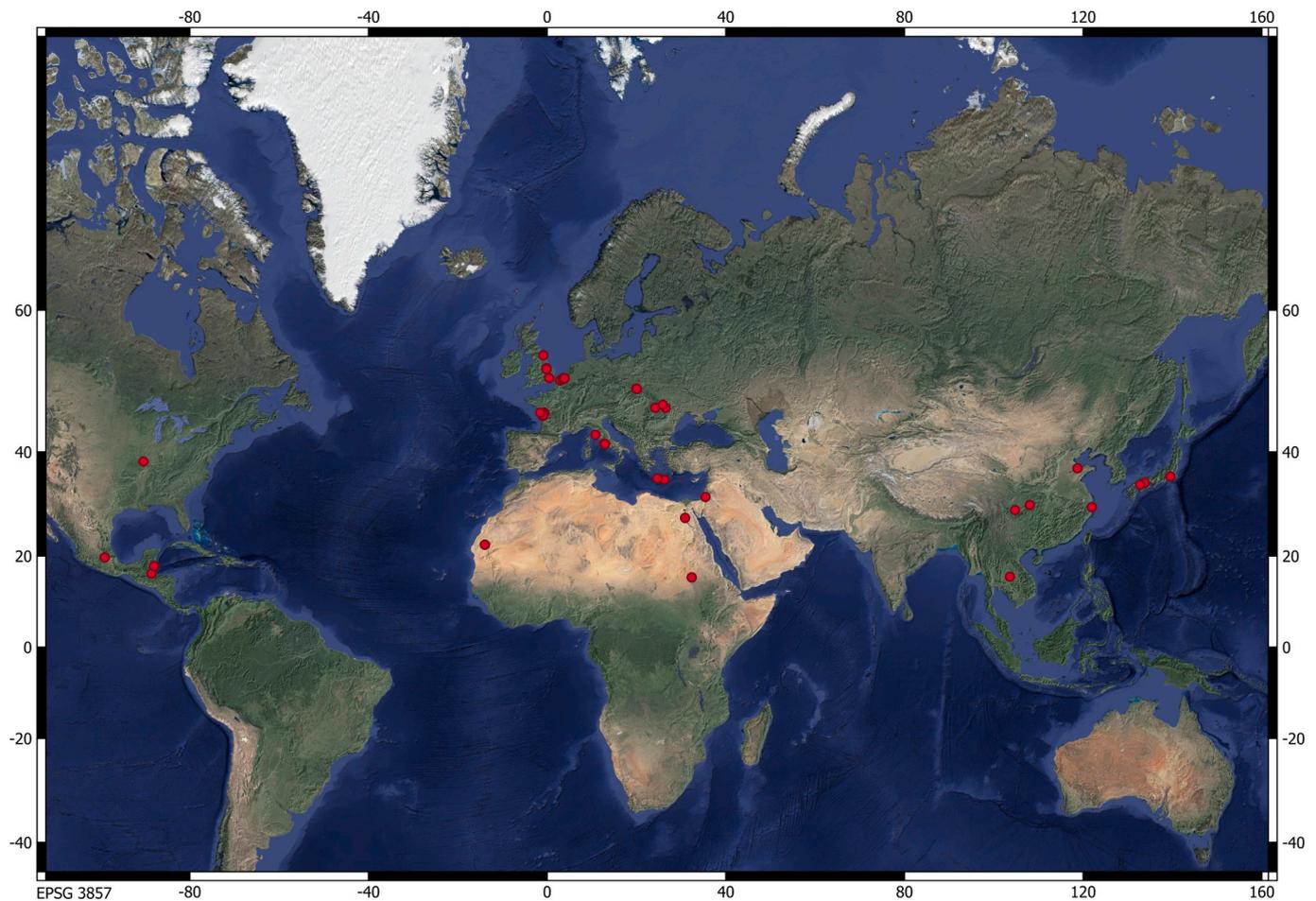


Fig. 1. Geographical distribution of the sites considered in the text. Maps at a larger scale with site labels are in the supplementary data (Figs. S1 and S2).

outlined in the 1998 abstract, the authors emphasize that although Bromine is not the compound showing the largest difference between marine and terrestrial concentrations, it is generally absent from the clays used in ceramic production, unlike Chlorine. In fact, the concentration of the latter in some ceramics that had not come into contact with seawater was found to be approximately 10 times higher than terrestrial levels (2000–6000 ppm). This finding underscores the challenge of using Chlorine as a tracer for seawater. Another set of experiments involved modern containers in which seawater had been evaporated, subsequently rinsed with distilled water. Here the XRF revealed Chlorine and Bromine concentrations of 10,000–15,000 ppm and 100–150 ppm, respectively. Furthermore, a separate analysis focused on ceramic fragments from the Iron Age briquetage site of Cowbit (England). The Bromine values for the six analysed samples ranged from 20 to 36 ppm, with an average of 25 ppm. While these values suggest exposure to seawater, the authors acknowledge that the method cannot definitively indicate salt production, as contact may have occurred during vessel manufacturing, usage, or post-depositional phases. However, they suggest that this challenge could be partly addressed by measuring similar concentrations in local soil samples (Aloupi et al., 2000).

Later, the same approach was put to the test using ceramic sherds originating from the South-Western Fens of Lincolnshire (England) which date back to the Iron Age and the Roman period. Some of these pottery fragments were associated with the briquetage process, while others, which were clearly unrelated to salt production, served as a control group. Although the specific outcomes of the analysis were not detailed in the referenced article, it was affirmed that the experiment yielded positive results. It was asserted that the bromine concentration, relative to its depth from the ceramic surface, could be considered a

reliable indicator of contact with sea salt. It is noteworthy that the same article also proposes an alternative method for achieving the same objective, involving the detection of ancient DNA (aDNA) from Halobacteria (microorganisms that thrive in high-salinity water) within the ceramic fabric. However, it should be emphasized that this particular technique has not yet undergone testing (Siotis and Aloupi-Siotis, 2020).

O. Weller, one of the foremost experts in ancient salt production, in the framework of his PhD conducted a series of XRF analyses on six Late Neolithic (3400–2900 BCE) small truncated-cone vessels from the ditches in the Champ-Durand enclosure (Nieul-sur-l'Autise, Vendée, France), near the Marais poitevin marshes, and found a chlorine (Cl) concentration 2 to 20 times higher than in contemporary domestic productions (Weller, 2000, 2002).

Later, using the same methodology, another 61 samples from eight similar French sites were analysed. In four out of the six sites (Champ-Durand, La Mastine, L'Angle, Couture), the analyses revealed a chlorine concentration at least two times higher than that found in domestic ceramics and at least five times higher than in the surrounding soil. The analyses conducted on La Sauzaie pottery yielded negative results; however, the furnace fragment returned a chlorine concentration value 5–10 times higher than that of domestic ceramics, confirming the connection of this structure with salt production. The only two measurements made at Coteau de Montigné did not allow for a conclusive decision, as the detection threshold was too close. Finally, the values from the last two sites (La Tricherie in Beaumont and Ferteval in Thouars) are very similar and did not support the salt hypothesis. Further observations were conducted on the results of the 35 samples from Champ-Durand, aimed at discerning the impact of additional variables: the position of the analysed fragment in relation to the vessel,

the burial depth of the fragment, and the condition of the internal surface. As previously observed, higher chlorine concentrations are located at the edges of the vessels, followed by the bottoms and then the walls. According to the authors, this phenomenon is attributed to both brine overflow during firing and, more significantly, the capillary rise of saltwater into the ceramic fabric up to the container's edge. Concerning burial depths, higher concentrations of chlorine are associated with reduced infiltration and stagnation of rainwater. Consequently, chlorine levels will be lower on the surface due to rainfall and at the bottom of the pits due to water stagnation. Ultimately, a diminished retention of chloride ions and their compounds was noted when the surface exhibited scaling and corrosion, thereby facilitating post-depositional dissolution and ion exchange processes. This phenomenon might also account for the extremely low chloride percentage in the ceramics from La Sauzaie, where the salt container ceramics display significant porosity due to the substantial amount of organic temper used in the ceramic fabric (Ard and Weller, 2012; Cassen and Weller, 2013).

At the Chinese site of Zhongba (China, 2000 and 200 BCE) some analyses using a Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) conducted on two suspected briquetage potsherds revealed that the concentrations of both sodium (Na) and chlorine (Cl) are at their highest on the interior surface of the ceramic artifacts and exhibit a distinct gradient with decreasing concentrations as one moves towards the exterior of the sherds. The author suggested that during the brine boiling process, sodium and chlorine precipitate from the solution and infiltrate the vessel wall. However, variations in diffusion rates result in distinct distributions of Na and Cl concentrations within the innermost 2.1 mm of the sherds (Flad et al., 2005).

A particular case is represented by the site dating to the Late Bronze Age of Pelliccione (also known as P13, Italy), from which some vessel bottoms have been recovered, displaying the so-called "salt-colour": a spectrum of pinks, whites, greys, and lavender on the inner surface, possibly resulting from direct contact with brine at moderately high temperatures (Nijboer et al., 2006).

In 2011, Horiuchi et al. suggested that chloride anions could be captured within the pottery matrix. This is because the pottery matrix, containing silicates, might act as an ion exchanger. Consequently, strongly bound Cl^- could have survived the dissolving action of meteoric waters. The authors proposed the use of an ammonium fluoride solution (NH_4F) as an extraction reagent to determine the quantity of chloride ions. To test the method, several vessels were analysed. One freshly made from a clay source where the original presence of salt could be excluded. Brine was boiled inside until salt precipitation occurred. Additionally, three fragments originated from the archaeological site of Hiroe-Hama, a known salt-making site dating back to 550–600 CE (Kurashiki, Okayama Prefecture, Japan). Excavators hypothesized that these fragments were used in salt production. Another set comprised three fragments of Jomon pottery (3000–2500 BCE) from Location 20 site on the campus of International Christian University (Tokyo, Japan) a settlement not involved in salt production. Finally, three types of ceramics from the Okiura site (Kamagari, Hiroshima Prefecture, Japan) were examined: fragments involved in salt production (500–600 CE), fragments not involved (300–800 CE), and fragments resembling salt-related pottery but lacking signs of secondary firing or flaking, for a total of twenty-three potsherds. Each fragment, prior to analysis, underwent a process simulating the dissolution and removal of salt from the surface by natural waters. In the fragments from Hiroe-Hama, chloride ions were identified in varying percentages depending on the analysed part of the vessel: higher concentrations were found in the middle sections and lower in the top sections, as observed also in the simulated vessel. From one of the three fragments from Location 20, which were not used for salt production, there is a concentration of Cl^- comparable to that found in the upper part of the simulated vessel. This has been interpreted as being due to the cooking of salty foods or the use of salt as a seasoning. In the potsherds from Okiura, generally, the vessels used in salt production show a higher concentration than the

others, although a clear demarcation line cannot be drawn. It also appears evident that the Cl^- concentration depends to some extent on the analysed part of the vessel (Horiuchi et al., 2011).

Later, the method was again tested by Raad et al. on forty-two samples, taken from some experimental vessels and from vessels from three different sites, both associated and non-associated with salt production: the prehistoric saline of Kimmswick (Missouri) in the USA and the salt production sites of Zhongba and Shuangwangcheng in China. Using the method proposed by Horiuchi et al., the analyses did not reveal a significant difference between the fragments likely used during salt production and the others, both in the archaeological and in the experimental vessels. Further, the SEM analysed on five salt-production potsherds and on one not used in the process, showed that Cl was evenly distributed in all samples, with no gradients from interior to exterior. Raad et al. conclude that the method proposed by Horiuchi lacks reliability, as the origin of bound chlorine could differ from salt production and might instead be intrinsic to the material of the vessel (Raad et al., 2014).

Some analyses were conducted on five Copper Age ceramic fragments believed to have played a role in salt production through the briquetage technique. These fragments were sourced from the Hălăbutoaia à Țolici and Salina de Cacica sites in Romania, with the primary objective of exploring their chemical composition and firing temperatures, both in the context of their initial production and subsequent utilization. The ceramic fragments were analysed through X-Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDX), Fourier Transformed Infrared Spectroscopy (FTIR), and Thermogravimetry/Differential Thermogravimetry/Difference Thermo Analysis (TG/DTG/DTA). The analyses not only confirmed local production but also revealed the presence of chlorine and a higher concentration of sodium exclusively within the darker section, located inside and at the bottom of the container where the firing occurred under reducing conditions. This phenomenon can be explained by the presence of cations in lower oxidation states that formed stable chloro-oxy-hydroxy complexes or less soluble hydrated chlorides. Conversely, the outer surfaces, characterized by a red colour indicative of firing in an oxidizing atmosphere, were effectively washed by meteoric and groundwater, resulting in the absence of any traces of salt. As for the temperature aspect, the impact of the second firing, which was carried out for salt production at around 360 °C, was amplified by the fluxing effect of the salt, thereby affecting the distribution of the coloured zones (red and dark grey). The primary firing temperature was estimated to fall within the range of 830–1000 °C (Sandu et al., 2012).

Another three potsherds (bases) from Hălăbutoaia à Țolici were subsequently analysed by Tencariu et al., and according to the authors, the results do not deviate much from the previous ones: two samples show the presence of chlorine and relatively high concentrations of sodium suggesting their use in the briquetage process. In the same contribution, the authors detail two experiments undertaken to produce salt using the briquetage technique. Subsequently, a vessel employed in the experiment underwent SEM-EDX analysis to ascertain the presence of sodium (Na) and chlorine (Cl) and the extent to which these elements had penetrated the ceramic fabric. The results revealed elevated concentrations of both elements on the inner surface of the ceramic. Internally, the chlorine concentration progressively diminished, becoming negligible beyond 2 mm from the inner surface (Tencariu et al., 2015).

In 2014, fifteen ceramic fragments from pottery believed to be associated with salt production at the Puntone di Scarlino - Campo da Gioco site underwent analysis using Optical Microscopy (OM), Polarised Light Microscopy (PLM), SEM-EDS, and (X-Ray Powder Diffraction) XRPD. The aim was to determine their chemical and physical properties, the temperature of the primary firing, and their origin, with the possibility of uncovering traces that could confirm salt production. No traces of NaCl were identified in the analysed fragments, but the authors emphasize that any potential traces could have been washed away by meteoric waters (Aranguren et al., 2014).

About 6000 ceramic samples from the entire Basin of Mexico underwent NAA analysis, leading to the identification of seven ceramic groups. Among these, two associated with the city-state of Xaltocan showed elevated sodium and potassium levels. Xaltocan was a city-state inhabited in the Postclassic period (950–1521 CE), in the Basin of Mexico. To interpret this anomaly and ascertain whether it resulted from post-depositional phenomena (such as salt production or the preservation or cooking of salted foods), a select number of samples underwent Laser Ablation-Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS) analyses and some experiments were conducted. The latter involved varying some parameters (clay, temper, water, and firing) in the pottery making process to determine the behaviour of sodium in raw clay and ceramics. The experiments yielded some interesting results. Among the samples treated with brine before firing, it appears that sodium migrated towards the surface of the ceramic fragment during drying and firing, especially at higher temperatures. Among the specimens soaked in brine after firing, ceramics fired at lower temperatures absorbed more sodium than those fired at higher temperatures. This is likely due to their lower degree of vitrification and higher porosity. In leaching experiments, it was observed that ceramics fired at lower temperatures experience a higher loss of sodium. Consequently, lower firing temperatures prove to be less effective in incorporating sodium into the ceramic structure. Additionally, through rinsing, nearly all of the sodium introduced by repeated saline soakings of fired tiles (those not treated with brine before firing) was eliminated. As for the LA-ICP-MS analyses, the results indicate that the temper and natural inclusions in the ceramics played a more significant role in contributing sodium but less potassium to their chemical composition, as inferred from the Neutron Activation Analysis (NAA). Based on all this data, the authors propose that the unusual levels of sodium and potassium in Xaltocan ceramics are likely not a result of post-depositional processes but rather stem from their presence in the original clay and/or the inclusion of saltwater during the manufacturing of the artifacts (Stoner et al., 2014).

At the site of Batardières 2, on the western Atlantic coast of France, a single kiln associated with some ceramic fragments typical of the European briquetage has been discovered. To confirm the involvement of the structure in salt production, chemical analyses were performed using XRF, on three potsherds. Two of them were recovered inside the kiln. One, not involved in the supposed briquetage, came from outside the hearth and was used together with a soil sample as reference. Concentrations of both chlorine and bromine were examined. The results have shown that the chlorine and bromine percentages within the ceramic fragments from the kiln are two to five times higher compared to those observed in the soil sample and the ceramic retrieved outside the kiln. Radiocarbon dating of a charcoal sample placed the structure's origin at the onset of the Bronze Age (Large et al., 2015).

In the Italian peninsula, in *Latium* region, the sole specimens of ceramic pedestals that are typically linked to salt production have been found in contexts from the Middle Bronze Age at the Caprolace site (Sabaudia). An analysis was then conducted on certain potsherds from the same contexts using SEM-EDS and Electron Micro Probe Analyzer (EMPA) techniques to uncover any indications of their involvement in the salt production process. Additionally, other fragments from the same site, dating to the Middle Bronze Age but slightly later, were subjected to analyses due to their discovery in contexts primarily yielding reddish jars. Following the approach proposed in Flad et al., (2005), the authors investigated the percentage difference of Na and Cl within the ceramic profiles by conducting transects between the inner and outer surfaces. However, due to inconclusive results, a closer examination was carried out on the composition and characteristics of salt crystals discovered within the ceramic fabric of a single specimen. Given that the morphology of NaCl (sodium chloride) crystals is influenced by the extent of supersaturation in the salt solution and/or the cooling rates, the presence or absence of the pure cubic form of NaCl, which occurs during gradual cooling, alongside the simultaneous presence of amorphous NaCl, formed during extremely rapid cooling, led the authors to

posit the potential separation or complete evaporation of the supersaturated NaCl solution within the container. This hypothesis aligns with the final stages of the salt production process (briquetage) but also corresponds to the production of *liquamen*, as detailed in the *Geoponica* (Alessandri et al., 2019).

At the Băile Figa site (Beclean town, Romania), analyses were conducted on eleven Bronze Age ceramic fragments with the specific purpose of investigating their utilization within the context of the salt extraction process, a hypothesis already well-founded at the site. These ceramic fragments were analysed using SEM-EDX. Those displaying traces of carbon were subjected to further examination via micro-FTIR. Nearly all the fragments exhibited varying percentages of Na and Cl traces, with one of them even revealing macroscopically visible salt crystals. The authors attributed the lower percentages of Na and Cl to interactions with the soil, while the higher concentrations were linked to the containers' use in the salt production process. Furthermore, the analyses confirmed that, with a single exception, all the vessels were produced in kilns that reached temperatures exceeding 800 °C in a reducing atmosphere (Vasilache et al., 2020).

At the Early Neolithic site of Street House in Loftus (England) Phase 2 evidence has been identified as a briquetage workshop. The evidence includes three areas of burnt material interpreted as hearths, along with some possible props or supports for oven furniture, and ceramic vessels likely for brine placed around them. Adjacent to the oven, there was also a pit with a clay lining interpreted as a tank for storing concentrated brine solution before the boiling process. To validate this hypothesis, some ceramic samples were analysed using XRF, which revealed, according to the authors, significant variations in the levels of chlorine (Sherlock, 2021).

In the heart of the Western Sahara, near the Lejuad XVII rockshelter site, three ceramic fragments dated through thermoluminescence between the ninth and third century BCE have been recovered. To understand their function, a comprehensive array of chemical analyses was carried out, including OM, SEM-EDS, Wavelength Dispersive-X-Ray Fluorescence Spectroscopy (WD-XRF), XRD, and Thermogravimetric Analysis (TGA). Additionally, X-ray micro-computed tomography (μ -CT) was employed to provide a clearer understanding of the ceramics' fabric. Despite the extensive data collected, no proxies of salt (NaCl) were found. However, the physical and chemical characteristics of the fragments, along with their distinctiveness from contemporary household ceramics, led the researchers to hypothesize that they were used for boiling brine to extract salt. Features such as the addition of mineral and organic temper, the use of a coarse fabric, and thick walls are typical of ceramics designed to withstand moderate thermal shocks for prolonged periods. Moreover, the relatively low firing temperature (not exceeding 900 °C) ruled out the possibility of these ceramics being crucibles, which was another hypothesis considered (Larreina-García et al., 2021).

In some locations along the Belgian and Dutch coastlines (Leffing in Belgium; Koudekerke, Ritthem, Aardenburg, 's-Heer Abtskerke, 's Gravenpolder and Middelburg in Netherlands), substantial deposits of vitrified ceramic material dated from I to III century CE have been discovered, which clearly cannot be attributed to pottery vessels. Through analyses conducted using techniques such as PLM, SEM-EDS, and XRD, the formation process of these slag deposits has been elucidated. These findings have been interpreted as the remnants of furnace bottoms, vitrified due to extremely high temperatures and periodically replaced. However, the clay available in the area lacks sufficient CaO, making it inherently resistant to vitrification. Therefore, the vitrification process must have occurred due to the presence of elevated concentrations of external fluxes in the environment, which effectively facilitated the process by lowering the melting point. Since vitrification is an unintended consequence, the origin of these external fluxes must have been located within the furnaces themselves. This could be attributed to the type of fuel used (wood, peat, sources of Ca, K) or the presence of brine (a source of Na and Mg). While the focus of the contribution's research question was related to the use and role of these slag materials

in the briquetage process, which was already well-documented at these sites, what is of particular interest here is the inverse reasoning: in the context of Ca-poor clay, the presence of vitrified ceramics within the furnaces might imply the deliberate addition of external fluxes, a phenomenon that can be effectively explained by the briquetage process (Dekoninck et al., 2022).

In the necropolis of the site of Ban Muang Bua (Thailand, Bronze Age), some funerary urns have been characterized using SEM-EDS, Proton Induced X-Ray Emission Spectroscopy (PIXE) and Synchrotron Radiation X-ray Tomographic Microscopy (SR XTM) primarily to investigate manufacturing techniques and origin. The presence in some samples of iron-rich kaolin clay in the ceramic fabric, typical of salt deposits in the area, has been considered by the authors as evidence of salt processing (Boonruang et al., 2022).

3.2. Analyses on soil

In the context of soil analyses as well, the primary objective is often to detect the chemical constituents linked to salt production rather than the salt itself (halite), which, due to its high solubility, is seldom preserved.

Some of the initial soil analyses were conducted in some Polish sites. In the Wieliczka's site XI (La Tène D1 – phase B1a roman period, 125 BCE – 30 CE), the analyses of the internal surface of a supposed settling basin indicate a NaCl content of 0.15%, whereas the surrounding soil averages only 0.02%. The filling soil inside the storing and/or decantation basin in Wieliczka's site IV (950–1100 CE) showed a NaCl content of 0.1%, in contrast to the surrounding soil, which exhibited only 0.008% NaCl (Jodłowski, 1977).

In the “tis Ouranias to Froudi” cave, on the island of Crete, the exceptional environmental conditions have enabled the remarkable preservation of crystals in the archaeological layers. The crystals, which have been found in undisturbed Minoan layers, upon undergoing chemical analysis (not further specified), were identified as NaCl and the iodine content revealed its marine origin (Kopaka and Chaniotakis, 2003).

At the Chinese site of Zhongba (China, 2000 and 200 BCE), soil layers linked to the presumed salt production through the briquetage technique were chemically analysed (XRF) in comparison to the impurities present in the local salt and brine deposits, primarily consisting of calcium, magnesium, and potassium. Control samples were taken from soils unrelated to this technique. The findings revealed a notably elevated presence of magnesium and calcium in both the soils and the structures associated with briquetage, such as the pits (Flad et al., 2005).

Later, from one of the archaeological test pits conducted at the site, 201 soil samples were collected from a section covering a time span from around 3000 to 1981. The aim was to identify, through ICP-MS and Inductively coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analysis, the ratios between the concentrations of Na, Ca, and Mg. The authors hypothesize that during the final stage of salt production, some impurities like $MgCl_2$ and $CaCl_2$ remained within the salt since, being more soluble than NaCl, they would precipitate later. As these compounds are harmful to health and have an unpleasant taste, they needed to be removed. To achieve this, it is likely that the salt was rinsed again using a saturated solution of NaCl and then boiled once more. The excess liquid, enriched with Mg and Ca, would be discarded. Thus, layers enriched with these two elements would likely indicate salt production activities, together with a decrease in the Na content. Ca was chosen as a proxy over Mg due to its greater stability. The findings reveal 21 periods characterized by a higher percentage of Ca compared to Na, suggesting active periods, and 14 periods with higher Na levels than Ca, indicating declines in salt production activity. Notably, 7 out of these 14 periods align with flood layers. Similar analyses were carried out at Yuxi, a non-salt production site located approximately 40 km from Zhongba. Here, the samples (47 in total) revealed a distinct pattern: while positive correlations were observable, negative ones were not. Moreover, there

was no clear correlation between higher Na content and lower Ca content in samples from flood layers (Zhu et al., 2008).

In the natural reserve of Stanford Wharf (United Kingdom) extensive archaeological fieldworks brought to light remains associated with briquetage dating from the Iron Age (400-100 BCE) to the late Roman period (410 CE). An extensive campaign of chemical analyses using SEM-EDS, FTIR and (Magnetic Susceptibility) MS was designed to enhance the interpretation of the finds. So called “white nodules”, identified as vesicular siliceous glass bodies, were found within the soil. Analyses indicate that these nodules are a result of fuel ash formed during the combustion of monocotyledonous plants. Two implications arise from this: first, that plants gathered from nearby marshes were employed as fuel, and second, that the resulting ash, which was rich in salt, was used by blending it with seawater to create brine. At the same site, researchers also examined some “green glaze”, which are strongly heated silicate glass pieces attached to the briquetage. They contained higher amounts of sodium, phosphorus, and iron compared to the fragments they were attached to. The authors propose that this is a result of the vessel's contact with the flame: iron causing the greenish colour and phosphorus deriving from the fuel. Although sodium levels are unusually high, their concentration decreases with distance from the glaze surface. This constitutes an additional indication of the containers being used in salt production. Lastly, traces of zinc were discovered, possibly attributed to the marine origin of the plants used as fuel. Within a Late Roman building, analyses conducted on the floor levels have revealed a very high enrichment of lead associated with ‘iron’ staining of the floors, suggesting the use of lead containers in the salt production process during this period (Macphail et al., 2012).

The aDNA of two halophilic archaea (*Natronomonas* and *Halorubrum*) has been identified in subsurface halite deposits in Death Valley, California (USA), dating back to 22,000 to 34,000 years BP (Sankaranarayanan et al., 2014). This demonstrates the long-term survival of halophilic archaea in ancient halite and could open the door to new applications in the field of salt archaeology (Afouda et al., 2020; McGenity, 2014).

The Maya site of Chan b'i in Belize is characterized by the almost exclusive presence of evidence related to briquetage. The site, dating to the Early Classic period (300–600 CE), was once situated on dry land but is now submerged. Soil samples were collected at 44 cm depth from the water surface, in a peat environment, for chemical analysis (ICP-MS), aiming to identify traces of anthropic activities. However, the results revealed significant variations in nine elements (P, Sr, Na, Mg, Al, K, Ca, Mn, and Fe) that have been linked to salt production. The observed phosphorus peak and the presence of magnesium and potassium in an area adjacent to a wooden structure suggested the existence of a designated disposal area for residues generated during the cleaning of zones where briquetage was employed, especially ash and charcoal. Additionally, near the same wooden structure, in an area abundant with remains of briquetage vessels, another concentration of potassium, aluminium, and iron has been identified. The authors suggest that this might be attributed to the mixture of sand used as a tempering agent within the briquetage vessels and the ashes resulting from fires (Sills et al., 2016).

In the Maya site of Marco Gonzalez (Ambergris Caye, Belize), salt-production activities are supposed to have taken place in the Late Classic period (600–750 CE). Soil chemistry and micromorphology analyses (SEM-EDS, XRF) has been utilized to verify the existence of briquetage and potentially uncover additional clues regarding the chaîne-opératoire. Six out of the seven highest salinity bulk soil samples contain ash, charcoal, and/or burnt residues from processing levels. The presence of unweathered ash deposits and burnt tidal flat sediments, which inherently contain soluble salts, suggests that the salinity variations observed across these samples likely arise from a mix of natural enrichment processes and human activities, particularly the collection of saline sediments to obtain brine (Graham et al., 2017; Macphail et al., 2017).

In the sites of Hălăbutoaia (Țolici) and Poiana Slatinei (Lunca) in Romania, microscopic analyses have revealed the presence of gypsum crystals in select soil samples dating back to the Early Neolithic and Copper Age. A subset of the samples also underwent SEM-EDS analysis, aiming to detect halite crystals that were not visible through microscopy. In Țolici, the analyses demonstrated the simultaneous presence of sodium and chlorine solely within the ash accumulations located in the lower strata, along with potassium and magnesium. Likewise, in Lunca, sodium, chlorine, and potassium elements were detected in deposits characterized mainly by ash and ceramic fragments. These findings, together with other pieces of evidence, have been interpreted as remnants of salt processing (Sordoillet et al., 2018).

In 2015, the Puntone di Scarlino – Campo da Gioco site (Tuscany, Italy) underwent geomagnetic investigations (MS), and excavation trenches were opened, revealing extensive soil dumping areas, layers comprising fragments of reddish jars, commonly associated with briquetage, as well as fireplaces and pits. Chemical analyses using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) were carried out on various soil samples to confirm the existence of salt production facilities and reconstruct their chaîne-opératoire. Analyses on samples from one of these pits indicated a notable concentration of magnesium, sodium, chlorine, and boron, suggesting the presence of solutions originating from the sea. The presence of ferroan-magnesian calcites in the pit fill points to prolonged existence of anoxic conditions. All these data suggested the use of the pit as a brine collector. High concentrations of Mg, K, S, and B were also observed in the dump area, which has been interpreted as the residual of the disposal of the “mother liquor”. The latter forms if, after the precipitation of NaCl, the evaporation process is halted before the so-called bitterns (which would add an unpleasant taste to the salt) also precipitate, and the liquid is decanted (Sevink et al., 2021a).

On the same site, physical-chemical (OM, ICP-OES, XRD, SEM-EDS) and aDNA analyses were carried out on soil samples obtained from within a pit, which was hypothesized to be linked to salt production. In this instance, the article’s primary focus was on dating briquetage salt production activities. Within the scope of the research, ancient DNA analyses were carried out; however, these analyses did not yield definitive results due to the absence of halophilic bacteria in the pit (Sevink et al., 2021b).

In the Neolithic site of Daxie (China), the so-called Phase 2 is characterized by 27 furnaces and numerous pottery fragments interpreted as remnants of briquetage. Radiocarbon dates for this phase range from 2469 to 2293. To reconstruct the chaîne-opératoire in detail, soil samples and sediment cores have been taken. Specifically, 37 samples were taken from one site profile (T0705S) and analysed using ICP-OES to measure alkaline earth metals, Sr, and Ba. Strontium is typically found in marine environments, while Barium indicates terrestrial settings. Of particular interest are the levels of these elements in cultural phases 5 and 6 of profile T0705S, where the absence of foraminifera and low Sr values suggest a terrestrial environment. Normally, this would correspond to high Barium concentrations, yet they are surprisingly low. Authors attribute this anomaly to the brine-enrichment process, which involves leaching soils with a significant amount of seawater, known to remove Ba. Moreover, the occurrence of amorphous CaCO₃ in the foraminiferal tests sampled from the discharged salty soils, as opposed to the natural deposits, prompts the authors to hypothesize that the salty soils were allowed to air-dry prior to the leaching phase. During this process, evaporation would have caused CaCO₃ to precipitate within the foraminiferal test chambers, and the calcium carbonate would then have acted as a barrier, thus preventing seawater from entering during the subsequent leaching stage. This initial evaporation process would also be confirmed by the presence of CaCO₃ nodules in the salty soils (Zheng et al., 2023).

At the archaeological site known as 16-D-4B in Al Khiday (Sudan) dating back to the Middle Mesolithic period, numerous waste pits from the village were discovered. These pits contained preserved fish bones

with traces of halite. SEM-EDS and XRPD analyses were then conducted on some bone and soil samples to understand the reason for this association. The analyses showed that halite is abundant in the fish bones and is pure (NaCl). Additionally, halite was observed on the inner surface of certain ceramic fragments and in the sediment filling the pits, albeit at lower concentrations (0.14–0.43 wt%) compared to the ceramic samples and fish bones (in both cases exceeding 1 wt%). Notably, the concentration of halite in the sediment outside the pits was minimal (less than 0.01 wt%). Based on these findings, the researchers concluded that the crystallization of halite on the bones was not natural but the salt was deliberately added by Mesolithic peoples, presumably to preserve the fish (Maritan et al., 2018).

3.3. Analyses on residues

In extremely rare instances, the contents of ceramic vessels have been preserved, in varying quantities and states of preservation, allowing for analyses aimed at identifying their composition, both organic and inorganic.

At the Chinese site of Zhongba (China, 2000-200 BCE), residues found at the bottom of vessels likely used for brine evaporation (briquetage) revealed Calcium carbonate as the dominant compound (XRD). Other residues analysed from a 2000-year-old salt-boiling pan in Zigong (China) and from a modern saltworks in Yunyang exhibited the same chemical composition, highlighting calcium carbonate as one of the most indicative residues of salt production (Flad et al., 2005).

In a vessel recovered from the necropolis of Antinoupolis (Egypt), dating back to the 6th and 7th centuries CE, the optical microscope revealed the presence of halite crystals. Alongside them, chemical elements typically associated with evaporitic salt were also identified through SEM-EDX and XRD (e.g., gypsum and silvite). In addition, analyses targeting organic constituents, Direct Exposure-Mass Spectrometry (DE-MS) and Gas Chromatography – Mass Spectrometry (GC-MS), revealed the presence of lipid material from fish, together with fish scales, observed by OM and analysed by EDX and FTIR. This collectively led the researchers of the study to speculate that the vessel possibly contained salt-preserved fish (Ribechini et al., 2009).

At the Jericho site in Palestine, SEM analysis of residues found on the inner surface of a so-called “teapot” dating back to the Bronze Age has revealed the presence of NaCl (sodium chloride) crystals near the spout (Nigro et al., 2021).

4. The citation graph

Through the analysis of the citations contained within each paper, we created a citation graph with the aim of investigate the existence of clusters associated with the nationality (grouped by continents) or type (ceramic and soil) of the analysed artifacts. However, except for research on ancient DNA—a relatively isolated branch in the graph (n. 28 and 33; Sankaranarayanan et al., 2014; Siotis and Aloupi-Siotis, 2020, respectively), the graph does not reveal the presence of such clusters, demonstrating low values for both Modularity (0.27) and Average Clustering Coefficient (0.242). The latter further suggests a generally weakly connected network.

5. Discussion

5.1. Ceramic

Most analyses on ceramics assume that during the evaporation phase inside the kiln, the chemical elements present in the brine migrate into the ceramic fabric. The detection of these elements, primarily through SEM-EDS and XRF (Fig. 2), would then constitute a reliable indication of the salt production process through briquetage technique. Clearly, the most sought-after elements are sodium and chlorine. When analysing ceramic fabric for these elements, two approaches have been commonly

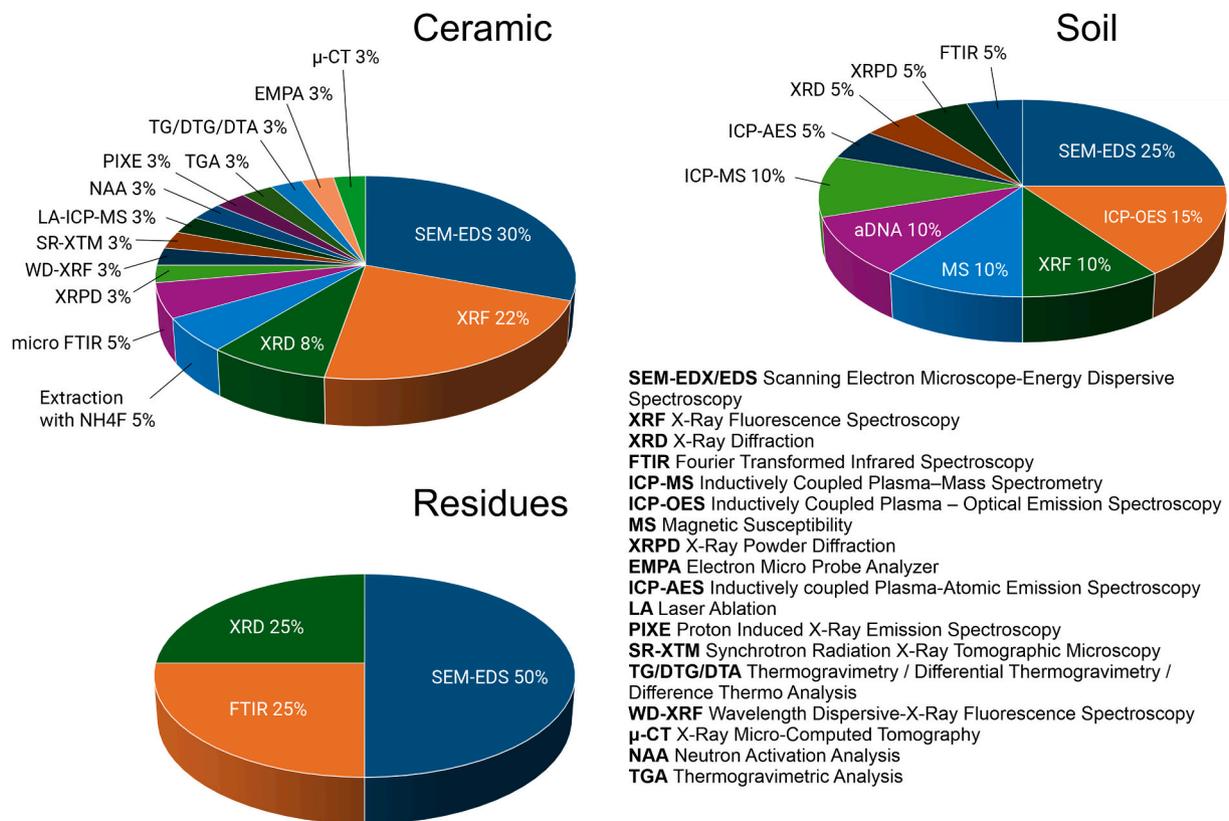


Fig. 2. Percentage of utilization of scientific instrumentation, in ceramic, soil and residues analyses.

adopted. The first involves comparing the sodium and chlorine percentages in suspected ceramic fragments with those measured in other contemporary ceramic fragments originating from the same or a nearby site. In this case, one would expect a higher concentration of Na and Cl in the fragments involved in the briquetage process (Jodłowski, 1977; Sandu et al., 2012; Sherlock, 2021; Tencariu et al., 2015; Vasilache et al., 2020). The second, less commonly utilized approach, involves measuring the variation in the percentage of these elements from the inner surface of the vessel towards the outer surface. In the case of briquetage, a concentration gradient that is higher at the inner surface and tends to decrease as one moves deeper into the vessel thickness is expected (Flad et al., 2005).

O. Weller, who extensively used the first approach, also highlighted some parameters that would influence this phenomenon and need to be considered during research design (Ard and Weller, 2012; Cassen and Weller, 2013; Weller, 2002). Firstly, the chlorine percentage somehow depends on the portion of the vessel analysed, as also observed by Horiuchi et al. (2011). Higher percentages of chlorine were found in the following order: on the rim, on the bottom, and finally in the walls. Additionally, the depth at which ceramics are found influences chlorine preservation due to meteoric and stagnant water that tends to "wash away" chemical components. For this reason, surface fragments or those near the surface and those at the bottom of pits where water stagnates are less suitable for analysis since the meteoric water can completely dissolve the Cl and Na (e.g. Aranguren et al., 2014; Sandu et al., 2012). Finally, ceramic porosity also plays a fundamental role, facilitating post-depositional dissolution of chemical elements trapped in the ceramic fabric.

Some scholars have raised objections to both approaches, arguing that chlorine naturally occurs in clay, so a portion of the chlorine detected in the analyses may already be present in the vessel at the time of manufacture (Raad et al., 2014; Stoner et al., 2014). To address this concern, the utilization of alternative elements as proxies has been

proposed, such as Bromine (Aloupi et al., 1998, 2000; Large et al., 2015; Siotis and Aloupi-Siotis, 2020) or Boron (Alessandri and Attema, 2022; Sevink et al., 2021a), which are found in significantly higher concentrations in seawater compared to terrestrial environments. However, strictly speaking, this would suggest contact of the ceramics with seawater, so this approach it is not able to distinguish a potential briquetage process from the boiling of a mixture, for example, of fish and salt.

In the literature, various other approaches have also been employed, though they are less commonly used.

One approach involves identifying the "salt-colour" phenomenon at the inner surface of the bottom of containers. This refers to a spectrum of pinks, whites, greys, and lavender hues, possibly resulting from direct contact with brine at moderately high temperatures (Nijboer et al., 2006).

Another approach consists of identifying the habitus of any residual salt crystals or those trapped in the microfissures of the ceramic during firing. Considering that their habitus is affected by the degree of supersaturation in the salt solution and/or the speed of cooling, the absence of pure cubic NaCl crystals, which develop during slow cooling, in conjunction with the simultaneous presence of amorphous NaCl, formed during rapid cooling, could suggest the complete evaporation of a supersaturated NaCl solution within the container, which is a potential stage in the briquetage process (Alessandri et al., 2019).

The last approach begins with the observation that in the presence of ceramics made with Ca-poor clay, the presence of vitrified specimens within furnaces might imply the deliberate addition of external fluxes which lower the temperature at which the vitrification process begins. This phenomenon can be effectively explained by the briquetage process since sodium and magnesium (from the brine) exhibit precisely this characteristic (Dekoninck et al., 2022).

5.2. Soil

Except for a few fortunate instances where salt crystals are preserved (Jodłowski, 1977; Kopaka and Chaniotakis, 2003; Maritan et al., 2018), the typical approach when examining soils for evidence of briquetage involves identifying abnormal concentrations of sodium, chlorine and/or the chemical compounds that constitute the residues of the processing like calcium, magnesium and potassium. (e.g. Becker et al., 2019 and reference therein). The most used instruments, like in the case of ceramic, are the SEM-EDS and XRF, but also the ICP, coupled with OES, AES or MS (Fig. 2).

Mirroring the approach seen in ceramics, two methodologies have been embraced. The prevalent method involves measuring the concentrations of these elements in the soil and subsequently comparing them with analogous measurements from adjacent soils that are unequivocally unrelated to salt production (Flad et al., 2005; Maritan et al., 2018; Sevink et al., 2021a; Zhu et al., 2008). In other instances, internal

variations in salinity as evidenced, for example, by pH anomalies (Graham et al., 2017; Macphail et al., 2017) or typical chemical elements (Sills et al., 2016; Sordoillet et al., 2018; Zheng et al., 2023) within the site have been regarded as evidence of anthropogenic activity linked to salt production.

Another line of research that remains underexplored is the study of ancient DNA (aDNA). In this case, the objective is to trace the DNA of halophilic organisms like the *Halobacterium salinarum* (Sankaranarayanan et al., 2014; Sevink et al., 2021b; Siotis and Aloupi-Siotis, 2020).

5.3. Residues

In the case of residues, the strategy adopted is similar to that commonly employed in soils, namely the search for salt crystals (Nigro et al., 2021; Ribechini et al., 2009) or residues of its production (Flad et al., 2005). As for the used instruments, the sample size is too small (4 cases, Fig. 2) to derive a trend.

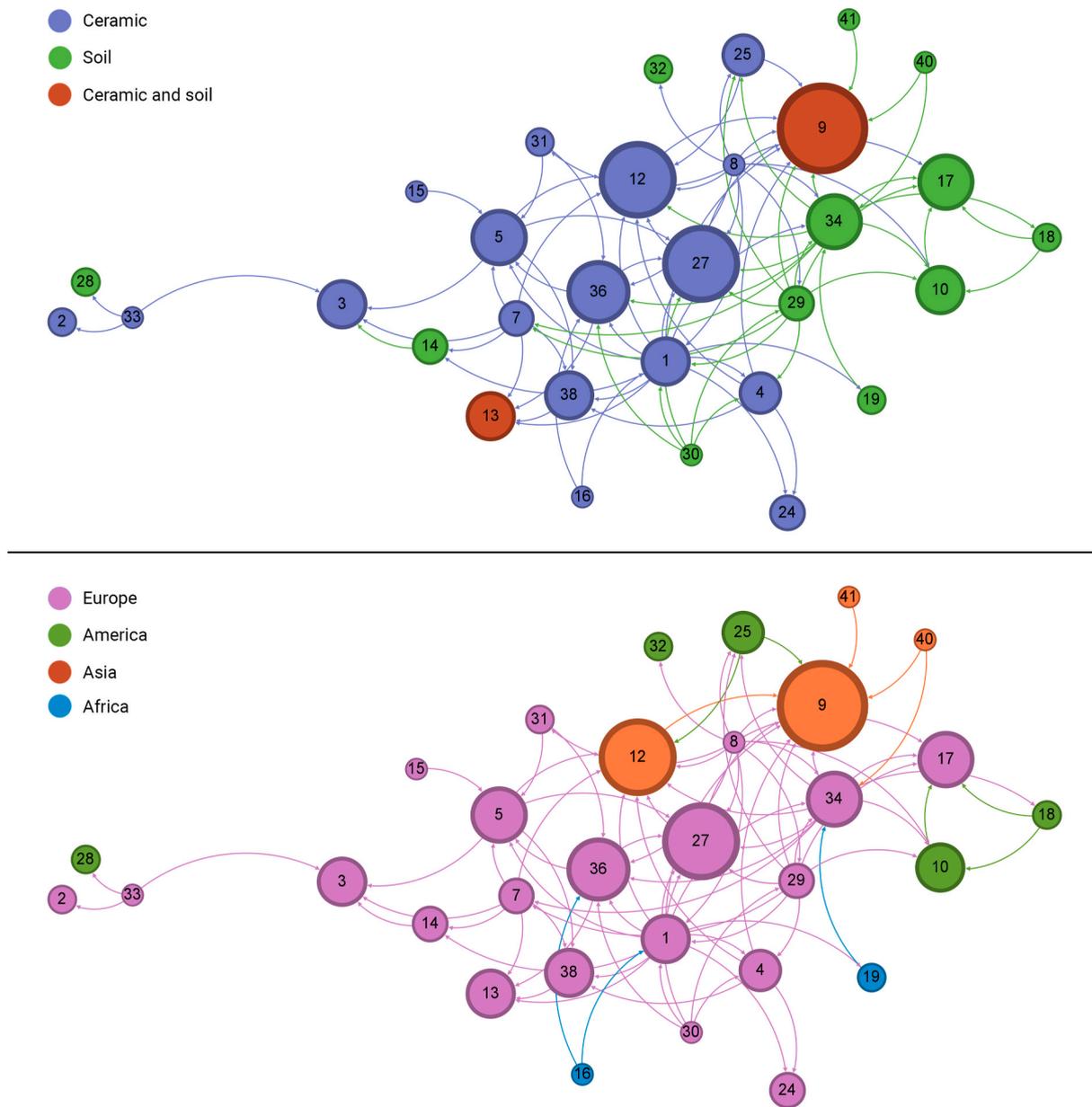


Fig. 3. Citation graphs of the papers discussed in this contribution. node sizes are proportional to the in-degree parameter, ForceAtlas2 layout. A: coloured by type of analysed artifacts; B, coloured by nationality of analysed artifacts. for the paper IDs and network properties refer to Table S7; the disconnected papers n. 6, 23, 26, 35 and 37 are out of sight. made with Gephi 0.10 (Bastian et al., 2009).

5.4. The citation graph

From the In-Degree citation graph of the analysed contributions (Fig. 3, Table S7), some interesting observations can be made. Not surprisingly, the most frequently cited works (n. 9, 12 and 27; Flad et al., 2005; Horiuchi et al., 2011; Sandu et al., 2012, respectively) are those which initially proposed best practices for identifying salt proxies and which have thus clearly oriented subsequent lines of research, at least at the European level. The value of the Average Clustering Coefficient points to a weakly connected network, which undoubtedly constitutes a limitation in the development of studies on the subject. When analysing and commenting this data, it's important to remember that it represents only a subset of the papers on salt in antiquity: taking the entire record into account, the overall picture might be different.

6. Conclusion

Despite the widespread application of chemical and physical techniques, a definitive method for identifying briquetage remains elusive. Traditionally, the probability of recognition relies on a combination of clues, with chemical indicators representing just one facet. The typical chemical-physical strategy involves detecting abnormal concentrations of salt or by-products associated with its production. These concentrations must be carefully juxtaposed with local and contemporaneous contexts that were assuredly not involved in the production process. Chlorine and sodium have proven to be somewhat unreliable proxies, while the potential implications of utilizing other chemical elements such as boron or bromine remain largely unexplored. Additionally, the dynamics of salt diffusion and accompanying components within the ceramic matrix during secondary firing (briquetage), though suggested by one study, demand a more thorough investigation to propose more effective sampling strategies.

On these grounds, the present review evidences the importance of a multidisciplinary analytical approach in archaeometry investigations applied to ancient salt production. Analytical methods applied to ceramic containers, e.g., ED-XRF (or only XRF) aiming at detecting the NaCl chemical signature, is a fundamental test due to its straightforward applicability; however, the compositional information should be improved by SEM-EDS and/or LA-ICP-MS aiming at distinguish and interpret the genesis of sodium chloride as related to either post-depositional processes or presence in the original clay and/or the inclusion of saltwater during the ceramic manufacture. Also, the SEM-EDS analysis of NaCl crystal habitus on pottery may provide inferences about the degree of supersaturation and/or the cooling rates of the salt solution (e.g., Alessandri et al., 2019).

Due to the high solubility of salt, recognising the environmental chemical signature of the production process, e.g., by soil analyses, is a complex yet fundamental clue. Microtextural analyses of soil specimens is a complex procedure and require uniform resin impregnation of undisturbed samples, de-airing and curing so that the soil structure maintain its *in situ* characteristics. This procedure allows the correct interpretation of microanalytical and bulk analysis data (eg., XRF, ICP-MS, ICP-AES, total and pyrogenic carbon contents, pH, magnetic susceptibility) in light of soil micromorphology and microtextural analyses by OM or SEM-EDS. Then, the results from soil analyses can be filtered through statistical analysis including clustering, principal component analysis, and inference tests.

In rare, favourable conditions, analyses on residual organic constituents by Mass Spectrometry (MS) coupled with Gas Chromatography (GC) is an essential method in the field of biomolecular archaeology to characterize animal fats and oil of various nature and origin. Furthermore, an entirely unexplored but potentially promising avenue is the "biological" approach, aiming to identify the DNA of halophile organisms.

Surprisingly, few experimental attempts have been made to replicate the briquetage technique, which could shed light on this and other issues

and should be utilized more extensively. Finally, the analysis of the citation graph, albeit to be approached with caution as it represents a subset of the entire bibliography concerning salt production in antiquity, has underscored the need for enhanced information exchange among research groups addressing this issue. In summary, it appears that some strategies to advance this field of study further could include.

- Enhancing the utilization of experimental archaeology, particularly in the context of briquetage. The reproduction of the briquetage technique, combined with a detailed analysis of the involved chemical and physical parameters, would aid in interpreting similar ancient remains and in selecting the most effective analytical techniques.
- Testing the use of Bromine and Boron. To date, although promising in theory, no extensive studies have been conducted on the use of these two proxies. When used alongside the classic chlorine and sodium, they could assist in identifying artifacts that have been in contact with seawater.
- To improve the connectiveness of the research network (about salt), several strategies can be suggested. One approach is to continue organizing and expand international conferences or workshops on the subject, akin to the international congresses on the anthropology of salt (ICAS) held since 2015, or the workshop on ancient salt production held in Rome (Salt and Power. Early States, Rome and Resource Control) in 2022, whose proceedings include this article. Another approach could be to develop a web platform that gathers all the sites where salt production is presumed, following the model used for ancient ports (<https://www.ancientportsantiques.com/>) (de Graauw, 2011, 2014), and keeping it updated in real time. Opening the database to collaboration from scholars worldwide would be an excellent way to connect them, keep everyone updated, and foster the development of new initiatives.

Credit author statement

Alessandri L: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Project administration; Sottili G: Conceptualization, Methodology, Investigation, Writing – original draft; Belardelli C: Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT 3.5 to improve the language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No unpublished data was used for the research described in the article.

Acknowledgments

This work was supported by the Istituto Italiano di Preistoria e Protostoria (MIURDM 44/2008 funds "Scienze per la preistoria", prot. 13411/21) and by the Netherlands Organisation for Scientific Research (NWO), grant 406.20.HW.013.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.quascirev.2024.108809>.

References

- Afouda, P., Dubourg, G., Raoult, D., 2020. Archeomicrobiology applied to environmental samples. *Microb. Pathog.* 143, 104140 <https://doi.org/10.1016/j.micpath.2020.104140>.
- Alessandri, L., Achino, K.F., Attema, P.A.J., de Novaes Nascimento, M., Gatta, M., Rolfo, M.F., Sevink, J., Sottili, G., van Gorp, W., 2019. Salt or fish (or salted fish)? The Bronze Age specialised sites along the Tyrrhenian coast of Central Italy: new insights from Caprolace settlement. *PLoS One* 14. <https://doi.org/10.1371/journal.pone.0224435>.
- Alessandri, L., Attema, P., 2022. From briquetage to salterns in protohistoric central Italy. Research of a fundamental subsistence commodity. *IpoTesi Preistoria* 14, 161–168. <https://doi.org/10.6092/issn.1974-7985/14338>.
- Aloupi, E., Karydas, A., Paradellis, T., Siotis, I., 2000. Salt tracers in ancient artefacts. In: *Proceedings of the 8th Workshop of the Cultural Foundation of the National Bank for Industrial Development*, pp. 47–55.
- Aloupi, E., Karydas, A., Paradellis, T., Siotis, I., 1998. Pilot Validation Study for the Use of Bromine as a Tracer of Sea and Salt Routes in Ancient Cultures.
- Antonites, A., 2016. The organization of salt production in early first millennium CE South Africa. *J. Anthropol. Archaeol.* 44, 31–42. <https://doi.org/10.1016/j.jaa.2016.08.001>.
- Aranguren, B.M., Cinquegrana, M.R., De Bonis, A., Guarino, V., Morra, V., Pacciarelli, M., 2014. Le strutture e lo scarico di olle del Puntone Nuovo di Scarlino (GR), e i siti costieri specializzati della protostoria mediotirrenica. *LXIV. Rivista di Scienze Preistoriche*, pp. 227–259.
- Ard, V., Weller, O., 2012. Les vases de “type Champ-Durand”: témoins d’une exploitation du sel au Néolithique récent dans le Marais poitevin. In: Joussaume, R. (Ed.), *L’enceinte Néolithique de Champ-Durand à Nieul-Sur-l’Autise (Vendée)*, pp. 309–333. Chauvigny.
- Bastian, M., Heymann, S., Jacomy, M., 2009. Gephi: an open source software for exploring and manipulating networks. *ICWSM 3*, 361–362. <https://doi.org/10.1609/icwsml.v3i1.13937>.
- Becker, F., Eser, R.A., Hoelzmann, P., Schütt, B., 2019. The environmental impact of ancient iron mining and smelting on Elba Island, Italy – a geochemical soil survey of the Magazzini site. *J. Geochem. Explor.* 205, 106307 <https://doi.org/10.1016/j.gexplo.2019.04.009>.
- Boonruang, C., Won-in, K., Nimsuwan, N., Pakawanit, P., Tippawan, U., Thongleum, C., Dararutana, P., 2022. Characterization of ancient burial pottery of ban Muang Bua archaeological site (northeastern Thailand) using X-ray spectroscopies. *Appl. Sci.* 12 <https://doi.org/10.3390/app12052568>.
- Booth, A., Sutton, A., Clowes, M., Martyn-St James, M., 2022. *Systematic Approaches to a Successful Literature Review*. SAGE Publications Inc.
- Cassen, S., Weller, O., 2013. Idées et faits relatifs à la production des sels marins et terrestres en Europe, du Vie au IIIe millénaire. In: Soares, J. (Ed.), *Pré-História Das Zonas Húmidas. Paisagens de Sal/Prehistory of Wetlands. Landscapes of Salt*. Museu de Arqueologia e Etnografia do Distrito de Setúbal/Assembleia Distal de Setúbal, Setúbal, pp. 255–304.
- de Graauw, A., 2014. *Geodatabase of Ancient Ports and Harbors, DARMC Scholarly Data Series, Data Contribution Series # 2013-2 (Version 1.1)*. DARMC, Center for Geographic Analysis, Cambridge: Center for Geographic Analysis. Harvard University.
- de Graauw, A., 2011. Ancient coastal settlements, ports and harbours | ancient ports - ports antiques. *Ancient Ports-Ports Antiques*. URL: <https://www.ancientportsantiques.com/>, 6.4.24.
- Dekoninck, M., Goemaere, E., Dewaele, S., De Grave, J., Leduc, T., Vandenberghe, D., De Clercq, W., 2022. Geochemical and mineralogical characterisation of vitrified waste material discovered in large quantities on Roman salt production sites along the southern North Sea coast. *J. Archaeol. Sci.* 146, 105665 <https://doi.org/10.1016/j.jas.2022.105665>.
- Efron, S.E., Ravid, R., 2018. *Writing the Literature Review: A Practical Guide*. Guilford Publications, New York, UNITED STATES.
- Flad, R.K., Zhu, J., Wang, C., Chen, P., von Falkenhausen, L., Sun, Z., Li, S., 2005. Archaeological and chemical evidence for early salt production in China. *Proc. Natl. Acad. Sci. U.S.A.* 102, 12618–12622. <https://doi.org/10.1073/pnas.0502985102>.
- Giovannini, A., 1985. *Le sel et la fortune de Rome*. *Athenaeum* 63, 373–386.
- Graham, E., Macphail, R., Turner, S., Crowther, J., Stegemann, J., Arroyo-Kalin, M., Duncan, L., Whittet, R., Rosique, C., Austin, P., 2017. The Marco Gonzalez Maya site, Ambergris Caye, Belize: assessing the impact of human activities by examining diachronic processes at the local scale. <https://doi.org/10.1016/j.quaint.2015.08.079>.
- Harding, A., 2021. *Salt: White Gold in Early Europe, Elements in the Archaeology of Europe*. Cambridge University Press, Cambridge. <https://doi.org/10.1017/9781009038973>.
- Harding, A., 2013. *Salt in Prehistoric Europe*. Sidestone, Leiden.
- Hocquet, J.-C., 2022. L’Adriatique, golfe de Venise? Commerce, ports et relations à la fin du Moyen Âge. *medieval* 13–32. <https://doi.org/10.14198/medieval.20224>.
- Hocquet, J.-C., 1979. *Le sel et la fortune de Venise*. In: *Voiliers et commerce en Méditerranée*, vol. 2. Presses de l’Université de Lille III, Lille, pp. 1200–1650.
- Horiuchi, A., Ochiai, N., Kurozumi, H., Miyata, Y., 2011. Detection of chloride from pottery as a marker for salt: a new analytical method validated using simulated salt-making pottery and applied to Japanese ceramics. *J. Archaeol. Sci.* 38, 2949–2956. <https://doi.org/10.1016/j.jas.2011.06.003>.
- Jodłowski, A., 1977. Die Salzgewinnung auf polnischem Boden in vorgeschichtlicher Zeit und im frühen Mittelalter. *Jahresschr. für Mitteldtsch. Vorgesch.* 61, 85–103.
- Kopaka, K., Chaniotakis, N., 2003. Just taste additive? Bronze Age salt from Zakros, Crete. *Oxf. J. Archaeol.* 22, 53–66. <https://doi.org/10.1111/1468-0092.00004>.
- Large, J.-M., Corson, S., Dupont, C., Weller, O., 2015. Indices d’exploitation de ressources marines à la fin du 2nd millénaire av. J.-C. : le foyer de l’âge du Bronze aux Batardières (Saint-Vincent-sur-Jard, Vendée). *Rev. Archéol. Ouest* 32, 97–112.
- Larreina-García, D., Saenz de Buruaga, A., Vinagre, A.T., Notario, B., 2021. Technical ceramics for salt production in Western Sahara. *Azania* 56, 344–370. <https://doi.org/10.1080/0067270X.2021.1966213>.
- Macphail, R.I., Crowther, J., Berna, F., 2012. Stanford Wharf, Essex (London Gateway Compensation sites a and b; compa 09): soil micromorphology and microchemistry, chemistry and magnetic susceptibility, and FTIR. In: Macphail, R.I., Crowther, J., Berna, F. (Eds.), *London Gateway. Iron Age and Roman Salt Making in the Thames Estuary. Excavation at Stanford Wharf Nature Reserve, Essex*. Oxford Archaeology, Oxford, pp. 1–193.
- Macphail, R.I., Graham, E., Crowther, J., Turner, S., 2017. Marco Gonzalez, Ambergris Caye, Belize: a geoarchaeological record of ground raising associated with surface soil formation and the presence of a Dark Earth. *J. Archaeol. Sci.* 77, 35–51. <https://doi.org/10.1016/j.jas.2016.06.003>.
- Maritan, L., Iacumin, P., Zerboni, A., Venturilli, G., Dal Sasso, G., Linsele, V., Talamo, S., Salvatori, S., Usai, D., 2018. Fish and salt: the successful recipe of White Nile Mesolithic hunter-gatherer-Fishers. *J. Archaeol. Sci.* 92, 48–62. <https://doi.org/10.1016/j.jas.2018.02.008>.
- McGenity, T.J., 2014. The immortal, halophilic superhero: *Halobacterium salinarum* - a long-lived poly-extremophile. *Microbiol. Today* 24–27.
- McKillop, H., Sills, E.C., Cellucci, V., 2014. The ancient Maya canoe and the canoe paddle from Paynes Creek national Park, Belize. *Research Reports in Belizean Archaeology* 11, 297–306.
- Nigro, L., Gallo, E., Mura, F., Rinaldi, T., 2021. Teapot or milkpot? About the content of a small, spouted jar from EB IV (2300-2000 B.C.E.) tell es-Sultan, ancient Jericho. *Mediterranean Archaeology and Archaeometry* 21, 281–290. <https://doi.org/10.5281/zenodo.4575728>.
- Nijboer, A.J., Attema, P.A.J., van Oortmerssen, G.J.M., 2006. Ceramics from a late Bronze Age saltern on the coast near Nettuno (Rome, Italy). *Palaeohistoria* 47/48, 141–205.
- Raad, D.R., Li, S., Flad, R.K., 2014. Testing a novel method to identify salt production pottery via release and detection of chloride ions. *J. Archaeol. Sci.* 43, 186–191. <https://doi.org/10.1016/j.jas.2014.01.004>.
- Reina, R.E., Monaghan, J., 1981. The ways of the Maya. salt production in Sacapulas, Guatemala. *Expedition* 13–33.
- Ribechini, E., Colombini, M.P., Giachi, G., Modugno, F., Pallecchi, P., 2009. A multi-analytical approach for the characterization of commodities in a ceramic jar from Antinoe (Egypt). *Archaeometry* 51, 480–494. <https://doi.org/10.1111/j.1475-4754.2008.00406.x>.
- Sandu, I., Weller, O., Stumbea, D., Alexianu, M., 2012. Analyses archéométrique sur les moules à sel chalcolithiques de l’est de la Roumanie. In: Nikolov, V., Bacvarov, K. (Eds.), *Salz Und Gold: Die Rolle Des Salzes Im Prähistorischen Europa/Salt and Gold: The Role of Salt in Prehistoric Europe*. Verlag Faber, Provardia, Veliko Tarnovo, pp. 143–154.
- Sankaranarayanan, K., Lowenstein, T.K., Timofeeff, M.N., Schubert, B.A., Lum, J.K., 2014. Characterization of ancient DNA supports long-term survival of haloarchaea. *Astrobiology* 14, 553–560. <https://doi.org/10.1089/ast.2014.1173>.
- Sevink, J., de Neef, W., Alessandri, L., van Hall, R.L., Ullrich, B., Attema, P.A.J., 2021a. Protohistoric briquetage at Puntone (Tuscany, Italy): principles and processes of an industry based on the leaching of saline lagoonal sediments. *Geoarchaeology* 36, 54–71. <https://doi.org/10.1002/gea.21820>.
- Sevink, J., Muzzer, G., Arienzo, I., Mormone, A., Piochi, M., Alessandri, L., van Hall, R.L., Palstra, S.W.L., Dee, M.W., 2021b. The protohistoric briquetage at Puntone (Tuscany, Italy): a multidisciplinary attempt to unravel its age and role in the salt supply of Early States in Tyrrhenian Central Italy. *J. Archaeol. Sci.: Report* 38, 103055. <https://doi.org/10.1016/j.jasrep.2021.103055>, 103055.
- Sherlock, S.J., 2021. Early neolithic salt production at Street House, Loftus, north-east england. *Antiquity* 95, 648–669. <https://doi.org/10.15184/ajqy.2021.25>.
- Sills, E.C., McKillop, H., Wells, E.C., 2016. Chemical signatures of ancient activities at Chan b’i - a submerged Maya salt works, Belize. *J. Archaeol. Sci.: Report* 9, 654–662. <https://doi.org/10.1016/j.jasrep.2016.08.024>.
- Siotis, I., Aloupi-Siotis, E., 2020. Experimental interpretation of the presence of female genitalia in Early Bronze Age ‘frying pan’-type ceramics from the Cyclades. *Archaeometry* 62, 285–296. <https://doi.org/10.1111/arc.12525>.
- Sordoulet, D., Weller, O., Rouge, N., Buatier, M., Sizun, J.-P., 2018. Earliest salt working in the world: from excavation to microscopy at the prehistoric sites of Țolici and Lunca (Romania). *J. Archaeol. Sci.* 89, 46–55. <https://doi.org/10.1016/j.jas.2017.11.003>.
- Stoner, W.D., Millhauser, J.K., Rodríguez-Alegría, E., Overholtzer, L., Glascock, M.D., 2014. Taken with a grain of salt: experimentation and the chemistry of archaeological ceramics from xaltocan, Mexico. *J. Archaeol. Method Theor* 21, 862–898. <https://doi.org/10.1007/s10816-013-9179-2>.
- Tencari, F.-A., Alexianu, M., Cotiugă, V., Vasilache, V., Sandu, I., 2015. Briquetage and salt cakes: an experimental approach of a prehistoric technique. *J. Archaeol. Sci.* 59, 118–131. <https://doi.org/10.1016/j.jas.2015.04.016>.

- Vasilache, V., Kavruk, V., Tencariu, F.-A., 2020. OM, SEM-EDX, and micro-FTIR analysis of the Bronze Age pottery from the Băile Figa salt production site (Transylvania, Romania). *Microsc. Res. Tech.* 83, 604–617. <https://doi.org/10.1002/jemt.23451>.
- Vyas, B.G., Labhasetwar, P.K., Yadav, A., Paital, A.R., 2022. A compendium of evaporation techniques for salt production from seawater and sub-soil brine. *Chem. Pap.* 76, 6659–6674. <https://doi.org/10.1007/s11696-022-02363-1>.
- Weller, O., 2002. Aux origines de la production du sel en Europe. *Vestiges, fonctions et enjeux archéologiques*. In: *Archéologie Du Sel: Techniques et Sociétés*, pp. 163–176. Colloque 12.2, XI^e Congrès UISPP.
- Weller, O., 2000. Les premières formes d'exploitation du sel durant le Néolithique et le Chalcolithique européens: de la reconnaissance des techniques à l'analyse des dimensions socio-économiques.
- Zheng, T., Lei, S., Wang (王张华), Z., Li, W., Mei, S., Wang, J., Meadows, M.E., 2023. Prehistoric sea-salt manufacture as an adaptation strategy to coastal flooding in East China. *Quat. Sci. Rev.* 302, 107966 <https://doi.org/10.1016/j.quascirev.2023.107966>.
- Zhu, C., Jiang, F., Ma, C., Xu, W., Huang, L., Zheng, C., Li, L., Sun, Z., 2008. Rise and decline of ancient salt industry revealed by Na and Ca concentrations in sediments at Zhongba site, Chongqing. *J. Geogr. Sci.* 18, 328–340. <https://doi.org/10.1007/s11442-008-0328-6>.