Protohistoric briquetage at Puntone (Tuscany, Italy): principles and processes of an industry based on the leaching of saline lagoonal sediments

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Abstract

A protohistoric (c.10th–5th c. BC) briquetage site at Puntone (Tuscany, Italy) was studied to unravel the salt production processes and materials involved. Geophysical surveys were used to identify kilns, pits, and dumps. One of these pits and a dump were excavated, followed by detailed chemical and physical analyses of the materials encountered. The pit had been used for holding brine, obtained by leaching of lagoonal sediment over a sieve, that afterwards was discarded to form large dumps. Phases distinguished indicate that the pit filled with fine sediment and was regularly “cleaned.” The presence of ferroan-magnesian calcite in the pit fill testifies to the prolonged presence of anoxic brine. The production processes could be reconstructed in detail by confronting the analytical results with known changes in composition of a brine upon evaporation. These pertain in particular to the accumulation of “bitterns” and increased B (boron) concentrations in a residual brine. Both could be traced in the materials studied, and were found to be far more indicative than the ubiquitously studied concentrations of Cl and Na.

Keywords

bitterns, briquetage, ferroan-magnesian calcite, geophysics, protohistory, salt production

1 INTRODUCTION

Salt has long been an important commodity and it is therefore not surprising that numerous archaeological studies have been devoted to its production (see e.g., Harding, 2013; Hocquet & Sarrazin, 2006; Nikolov & Bacvarov, 2012; Weller, 2002). Production techniques have ranged from mining (rock salt) and burning material containing salts (plants and peat), to evaporation of saline waters to produce a brine from which salt is precipitated. Brines can be obtained in many ways, from collecting saline spring and seepage waters, or salt lake water (e.g., sebkhas), to evaporation of seawater and leaching saline coastal sediments (see e.g., Weller, 2015). Brine produced by evaporation of sea water is by far the dominant raw material for salt production in the drier and warmer coastal areas of the world.

Early salt production techniques based on evaporation of brines have been extensively studied, in many cases supported by ethnographic studies of such salt production in nonindustrial societies (see e.g., Cassen & Weller, 2013; Flad et al., 2005; Graham et al., 2015; Parsons, 2001; Weller, 2015; Williams, 2002). Two broad categories are distinguished: salt production using solar energy to evaporate a brine, and production based on boiling brine held in some sort of container (Weller, 2015). The first technique prevailed in Mediterranean and warmer (semi-)tropical climates favouring rapid evaporation and was often based on evaporation from brines in salt pans.
or salterns. The second was more common in temperate and humid climates which are less appropriate for solar evaporation but has also been employed in warmer climates. At a more detailed level, a range of key techniques have been distinguished for obtaining a brine and for evaporating a brine to obtain solid salt, as described in the many reviews and handbooks dealing with early salt production (see literature cited above).

In early modern chemistry, the study of the geochemical processes involved in the evaporation of sea water and the precipitation of salt was an important topic. Already in 1849 Usiglio published the first experimental study (Usiglio, 1849) and he was soon followed by others (for a concise description of this history, see Stewart, 1963). Later relevant studies include those by Hardie and Eugster (1980), McCaffrey et al. (1987), Vengosh, Starinsky, Kolodny, Chivas, and Raab (1992), Akridge (2008), Babel and Schreiber (2014), and Hussein, Zohdy, and Abdelkreem (2017). The results from extensive fundamental research provide the foundation for modern seawater-based salt industries, which produce a wide range of commodities. Important aspects are the precipitation of “bitterns” at specific stages in the evaporation process (see Hussein et al., 2017) and the productivity of various salt production systems in terms of ratios between brine volume processed, salt produced, and energy needed. These ratios were a crucial economic driver for the development of modern vacuum evaporation techniques and the trend towards combining seawater desalination with salt production (see e.g., Cheng, Song, & Cheng, 2015; Sorour, Hani, Shaalan & Al-Bazedi, 2015) while bitterns are important in the modern salt industry as a major source of elements such as Mg, K, B, and Li.

Remarkably, in archaeological studies on early salt production the focus has been on material remains in the form of salterns, furnaces, kilns, and ceramics used, whereas fundamental aspects of the salt production process have received far lesser attention. Thus, geochemical analyses rarely go beyond the concentrations of sodium and chlorine in archaeological materials (see e.g., Alessandri et al., 2019; Flad et al., 2005; Macphail, Crowther, & Berna, 2012; Raad, Li, & Flad, 2014; Sandu, Weller, Stumbea, & Alexianu, 2012; Sordoillet, Weller, Rouge, Buatier, & Sizun, 2018; Tencariu, Alexianu, Cotiugă, Vasilache, & Sandu, 2015). Moreover, most of the limited number of archaeological studies incorporating geochemical aspects are from the last decade and of these only a few deal with early Italian salt production sites (see Alessandri et al., 2019).

In early times, salt production flourished along the Tyrrenian coast of Central Italy with many known sites where salt was produced, largely based on salterns and solar evaporation. Salt was also produced by boiling brine in ceramic vessels, referred to as briquetage (see e.g., Harding, 2013; Hocquet & Sarrazin, 2006; Tencariu et al., 2015). The later results from extensive research may well represent an early (protohistoric) small-scale type of salt industry that later on was replaced by larger scaled saltern-based industries. Review papers on these production sites describing overall trends are by Attema and Alessandri (2012) and Alessandri et al. (2019). In Central Tuscany, major production complexes were situated in the Piombino/Follonica coastal area, where many excavations have taken place (Aranguren, 1995; Aranguren, 2002; Aranguren & Castelli, 2011; Aranguren et al., 2014; Baratti, 2010; Barbaranelli, 1956; Giroldini, 2012). Recent excavations at Puntone Campo da Gioco (Figure 1) led to the discovery of a protohistoric salt production site based on briquetage, further inland than earlier finds at Puntone (Aranguren et al., 2014). More detailed research on its structure and age was carried out over three excavation campaigns between 2015 and 2017. Cinquegrana...
(in prep.) typologically dated ceramics to the 8th–6th c. BC, based on diagnostic features related to the production process. More recent Roman pottery was attributed to a Roman villa with an agricultural vocation (1st–2nd c. AD).

The main archaeological features linked to salt production found thus far in these and earlier excavations at the Puntone site have included: (a) pottery kilns and dumps of pottery fragments, typical for briquetage sites, (b) large dumps of lagoonal sediment that could conceivably have served as raw material for brine production, (c) firing pits apparently used for heating brine-containing pots, and (d) former pits that have somewhat tentatively been described as having held brine and now are filled with light-colored calcareous sand. The general impression is that of a low but continuous density of material structures and dumps. However, these may extend over a considerable area along the edge of the lagoon and continue well outside the modest area of c. 1 ha that we were allowed to investigate.

In 2015, Eastern Atlas conducted a geophysical survey of the site, including a full-coverage magnetic gradiometry survey and two targeted ground penetrating radar (GPR) surveys. Three types of magnetic anomalies were observed, representing the main archaeological features described above: (a) pyrotechnological features (kilns or fire pits), identified by their very high amplitudes and dipole characteristics, (b) pits or deposits with positive magnetic amplitudes, and (c) crescent-shaped features with negative magnetic amplitudes, which were identified as dumps of lagoonal sediment (Figure 2).

Using results from this survey, several areas were excavated in the subsequent campaigns (see Figure 3). These included a pit with positive magnetic amplitude, which may have held brine (area B) and crescent-shaped features, interpreted as dumps (areas B and C). More extensive descriptions of the archaeological features and phenomena can be found in the studies cited and in the forthcoming PhD thesis by Cinquegrana.

In the archaeological campaigns, emphasis was placed on the study of structures and artefacts. An obvious remaining question was whether the production techniques employed could be reconstructed based on an approach that was more oriented towards the physicochemical characteristics of the features and materials encountered. These techniques can be subdivided into the production of brine, the storage of the brine produced, and the production of salt by briquetage, including the removal of bitterns. To that purpose, we studied a representative pit (B2) and associated crescent-shaped dump with intercalated pottery debris layer (area C), paying particular attention to physicochemical characteristics of their materials, and the phases in their formation, as well as to the geological setting of the site. Results suggest a complex phasing and origin of the various materials. The data have allowed us to infer novel information on production processes at the site and highlight the relevance of this approach for studies on early salt production.

In this paper, we deal with the following three topics:

- The local geology and soils.
- The characteristics and phasing of the pit fill and dumps, relevant for establishing the functioning of this type of pit as a collector/store of brine, produced by leaching of lagoonal sediment. Special attention is paid to the geomagnetic properties of the various materials encountered in and associated with this pit.
- The salt production processes. This aims at a more detailed description of the briquetage process, based on the geochemical principles behind this process and dedicated chemical analyses.

## 2 | MATERIALS AND METHODS

### 2.1 | The site and its geology

In Figure 2, results from the geophysical surveys are presented (a) along with their interpretation (b). The latter was supported by a series of corings in the various features distinguished. Areas excavated in the archaeological campaigns are also indicated in Figure 2b. Figure 3 provides more detailed information on the areas and features studied. The excavations showed that pit B2 (area B) had a stratified sandy fill. Excavations in areas B and C showed that the crescent-shaped fans were indeed dumps, consisting of irregularly stacked layers of quartzitic sands with variable amounts of secondary carbonates. In area C, the dump contained a layer of fragments of ceramic vessels (Figure 4), assumed to have been used in salt production. Similar layers of ceramic fragments were also encountered in corings in other, not yet excavated dumps. The dimensions of the dumps were such that large volumes of sand must have been processed to extract salt, pits (like pit B2) presumably being used to store the brine thus obtained (Aranguren & Castelli, 2011).

The local geology is depicted in Figure 5. The site is on the lower slope of a Pleistocene alluvial fan complex (units dt and f²), composed of sediment derived from Macigno sandstone (unit mg), and locally covered by Holocene fan sediments (unit a). The sandstone crops out on the overlying slopes. The lagoon was in open connection with the sea until recently (e.g., Cappuccini, 2011; Gioldini, 2012). Unlike in many other areas along the Tyrrhenian coast, Pleistocene marine terraces are completely absent, evidencing tectonic subsidence during the later part of the Quaternary, as also observed in the nearby Grosseto basin (e.g., Bisemi & Van Geel, 2005; Lambeck, Antonioli, Purcell, & Silenzi, 2004; Sevink, Beemster, & Van Stiphout, 1986). The Macigno formation (Late Oligocene-Miocene) consists of grey to bluish-grey, well-consolidated, poorly to moderately sorted siliciclastic sandstone or greywacke. It may contain some calcium carbonate (generally < 5%), while iron contents range from 4% to 7% (Fe₂O₃; Cornamusini, 2002; Deneke & Günther, 1981; Dinelli, Lucchini, Mordenti, & Paganeli, 1999).

### 2.2 | Field methods

In 2015, Eastern Atlas GmbH & CoKG started with a magnetic gradiometry survey, using a LEA-MAX mobile cart system mounted with
six Foerster FEREX 4.031 CON 400 fluxgate gradiometer probes (Ullrich, 2016). Next, a GPR survey was undertaken of two smaller areas using a GSSI SIR-3000 system with a 270 MHz antenna. In 2016 and 2017, Magnetic susceptibility (MS) measurements were obtained using a Bartington MS3 meter and a MS2D loop on excavation levels, and a MS2F probe on vertical sections across excavated features. MS data were recorded and processed using the manufacturer software Bartsoft.
In 2016 and 2017, the locations for excavation were chosen on the basis of the magnetometry data plus additional information from the GPR survey (Figure 2). Relevant areas are B (pits) and C (positive magnetic dump of pottery fragments and crescent-shaped negative magnetic anomaly). The circular pit B2 in area B (Figures 3 and 6b) was described and sampled per stratigraphic layer. Samples were also taken from sections in area C: C1 is in sands, while C2 holds a layer of ceramic debris (Figure 4). Lastly, a Macigno soil was sampled near to the pit (at a distance of about 1 m).

2.3 | Lab analyses

For MS analysis of individual materials, samples from the layers identified in the pit were treated with acetic acid and HCl, respectively, to remove carbonates (see below). This was followed by treatment with 5% H$_2$O$_2$ to remove organic matter, after which samples were washed and filtered over a 0.2 µm filter. Residues were analysed using a Bartington MS3 meter coupled with a MS2B laboratory meter.

Electrical conductivity/salinity and pH were measured in soil extracts with a 1:2.5 weight ratio (solid/water). After filtering the soil extracts over a 0.2 µm filter, Cl was measured using a segmented flow auto-analyser (SAN++, Skalar). Other water soluble elements (B, Ca, K, Mg, Na, P, and S) were measured using ICP-OES (Optima-8000, Perkin Elmer).

To distinguish between readily and poorly soluble carbonates, samples were treated with acetic acid and with hydrochloric acid, after which residues were weighed. For total carbonates, a 100 g sample was treated with an excess amount of HCl (4 M). In the extract, Ca, Fe, and Mg were estimated using ICP-OES. In the residue, C, N, and S were determined by elemental analyser (Vario El cube). For a more selective dissolution of

FIGURE 3 Details of geophysical survey with locations of areas B and C, and features (B1 and B2) in area B (below). Surface of the features after removal of topsoil material, with pits in area B and exposed layer of pottery fragments in area C. The locations of sample profiles C1 and C2 are indicated with orange dots [Color figure can be viewed at wileyonlinelibrary.com]
carbonates (only calcium carbonates), 200 g samples were treated with acetic acid (0.25 M) for 2 hr, followed by washing with demineralized water and centrifugation. This procedure was repeated four times and the supernatant was analysed using ICP-OES.

For microscopic study, samples were treated with 5% H2O2 to remove organic matter followed by sieving over a 105 µm sieve. Fossils present in these fractions were identified by Wim Kuiper. For Layer 7 a thin section was prepared from a resin-impregnated undisturbed sample.

Radiocarbon dating was performed on charcoal and mollusc shells from the fractions >105 µm obtained by wet sieving. Charcoal was pretreated using the ABA-procedure. Samples were dated by the AMS-method at the CIO lab in Groningen, The Netherlands. Values obtained are presented as 14C years BP and have been calibrated using the software OxCal v4.3 (Ramsey & Lee, 2013) and the IntCal13 and Marine13 curves (Reimer et al., 2013). The DeltaR (22 ± 39) has been calculated using the Marine Reservoir Correction Database (http://calib.org/marine/) and is the result of an average of two estimated values (Naples: Siani et al., 2000; Liguro-Provençal Basin: Tisnérat-Laborde et al., 2013).

3 | RESULTS

3.1 | Local geology and soils

Results described below are based on corings and observations in natural exposures and excavation trenches at the site and its surroundings. The fan deposits are more or less matrix supported conglomerates with rounded Macigno sandstone blocks up to several decimeters in diameter. In the upper meters strongly developed soils occur, often as stacked paleosols reflecting the alternation of stable and unstable phases during the Quaternary. The upper part of this "paleosol complex" consists of a thick reddish-brown (5–7.5 YR) clayey argic B horizon, formed by prominent illuviation of clay during the Late Pleistocene (e.g., Gardin & Vinci, 2006; Sevink et al., 1986). Soils classify as Chromic and Ferric Luvisols, or as Podzoluvisols where soils are not eroded and in more level positions (WRB FAO, 1998).

Soils are generally more or less truncated, with the clayey argic B horizon close to the surface. This horizon is very slowly permeable, and exhibits pronounced stagnic properties. Even in deep incisions, soils and sediments are completely free of carbonates. In line with these general observations, in the archaeological trenches and pits a strongly developed clayey argic B horizon was encountered below the archaeological layers.

Corings in the adjacent lagoon showed the presence of loamy sandy, quartzitic sediment holding some shells, with an overall thin top layer of finer sediment. Organic (peat) layers were not encountered, but in deeper corings close to the foot slope of the alluvial fans, peat layers were found at several meters depth. Preliminary 14C dating of peat from one of these cores indicate that the Neolithic–Early Bronze Age transition is found at a depth of between 2 and 3 m.

On the foot slopes and in the hills above, depicted in Figure 1, there are no springs and no permanent rivers carrying water in the dry summer season. The site is a few meters above sea level and thus was very close to the open lagoon.
3.2 Pit fills and crescent-shaped deposits

Figures 2 and 3 show results from the geophysical survey, with the pit and the crescent-shaped features. In Figure 6a a cross section of the pit is presented, while Figure 6b shows a photograph of the pit. Sections through the crescent-shaped deposits are depicted in Figures 4 and 7a,b.

3.2.1 General characteristics and phasing

In relation to the pit, four phases were distinguished, evidencing the complex history of this site and its associated deposits. No archaeological materials (such as ceramic fragments) were found that would allow for dating the phases.

The phases distinguished are as follows:

- **Phase 1**: Stacked Layers 16, 15, 14, 37, 17, 33, and so forth (left), and 16, 27, and 30 (right). Layer 16 rests on the "natural" soil, contains charcoal, and consists of "reworked" soil. Layers 15, 17, 30, and most other overlying layers (24, 33, etc.) are composed of light-colored, calcareous quartzitic sand. Layers 14/27 consist of reworked "Macigno-type" paleosol material. Downslope, the individual layers of this complex Phase 1 grade into deposits, forming the lower strata of a crescent-shaped fan. The later excavation of a large pit at the start of Phase 2, destroyed all evidence of an earlier
pit. Nevertheless, the existence of Layers 14 and 27 suggests that a fill was excavated to deepen an existing pit.

- **Phase 2**: Layers 5, 20, 22, and 23, representing the fill of a deep pit. Layer 5 exhibits prominent iron (hydr)oxide accumulation and gleicy features, dating from the later Stage 3, (associated with the wall of the pit in Phase 3). Layer 2 probably dates from Phase 2 but its stratigraphic position is not clear.

- **Phase 3**: Next pit phase postdating Layer 5 and earlier strata, filled in by Layers 18 and 19 (grey clay). The size of the pit was smaller than in Phase 2. The gleicy features are associated with this pit.

- **Phase 4**: The size of the pit was reduced, and the pit wall was “plastered” with clay (Layer 8). It postdates Layer 19 and was filled with Layers 13, 7, and 6.

Material encountered in the Layers 15, 37, 17, and 33/30 (Phase 1), 22 and 23 (Phase 2), 19 (Phase 3), 13, 7, and 6 (Phase 4), and 2 is all very similar: light coloured, calcareous quartzitic sand.

As to the crescent-shaped deposit, the calcareous sands that strongly resemble those described above, regularly contain marine shells (2–4 cm in size) notably of the marine species *Aporrhais pespelecan*. They consist of irregularly stacked layers with slight differences in composition (Figure 7a). Stratification is often highly irregular and complex, testifying to the multiphased nature of these deposits (Figure 7b). In some places, intercalated strata consisting of fragments of coarse ware ceramics were encountered. Figure 4b shows such a stratum which was sampled for chemical analyses. The overlying and underlying sand lacks any sign of remobilization of carbonates. The ceramic fragments are carbonate-encrusted but are not cemented and occur as a loose assemblage.

### 3.2.2 The pit complex: Composition and geophysical characteristics

Readily dissolving carbonates form only a minor component of the calcareous quartzitic sand, whereas “total carbonates” constitute up to about one-third of the total mass and consist of carbonates, relatively high in iron and magnesium (Table 1). Fe contents are particularly high in Layers 19 and 17, with distinctly lower Mg values.

The fractions >105 µm largely consist of angular quartz, with in addition some detrital feldspar and mica, and as second major component fine-grained aggregates of secondary carbonates (Figure 8). Fossil shell material was found in variable amounts and is typically from a shallow coastal marine environment. All shell material is small in size (<c. 1 mm) and includes small Foraminifers (abundant, various species) and lesser Polychaeta, Bryozoa, Ostracoda, Bivalvia, Gastropoda, Echinoderma, and Porifera. In samples from Layers 6, 7, and 13 (Phase 4) shells are abundant, whereas in the other samples the shell content is distinctly lower, and shells may even be rare (Layers 18 and 19, Phase 3). What is remarkable is the perfect preservation of juvenile shells and the absence of postdepositional dissolution of these shells. This is evidenced by the thin section of Layer 7, with abundant secondary carbonates covering the fully intact fossils (Figure 8c,d). Shells largely consist of calcium carbonate, which means that concentrations of Fe and Mg in the secondary carbonates must be higher than indicated in Table 4. In what follows, these secondary carbonates are referred to as ferroan-magnesian calcites.

Though both calcium carbonate and quartz are diamagnetic, that is they are repelled by a magnet (Ivakhnenko & Potter, 2004), the quartzitic sands show up clearly in the survey, as is also evidenced by the MS measurements (Figure 9). The Macigno soil and layers derived from that...

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**FIGURE 7** (a) Inclined dump of irregularly alternating sands with varying carbonate content, area A; (b) irregularly alternating calcareous sands in area B—wall opposite pit (see 6b) [Color figure can be viewed at wileyonlinelibrary.com]
material exhibit low values for MS, whereas it is particularly the highly calcareous quartzitic sand in and around the pit that shows high values.

In contrast to quartz and calcium carbonates, there are also paramagnetic carbonates with a weak positive MS, such as siderite (FeCO₃). Salts may be paramagnetic or diamagnetic, such as NaCl (Heinrich, Schmidt, Schramm, & Mertineit, 2017). Evidently, after being leached by infiltrating excess precipitation over a period of millennia, the chances of preservation of relevant amounts of soluble salts are nil. This leads to a further question: why do the sandy deposits at Puntone produce the unexpectedly elevated positive magnetic signatures in the pit features as well as the expected negative magnetic anomalies in the crescent-shaped features?

Table 1 shows that after removal of the carbonates, the magnetic properties were as expected for this quartzitic material. The aberrant behavior is thus linked to the presence of the carbonates. Ferroan calcites are known to have low magnetic susceptibilities (paramagnetic; Hunt, Moskowitz, & Banerjee, 1995; Ivakhnenko & Potter, 2004). Samples from Layers 7 and 13 behave rather differently, largely retaining their magnetic properties after removal of the carbonates. Here, other minerals may play a role such as magnetotactic bacteria, which may have lived in a brine collected in the pit (Faivre & Schuler, 2008).

### 3.2.3 Soluble elements

Table 2 presents the results from the chemical analyses. It shows that values for Mg, Na, and B in the pit and associated deposits are distinctly higher than those for the nearby “Macigno soil.” Even more prominent, however, are the differences in the various ratios, including Na/Cl (higher), Mg/Na (distinctly higher), and B/Na. These ratios clearly point to a significant contribution from elements of marine origin. However, total soluble salt contents, defined as the sum of Mg, Na, K, S, and Cl, remain relatively low, implying that salts, even if initially present in higher concentrations, have largely been leached over the following millennia, as is to be expected given the high mobility of the ions concerned (see below).

In the dump, the highest values for elements and ratios indicative for a marine origin are found in profile C2 (Table 3). B values are also very high, as are S values in the lower part of the section. Remarkably, the highest values are encountered in the layer composed of ceramic fragments. In profile C1, values are lower but still indicative of a significant marine contribution. Total soluble salt contents reach their highest values in the lower part of C2 below the layer with ceramic fragments, which are assumed to be the remains of ceramic vessels in which solid salt was produced.

Differences exist in mobility between monovalent and bivalent cations, and between anions and cations (McBride, 1994). Over time, leaching by infiltrating rainwater will lead to an increase in the ratio between bi- and monovalent cations (e.g., Mg/Na) and between cations and anions (e.g., Na/Cl). This is evidenced in the data, where the lowest Na/Cl ratios are found in samples with the highest concentrations of these elements and thus the least leaching. The various materials can be interpreted as being more or less leached, with corresponding changes in both concentrations and element ratios; C2 exhibits the most prominent saline conditions, notably in and below the ceramics layer.

The values for B are particularly interesting, since B-concentrations in marine deposits are considerably higher than in terrestrial deposits, and B-concentrations can be used as a facies indicator (Frederickson & Reynolds, 1960; Harder, 1970; Vengosh et al., 1992). Boron (B) is relatively tightly bound in micaceous minerals and may be less rapidly leached (see e.g., Goldberg, Suarez, & Shouse, 2008). Our values concern extractable B and suggest that the samples contain a significant pool of total B. The B/Cl ratios are far higher than those for seawater and thus point to earlier direct contact with a highly saline brine in which B concentrations would have reached high values (see Section 4.3).

### Table 1

| Layer | Carbonates HAc (%) | Carbonates HCl (%) | Fe (%) | Ca (%) | Mg (%) | C (%) | N (%) | S (%) | Ac | HCl |
|-------|--------------------|--------------------|--------|--------|--------|-------|-------|-------|-----|-----|
| 6     | 1.41               | 32.0               | 8.62   | 73.59  | 17.79  | 0.79  | 0.039 | 0.031 | 11.3 | 0.94 |
| 7     | 1.71               | 36.1               | 5.53   | 80.53  | 13.94  | 1.63  | 0.081 | 0.049 | 18.6 | 11.6 |
| 13    | 0.69               | 31.9               | 6.45   | 81.41  | 12.14  | 1.41  | 0.083 | 0.051 | 13.9 | 10.4 |
| 19    | 3.93               | 28.2               | 20.84  | 70.63  | 8.54   | 0.54  | 0.050 | 0.022 | 5.91 | 0.02 |
| 20    | 2.38               | 15.4               | 7.04   | 74.87  | 18.09  | 0.27  | 0.030 | 0.022 | 5.69 | 0.03 |
| 15a   | 1.57               | 22.7               | 8.78   | 80.78  | 10.44  | 0.29  | 0.010 | 0.014 | 3.86 | 0.04 |
| 15b   | 1.55               | 29.3               | 7.73   | 81.65  | 10.62  | 0.46  | 0.020 | 0.015 | 1.57 | 0.09 |
| 17    | 1.63               | 23.5               | 13.22  | 77.27  | 9.52   | 0.14  | 0.010 | 0.013 | 0.70 | 0.14 |

Note: Chemical composition of the carbonates (sum of Fe, Ca, Mg = 100%); C, N, and S content of carbonate-free residues. Magnetic susceptibility of the Ac and HCl treated fractions in $\text{Si}^4\text{10}^3$.  

**TABLE 1** Readily dissolved (HAc) and total carbonates (HCl)
3.2.4 | Radiocarbon dating

Layer 16 (Figure 6a) was the only sediment containing charcoal that could be dated. In the other layers, no charcoal or identifiable plant macro remains were found. For that reason, $^{14}$C datings were performed on two shell samples (Table 4 and Figure 10).

Layer 16 forms the earliest layer that must be contemporary with the outset of Phase 1, setting it at 1,073–875 cal BC. This is in line with the dating by Aranguren et al. (2014) and suggests that salt production started in the late Final Bronze Age to Early Iron Age (Van der Plicht & Nijboer, 2018). Ages found for the shells obviously have to be corrected for the seawater reservoir effect, as shown in Figure 10 (910–739 cal BC for US13 and 726–416 cal BC for US 6). These corrected values are lower than those reported by Sabatier et al. (2010) and may be open to question (see e.g., Lowe et al., 2007). Furthermore, shells may date from before the “harvest” of the sand as raw material and thus “true” ages might well be lower.

4 | DISCUSSION

Alessandri et al. (2019) have produced a major overview of the briquetage sites along the Tyrrenian coast of central Italy, which includes the Puntone site. Briquetage as a salt production technique involves obtaining a brine, storing this brine, boiling the brine in ceramic vessels over a fire, and then breaking the vessels to extract the solid salt (Harding, 2013).

4.1 | Brine production

Brines can be obtained in various ways, such as by evaporation of seawater in salinas, but other techniques may also have been used. At our site, no indication was found for the earlier existence of salinas or other installations, based on solar evaporation. In contrast, strong circumstantial evidence was found for the production of brine by leaching of sediment, “harvested” from the adjacent lagoon (Aranguren et al., 2014). In this nearby open and very shallow lagoon, salt must have seasonally accumulated at the surface, a phenomenon
# Table 2

Chemical composition, pH, EC and elemental ratios of water extracts from individual layers from the pit and Macigno soil

| Unit | Location/Depth | pH  | H₂O (mg/kg) | Mg (mg/kg) | Ca (mg/kg) | Na (mg/kg) | K (mg/kg) | B (mg/kg) | P (mg/kg) | S (mg/kg) | Cl (mg/kg) | Soluble (mg/kg) | Na/Cl | Mg/Na *100 | Mg/Ca *100 | B/Na *100 | B/Mg *100 | B/Cl *100 |
|------|----------------|-----|-------------|------------|------------|------------|-----------|-----------|-----------|-----------|------------|-----------------|--------|------------|------------|-----------|------------|-----------|
| Pit  | Pit top        | 7.95| 210         | 16.3       | 87.1       | 8.6        | 0.36      | 0.42      | 0.42      | 2.30      | 2.31       | 30               | 3.73   | 0.19       | 4.9        | 257       | 18.2       |
|      | Pit fill       | 7.67| 268         | 20.8       | 109.6      | n.d.       | 0.45      | 0.52      | 0.35      | 3.38      | 2.84       | nd.             | 3.75   | 0.19       | 4.9        | 248       | 18.1       |
|      | Pit fill l     | 7.67| 228         | 17.0       | 87.7       | 11.1       | 1.08      | 0.55      | 0.26      | 2.62      | 3.55       | 35               | 3.13   | 0.19       | 5.0        | 323       | 15.5       |
|      | Pit fill l     | 7.68| 227         | 19.3       | 62.6       | 15.9       | 2.11      | 0.78      | 0.25      | 3.23      | 4.44       | 45               | 3.58   | 0.31       | 4.9        | 405       | 17.7       |
|      | Pit fill l     | 7.75| 167         | 12.2       | 46.1       | 10.9       | 0.80      | 0.53      | 0.19      | 1.87      | 3.82       | 29               | 2.84   | 0.26       | 4.9        | 438       | 14.0       |
|      | Pit fill l     | 8.31| 192         | 14.2       | 49.1       | 12.8       | 1.71      | 0.63      | 0.17      | 2.51      | nd.         | nd.             | nd.    | 0.29       | 4.9        | 444       | nd.        |
| 5    | Pit wall       | 8.21| 171         | 9.0        | 53.9       | 10.2       | 1.07      | 0.42      | 0.17      | 2.42      | 2.49       | 25               | 4.11   | 0.17       | 4.2        | 470       | 17.1       |
| 8    | Pit wall       | 7.9 | 185         | 11.7       | 64.6       | 12.9       | 1.74      | 0.53      | 0.18      | 3.05      | 2.22       | 32               | 5.82   | 0.18       | 4.1        | 456       | 24.0       |
| 17   | Side pit       | 7.76| 188         | 12.3       | 66.0       | 8.3        | 1.91      | 0.38      | 0.17      | 3.12      | 3.55       | 29               | 2.33   | 0.19       | 4.7        | 314       | 10.8       |
| 14a  | Side pit       | 7.75| 176         | 12.3       | 53.6       | 9.3        | 1.23      | 0.46      | 0.09      | 2.35      | 2.36       | 27               | 3.93   | 0.23       | 5.0        | 378       | 19.7       |
| 14b  | Side pit       | 7.77| 175         | 13.2       | 58.8       | 10.3       | 0.98      | 0.55      | 0.09      | 3.02      | 2.57       | 30               | 4.02   | 0.22       | 5.3        | 418       | 21.4       |
| 15a  | Side pit       | 7.92| 151         | 15.4       | 59.4       | 10.9       | 0.53      | 0.50      | 0.14      | 3.12      | 3.06       | 33               | 3.57   | 0.26       | 4.6        | 323       | 16.3       |
| 15b  | Side pit       | 7.81| 196         | 17.7       | 58.6       | 10.6       | 0.62      | 0.57      | 0.11      | 3.01      | 3.37       | 35               | 3.14   | 0.30       | 5.4        | 324       | 17.0       |
| 16a  | Side pit       | 7.73| 163         | 12.4       | 48.1       | 11.1       | 1.14      | 0.50      | 0.12      | 1.45      | 3.82       | 30               | 2.92   | 0.26       | 4.5        | 400       | 13.0       |
| 16b  | Side pit       | 8.47| 178         | 11.8       | 48.7       | 10.9       | 1.05      | 0.44      | 0.13      | 1.12      | 4.44       | 29               | 2.46   | 0.24       | 4.0        | 370       | 9.8        |
| 16r  | Side pit r     | 8.38| 163         | 10.8       | 54.6       | 12.1       | 1.02      | 0.46      | 0.13      | 2.22      | 3.99       | 30               | 3.02   | 0.20       | 3.8        | 422       | 11.4       |

| Macigno soil | | | | | | | | | | | | | | | | | | | |
| 34 | 30-40 cm | 7.94 | 134 | 6.6 | 52.1 | 9.7 | 0.94 | 0.25 | 0.41 | 1.90 | 4.44 | 24 | 2.19 | 0.68 | 0.13 | 2.6 | 384 | 5.7 |
| 35 | 40-50 cm | 8.28 | 149 | 6.7 | 51.7 | 9.3 | 0.87 | 0.25 | 0.54 | 2.07 | 4.26 | 23 | 2.19 | 0.72 | 0.13 | 2.6 | 369 | 5.8 |
| 36 | 50-60 cm | 8.21 | 144 | 7.1 | 48.8 | 9.5 | 1.39 | 0.24 | 0.54 | 1.83 | 3.46 | 23 | 2.75 | 0.74 | 0.14 | 2.5 | 337 | 6.9 |
| 37 | 60-70 cm | 8.25 | 142 | 8.8 | 42.8 | 8.9 | 1.80 | 0.24 | 0.28 | 1.09 | 2.40 | 23 | 3.73 | 0.99 | 0.21 | 2.7 | 272 | 10.0 |

Note: Soluble salts = Mg + Na + K + S + Cl.
Abbreviations: *100 = multiplied by 100; l = left side; n.d. = missing value; r = right side.
TABLE 3  Chemical composition, pH, EC, and elemental ratios of water extracts from the two profiles in the dump of area

| Profile | Cm depth (mm) | pH  | H₂O (µS/cm) | EC (µS/cm) | Mg (mg/kg) | Ca (mg/kg) | Na (mg/kg) | K (mg/kg) | B (mg/kg) | P (mg/kg) | S (mg/kg) | Soluble (mg/kg) | Na/Cl | Mg/Na | Mg/Ca | B/Na *100 | B/Mg *100 | B/Cl *100 |
|---------|--------------|-----|-------------|------------|------------|------------|------------|----------|----------|----------|----------|---------------|-------|-------|-------|----------|----------|-----------|
| C1      | 0-10         | 7.59| 183         | 10.0       | 80.4       | 8.1        | 1.56       | 0.573    | 0.51     | 4.00     | 231      | 26             | 3.49  | 1.24  | 0.12  | 7.1       | 5.73     | 248       |
|         | 10-20        | 8.44| 131         | 7.5        | 59.2       | 5.0        | 0.94       | 0.23     | 0.40     | 2.22     | nd.      | nd.            | nd.   | 1.51  | 0.13  | 4.6       | 3.02     | nd.       |
|         | 20-30        | 8.45| 135         | 7.2        | 56.5       | 4.7        | 0.67       | 0.22     | 0.29     | 2.10     | 1.95     | 17             | 2.39  | 1.54  | 0.13  | 4.8       | 3.12     | 11.4      |
|         | 30-40        | 8.25| 183         | 10.8       | 69.6       | 7.4        | 0.53       | 0.36     | 0.13     | 3.14     | 4.79     | 27             | 1.55  | 1.46  | 0.16  | 4.9       | 3.33     | 7.5       |
|         | 40-50        | 7.66| 195         | 14.5       | 84.0       | 10.1       | 1.33       | 0.48     | 0.16     | 8.35     | 8.25     | 42             | 1.22  | 1.44  | 0.17  | 4.8       | 3.34     | 5.9       |
|         | 50-60        | 7.93| 147         | 11.4       | 68.1       | 10.5       | 0.64       | 0.36     | 0.15     | 3.55     | 5.86     | 32             | 1.79  | 1.08  | 0.17  | 3.4       | 3.15     | 6.1       |
|         | 60-70        | 8.08| 134         | 8.7        | 56.3       | 7.7        | 0.41       | 0.43     | 0.14     | 2.90     | 3.28     | 23             | 2.34  | 1.13  | 0.15  | 5.6       | 4.91     | 130       |
|         | 70-80        | 8.08| 136         | 8.8        | 51.1       | 8.8        | 0.70       | 0.38     | 0.11     | 2.71     | 3.11     | 24             | 2.85  | 0.99  | 0.17  | 4.3       | 4.35     | 12.3      |
|         | 80-90        | 8.09| 125         | 8.4        | 49.2       | 7.8        | 0.63       | 0.36     | 0.10     | 2.68     | 3.28     | 23             | 2.38  | 1.07  | 0.17  | 4.6       | 4.28     | 10.9      |
| C2      | 0-10         | 8.13| 201         | 12.0       | 79.0       | 10.4       | 0.39       | 0.76     | 0.14     | 4.85     | 4.44     | 32             | 2.34  | 1.16  | 0.15  | 7.3       | 6.32     | 17.2      |
|         | 10-20        | 7.95| 243         | 13.8       | 92.8       | 17.3       | 0.70       | 0.64     | 0.31     | 6.85     | 15.18    | 54             | 1.14  | 0.80  | 0.15  | 3.7       | 4.63     | 4.2       |
|         | 20-30        | 7.76| 295         | 18.0       | 108.4      | 25.0       | 0.44       | 1.49     | 0.28     | 8.75     | 15.04    | 67             | 1.66  | 0.72  | 0.17  | 5.9       | 8.24     | 9.9       |
|         | 30-40        | 7.91| 260         | 19.9       | 90.1       | 29.3       | 0.33       | 1.40     | 0.17     | 7.89     | 23.96    | 81             | 1.22  | 0.68  | 0.22  | 4.8       | 7.03     | 5.8       |
|         | 40-50        | 7.81| 194         | 15.4       | 69.7       | 18.3       | 0.34       | 1.00     | 0.11     | 5.72     | 17.93    | 58             | 1.02  | 0.84  | 0.22  | 5.4       | 6.48     | 5.6       |
|         | 50-60        | 7.92| 154         | 12.6       | 58.0       | 13.7       | 0.34       | 0.67     | 0.09     | 4.87     | 14.33    | 46             | 0.96  | 0.92  | 0.22  | 4.8       | 5.28     | 4.6       |
|         | 60-70        | 7.90| 191         | 16.3       | 76.2       | 14.3       | 0.26       | 0.80     | 0.15     | 11.64    | 12.34    | 55             | 1.16  | 1.14  | 0.21  | 5.6       | 4.95     | 6.5       |
|         | 70-80        | 8.15| 251         | 20.1       | 80.5       | 13.3       | 0.44       | 0.58     | 0.08     | 29.10    | 14.20    | 77             | 0.93  | 1.52  | 0.25  | 4.4       | 2.88     | 4.1       |
|         | 80-90        | 7.85| 288         | 27.4       | 98.6       | 17.6       | 0.22       | 0.75     | 0.09     | 54.69    | 22.54    | 122            | 0.78  | 1.56  | 0.28  | 4.2       | 2.73     | 3.3       |
| Eastern | Med. Sea     |     |             |            |            |            |            |         |          |          |          |                |       |       |       |          |          |           |
|         | 1403         | 423 | 11800       | 463        | 13.23      | 21200      | 0.56       | 0.119    | 3.32     | 0.112    | 0.94     | 0.06             |       |       |       |          |          |           |

Note: Soluble salts = Mg + Na + K + S + Cl. Composition Eastern Mediterranean Sea is from https://www.lenntech.com/composition-seawater.htm
Abbreviations: C*100 = multiplied by 100; n.d. = missing value; ceram. = layer with ceramic sherds.
that can still be observed in the current lagoon and which has been well described for many coastal lagoons (e.g., Summa, Margiotta, & Tateo, 2019). The highly saline sediment constitutes an excellent raw material for brine production, which can be obtained by leaching the sediment with sea water. Sea water would have been used since there was no local source of fresh water. The large volume of the crescent-shaped dumps—at least 2,000 m$^3$ cubic meters—testifies to their massive use as salt source. No other explanation can be devised for the existence of the dumps. The question remains, however, of exactly how the brine was produced.

Two basic techniques are known from ethnographic studies (Cassen & Weller, 2013; Harding, 2013; Parsons, 2001; Sebillaud, Liu, & Wang, 2017; Weller, 2015; Williams, 2002). Technique 1 consists of leaching sediment in a pit or container, which at its base has a "drain" through which the leachate is collected in containers. Technique 2 consists of leaching sediment over a "sieve" and collecting the leachate in a container or pit. The sieve may be a piece of tightly woven fabric, placed over the pit, or similar construction involving another sort of sieve. In the excavated pit there was no trace of a drainage pipe, implying that technique 1 can be completely ruled out. Conversely, there were strong indications for the use of a "sieve" method, and these are described below in more detail.

The sands of the dumps contain relatively large mollusc shells, whereas in the pit these are completely absent. The material in the pit holds only small sized shells (< 1 mm), which suggests that the material was indeed "sieved." Small amounts of finer sediment, including small shells, would have passed through this sieve to gradually accumulate in the pit and ultimately filling it. This would have necessitated a regular cleaning-up of the pit after which operations could be resumed and readily explains the several phases in its use, as described in Section 3.2.1.

In summary, it is likely that the lagoonal sediment was collected during the dry season, when salt crusts formed in the topsoil. We conclude that after having been leached, the residual sediment was dumped, forming large crescent-shaped fans. For this leaching, a "sieve" was used with some fine sediment passing through it. What type of "sieve" remains obscure, but the mesh must have been small (c. 1 mm). The sediment that washed through the sieve gradually filled the pit and necessitated a regular "clean-up." The overall process is tentatively depicted in Figure 11. The several fans and associated pits (Figure 2) suggest that several sieve-pit-dump systems were operative.

### 4.2 The function of the pit

The soil into which the pit was dug is quite impervious, allowing for its use as a brine collector and container. The presence of a layer of "clay plaster" (Layer 8) suggests that cleaning was accompanied by plastering the pit wall to reduce infiltration losses. That the pit indeed had a reservoir function can be concluded from the pronounced hydromorphic properties in the walls of the pit (Layers 5, Figure 6a,b), which can only result from anoxic conditions brought about by prolonged water stagnation. There is also other evidence
for such prolonged existence of anoxic conditions in the form of ferroan-magnesian calcites in the pit fill.

Carbonates that eventually formed in the lagoonal sediment upon strong evaporation during the dry summer season may hold some magnesium. However, formation of ferroan-magnesian calcites under such conditions can be ruled out (Aqrawi, 1995; Romanek et al., 2009; Wittkop, Teranes, Lubenow, & Dean, 2014). This is supported by the distinctly diamagnetic character of the dumps, confirming that the processed sands do not hold such paramagnetic carbonates.

As described above, the Macigno sandstone and soils in sediments derived from this rock, are relatively high in iron (4–7%). It is very likely that upon reduction in an anoxic environment, that is in a pit filled with brine, ferrous iron reached the concentration levels required for these specific carbonates to form (Barnaby & Rimstidt, 1989; Pye, Dickson, Schiavon, Coleman, & Cox, 1990). Obviously, their precipitation additionally requires evaporative losses from the brine. Such precipitation must have been significant given the carbonate contents in the pit fill, relative to what might have been expected in the original lagoonal sediment, which contained only minor amounts of carbonate (up to 10% or so). Additional evidence for prolonged storage of brine in the pit is provided by the chemical analyses in Table 2 (discussed in Section 3.2.4). The relatively high B concentrations in particular are highly indicative for such a use of the pit, since these higher concentrations and associated increases in the ratios B/Na and B/Cl can only be explained by their residual concentration in a residual brine.

In summary, evidence for the use of the pit as a brine collector is abundant: (a) the distinct iron redistribution in the walls of the pit; (b) the ferroan-magnesian carbonates, which can only be formed upon reduction of iron-rich paleosol-derived material under prolonged anoxic conditions and subsequent precipitation of the ferrous iron released as carbonate; and (c) the relatively high

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**FIGURE 10** Calibrations of radiocarbon ages (Marine curves in green) [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 11** Presumed phases in the salt production processes at Puntone [Color figure can be viewed at wileyonlinelibrary.com]
amounts of "marine elements" such as Mg, Na, Cl, and B in the fill and walls of the pit. There are quite a few descriptions of modern analogues of such "sieve over a brine-collecting pit" systems using saline topsoil material in ethnographic studies on salt production in coastal areas. One of the best examples is from Central America (Williams, 2002).

From the study of the pit and directly associated deposits we concluded that at least four major phases could be distinguished. Each of these consisted of more or less distinct subphases, as evidenced for example by the complex built-up of successive layers around the pit B2 during Phase 1. Though little is known about the existence and use of a pit in this Phase 1, throughout the whole period saline lagoonal sediment was used as a primary salt source. Production must have started at the latest c. 1073–850 cal BC and probably lasted until the 4th c. BC.

### 4.3 | Briquetage

Studies on modern salt production emphasize that upon evaporation of a brine, undesired salts must be removed, and they describe methods by which this can be achieved most efficiently (see e.g., Hussein et al., 2017). These salts include calcium carbonate (calcite) and calcium sulfate (gypsum), which in the main precipitate before the principal production stage at which sodium chloride (halite) precipitates. Salts such as magnesium sulfates precipitate at a later stage (Usigio, 1849 and later authors such as Babel & Schreiber, 2014).

The carbonates we found cannot have other than a marine origin, that is they were either present as fossils and other carbonates in the lagoonal sediment or were precipitated from the brine and seawater that were used in the process. The deeply weathered soil in the Macigno-derived fan deposits was completely free of carbonates and only played a role as a source of ferrous iron that coprecipitated with magnesium and calcium to form the ferroan-magnesian calcites causing the deviating magnetic behavior of the materials from the pit fill. Quite significant amounts of carbonates must have precipitated in the pit as evidenced by the occurrence of the ferroan-magnesian calcites, which cannot have formed in anoxic environment (open lagoon). This suggests that the brine that was used stood in the pit for significant periods of time and over that period lost most of its carbonates and gypsum as a result of evaporation and concurrent precipitation.

Other undesired salts would have been "bitterns" (Mg-salts) that precipitate at a late stage of evaporation of brines, which in our case is upon their heating in a vessel (McCaffrey et al., 1987; Hussein et al., 2017). Basically, two methods exist to produce relatively pure halite by heating brines in a vessel: (a) Collection of halite crystals from an evaporating brine and separate processing of these crystals, and (b) Decantation of residual brine at a late stage, which serves to remove the still dissolved "bitterns" from the halite (NaCl) crystals that already have been formed. In other words, relatively pure halite can be produced by decanting the residual "mother liquor" (c.f. McCaffrey et al., 1987) before the precipitation of "bitterns" and after successive replenishments of the brine to a stage that the vessel is sufficiently filled with solid salt. The fundamentals of these methods have been described by McCaffrey et al. (1987) and Akridge (2008). In Method 1, halite crystals need to be collected repeatedly from a hot brine in vessels on a fire. Method 2 is easily applicable and efficient, rather than the mechanical separation of salt crystals from a brine in a vessel. In this Method 2, a vessel on a fire can be replenished with brine until sufficient halite has accumulated. The vessel is then removed from the fire or the fire extinguished and after cooling the residual liquid is decanted. Evidently, Method 1 would not formally fall under the definition of briquetage—briquetage includes the breaking of the ceramic vessel to collect the solid salt it contains—and is very unlikely to have produced the large mass of typical ceramic fragments.

Decantation or harvesting of the salt crystals inevitably produces a "mother liquor" that is enriched in Mg, K, S, and B (see e.g., Babel & Schreiber, 2014). This is what was observed in the chemical analyses of the dump and pit samples (Tables 2 and 3), which suggests that this "mother liquor" was indeed disposed of. This aspect of the briquetage process—the need to remove "bitterns"—seems to have been fully overlooked in recent studies. This conclusion is in line with the statement by Gouletquer and Weller (2015, p. 25) that "the research about the processes taking place before firing are dramatically lacking." We did not find decisive evidence in favor of one of the potential methods to remove the "bitterns" but consider the second process—decantation—to be far more efficient and applicable in the context that we studied. Decantation is therefore assumed to have been an integral part of the salt production process at Puntone (Figure 11).

### 5 | GENERAL DISCUSSION AND CONCLUSIONS

The various steps in the salt production that we reconstructed are summarized in Figure 11. It is not clear whether the briquetage system at Puntone is unique in its use of saline lagoonal sediment in such a "sieve-brine pit-briquetage with decantation" system. A few similar pits associated with large Iron Age potsherd dumps and lined with clay have been found at La Mattonara (Toti, 1962) and Torre Chiaruccia (Barbaranelli, 1956), respectively. These excavations were, however, poorly documented and it is therefore uncertain what function these pits had. Most protohistoric briquetage industries described in the literature appeared to use a salinas system to produce a brine and how "bitterns" were dealt with in that type of salt production process is rarely described in detail (Harding, 2013).

For a reliable estimate of the productivity of the salt production system studied more information is required concerning such parameters as the volumes of briquetage debris and of raw material used, and the time span over which production took place. At our site, a considerable volume of lagoonal sediment was leached (c. 2000 m³) and it seems most likely that several sieve-pit-briquetage systems were operative. However, thus far near Puntone only a small area was surveyed and excavated, and the total size of the site is not yet known. At the level of the region and beyond, insight into the scale of
this type of briquetage might be significantly increased by more systematic geophysical prospections, as carried out in the present project. These should be performed on a broad landscape scale along the borders of those (former) coastal lagoons that in protohistory were open to the sea. Moreover, excavations should not only target pyrotechnological features (kilns or fire pits) and ceramic debris but also sand dumps and sand pits to reconstruct the chaîne opératoire of the briquetage.

Our radiocarbon data suggest that at Puntone the industry started in the Late Bronze Age/Early Iron Age (around the 10th c. BC) and eventually lasted well into the 5th c. BC, but this has not yet been corroborated by the typology-based ceramics datings. Though the total dimensions of the production complex are still uncertain, it is evident that the dimensions of a sieve-pit-briquetage system were smaller and its logistics far less complex than those of the well-known salinas systems that operated in the Piombino area and in many other Mediterranean coastal areas later in the first millennium BC. Population increase in the course of this millennium undoubtedly necessitated the upscaling of the salt production and the salinas systems may have gradually replaced protohistoric briquetage systems based on small-scale brine production by leaching lagoonal sediment.

Recent studies of protohistoric salt production by briquetage increasingly pay attention to salt in ceramic materials, employing a variety of modern analytical techniques to prove their salt production function (Flad et al., 2005; Graham et al., 2015; Macphail et al., 2012; Raad et al., 2014; Sandu et al., 2012; Sordoillet et al., 2018; Tencaru et al., 2015). Results are not always conclusive, since often no hard evidence is found for the use of these ceramics as brine/salt containers (e.g., Raad et al., 2014). This is not surprising since Na and Cl are highly mobile elements that are easily leached by infiltrating water. Moreover, in Mediterranean coastal areas salt-spray has a strong impact on the chemical composition of infiltrating water (Manca, Capelli, & Tuccimei, 2015), an impact that is neglected as a potential cause of relatively high Cl (and Na) concentrations currently found in these ceramics. In conclusion, we believe that the focus on residual Cl is not particularly useful as a means to better understand the processes involved. Aspects that thus far have received only marginal attention in relation to a production site include (a) the strong enrichment of other elements in the residual brine or "mother liquor," and the associated changes in element ratios relative to Na and Cl, and (b) the higher concentrations of boron and its indicator function. Both phenomena are far less sensitive to later leaching and to salt-spray and, as strongly suggested by our observations, are more accurately indicative of the processes involved in salt production by briquetage.

Our study demonstrates the value of a multidisciplinary approach in the study of such briquetage systems, with emphasis on the physicochemical characteristics of materials at site level and on an adequate insight into the geochemical aspects of salt production by evaporation. It provides a deep insight into the techniques used in protohistoric salt production, where brine was not produced by solar evaporation in salinas, but by leaching of saline lagoonal sediment.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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