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## Earliest salt working in the world: From excavation to microscopy at the prehistoric sites of Țolici and Lunca (Romania)

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### ► To cite this version:

Dominique Sordoillet, Olivier Weller, Nicolas Rouge, Martine Buatier, Jean-Pierre Sizun. Earliest salt working in the world: From excavation to microscopy at the prehistoric sites of Țolici and Lunca (Romania). *Journal of Archaeological Science*, 2018, 89, pp.46 - 55. 10.1016/j.jas.2017.11.003 . hal-01676289

**HAL Id: hal-01676289**

**<https://hal.science/hal-01676289>**

Submitted on 11 Dec 2023

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1 **Earliest salt working in the world: from excavation to microscopy at the prehistoric sites of Tolici**  
2 **and Lunca (Romania)**

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**Abstract**

Since the Early Neolithic, salt has played an important role in the social and economic development of populations. Consequently, the study and comprehension of salt management strategies have become a significant component of current archaeological research. This study is part of an interdisciplinary research program consisting of excavations and detailed analyses at two earliest salt working sites situated in the sub-Carpathian region of Romania, Lunca and Tolici (county Neamt). These remarkably well-preserved sites are characterized by stratified deposits of several meters thick. Detailed stratigraphic descriptions were followed by optical microscopy analysis (soil micromorphology) and scanning electron microscopy (SEM) coupled with geochemical analysis (EDS). The aim of these analyses was to identify specific sedimentary, petrographic and chemical characteristics that could be linked to salt working process. The results enable us to describe the main site formation process over time and to detect chemical components of edible salt (Na and Cl) in Early Neolithic ashes. These new data and consolidate previous interpretations of the operating procedures implemented from the Early Neolithic to the Early Bronze Age. Two techniques appear to have been preferentially adopted: pouring natural brine onto combustion structures during the Early Neolithic and evaporation in specific ceramic containers from the Chalcolithic onwards.

**Keywords:**

Neolithic; salt working; brine; hearth; micromorphology; SEM-EDS; Romania

52 **1. Introduction**

53  
54 Since the Early Neolithic, salt has played an important role in societies for the consumption and  
55 conservation of foodstuffs, livestock farming or for therapeutic purposes (Weller 2015). The control  
56 of deposits and production sites, the mastery of extraction techniques and the transport of salt over  
57 long distances all contributed to the social and economic development of populations. Consequently,  
58 the study and comprehension of salt management strategies have become a significant component of  
59 current archaeological research, as shown by recent studies and collective works in Europe (Alexianu  
60 et al. 2011; Biddulph et al. 2012; Nikolov, Bacvarov 2012; Harding 2013, Alexianu et al. 2015;  
61 Brigand, Weller 2015) as well as in Asia (Flad 2011; Horiuchi et al. 2011; Kawashima 2015), America  
62 (McKillop 2005; Williams 2015; Graham et al. 2017) or Africa (Alabi 2000; Antonites 2016).

63 Since 2003, the Franco-Romanian research program "The prehistoric exploitation of salt springs in  
64 Moldova", aims to describe the different technical, socio-economic or ecological aspects of salt  
65 exploitation in this region in the north-east of Romania, from the early Neolithic until the end of the  
66 Chalcolithic (6000-3500BC). Several approaches contribute to this research: prospecting and  
67 recording salt springs and archaeological sites, spatial analyses of territorial dynamics, ethnographic  
68 investigations among riverine communities, archaeological excavations and paleo-environmental and  
69 geo-archaeological studies (see the compilation of studies in Alexianu et al. 2016; Brigand and Weller  
70 2018). The study zone is located along the Carpathian thrust on the Moldavia Plain (Fig. 1). On the  
71 north-south branch of this thrust, more than 200 salt springs and fifteen archaeological sites linked to  
72 salt exploitation were recorded during archaeological survey (Weller et al. 2008a; Weller and Brigand  
73 2017). This dense concentration of sites is due to the upwelling of brine springs in sub-Carpathian  
74 Tertiary argillites rich in salt, through the numerous fault lines running through the massif.

75 Two of them which have our attention are Halabutoaia, near Tolici, and Poiana Slatinei, in Lunca  
76 (county Neamt) (Fig. 1 and 2). The site of Poiana Slatinei was first excavated in 1984-1987 by a team  
77 led by G. Dumitroaia (1987), These first excavations highlighted the potential of the site about the  
78 question of salt making since Neolithic time, so we decided to re-excavate the site in 2004 and to  
79 implement new methods of investigation as micromorphology (Weller et al. 2008b). The site of  
80 Halabutoaia was discovered during prospection in 2005, then excavated and studied by our team from  
81 2007 onwards (Weller et al. 2008a, 2015; Danu et al. 2010). Both sites are located near salt springs  
82 which are still used today and currently represent the oldest known salt production sites in Europe  
83 (Weller and Dumitroaia 2005; Weller et al. 2015). They occur as thick archaeological sedimentary  
84 accumulations, which are several metres high and comprise numerous lenticular layers of clay, ash  
85 and charcoal. The salinity of both mineral springs is very high, with extreme chlorine and sodium  
86 contents (Table 1).

87 The location of the sites near salt sources still in use today and the presence of thick stratified  
88 archaeological sedimentary accumulations, the upper part of which contain pottery generally used for

89 making salt blocks (called briquetages), give rise to the following working hypotheses: a) at Lunca,  
90 like at Tolici, the whole sedimentary sequence, and not just the upper part, may be linked to salt  
91 making ; b) the sedimentary changes in these sequences may reflect the evolution of exploitation  
92 techniques during the course of time. Therefore a detailed study of these deposits was carried out,  
93 beginning with chrono-stratigraphic description in the field, and followed by soil micromorphology  
94 and scanning electron microscopy (SEM) coupled with geochemical analysis (EDS). The aim of these  
95 analyses was to identify specific sedimentary and petrographic characteristics that could be linked to  
96 salt making process and perhaps to detect chemical components of edible salt (Na and Cl). Such  
97 combined use of soil micromorphology and SEM-EDS has already obtained pertinent results from salt  
98 working sites, as at the Iron Age and Roman coastal site of Essex (Macphail et al. 2012) or at Maya  
99 Marco Gonzalez, Belize (Macphail et al. 2017). Other workers employing SEM-EDS found traces of  
100 Na and Cl in pottery from the first millennium BC (Flad et al. 2005) and, in Romania, identified salt  
101 in briquetage at the early 4th millennium sites of Tolici and Cacica (Weller 2000; Sandu et al. 2012;  
102 Tencariu et al. 2015). However, to our knowledge, no analysis of this type has yet been conducted on  
103 sedimentary deposits produced by the first exploitation of salt springs during the 6th millennium B.C.  
104 These new data would be able to provide a much better understanding of salt working processes and  
105 test the hypothesis of pouring brine on earth, previously proposed to explain salt making at Early  
106 Neolithic of Lunca (Weller et al. 2008b; Dufraisse et al 2010). Identifying edible salt in deposits dating  
107 to the second quarter of 6th millennium at Lunca and Tolici could be an important first step for any  
108 discussion of salt making in the early European Neolithic.

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## 110 **2. Material and method**

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### 112 **2.1. Stratigraphic study and sampling**

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#### 114 2.1.1. General principles

115 The stratigraphic study of both sites was based on classically used methods in archaeology (Loustaud  
116 1985; Wheeler 1989; Sordoillet 2009; Harris 2014). Stratigraphic sections were drawn and the main  
117 pedo-sedimentary characteristics of the deposits were described. The main types of deposits were  
118 identified and the first hypotheses concerning site formation processes were advanced, guiding our  
119 sampling strategy. The micromorphological samples were taken from the stratigraphic profiles by  
120 removing blocks of sediment (Murphy 1986). At both sites we have tried to realise the most regular  
121 sampling as possible, in the different deposits and periods. It was relatively easy to do at Tolici, where  
122 we had a complete archaeological sequence, but not at Lunca, where most of the Chalcolithic and  
123 Bronze Age deposits have been removed. The micromorphological samples were also used for making  
124 uncovered thin sections for the scanning electronic microscope and spectrometry studies (Table 2).

125 The location of these uncovered thin sections was chosen according to the micromorphological results,  
126 in order to get chemical composition of specific components that were believed to be salt residues.

### 128 2.1.2. The site of Tolici

129 The Tolici site forms a circular mound of about twenty meters in diameter (Fig. 1). The trench in the  
130 median part allowed the study of the 7-m-thick stratified anthropogenic accumulation (Fig. 2a-b). The  
131 main litho-stratigraphic characteristics of the 29 recorded strata reveal abundant combustion structures,  
132 as shown by the superposition of ashy-charcoal residues on reddened clays. The earliest deposits show  
133 the presence of elongated hollow shapes (Fig. 2a), while the latest deposits are horizontal (Fig. 2b).  
134 These elongated hollows have a gentle slope toward the stream running at the foot of the depositional  
135 mound. White ashy deposits are preserved inside and their outer edges are rubefied. Radiocarbon  
136 dating and typical ceramic material place the beginning of exploitation at around 5700 BC and the  
137 end towards 3500 BC (Weller et al. 2015).

138 Seventeen micromorphological samples were taken from deposits that were considered to be  
139 representative of the whole accumulation (Fig. 3a-b). These samples were also used for making five  
140 smaller uncovered thin sections for the SEM-EDS study. The chronological distribution of the samples  
141 is as follows: eight micromorphological thin sections for the Early Neolithic deposits (Cris cultural  
142 period), one thin section for the Middle Neolithic (Linear Pottery), two thin sections for the final  
143 Neolithic (Precucuteni), and six thin sections from the Chalcolithic (Cucuteni). SEM-EDS analyses  
144 were conducted on all these different exploitation periods, apart from the Middle Neolithic, where the  
145 deposits showed signs of mixing with the surrounding levels.

### 147 2.1.3. The site of Lunca

148 The site of Lunca forms a vast dome 65 m long by 25 m wide (Fig. 1). Two of the 1995 excavation  
149 sectors were reopened in 2004 and permitted the study of several sections, revealing a 3-m-thick  
150 stratified accumulation (Fig. 2c-d). Several tens of lenticular layers, with varied textures and colours,  
151 were brought to light and about a hundred combustion structures were recorded, sometimes with  
152 hollow or trough shapes, like at Tolici. Charcoal dating shows that the first exploitations date to about  
153 6000 BC at the earliest, with a phase of intensification at about 5900-5600 BC, and the most recent at  
154 about 1500 BC (Weller, Dumitroaia 2005).

155 Samples were taken from different points of the site, using residual sedimentary sequences not  
156 reworked by the earlier excavations (Weller et al. 2008b; Dufraisse et al. 2010). Twelve  
157 micromorphological samples are from the Early Neolithic deposits, located in the centre of the site,  
158 and three are from the Bronze Age levels, located on the eastern edge of the site. SEM-EDS analyses  
159 were carried out on five thin sections from the well preserved Early Neolithic deposits.

## 161 2.2. Micromorphology and scanning electronic microscopy

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Sample consolidation and micromorphological thin section manufacture were carried out by Th. Beckmann (Schwülper-Lagesbüttel, Germany), who also produced smaller uncovered thin sections for the scanning electron microscope. The locations for these smaller thin sections were selected in accordance with the micromorphological results, by targeting the sectors with crystallitic assemblages possibly linked to salt manufacture.

Established descriptive methods were applied to the micromorphological thin sections (Bullock et al. 1985; Courty et al. 1989). Each microstratigraphic unit identified in the thin sections was described and numbered in relation to its field number. The description of the sedimentary microfacies was carried out at the Chrono-environment laboratory at Besançon (France), employing a Leica DMLM microscope equipped with a DFC320 camera. The observation of the different types of organic, mineral and anthropogenic components, as well as the microstructure of the deposits result in the identification of the archaeo-sedimentary processes involved in site formation and enable us to advance hypotheses concerning salt fabrication techniques. As this salt production involves the neof ormation of crystals by the evaporation of brines, particular attention was paid to the identification of these salt crystals and their stratigraphic position. During this micromorphological study, some specific features, believed to be salt residues, were selected for spectrometric analysis.

The scanning electron microscopy - energy dispersive X-ray spectroscopy analyses (SEM-EDS), were carried out at Besançon (France), initially in the UMR 6213 laboratory – Utinam, then in the UMR 6174 facility - Femto. The samples were examined with JEOL 5600 and FEI 450 microscopes, respectively coupled with EDS Fondis Electronic and Edax systems. In some cases, the analyses focused on specific crystalline forms (spot mode), and in others on average measurements over larger zones (window mode over about 10 µm). For these analyses, the thin sections were covered with a 20 nm layer of carbon by thermal sublimation using a Cressington 108 evaporator. The electronic microscopy observations were conducted with Backscatter Electron Images in composition mode. For each site, five uncovered thin sections underwent SEM-EDS analyses (Table 2, Fig. 6). At Tolici, 65 measurements were made, and at Lunca, 23 measurements were taken. The aim was to verify if edible salt residues, characterised by Na and Cl elements, could exist in the archaeological deposits, despite the fact that no halite crystal has been recognized during the micromorphological observations.

### **3. Results and preliminary discussion**

#### **3.1. Micromorphology**

Five main deposit facies have been identified during the stratigraphic and micromorphological studies of the two archaeological mounds. They appear in the form of superimposed layers of various thickness and length. They have been named according to their most striking characteristics: yellowish to

199 greenish massive clay layers, reddened clayey lenses, charcoal-rich and ashy beds, microstratified fine  
200 deposits (identified only in thin section) and heterogeneous brownish accumulations. Different salt  
201 crystals have been observed in these deposits and are summarised at the end of this section.

### 203 3.1.1. Yellowish to greenish massive clay layers

204 At both sites, yellowish to greenish clays form the substratum of the archaeological deposits. The same  
205 kind of clays are also present as interstratified beds in the archaeological mounds. The thickness of  
206 these clay beds ranges from a few millimetres to a few centimètres.

207 Under the microscope, the clay forming the substratum at Lunca, just below the first archaeological  
208 levels, is homogeneous and massive, but penetrated by a few biological channels (Fig. 4a). Sand- and  
209 silt-size quartz, granite and gneiss, very numerous organic plant fragments and grass phytoliths are  
210 scattered in the groundmass. Pedofeatures consist of oxidized or yellow clay coatings and dusty clay  
211 intercalations. A few gypsum crystals are present.

212 Yellowish clay layers interbedded in the archaeological mounds, have the same massive fabric as the  
213 substratum, or show particule redistribution evident as banded distribution patterns or parallel striated  
214 b-fabrics (Fig. 4b). These dense and massive beds are in some ways similar to constructed floors or  
215 clay plastering (Boivin 2000; Weller et al. 2008b; Karkanas and Van de Moortel 2014). These  
216 supposed floors would have been made with wet and plastic clay that had been collected locally. As  
217 in the substratum, crystallitic material, but mostly gypsum, is presents in these clay layers.

### 219 3.1.2. Reddened clayey lenses

220 Numerous reddened silty clayey lenses, from a few centimetres to a few metres in diameter, and a few  
221 millimetres to a few centimetres in thickness, are interbedded in the archaeological mounds. Most of  
222 them were overlain by microstratified ashes and charcoal (Fig. 2d and 4a). The microscopic study  
223 revealed that their fabric and microstructure are approximately similar to those of the greenish clays,  
224 and that the main difference is the reddening of the matrix (Fig. 4c-d). This rubefaction, brought about  
225 by fire, decreases from the top to the bottom indicating *in situ* fire places (Dammers and Joergensen  
226 1996; Linford and Canti 2001; Weller et al. 2008b).

### 228 3.1.3. Charcoal-rich and ashy beds

229 The charcoal-rich beds are often located over the rubefied clay lenses, and in some cases on greenish,  
230 gray or gray-brown deposits. The ashy layers are superimposed on charcoal-rich beds or on rubefied  
231 clayey lenses (*in situ* hearths). These combustion deposits are characterized by microstratified ashes  
232 and charcoals (Fig. 4e), and contain various amounts of sherds, fragments of mudbrick, aggregates of  
233 heated or melted clays, vitreous slag, and leaf or grass phytoliths (Canti 2003). The different  
234 combustion residues indicate temperature from 300°C to more than 1000°C, but salt can bring down  
235 the melting points. The calcitic wood ash crystals are often altered and, in some case, calcium

236 carbonate (resulting from the dissolution of ashes) recrystallizes lower down and cements the charcoal-  
237 rich deposits (Dufraisse et al. 2010). This charcoal is generally characterised by strong fragmentation  
238 and vitrified surfaces. Often, thick clay or silty clay coatings and intercalations are present inside the  
239 porosity of charcoal and ash accumulations, indicating significant amounts of dusty water through-  
240 flow (Fig. 4f-i). Crystals or vesicular isotropic nodules which may correspond to salt residues, are  
241 present in these deposits (Fig. 4i and 6).

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#### 243 3.1.4. Microstratified fine deposits

244 Fine microstratified deposits, a few millimetres to one centimetre in thickness, and extending over a  
245 few centimetres, have been identified during the microscopic observations (Fig. 4j-k), while they were  
246 simply described as greenish clays in field profiles. In these beds, at least ten thin lenses of fine sands,  
247 silts or clays are superimposed, with upward-fining characteristics and a relatively high fine charcoal  
248 content. These laminated deposits are interpreted as waterlaid deposits. Periodic settling phases in  
249 quiet standing water could have led to such microstratified layers. The limpid and dusty clay  
250 intercalations observed in the ashy and charcoal-rich layers (Fig. 4f-h), are believed to be linked to the  
251 same sedimentation process. Water infiltration through the deposits would have led to the migration  
252 and the trapping of clay and micro-charcoals in voids. At both sites, these fine microstratified deposits  
253 are particularly characteristic of the Early Neolithic.

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#### 255 3.1.5. Heterogeneous and chaotic accumulations

256 This last deposit facies appears as heterogeneous accumulations of ashes, charcoal, broken pottery and  
257 fragments of fired earth, in variable quantities from one layer to another, which have an open structure  
258 and no preferentially orientated components (Fig. 4l). Such deposits are believed to result from the  
259 remains of demolition and accumulations resulting from human activities (Courty et al. 1989). In our  
260 case, these dump facies could be associated with salt working, as in the case of the Maya site of Marco  
261 Gonzalez in Belize (Macphail et al. 2017). At Lunca and Tolici, such dumped deposits exist for all  
262 occupation periods, but are most frequent from the Chalcolithic onwards.

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#### 264 3.1.6. Salt crystals

265 At both sites, the different archaeological facies revealed the presence of crystals petrologically  
266 identified as salts. Salt crystals are naturally present in the clayey substratum at Lunca, but some of  
267 those observed in archaeological layers could be linked to salt-making. Fibro-radial crystals, observed  
268 in natural and archaeological deposits, are identified as sulfate salts ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; from the gypsum  
269 family; selenite, Fig. 5a). Gypsum crystals are also present as elongated laths in the Chalcolithic  
270 deposits of Tolici (Fig. 5b). Lastly, at Lunca, a Neolithic ash level contained small orthorhombic  
271 crystals of thenardite (Fig. 5c), a sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). But no sodium chloride crystals ( $\text{NaCl}$ ,  
272 halite) were identified in thin sections, which can be explained by the high solubility of this edible salt.

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### **3.2. Scanning Electron Microscope Analyses (SEM-EDS)**

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For each site, five thin sections underwent SEM-EDS analyses (Table 2, Fig. 6). The aim was to verify if edible salt residues, characterised by Na and Cl elements, could exist in the archaeological deposits, despite the fact that no halite crystal has been recognized during the micromorphological observations. Measurements were done on specific features and over larger zones selected during micromorphological study.

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At Tolici, analyses concern the sedimentary accumulations from the Early Neolithic to the Chalcolithic (Fig. 6). No less than 65 measurements were made at different points of the five thin sections. The results only rarely reveal the presence of chlorine in association with sodium and these two elements were only detected together in the deepest deposits from Tolici, in the Early Neolithic hollow structures (Fig. 6d). These elements were associated with potassium and magnesium in ashy accumulations. Some were included in the composition of small crystals, but larger amounts were located in massive units with a melted aspect (Fig. 6c).

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At Lunca, 23 measurements were taken on the five thin sections from the Early Neolithic deposits. Sodium, potassium and chlorine elements were detected in ashes and waste deposits, associated with sherds.

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In conclusion, presence of Na and Cl in the Neolithic ashes, and not in the more recent deposits, seem to indicate that different techniques to collect salt have been used over time. Maybe, leaching could have contributed to the removing of Na and Cl in recent deposits, but if so, why not in the older ones ? Salt could have move through porous deposits as found in porous ceramics (Raad et al. 2014), but in this case why did it stop in the Early Neolithic ashes and not in the other deposits ? It certainly would be useful to get complementary data from other sites to go farther in the discussion.

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### **4. Discussion and conclusion**

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Archaeological and stratigraphic study, soil micromorphology and SEM/EDS analyses conducted at Lunca and Tolici enabled us to identify the main sedimentary processes involved in site formation and to be able to discuss their link with salt-working techniques.

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At both sites, the excavation and chrono-stratigraphic study showed that the most recent deposits, which are generally more recent than 4300 BC, contained remains of salt moulds (briquetages), whereas the older deposits were characterized by vast combustion structures. Due to the absence of briquetage in the early deposits, the hypothesis has been advanced that pouring of brine onto hot embers could be a salt making process during the Early Neolithic. This hypothesis is partly based on descriptions by Ancient writers (Varro, Pliny the Elder and Tacitus, see Moinier, Weller 2015: 43-44), but also upon 18th century ethno-historic records, which describe Romanian farmers pouring brine

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310 onto embers (Ceausu 1982: 379). This technique was also experimentally tested by pouring salt water  
311 with a concentration of 30 g/l NaCl, onto a fire, which led to the recovery, after evaporation, of a grey  
312 salt with a high sodium chloride content (Dufraisse et al. 2004).

313 Micromorphology of the Early Neolithic deposits reveals the presence of numerous *in situ* hearths,  
314 characterised by microstratified charcoal-rich and ashy beds overlying reddened deposits. At first,  
315 these hearth fires were lit on yellowish silty clay layers showing characteristics of man-made floors  
316 (Karkanas and Van de Moortel 2014; Macphail et al. 2017), and became reddened in their upper parts.  
317 These hearths have been used repeatedly, with considerable supplies of fuel (Dufraisse et al 2010).  
318 The presence of clay, dusty clay or silty clay waterlaid deposits, interbedded in the combustion  
319 residues, seem to be consistent with the hypothesis of salt making carried out by pouring brine onto  
320 hearth embers. The existence of neoformed automorphic crystals similar to those characterizing  
321 evaporite contexts (Warren 2006; Mees and Tursina 2010) could be evidence of the evaporation of  
322 brine. Although the neoformed salts observed with the optical microscope are not edible salt (halite),  
323 the identification of Na and Cl with SEM-EDS in the Early Neolithic ashes at Lunca and Tolici, and  
324 never in the more recent ashy deposits, also seems to support the link between the hearth structures  
325 and the brine evaporation. In this case, the hollow shape of the combustion structures excavated at  
326 Tolici would be designed to avoid the excessive dispersion of the brine and concomitant concentration  
327 of salt.

328 On the other hand, during the Chalcolithic, dumped deposits take precedence over microlayered  
329 combustion beds and waterlaid deposits, underlining the evolution of salt-making techniques. The very  
330 abundant sherds characterizing these discharge facies are not only from pottery used for transporting  
331 and storing brines, but also represent the remains of salt moulds (briquetages), which were widely used  
332 at that time (Tencariu et al. 2015).

333 Finally, although more research is required, the analyses of the sedimentary facies of the sites of Lunca  
334 and Tolici, using optical and electronic microscopy associated with dispersive energy X-ray  
335 spectrometry, is already helping our team to discern several aspects of the likely techniques used to  
336 produce edible salt. The combustion and waterlaid deposits, the neoformed salt crystals, and the  
337 presence of Na and Cl elements in ashes, seem to attest to salt making by the direct evaporation of  
338 brine on embers, during the Early Neolithic, or about 6000-5300 BC. At both of the studied sites,  
339 exploitation techniques change after 4300 BC during the Chalcolithic, with the advent of briquetage  
340 use, but which disappear at the beginning of the Bronze Age.

341 In addition to these advances in understanding salt making processes, one positive result is that the  
342 identification of Na and Cl with SEM-EDS has improved our detection of edible salt in  
343 micromorphological thin sections. Edible salt, which is an invisible substance before crystallisation  
344 and which is easily soluble in water, appear as isotropic colourless vitreous nodules with vesicular  
345 porosity (Fig. 6). Of course, care is needed in order not to confuse these salt-associated nodules with  
346 melted phytoliths that have similar aspect. Continued microscopic analyses, or other bulk soil

347 chemistry analyses, at Tolici, Lunca and other production sites will undoubtedly provide more  
348 information on salt making deposits and the processes involved. Other components of the  
349 interdisciplinary study are currently being explored, such as the evaluation of the environmental impact  
350 of exploitation techniques, the underlying social functions and the different uses of this earliest salt  
351 working in the world.

352

### 353 **Acknowledgements**

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355 We would like to thank the Commission for Foreign Excavations (French Ministry of Foreign Affairs),  
356 the National Institute of Preventive Archaeological Research (INRAP) and the National Centre of  
357 Scientific Research (CNRS, UMR 8215 Trajectoires and UMR 6249 Chrono-environnement) for their  
358 support. The authors also thank the History & Archaeology Museum of Neamt for their continued  
359 cooperation. This work was partly supported by the French RENATECH network and the FEMTO-  
360 ST technological facility. We also express our gratitude to Isabelle Jouffroy-Bapicot, Jacques Mudry,  
361 Christophe Loup, Bruno Régent, Louise Byrne, Boris Vannière and Nick Marriner for their help during  
362 different stages of this work. Finally, we greatly thank the reviewers of this article for their constructive  
363 comments.

364

### 365 **Bibliography**

366

367 Alabi, R.A., 2000. Gberefu and Agorin sea beach: intensive salt-making site of the south-west coast  
368 of Nigeria. *West African Journal of Archaeology* 30, 41-67.

369 Antonites, A., 2016. The organization of salt production in early first millennium CE South Africa,  
370 *Journal of Anthropological Archaeology* 44, 31-42.

371 Alexianu, M., Weller, O., Curcă, R. (Eds.), 2011. *Archaeology and Anthropology of salt. A diachronic  
372 approach. Proceedings of the International Colloquium (Iași, Romania, 2008). BAR International  
373 Series 2198. Archaeopress, Oxford.*

374 Alexianu, M., Curcă, R., Cotiugă, V. (Eds.), 2015. *Salt Effect. From the ethnoarchaeology to the  
375 anthropology of salt. BAR International Series 2760. Archaeopress, Oxford.*

376 Alexianu, M., Weller, O., Curcă, R., Brigand, R., Asăndulesei, M., 2016. *White Gold. French and  
377 Romanian Projects on Salt in the Extra-Carpathian Areas of Romania. Parthenon Verlag,  
378 Kaiserslautern.*

379 Biddulph, E., Foreman, S., Stafford, E., Stansbie, D., Nicholson, R., 2012. *London Gateway. Iron Age  
380 and Roman salt making in the Thames Estuary; Excavations at Stanford Wharf Nature Reserve, Essex.  
381 Oxford Archaeology monograph 18, Oxford.*

382 Boivin, N. L., 1999, Life rhythms and floor sequences: excavating time in rural Rajasthan and Neolithic  
383 Çatalhöyük. *World Archaeology* 31 (3) 367-388.

384 Brigand, R., Weller, O. (Eds.), 2015. *Archaeology of Salt. Approaching an invisible past*. Sidestone  
385 Press, Leiden.

386 Brigand, R., Weller, O., 2018. Neo-Eneolithic settlement pattern and salt exploitation in Romanian  
387 Moldavia. *J. Archaeol. Sci. Rep.* 17, 68-78.

388 Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G., Tursina, T., Babel, U., 1985. *Handbook for soil  
389 thin section description*. Waine Research Publications, London.

390 Canti, M., 2003. Aspects of the chemical and microscopic characteristics of plant ashes found in  
391 archaeological soils. *Catena* 54, 339-361.

392 Ceausu, M., 1982. Contributii la istoricul exploatarei sarii la sfirsitul secolului al XVIII-lea si în prima  
393 jumătate a secolului al XIX-lea în Bucovina. *Suceava IX*, 377-392.

394 Courty, M.-A., Goldberg, P., Macphail, R-I., 1989. *Soils and micromorphology in archaeology*.  
395 *Cambridge manuals in Archaeology*, Cambridge University Press, Cambridge.

396 Dammers, K., Joergensen, R. G., 1996. Progressive loss of Carbon and Nitrogen from simulated daub  
397 on heating. *J. Archaeol. Sci.* 23, 639-648.

398 Danu, M., Gauthier, E., Weller, O., 2010. Human impact and vegetation history on salt spring  
399 exploitation (Halabutoaia-Tolici, Petricani, Neamt, Romania). *International Journal of Conservation  
400 Science* 1 (3), 167-173.

401 Dufraisse, A., Gauthier, E., Pétrequin, A.M., Pétrequin, P., Weller O., 2004. Techniques d'exploitation  
402 préhistorique du sel en Franche-Comté et en Bourgogne. In: Bodu, P., Constantin, C. (Eds.),  
403 *Approches fonctionnelles en Préhistoire. Actes du XXVe Congrès Préhistorique de France (Nanterre,  
404 2000)*. Société Préhistorique Française, Paris, 427-444.

405 Dufraisse, A., Sordoillet, D., Weller, O., 2010. The alteration of Neolithic wood charcoal from the salt  
406 spring of Poiana Slatinei in Lunca (Neamt, Romania): a natural evolution or consequence of  
407 exploitation techniques ?, in: Théry-Parisot, I., Chabal, L., Costamagno, S. (Eds.), *Taphonomie de la  
408 combustion des résidus organiques et des structures de combustion en contexte archéologique. Actes  
409 de la table ronde du CEPAM (Nice, 2008)*. *Palethnologie* 2, 121-132.

410 Dumitroaia, G., 1987. La station archéologique de Lunca-Poiana Slatinei, in: Petrescu-Dîmbovita, M.,  
411 Ursulescu, N., Monah, D., Chirica, V. (Eds.), *La civilisation de Cucuteni en contexte européen*. Editura  
412 Universității Alexandru Ioan Cuza, Iași, 253-258.

413 Flad, R., Zhu, J., Wang, C., Chen, P., von Falkenhausen, L., Sun, Z., Li, S., 2005. Archaeological and  
414 chemical evidence for yearly salt production in China. *PNAS* 102 (35), 12618-12622.

415 Flad, R.K., 2011. *Salt Production and Social Hierarchy in Ancient China: An Archaeological  
416 Investigation of Specialization in Chinas Three Gorges*. Cambridge University Press, Cambridge.

417 Graham, E., Macphail, R., Turner, S., Crowther, J., Stegeman, J., Arroyo-Kalin, M., Duncan, L.,  
418 Whittet, R., Rosique, C., Austin, P., 2017. The Marco Gonzalez Maya site, Ambergris Caye, Belize:  
419 Assessing the impact of human activities by examining diachronic processes at the local scale.  
420 *Quaternary International* 437 (B), 115–142. doi:10.1016/j.quaint.2015.08.079

421 Harding, A., 2013. Salt in Prehistoric Europe. Sidestone Press, Leiden.

422 Harris, E.C., 2014. Principles of Archaeological Stratigraphy. Second ed. Elsevier Science, Kent.

423 Horiuchi, A., Ochiai, N., Kurosumi, H., Miyata, Y., 2011. Detection of chloride from pottery as a  
424 marker for salt: a new analytical method validated using simulated salt-making pottery and applied to  
425 Japanese ceramics. *J. Archaeol. Sci.* 38 (11), 2949-2956.

426 Karkanias, P., Van de Moortel, A., 2014. Micromorphological analysis of sediments at the Bronze Age  
427 site of Mitrou, central Greece : patterns of floor construction and maintenance. *J. Archaeol. Sci.* 43,  
428 198-213. doi:10.1016/j.jas.2014.01.007.

429 Kawashima, T., 2015. Prehistoric salt production in Japan, in: Brigand, R., Weller, O. (Eds.),  
430 Archaeology of Salt. Approaching an invisible past. Sidestone Press, Leiden, 125-138.

431 Linford, N. T., Canti, M. G., 2001. Geophysical Evidence for Fires in Antiquity: Preliminary Results  
432 from an Experimental Study. Paper Given at the EGS XXIV General Assembly in The Hague, April  
433 1999. *Archaeol. Prospect.* 8, 211-225.

434 Loustaud, J.-P., 1985. Techniques de fouilles terrestres, in: Pelletier, A. (Ed.), *L'archéologie et ses*  
435 *méthodes. Prospection, fouille, analyse, restauration.* Horvath, Roanne-Le Coteau, 61-81.

436 McKillop, H., 2005. Finds in Belize document Late Classic Maya salt making and canoe transport.  
437 *PNAS* 102 (15), 5630-5634.

438 Macphail, R.I., Crowther, J., Berna, F., 2012. Stanford Warf, Essex (London Gateway Compensation  
439 sites A and B; compa 09): Soil micromorphology and microchemistry, chemistry and magnetic  
440 susceptibility, and FTIR, in: Biddulph, E. et al., London Gateway. Iron Age and Roman Salt Making  
441 in the Thames Estuary; Excavations at Stanford Wharf Nature Reserve, Essex.  
442 <https://library.thehumanjourney.net/909/> (chap. 24, accessed 2017.06.30).

443 Macphail, R.I., Graham, E., Crowther, J., Turner, S., 2017. Marco Gonzalez, Ambergris Caye, Belize:  
444 A geoarchaeological record of ground raising associated with surface soil formation and the presence  
445 of a Dark Earth. *J. Archaeol. Sci.* 77, 35–51. doi:10.1016/j.jas.2016.06.003

446 Mees, F., Tursina, T. V., 2010. Salt minerals in saline soils and salt crusts. In Stoops, G., Marcelino,  
447 V., Mees, F., (Eds.), *Interpretation of Micromorphological Features of Soils and Regoliths.* Elsevier,  
448 Amsterdam, 441-469.

449 Moinier, B., Weller, O., 2015. *Le sel dans l'Antiquité ou les cristaux d'Aphrodite.* Les Belles Lettres,  
450 Paris.

451 Murphy, C.P., 1986. Thin section preparation of soils and sediments. AB Academic Publishers,  
452 Berkhamsted.

453 Nikolov, V., Bacvarov, K. (Eds.), 2012. Salt and Gold: The Role of Salt in Prehistoric Europe. Acts  
454 of international colloquium Humboldt-Kolleg (Provadia-Bulgaria, 2010). Faber, Veliko Tarnovo.

455 Raad, D. R., Li, S., Flad, R. K. 2014. Testing a novel method to identify salt production pottery via  
456 release and detection of chloride ions. *J. Archaeol. Sci.* 43, 186-191.

- 457 Sandu, I., Weller, O., Stumbea, D., Alexianu, M., 2012. Analyses archéométriques sur les moules à  
458 sel chalcolithiques de l'est de la Roumanie, in: Nikolov, V., Bacvarov K. (Eds.), *Salt and Gold: The*  
459 *Role of Salt in Prehistoric Europe*. Faber, Veliko Tarnovo, 143-154.
- 460 Sordoillet, D., 2009. *Géoarchéologie de sites préhistoriques : Le Gardon (Ain), Montou (Pyrénées-*  
461 *Orientales) et Saint-Alban (Isère)*. DAF 103. Maison des Sciences de l'Homme, Paris.
- 462 Tencariu, F.-A., Alexianu, M., Cotiuga, V., Vasilache, V., Sandu, I., 2015. Briquetage and salt cakes:  
463 an experimental approach of a prehistoric technique. *J. Archaeol. Sci.* 59, 118-131.
- 464 Warren, J.K., 2006. *Evaporites. Sediments, Resources and Hydrocarbons*. Springer, Berlin-New York.
- 465 Weller, O., 2000. *Les premières formes d'exploitation du sel durant le Néolithique et le Chalcolithique*  
466 *européens : de la reconnaissance des techniques à l'analyse des dimensions socio-économiques*. PhD  
467 diss., University of Panthéon-Sorbonne, Paris, unpublished.
- 468 Weller, O., Dumitroaia, G., 2005. The earliest salt production in the world: an early Neolithic  
469 exploitation in Poiana Slatinei-Lunca, Romania. *Antiquity* 79 (306).  
470 <http://antiquity.ac.uk/projgall/weller306/> (accessed 2017.06.30).
- 471 Weller, O., Brigand, R., Alexianu M., 2008a. Recherches systématiques autour des sources salées de  
472 Moldavie. Bilan des prospections 2004-2007. *Memoria Antiquitatis* XXIV (2007), 121-190.
- 473 Weller, O., Dumitroaia, G., Sordoillet, D., Dufraisse, A., Gauthier, E. 2008b. Première exploitation de  
474 sel en Europe. Techniques et gestion de l'exploitation de la source salée de Poiana Slatinei à Lunca  
475 (Neamt, Roumanie), in: Weller, O., Dufraisse, A., Pétrequin, P. (Eds.), *Sel, eau et forêt. D'hier à*  
476 *aujourd'hui*. Actes de colloque international (Arc-et-Senans, 2006). Cahiers de la MSH Nicolas  
477 Ledoux 12 (Homme et Environnement 1). PUFC, Besançon, 205-230.
- 478 Weller, O., Brigand, R., 2017. Recherches systématiques autour des sources salées de Moldavie. Bilan  
479 2011-2013 et synthèse de 10 ans de prospections. *Memoria Antiquitatis*, XXXI-XXXII (2016), 163-  
480 270.
- 481 Weller, O., 2015. First salt making in Europe: an overview from Neolithic times. *Documenta*  
482 *Praehistorica* 42, 185-196.
- 483 Weller, O., Brigand, R., Dumitroaia, G., Garvăn, D., Munteanu, R., 2015. A pinch of salt in the  
484 Prehistoric Eastern Carpathians Mountains (Ro.), in: Alexianu, M., Curcă, R.-G., Cotiugă, V. (Eds.),  
485 *Salt Effect. From the Ethnoarchaeology to the Anthropology of Salt*. BAR International Series 2760.  
486 Archaeopress, Oxford, 125–133.
- 487 Wheeler, M., 1989. *Archéologie : la voix de la terre*, Trad. *Archaeology from the Earth* (1968, Penguin,  
488 London), Edisud, Aix-en-Provence.
- 489 Williams, E., 2015. *The Salt of the Earth: Ethnoarchaeology of Salt Production in Michoacán, Western*  
490 *Mexico*. BAR International Series 2725. Archaeopress, Oxford.

491

492

493 Figure captions

494 A rajouter à la légende de la figure 3 :  
495 Samples  $\mu 1$  to  $\mu 4$  were taken when the site was discovered, at the base of the archaeological mound  
496 (Fig. 3a). The 13 other samples are from the trench excavated in the archaeological accumulation the  
497 following year (Fig. 3b).

## Earliest salt working in the world: from excavation to microscopy at the prehistoric sites of Tolici and Lunca (Romania)

Sordoillet D., Weller O., Rouge N., Buatier M., Sizun J.-P.

### Figures captions

#### Fig. 1. Location of the archaeological sites

The extension of the archaeological deposits is approximately indicated by white dotted ellipses.

*(1.5 column ; color online)*

#### Fig.2. Stratigraphic sections at the Tolici (a-b) and Lunca (c-d) excavations

**a** - Elongated hollow with white ashy deposits and rubefied outer edges, at the base of the archaeological mound (see also figure 3); **b** - horizontal stratification of the deposits in the upper part of the mound; **c** - north section of pit 1, with multiple superimposed hollow hearths above massive grey Tertiary clays (scale: 50 cm); **d** - detail of the previous section showing the overlapping white ashes, lenticular charcoal and rubefied layers.

*(1.5 column ; color online)*

#### Fig. 3. Stratigraphic section and sampling

**a** - First samples from the elongated hollow at the base of the archaeological mound at Tolici, when it was discovered (samples 3 and 4 were taken 1 metre higher, in Cucuteni horizontal levels ; see also online AppendixA-FigA1-A5); **b** - illustration of sampling from the different levels of the main stratigraphic section.

*(full page width ; color online)*

#### Fig. 4. Archaeological micro-sedimentary facies

**a** – Scan of thin section from Lunca, with yellowish clay of substratum at the bottom, and charcoals layers upon reddened clay in the upper part; **b** – Banded distribution of silt and clay in an interbedded yellowish layer at Tolici; **c** – Superimposed lenses of silt and clay, reddened by fire; **d** – Same kind of deposit as c, partly deformed by the fall of a grain of sand; **e** - Hearth deposits with microstratified white ashes and wood charcoal; **f** - Charcoals and ashes with limpid clay intercalations overlying cooked clay “floor” at Lunca; **g** – White ashes with limpid and dusty clay intercalations at Tolici; **h** – Detail of previous thin section showing several superimposed layers of silt and fine sand with many charcoal particles, and clay or dusty clay lenses ; **i** – Isotropic white vesicular nodule and leaf residue embedded in microlayered clays; **j** - Scan of thin section from Lunca with fine microstratified deposits; **k** – Detail of previous thin section showing fining up from fine sand to dusty clay in successive layers: **l** – heterogeneous deposit, with charcoal and sherds.

*cf* - clay “floor”; *ch* - wood charcoal; *dc* - dusty clay; *fs*- fine sand; *lc*-limpid clay; *lr*- leaf residue; *rc* – rubefied clay; *sh*- sherd; *vn*- vesicular nodule; *wa*- white ashes.

PPL – plane polarised light; XPL – cross polarised light.

*(full page width color online)*

#### Fig. 5. Salt crystals

**a** – Fibrous selenite crystal ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in rufedied Neolithic deposit at Lunca; **b** – elongated gypsum crystals in Chalcolithic ash deposit at Tolici; **c** – orthorhombic thenardite crystal ( $\text{Na}_2\text{SO}_4$ ) in Neolithic ashes at Lunca;

PPL – plane polarised light; XPL – cross-polarised light.

*(single column size color online)*

**Fig. 6.** Example of SEM-EDS analysis (Tol- $\mu$ 15): **a** – uncovered thin section before carbon coating; **b** – optical microscope views; **c** – electronic microscope views; **d** – chemical analysis diagrams.

(supplementary results online: AppendixA-FigA6-A22)

*(1.5 column ; color online)*

**Table 1**

	Cl (mg/l)	SO <sub>4</sub> (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	K (mg/l)
Poiana Slatina, Lunca, summer 2004	158,000.00	9,400.00	760.00	94,000.00	210.00	80.00
Halabutoaia, Tolici, summer 2007	190,597.00	7,463.00	1,040.00	113,000.00	190.00	35.00

**Table 1.** Chemical composition of the spring waters from Tolici and Lunca  
Analyses J. Mudry and C. Loup, Laboratoire de Chimie des Eaux, Université de Franche-Comté.

**Table 2**

	Cultural period	Micromorphology	SEM-EDS (number of analyses)
Tolici	Cucuteni (Chalcolithic)	$\mu$ 3, 4, 5, 6, 7, 8, 9, 10	$\mu$ 6e- (5) $\mu$ 10e- (18)
	Precucuteni (Late Neolithic)	$\mu$ 11, $\mu$ 12	$\mu$ 11e- (10)
	Linear Pottery (Middle Neolithic)	$\mu$ 13	
	Cris (Early Neolithic)	$\mu$ 1, 2 $\mu$ 14, 15, 16, 17	$\mu$ 15e- (13) $\mu$ 17e- (10)
Lunca	Cucuteni (Chalcolithic)	Excavation SXI : $\mu$ 12, 13, 14	
	Cris (Early Neolithic)	Excavation S1-02, section : - W : $\mu$ 1, 2, 3, 6, 7 - N : $\mu$ 8 - E : $\mu$ 9, 10, 11 - S : $\mu$ 15, 16	$\mu$ 1e- (7) $\mu$ 3e- (5) $\mu$ 6e- (3) $\mu$ 7e- (7) $\mu$ 10e- (10)

**Table 2.** List of the analysed samples

Figure 1

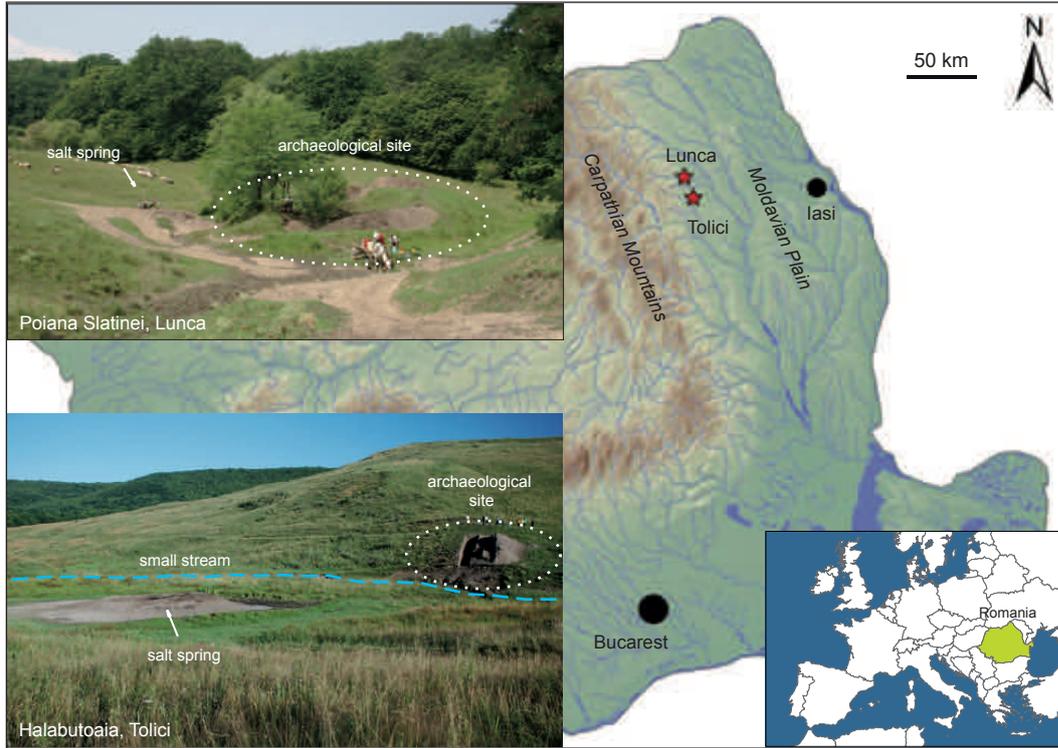


Figure 2



Figure 3

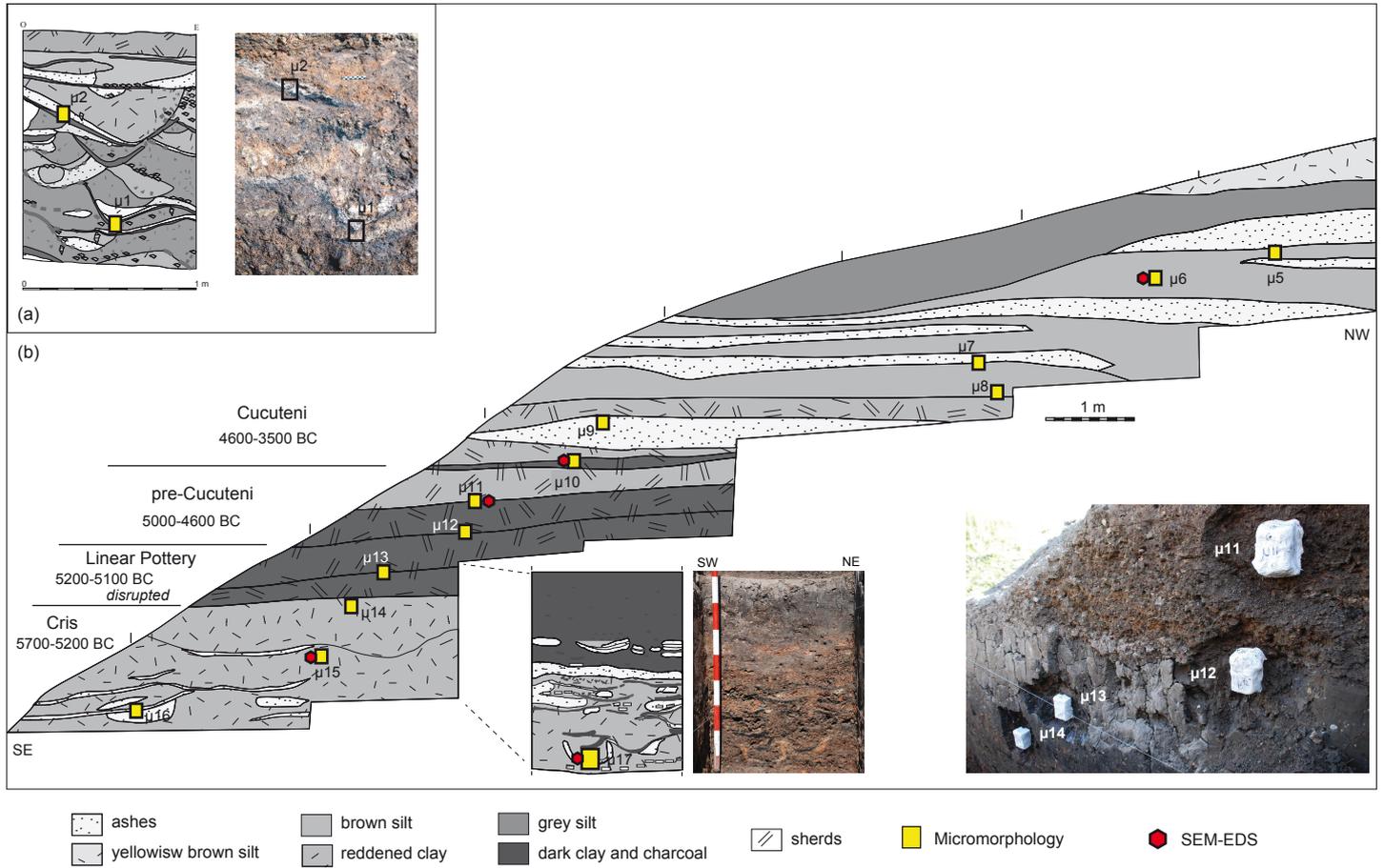


Figure 4

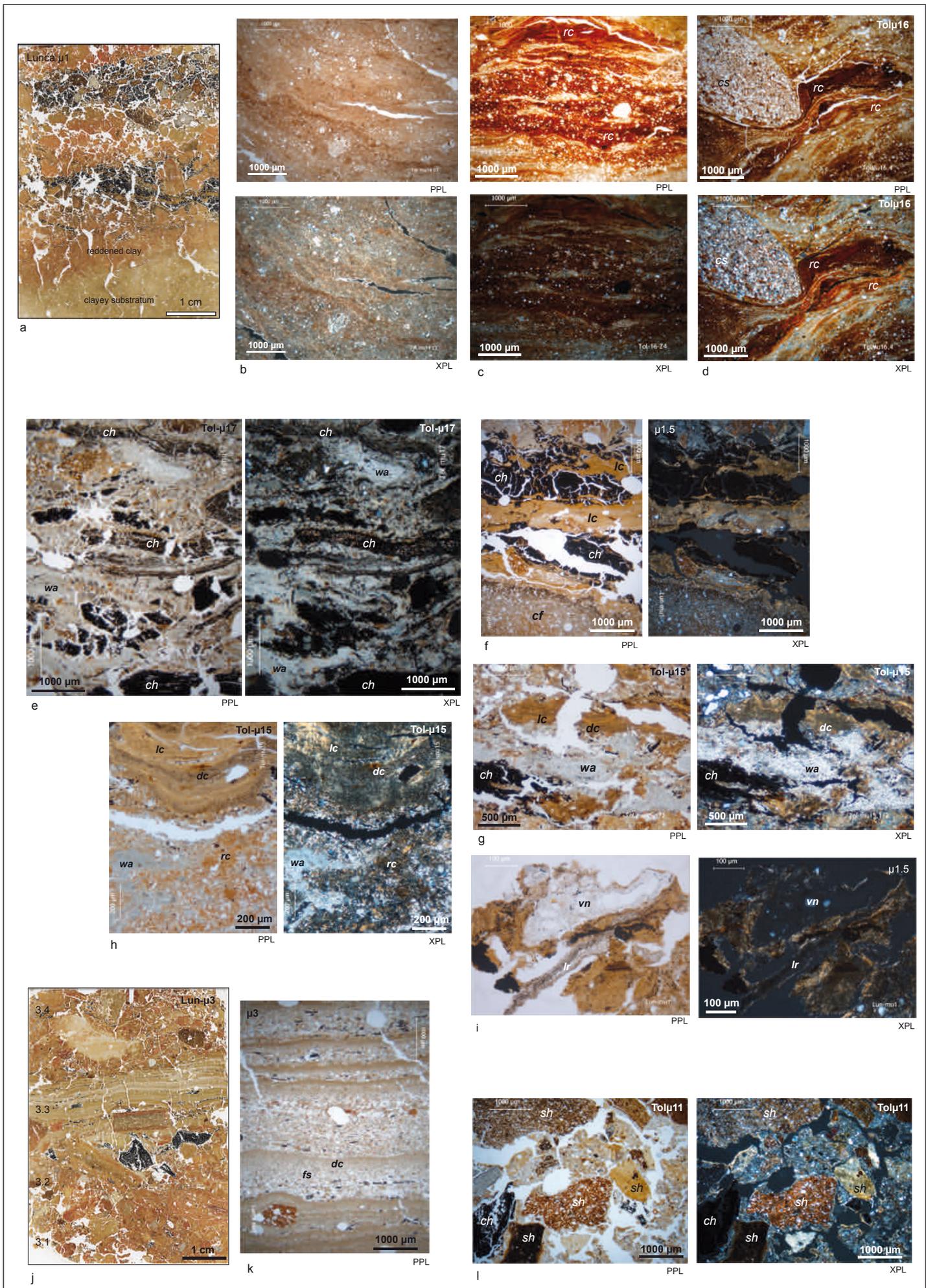


Figure 5

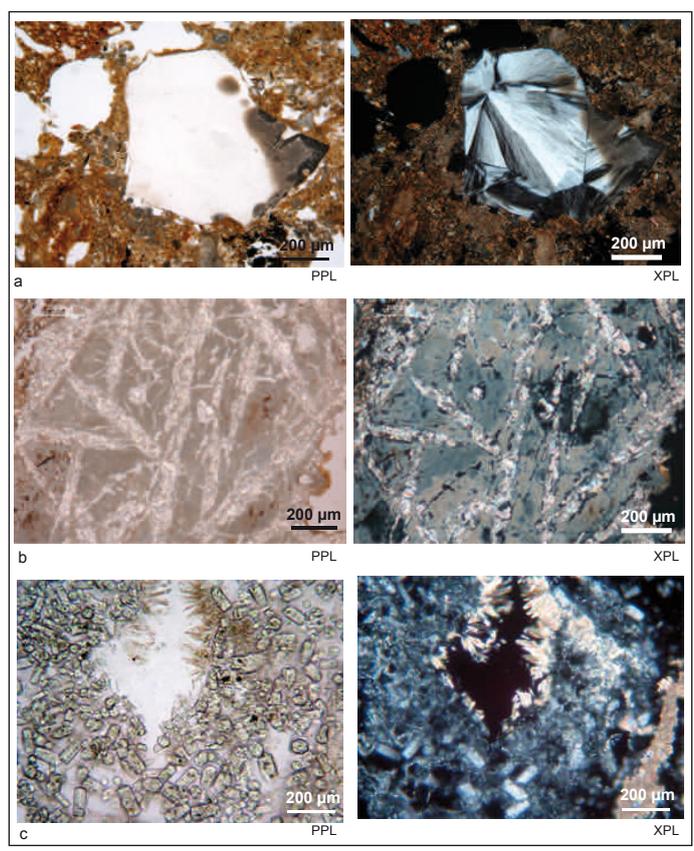


Figure 6

