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Ceramic-faience hybrids were used to recycle bronze in North-Western European Iron Age egg-shaped crucibles

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ABSTRACT

We investigated the characteristics of a group of 13 Middle Iron Age egg-shaped crucibles and crucible fragments from Tilburg (The Netherlands). We used a combination of optical and chemical analyses, including hand-held XRF, microCT scanning and 3-D printing polarizing light microscopy and SEM-EDX. The chemical analyses confirmed that the crucibles were used for copper alloy metallurgy. Impressions in the lids of the crucibles turned out to be imprints of copper alloy scrap, including fragments of twisted wire and fibulae. Most remarkable, however, is the large proportion of sheet metal among the scrap.

In order to make crucibles from the local, non-refractory clays, a hitherto unknown ceramic-faience hybrid was used: A combination of clay and halophytic plant ash was mixed with silt into a paste, and this was used to construct the crucible. During firing, the flux would promote melting of the clays and probably prevent catastrophic failure of the crucibles. The resulting glassy groundmass – in which silt grains are embedded and partially dissolved – is rich in Al_2O_3 as well as in Na_2O, K_2O, CaO, MgO and Fe_2O_3.

It is likely that this technique of crucible manufacture was widespread in Late Prehistory in areas where no refractory clays were available.

1. Introduction

In areas with no mineable primary sources of metal, the adoption and persistent use of metallurgy invariably implies that raw materials must have been obtained from further away. This is the case in the low countries when it concerns the introduction of copper-alloy metallurgy. Some Bronze Age and Iron Age copper and bronze artefacts from the low countries have foreign typologies, and are therefore probably imported as such. Others, however, display typological groups that indicate that they were produced locally or in the region. A few scarce mould and crucible remains support such local production of copper alloy artefacts (Louwe Kooijmans et al., 2005). However, this does not indicate how the metals for this local metallurgical production were obtained.

"Fresh" ingots may have been obtained directly from the mining and production areas. It is also possible that copper alloy objects were imported, at least some of which were scrapped and remolten when they were broken or obsolete. Finally, scrap metal may have been imported as raw material, meant for local recycling. Most likely is that there was

a combination of these three pathways.

An often overlooked factor in metallurgy is that metals may not be the only raw material that needed to be sourced by prehistoric metalworkers. The same may have been the case for materials that were suitable for making moulds and crucibles. In internally heated crucibles – where the charge was buried underneath charcoal and thus heated from the top – the charge was in the hottest part of the installation. Some melting or slagging at the charge-crucible interface was acceptable, and most of the crucible remained at temperatures below the melting point of the metal processed (Martinón-Torres and Rehren, 2014). Such crucibles are, however, not known from the low countries. Here, externally heated crucibles were used, which were placed in an oven or on a charcoal bed with the charge inside them. These crucibles would need to transfer heat from the oven atmosphere to the charge, and still keep functioning at temperatures exceeding the melting point of the metals inside. Cracking or slumping of the crucibles would lead to catastrophic loss of the charge. Especially for externally heated crucibles, therefore, the demands on the raw material properties are high. Most clays are incapable of withstanding the temperature range needed
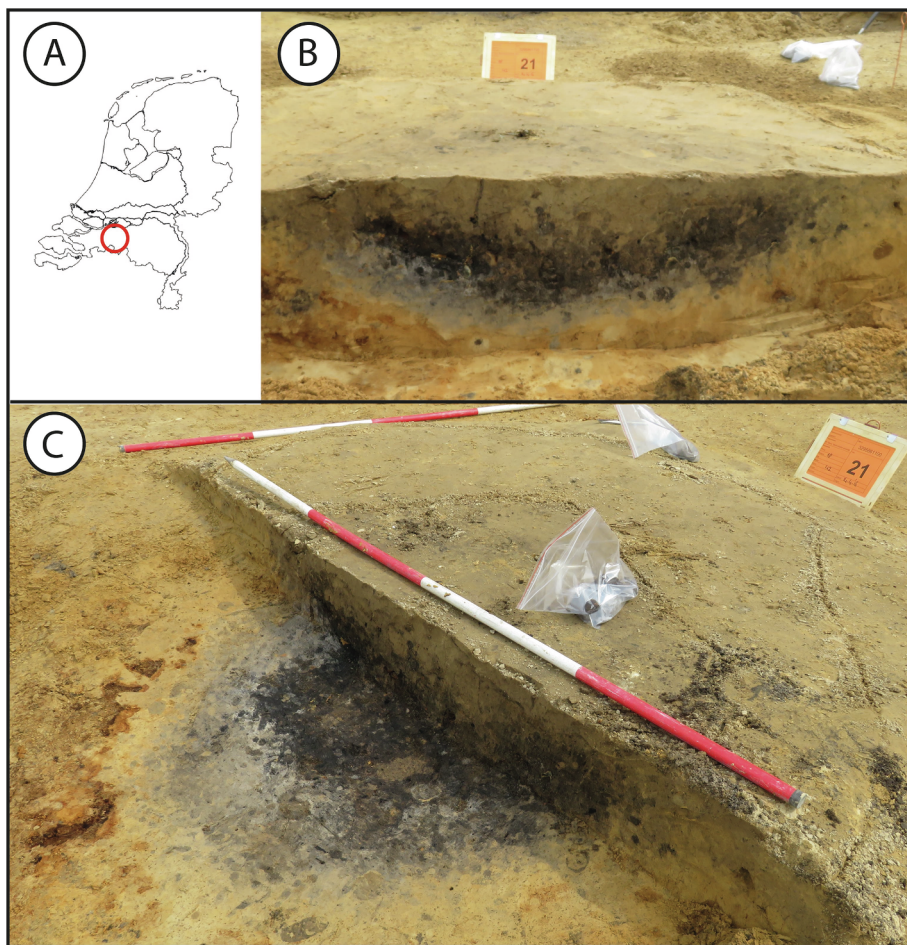
Fig. 1. Site data. A: Location of Tilburg in the Netherlands. B,C: Field photographs of the find location.

for copper alloy metallurgy. Martinón-Torres and Rehren (2014) indicate that special care was taken to process available clays, e.g. by adding temper, to deal with this problem. Later, specific "refractory" high-Al_2O_3 (and therefore kaolinite –rich) clays were used for such metallurgical ceramics. Specific additives were also sometimes used to alter behaviour of clays, e.g. marly limestone, marl or ash (roman double-layered crucibles; Koenig et al., 2013) and bone ash (in post-medieval cupels; Bayley and Rehren, 2007).

In this paper, we report on investigations of a series of Middle Iron Age crucibles from Tilburg (The Netherlands) that shed new light on this issue. The crucibles were found during digging activities associated with a redevelopment. An amateur archaeologist encountered a round pit, that contained prehistoric ceramics. A follow-up excavation by TRANSECT B.V., commissioned by Tilburg municipality, revealed a pit with a round top and rectangular base with a charcoal-rich layer at the base of the feature (Fig. 1). The feature contained 89 fragments of pottery, which was attributed to the Middle Iron age on typological grounds. This was confirmed by a ^{14}C-dating of 450–405 cal. yr. BC on a charred grain from the charcoal layer. Apart from the ceramic remains, some oven wall fragments, fragments of animal bone, stone, iron smithing slag, and corroded fragments of iron were found in the pit feature (Verhagen, 2018).

Remains of 13 crucibles were among the recovered material (see Fig. 2 for examples; Table 1 for a list of all recovered crucibles). Only a few are complete: the rest consists of fragmented and mostly incomplete ones. The complete one are similar in shape and size to goose eggs, with a small hole in the top. They show a molten outside surface, sometimes with red or greenish staining. A few white powdery fragments were observed on some of the fragments.
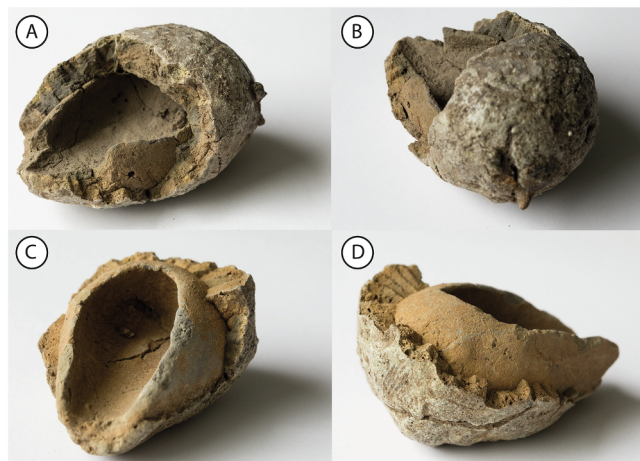
Fig. 2. Photographs of two broken crucibles (A, B #3; C, D # 13), showing the cradle inside a mantle with glassy outside. Note also the cracking pattern in the mantle.

Egg-shaped crucibles are relatively rare, but they have been encountered previously ,e.g. in Middle and Late Iron Age context in North-Western Europe, with examples from Switzerland (Mauvilly et al., 1998), France (Zaour et al., s.d.), Germany (Simons, 1989; Rehren, 2002) and The Netherlands (Hazen, 2015); see Modarressi-Tehrani (2004) for a comprehensive overview. Rehren (2002) and Modarressi-Tehrani (2004) have determined that the La Tène period crucibles from Cologne and from Hochdorf were used to process copper alloys.

Table 1
Dimensions and other characteristics of recovered crucibles and crucible fragments.

Crucible nr.	State	With lid?	Other features	Outside dimensions (mm) Length	Breadth	Width	Cavity dimensions (mm) Breadth	Length	Width	Volume (cm³)	Impressions tong marks outside	Impressions charge on inside	Remarks
1	Almost complete, broken	+		>70	54	43	18	>50	23	>9	+	+	
2	Almost complete	+		72	60	47	20	57	26	14	+		
3	Incomplete fragment and lid	+	Reddish colour on lid	71	63	47	18	>55	38			+	
4	Incomplete fragments	+		>55	57	48	18	>37	33			+	
5	Complete	+		88	64	52	24	72	23		+		
6	Almost complete	+	White porous material	74	58	50	28	52	25	11	+	+	
7	Incomplete fragment			65	50	45	24	53	25				
8	Complete, broken	+		81	58	50	24	61	23	17			
9	Almost complete	+		72	58	49	16	50	26	13		+	
10	Incomplete fragment			?	?	?	?	?	?				
11	Incomplete fragments	+	White porous material	>64	>43	?	?	>60	33		+		
12	Incomplete fragments		Brick red colour on crucible wall	>70	60	?	22	>70	25				Irregular cradle shape
13	Incomplete fragments			45	41	?	?	>33	24				

The crucibles were subjected to a series of subsequent analysis techniques to try and elucidate the way that these objects were made and used: First, semi-quantitative hand-held (HH) XRF analyses were done to ascertain that the crucibles were indeed used in copper alloy processing. A probe was used to check for metal fragments inside the undamaged crucibles. Subsequently, micro-CT scanning and 3-D printing was used to study their construction and recreate morphological features. To further study the mineralogical and chemical composition, thin sections were made which were studied first with polarization microscopy and subsequently with SEM-EDX.

2. Materials and methods

Hand-held XRF analyses were done on the outside of the crucibles, using a Thermo Scientific Niton XL3t energy-dispersive hand-held XRF analyzer. See Huisman et al., 2017 on machine specification and calibration methods. A special focus was on the areas where the outside surface had red staining. The measurement results should be treated as indicative only: The analyzed surface is not flat and not smooth – which affects the analyses of light elements disproportionally. Moreover, the analyses will be influenced by surface effects.

Micro CT scanning was done using a Nanotom (General Electrics) equipped with a 180 kV X-ray tube and a diamond target at Delft Univeristy. The data was processed using AVISO; see Ngan-Tillard et al. (2018) for the methodology. This data was used to make 3-D prints using a Formlabs (model Form2) 3D printer.

Five fragments in total from crucibles 11, 12 and 13 Fig. Supplementary figure 1 and one fragment of white powdery material from crucible 11 were selected for microscopic and submicroscopic analyses. (A second white fragment disintegrated during a sampling attempt). They were impregnated with a polyester resin under vacuum in the Cultural Heritage Lab in Amersfoort. Subsequently, they were cut and mounted on glass plates and ground and lapped c. 30 μm thin sections. No cover slip was applied. The white fragment was too small to be made into a thin section, so here only a polished cross-section was made. The sections were scanned on a flatbed slide scanner, and subsequently studied with a Leitz-Wild M420 binocular microscope with incident, transmitted and polarized light and a Zeiss Axioskop 40 polarization microscope, both with MRc5 digital cameras. Areas of interest were marked with copper tape. The thin sections were subsequently studied with a Thermo Scientific NovaNano SEM450 Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (standardless EDX with silicon drift detector using Pathfinder software from Thermo Scientific) at the Cultural Heritage Laboratory in Amsterdam, using the copper tape markings as guide to the most important areas of interest. The accelerating voltage was 20 kV and the pressure in the chamber 30 Pa. The brittleness of the crucible materials made it difficult to properly polish the embedded fragments, so some of the backscatter images produced are suboptimal.

3. Results

3.1. Crucible shape and properties

In total 13 crucibles were recovered: some undamaged but most were broken and incomplete; see Table 1 for an overview (Supplementary information 1 for an overview of the microCT scans). The crucibles typically are egg-shaped, (7–8, 5 cm in length, widths of c. 5–7 cm) with a small round hole in the top. The outside is typically glassy with a grey colour. Some non-glassy parts occur, which have a brick-orange colour. Most of the crucibles show extensive cracking of the surface layers, and some have fragmented because of this cracking. Fragments of iron are sporadically embedded in the glassy outside surface of some crucibles, usually surrounded by a dark green stain in the glassy surface. The broken crucibles revealed that their insides were not glassy but had the appearance of micro-porous ceramics. Inside
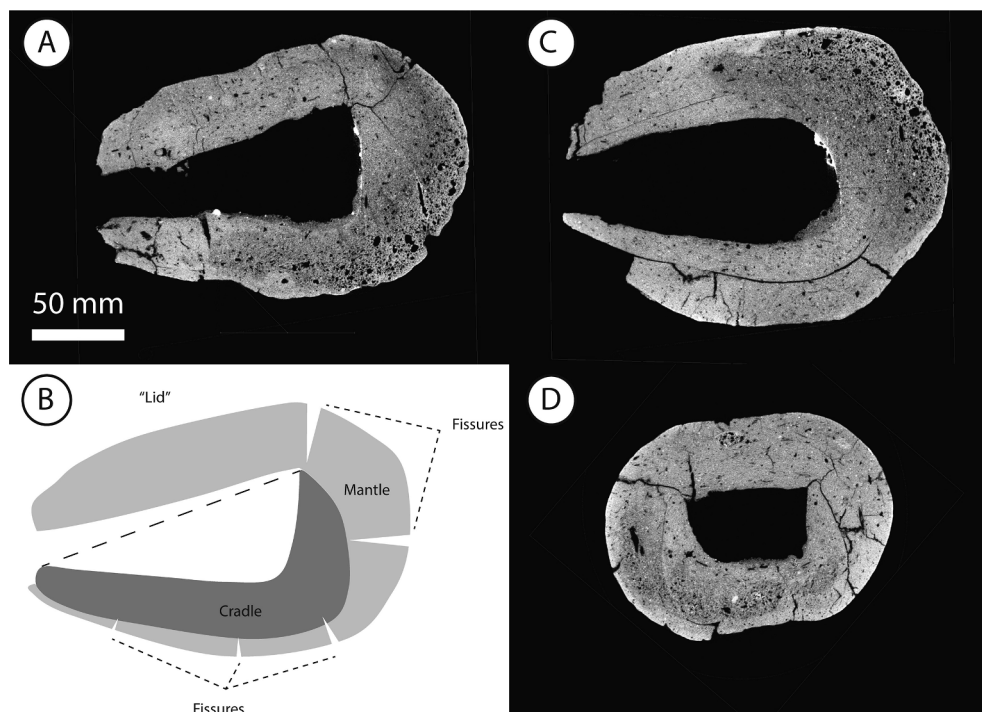
Fig. 3. Construction of the egg-shaped crucibles. A: microCT scan of crucible #6; vertical length-wise section. Note that the cradle and the mantle are not readily distinguishable, that there is a concentration of vesicles in the mantle on the right, and that the glassy surface has slightly higher attenuation. Observations with a probe showed that the highly attenuating spots on the crucible floor consisted of white powdery material. B: Schematic cross-section to a crucible, based on A, with nomenclature. C: Horizontal length-wise section of crucible #6. Note the vesicular material in the upper right part. The cradle is delineated by fissuring. D: Verticalcross-sections of crucible #6, showing how the cavitiy is flattened by the lid.

colours were typically greyish, although one fragment showed brick-orange colours as well.

The broken, incomplete crucibles made clear that each crucible consists of a thin-walled cradle-like inside, that is surrounded by and embedded in a thicker mantle (Fig. 2). With the aid of micro-CT scans, a cross-section of a typical crucible could be reconstructed (Fig. 3). It shows how the cradle is embedded in the outer mantle. However, the microCT scans does not reveal a visible distinction in their groundmasses (Fig. 3A). The outside surface is more attenuating than the rest, probably because of lower microporosity of the groundmass. The part where the mantle surrounds the open part of the cradle is usually slightly thinner, and is referred to as "lid" (see Fig. 3D). The floor of the cradles is flat, and therefore differs from the pointed cradle floors observed in Rehren (2002) and Hazen (2015). Based on mCT scans of the 6 more or less complete crucibles, the inside volume is estimated at 11–12 cm^3 (Table 1)

The iron fragments that were visible in the glassy surface layer in crucible 3 constitutes the largest of the segmented and visualized high-attenuation parts of Fig. 4. These images demonstrate how small and irregular these objects are. Some of the iron fragments are more or less flat and have a smooth surface, but others have a ragged boundary with many pores, suggesting that the iron and the molten crucible materials have reacted, or that iron dissolved into the glassy material.

3.2. Indentations

Several of the crucibles show rectangular indentations on the outside glassy surface, probably as a result of gripping the objects while still hot and (partially) molten with an iron tool (Fig. 5A; see also Rehren, 2002 for similar indentations).

Six of the recovered lids or complete crucibles showed impressions on the inside. They can be recognized as impressions of scrap fragments (Fig. 5B, C). Modarressi-Tehrani (2004) found such impressions in two of the Hochdorf crucibles as well. The micro-CT scans of the lids and complete, undamaged crucibles provided sharp 3-D digital models of the impressions (Fig. 5D, E). The 3-D prints of the negatives (Fig. 5F) made it possible to have life-size replicas of the objects that made the impressions, even the impressions that were hidden inside some of the
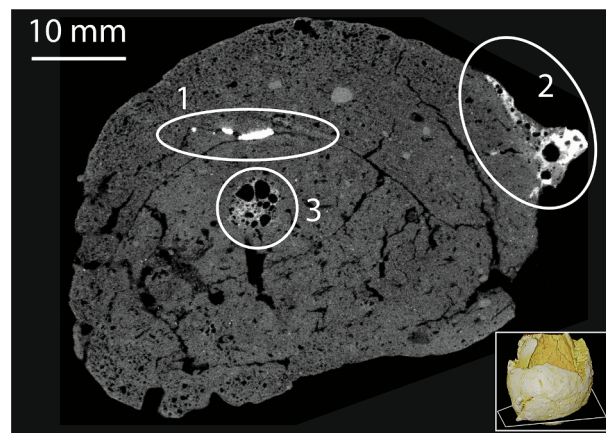
Fig. 4. Distribution of highly attenuating material in crucible 3. Cross-section (microCT scan data); the cross section position is shown in the insert (lower right). The fragments marked with "1" are flat and smooth, and are probably fragments of hammerscale. They are associated with the contact between cradle and mantle. Fragment "2" shows ragged edges and bubble which indicate that some sort of reaction has occurred. "3" marks a vesicular domain with high attenuation, similar to slag.

undamaged crucibles. Based on direct observations, on 3-D rendered images of the impressions on screen and on the 3-D printed negatives of these imprints, an overview could me made of the scrap fragments that had made the impressions (see Fig. 6). They include several twisted rods, a decorated rod and one or more fragments of what probably were fibulae. The overlarge majority of the fragments, however, consisted of folded or rolled-up fragments of thin plate.

3.3. Composition

Photomicrographs and SEM images of the thin sections are presented in Fig. 7 (see Supplementary Information S2 for photographs of the samples, and for scans of the thin sections). Microscopic observations on the thin sections revealed that the crucibles consist of an

Fig. 5. Indentations. A: Micro CT scan of crucible 1, showing rectangular impressions on the outside surface. B, C: Photographs of lids with indenta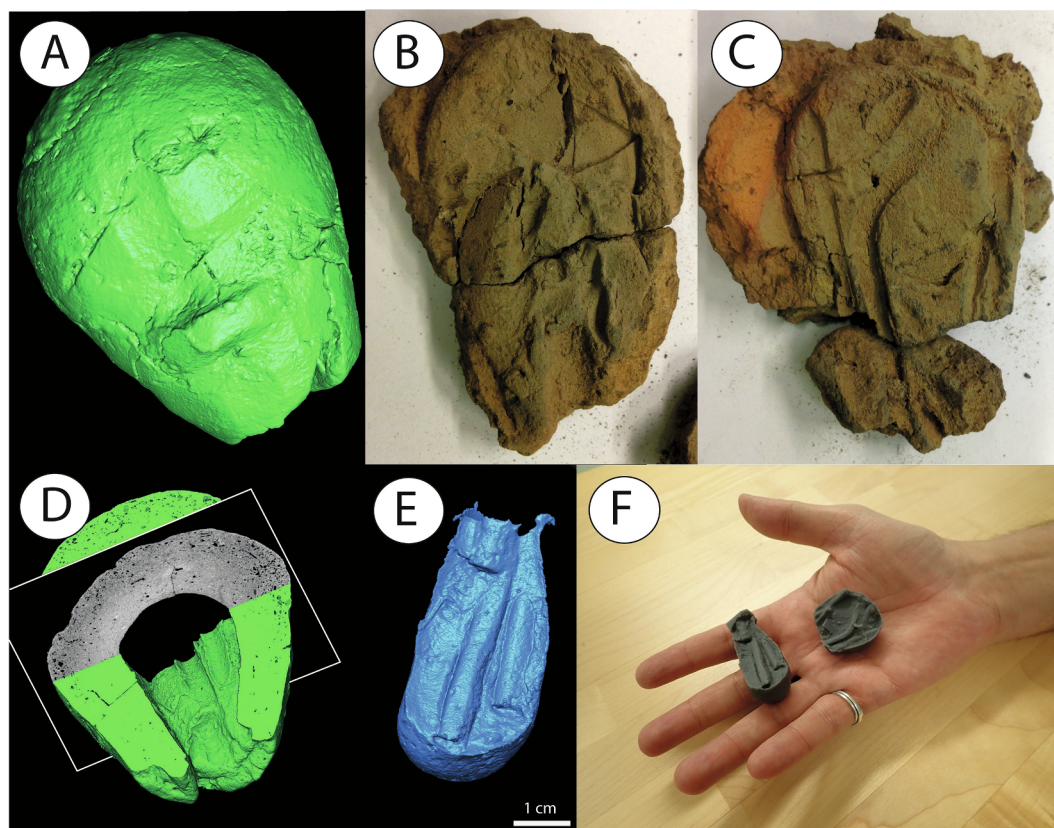tions of scrap remains. In 4B, (crucible nr. 4), impressions of folder sheet metal and twisted wires can be discerned. In 4C (crucible nr. 11, impressions of several rods can be seen. The bent one was probably part of a fibula. (see also Fig. 6). D: microCT-scan of the interior of crucible 1. The indentations in the lid are from rolled-up fragments of sheet metal. E: Negative of the cavity in crucible 1, showing the shape of the inside cavity as well as the positives of the scrap metal indentations on the lid. F: Examples of life-size 3-D prints of the inside of complete crucibles.

overall transparent colourless isotropic glassy matrix in which silt and fine sand grains are embedded (Fig. 7A, B, C). The sand and silt grains are dominantly quartz, but minor amounts of heavy minerals (zircon, titanium oxide, ilmenite, monazite, xenotime and unidentified pyroxenes or amphiboles), light minerals (feldspars, micas) and some kaolinite or haloysite grains were identified as well with polarization microscope and SEM-EDX.

The glassy material is vesicular at the outside of the crucible, but more massive on the inside. The very surface often consists of a thin layer of non-vesicular glass (Fig. 7A, B, C). It is remarkable that the fine groundmass has no birefringent properties anywhere in the crucible fragments. SEM imaging also found silt and sand grains embedded in a massive matrix of lighter material (i.e. darker grey) in the outer regions of the crucible samples. Here, the quartz grains show a gradual boundary of a few microns with the surrounding glass matrix, indicating that they were partially molten or dissolved into the glass (Fig. 7D). Towards the inside of the crucibles, however, this glassy material all but disappears, and only minor amounts are still present between the grains. This material is more grey in SEM images, and is tentative identified as only partially fused protoglass. Here, the grain boundaries are sharp, even when touching the proto-glass material (Fig. 7D, E).

In crucible nr. 13, the groundmass inside part of the crucible has parallel elongated pores. Some of them contain recognizable charred plant tissue fragments (Fig. 7F) or partially molten silica phytoliths (Fig. 7G). SEM revealed several instances where the intergranular glassy material forms pseudomorphs of organic tissue (Fig. 7H). (In these resin-impregnated samples, the charred material itself is indistinguishable from the resin itself by SEM). Towards the outside of the

crucible, these pores seem to become less frequent and then disappear. There is no clear compositional difference between the inside "cradle" part and the outside "mantle", and there is no clear boundary between the two.

Compositional data on the composition of the intergranular glass and proto-glass are given in Table 2. They include spot and area analyses throughout the thickness of the studied crucible fragments. In addition, some line scans are available, spanning the gradual boundary between glass and quartz grain in the outer part of crucible (Supplementary Information S3, S4, S5). The glassy groundmass seems to have the same characteristics throughout the thickness of the crucibles, being dominated by silica, and having additionally high (i.e. percent-range) concentrations of Al_2O_3, K_2O, Na_2O, MgO, CaO, and variable concentrations of other main elements like Fe_2O_3, P_2O_5 and TiO_2. Al_2O_3 concentration in the glassy material proper varies between 2 and 30%. The protoglass has higher Al_2O_3 concentrations, i.e. between 18 and 43%, with most values > 30%. Na_2O concentrations range between 0 and 8% in both groups, and K_2O concentrations between 0 and c. 12%. However, there seems to be a pattern, where higher Al_2O_3 concentrations (>20%) correlate with lower K_2O concentrations (<5%), but not with lower Na_2O concentrations (see also Supplementary information S6, S7).

3.4. Secondary components

As mentioned in the introduction, the glassy surface of some of the crucibles have macroscopically visible reddish staining, especially around the top hole. The hand-held XRF analyses on the surfaces of the crucibles showed elevated concentrations of Cu in most of the analyses,
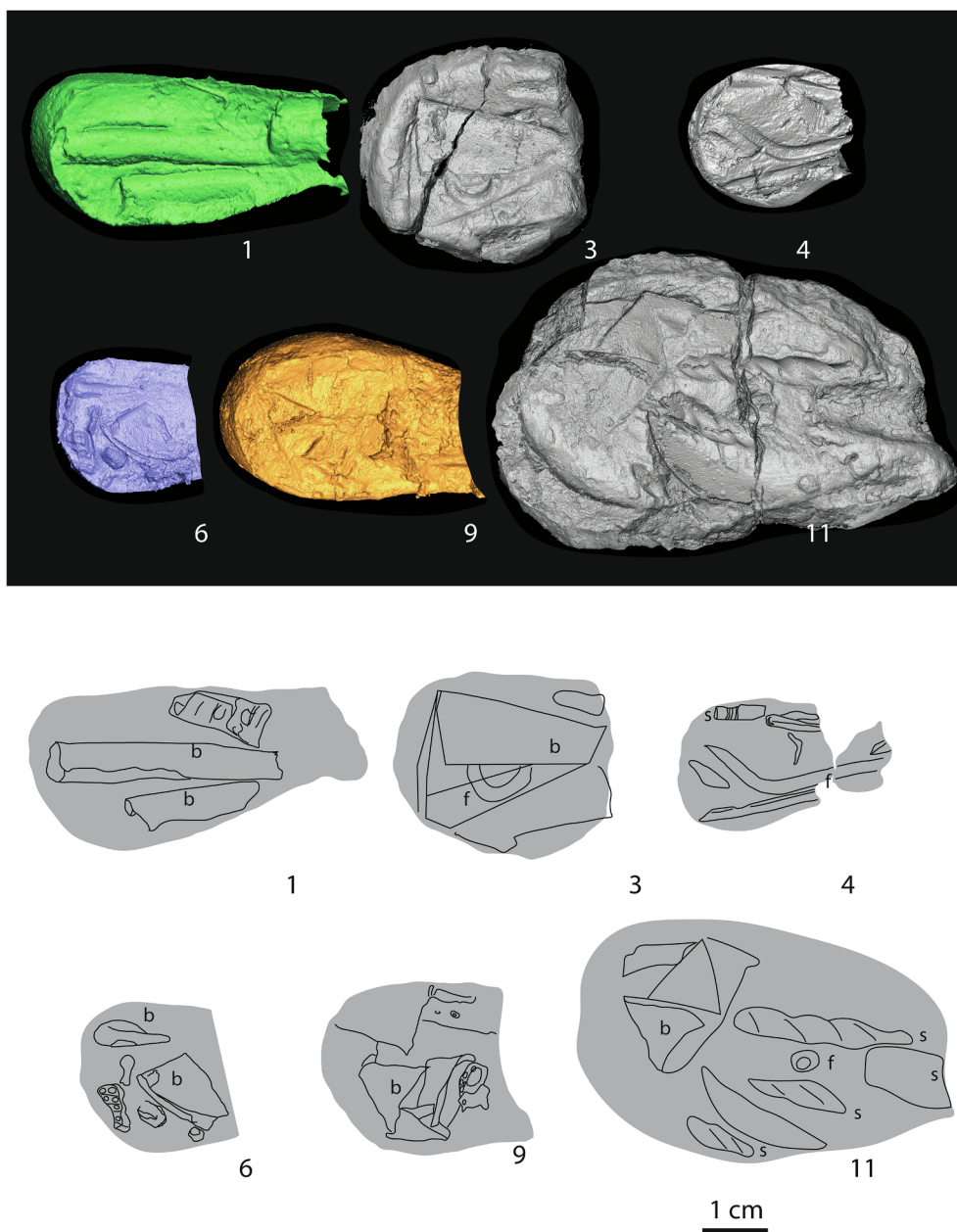
Fig. 6. mCT scans and drawings of the impressions in the recovered crucible lids, and their identification. Based on macroscopic observations, micro CT scans and 3D prints. Numbers indicate the crucible nr. f: possible fibula fragment, s: twisted rods or wires, b: fragments of plate metal.

and higher concentrations of Sn, Pb and Zn in some (Supplementary Information S8). Purplish red and green/blue staining was also observed in thin sections of the outer crucible surface of crucible 11 (Fig. 8 A – C). Although they probably represent dissolved copper (blue-green) or very finely distributed metallic copper globules (red; see Kunicki-Goldfinger et al., 2014), no copper wat detected on these spots by SEM-EDX. The copper concentrations were probably too low to be detectable by EDX. The crucible walls contain local domains with brown staining (Fig. 8 D). With SEM-EDX they were recognized as zones in which euhedral iron minerals occurred within the glassy matrix (Fig. 8F). Locally, concentrations of iron-rich globules also occur in the glass (Fig. 8E). The brick-orange zones in crucible 12 are under the microscope characterized by a dark reddish (PPL) to bright orange-red (XPL) colour in the glassy material, probably ferrous oxides (Fig. 8G). SEM-EDX did, however, not show higher concentrations of iron oxides in these zones, nor were iron-bearing minerals found. This indicates that

the red colouring is the result of oxidizing of iron oxides in the glassy phase, and not increased iron concentrations. Moreover, this oxidation process did not produce large enough minerals to be detectable by SEM.

A green stain in the glassy phase was bordered by iron oxide precipitates (Fig. 8H, I, J). SEM-EDX observations included platy and empty globular iron oxide phase (Fig. 8K, L) and cavity infills (Fig. 8M). These observations probably reflect occasions where metallic iron fragments – probably hammerscale- have become embedded into the crucible. Rehren (2002) mentions hammerscale in a similar position. The globular iron oxides in Fig. 8L especially may be related to chlorine-catalyzed corrosion of metallic iron (Selwyn et al., 1999). Euhedral TiO_2 minerals were observed in several instances by SEM EDX, embedded in the glassy matrix (e.g. Fig. 8 N).
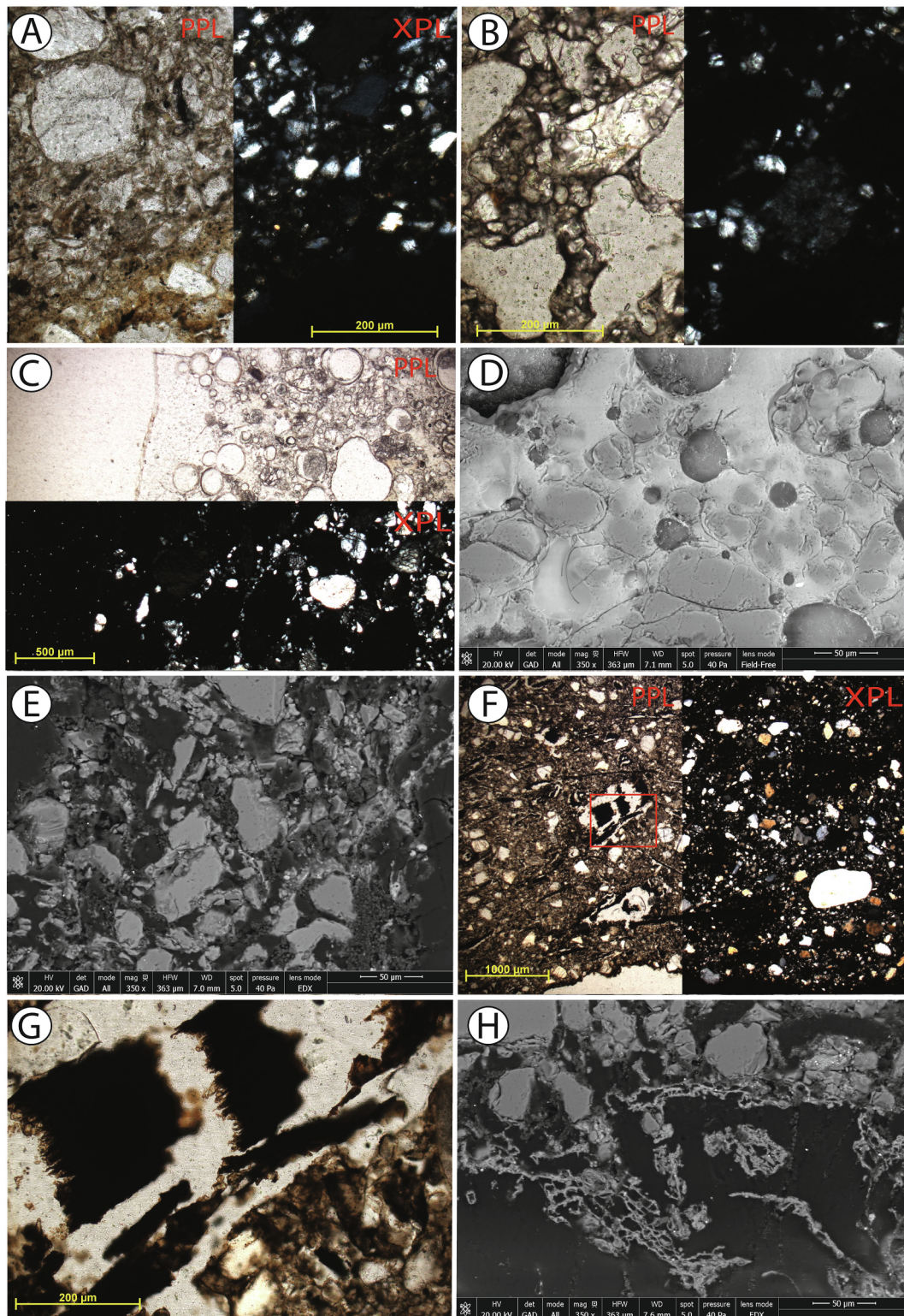
Fig. 7. Micrographs and SEM images of the investigated crucible fragments. PPL = plane polarized light, XPL = crossed polarizers. A: Inside edge of crucible 12, showing quartz grains in isotropic glassy matrix. B: Centre of crucible 13, showing large, somewhat irregular rounded vesicles. C: Outer edge of crucible 13, showing vesicular material, bordered by a thin band of massive glass. D: SEM backscatter image of the outside part of crucible 13. Quartz grains (grey) embedded in glassy (light grey – white) groundmass. Note the gradual boundaries between grains and glassy material. E: SEM backscatter image of the inside part of crucible 13, showing quartz grains (light grey) with some granular matrix material (grey; granular) and resin-filled pores (also grey; massive). F: Inside groundmass of crucible 13, showing ample pores that are filled with charred organic matter. Area of figure G is indicated. G: Magnification of one of the charred organic remains in figure F. H: SEM image of crucible 13 showing some organic structures – probably partially molten phytolith structures.

Table 2
SEM-EDX analysis results on the intergranular glassy material from spot and area measurements; sections from crucible nrs. 11, 12 and 13.

Object nr	Area	Lab code	Material analyzed	SiO₂ (%)	Al₂O₃ (%)	TiO₂ (%)	Fe₂O₃ (%)	MnO (%)	MgO (%)	CaO (%)	K₂O (%)	Na₂O (%)	P₂O₅ (%)	SO₃ (%)
11	Outer zone	11 1 1	Glass	62.65	16.78	0.00	5.02	0.00	1.23	0.00	10.78	3.54	0.00	0.00
11	Outer zone	11 4 2	Glass	56.41	8.98	0.61	2.74	0.00	3.05	11.13	9.32	6.34	0.42	0.00
11	Outer zone	11 2(1) 1	Glass	51.54	26.12	0.00	7.63	0.00	0.58	2.60	2.96	4.72	2.39	1.45
11	Outer zone	11 2(1) 2	Glass	32.52	23.39	1.40	28.60	0.00	0.93	1.04	1.86	5.79	3.63	0.00
11	Outer zone	11 2(1) 3	Glass	52.16	5.55	0.47	25.84	0.00	1.26	6.10	5.86	2.04	0.43	0.00
11	Outer zone	11 2(4) 1	Glass	56.28	6.02	0.63	9.11	0.00	3.44	17.86	2.73	2.69	0.86	0.00
11	Outer zone	11 2(6) 1	Glass	71.87	11.06	1.33	4.06	0.00	0.59	0.87	3.72	5.30	0.41	0.00
11	Outer zone	11 2(6) 4	Glass	80.29	4.60	0.00	2.48	0.00	1.16	1.83	1.74	7.90	0.00	0.00
11	Outer zone	11 2(6) 5	Glass	96.34	1.65	0.00	0.00	0.00	0.00	0.00	0.35	1.16	0.00	0.00
11	Outer zone	11 2(7) 3	Glass	79.38	7.57	0.87	2.86	0.00	0.73	0.73	2.54	4.79	0.00	0.00
11	Outer zone	11 2(8) 2	Glass	78.57	8.49	0.75	3.08	0.00	0.75	0.63	3.27	3.65	0.00	0.00
11	Outer zone	11 2(9) 1	Glass	71.64	13.51	0.62	4.91	0.00	0.93	0.65	3.38	4.00	0.00	0.00
11	Outer zone	11 2(13) 1	Glass	88.69	4.50	0.00	0.00	0.00	0.57	0.00	2.17	4.07	0.00	0.00
11	Outer zone	11 2(13) 3	Glass	88.61	3.97	0.46	1.70	0.00	0.46	0.64	0.83	2.62	0.00	0.00
11	Inner zone	11 2(18) 1	Glass	69.21	15.06	0.00	4.29	0.00	1.04	0.00	4.71	5.69	0.00	0.00
11	Inner zone	11 2(18) 2	Glass	79.30	9.46	0.00	2.78	0.00	0.46	0.00	4.22	3.77	0.00	0.00
11	Inner zone	11 2(20) 3	Glass	64.19	21.25	1.02	5.41	0.00	1.22	0.68	3.56	2.05	0.00	0.00
12	Outer zone	12 1 3	Protoglass	26.13	31.45	2.34	27.47	0.00	0.00	0.66	0.43	3.92	2.69	3.52
12	Outer zone	12 3 1	Protoglass	34.69	36.18	0.90	13.49	2.44	1.80	1.89	0.98	5.81	0.62	0.67
12	Middle zone	12 1 1 – 7	Area	73.80	12.00	1.22	4.54	0.00	0.41	0.68	3.11	3.50	0.00	0.00
12	Inner zone	12 5 1–10	Protoglass	35.40	43.21	0.71	12.41	0.00	0.00	0.59	0.77	0.00	4.37	2.12
12	Inner zone	12 5 2–10	Protoglass	61.72	24.14	1.27	7.90	0.00	0.64	0.00	1.39	0.00	2.18	0.00
12	Outer zone	12 1 1 – 1	Area	71.45	13.23	0.00	6.40	0.00	1.40	0.78	2.04	4.69	0.00	0.00
12	Outer zone	12 2 1 – 1	Area	71.27	13.29	0.00	8.22	0.00	1.07	0.00	2.33	3.82	0.00	0.00
12	Outer zone	12 3 8 – 2	Protoglass	42.99	34.02	2.66	10.75	0.00	3.04	0.00	3.32	1.64	0.00	0.00
12	Outer zone	12 3 9 – 2	Protoglass	32.75	17.86	0.34	26.72	0.52	0.00	19.71	0.00	1.44	0.46	0.00
12	Middle zone	12 4 3 – 3	Protoglass	30.07	20.00	0.00	38.08	0.00	9.99	0.00	1.86	0.00	0.00	0.00
12	Middle zone	12 4 5 – 3	Protoglass	47.18	38.35	0.00	3.84	0.00	1.63	0.00	4.90	4.09	0.00	0.00
12	Middle zone	12 5 2 – 4	Protoglass	60.44	17.59	0.00	0.00	0.00	0.00	0.00	13.46	8.51	0.00	0.00
12	Middle zone	12 1 1 – 5	Area	72.16	13.49	0.85	4.01	0.00	0.43	0.71	4.18	3.66	0.00	0.00
12	Middle zone	12 1 2 – 5	Protoglass	41.46	25.40	2.19	17.33	0.00	6.29	0.00	3.28	2.74	0.00	0.00
12	Middle zone	12 1 6 – 5	Protoglass	64.87	17.56	0.72	4.02	0.00	1.08	0.91	4.72	5.69	0.00	0.00
12	Middle zone	12 3 3 – 6	Protoglass	49.93	33.01	0.44	6.05	0.00	2.65	0.00	3.86	3.80	0.00	0.00
13	Outer zone	13 1 2 – 1	Glass	69.58	7.95	0.47	10.43	0.00	0.47	1.18	4.94	4.70	0.00	0.00
13	Outer zone	13 1 3 – 1	Glass	49.05	25.28	1.45	13.72	0.00	0.48	0.81	1.94	3.71	2.67	0.00
13	Outer zone	13 3 3 – 1	Glass	63.09	11.77	0.84	11.63	0.00	1.00	0.84	4.57	5.29	0.46	0.00
13	Outer zone	13 1 5 – 1	Glass	40.72	25.76	1.03	21.24	0.00	1.61	0.62	3.20	4.00	1.21	0.00
13	Outer zone	13 1 6 – 1	Glass	23.11	25.59	1.01	41.05	0.00	1.15	0.48	0.79	1.03	4.55	0.65
13	Outer zone	13 1 1 – 2	Glass	62.03	4.76	0.87	5.22	0.79	1.74	15.09	5.70	2.49	0.80	0.00
13	Outer zone	13 1 2 – 2	Glass	64.04	11.61	1.10	3.51	0.00	0.63	5.69	9.13	3.62	0.00	0.00
13	Outer zone	13 1 3 – 2	Glass	81.36	2.19	0.00	6.44	0.00	0.00	4.97	3.73	1.31	0.00	0.00
13	Inner zone	13 1 4 – 1	Protoglass	57.85	20.47	0.66	13.51	0.00	0.99	0.00	2.87	2.36	0.90	0.00
13	Middle zone	13 2 3–2	Glass	55.42	29.89	0.91	0.94	0.56	1.27	2.90	4.17	3.39	0.00	0.00
13	Middle zone	13 3 1–2	Protoglass	54.16	35.81	0.00	3.76	0.00	0.00	1.47	0.96	2.52	0.00	1.32
13	Inner zone	13 13 2–7	Glass	66.96	18.15	0.00	0.72	0.00	1.01	1.70	6.63	4.84	0.00	0.00
13	Inner zone	13 2 3–9	Glass	76.01	9.24	1.70	3.06	0.00	0.34	0.00	6.68	1.95	0.00	0.00
13	Inner zone	13 2 4–9	Glass	64.61	15.78	0.85	5.38	0.00	0.68	1.43	6.86	3.90	0.00	0.00
13	Inner zone	13 4 3–10	Glass	60.95	18.37	1.22	4.48	0.00	1.39	1.17	7.42	4.25	0.00	0.00
13	Inner zone	13 5 1–13	Organic pseudomorphs	13.50	13.95	0.72	65.80	0.00	0.00	0.61	0.00	0.00	4.98	0.00
13	Inner zone	13 5 2–13	Organic pseudomorphs	89.94	5.59	0.00	2.64	0.00	0.31	0.52	1.01	0.00	0.00	0.00
13	Inner zone	13 5 3–13	Organic pseudomorphs	12.49	9.51	0.00	73.02	0.00	0.00	0.74	0.00	0.00	4.25	0.00

3.5. White material

The small fragment of white powdery material appeared under the microscope as an irregular cluster of white material with reddish domains (Fig. 9A). SEM-EDX shows that the material is dominantly glassy, with embedded silt grains – like the crucible. However, the glass is riddled with lath- or needle-shaped cavities (Fig. 9B) and it contains ubiquitous small spheres (~300–400 nm) of metallic copper (Fig. 9C,D). Moreover, clusters of needle-shaped tin oxide minerals occur scattered through the fragment (Fig. 9E).

4. Discussion

4.1. Use of crucible and implications

There is little doubt that the crucibles were used in the melting of processing bronze: Copper has dissolved in the glassy phase on the outside of some of the crucible, whereas that white brittle fragments that contain copper and tin compounds are probably dross - a waste material that floated on top of the molten metal (see e.g Rademakers, 2015). The separation of the two metals in different precipitates (i.e. metallic copper and tin oxides minerals) makes it impossible to reconstruct the original composition of the material processed in these crucible, but it is clear that it was some variety of tin-bronze. This is in line with Rehren (2002) and Modarressi-Tehrani (2004) who found remains of bronze in Iron Age egg-shaped crucibles from Cologne and Hochdorf. Our evidence that these crucibles were used for scrap recycling, in the form of indentations of recognizable bronze objects in six of the recovered crucible lids, is in line with two of Modarressi-Tehrani's (2004) crucibles.

Archaeologically speaking, one of the most striking results of this study is that bronze plate fragments were recycled in Tilburg. This may have come in different scenarios: The simplest explanation is that a plate object was scrapped and subsequently recycled on site. If this is the case, there are some important implications: From the whole of the Netherlands, only a few Iron Age copper-alloy plate objects are known - most of them from the Early Iron Age - including eight bronze buckets (*situlae*) and a basin. These objects come from high-status burials and from wetland depositions, thought to be related to an elite gift-exchange network (van der Vaart-Verschoof, 2017). Because of their paucity and their find contexts, these objects are generally thought to have been regarded as important, very special ritual objects. Indications that at least one plate object was used as raw material for recycling may be at odds to this theory. It even begs the question whether the paucity of this type of object is because they were readily recycled.

There are, however, other options. One option is that the metalworker in Tilburg had done repair-work on a plate object, and subsequently recycled the refuse from that. After all, some of the known *situlae* have repair pieces (van der Vaart-Verschoof, 2017). If *situlae* and basins were rare, however, it is questionable whether local craftsmen would have the tools and technology to do the repairs themselves. Another option is that the Tilburg metalworker had imported scrap metal, including scrap from plate objects and/or cut-offs from repair-work, from further away.

4.2. Crucible technology

The presence of a range of light and heavy minerals in the sand/silt component of the crucible matrix indicate that this material has a sedimentary origin. Although the number of heavy minerals encountered is too low for a quantitive comparison, occurrences of zircon, rutile, monazite and xenotime are in line with the fine heavy mineral fraction in the local Late Pleistocene coversands (e.g. Schokker, 2003) and in the underlying Early Pleistocene sediments of the Waalre formation (formerly known as Tegelen and Kedichem formations; see Huisman and Kiden, 1998; Huisman and Klaver, 2007). This makes it likely that a local sediment source was used as raw material for making the crucibles.

The glassy material throughout the crucible cross-sections contain in general Al_2O_3 concentrations of a few % to >20%, with most of the higher Al_2O_3 percentages in the proto-glass. This indicates that clays contributed strongly to the overall glass composition. Moreover, the proto-glass seems to have a larger contribution of high - Al_2O_3 clays. The concentrations of K_2O, Na_2O and MgO, however, far exceed that of the composition of clays in the region: Huisman & Kiden (1998) and Schokker, 2003) found that Na_2O concentrations do not exceed 1 to 1,5%; > 4000 analyses from Late Neogene to Holocene clastic sediment composition data (www.dinoloket.nl) give the same range for clastic sediments from the whole of the Netherlands. Moreover, these maximum Na_2O - concentrations occur in (feldspar-bearing) fine sands and silts, not in clays. The only deposits in the Netherlands that have Na_2O concentrations >1.5% are from the Early Holocene Basal peat (Naaldwijk formation), a marine-influenced or coastal organic deposit. These high Na_2O concentrations are accompanied by high MgO values, in the same range as found in the Tilburg crucible glassy phase. However, Basal peat has low Al_2O_3 and was unreachable (buried) during Late Prehistory, whereas K_2O concentrations in the crucibles exceeds both the Netherlands' clays as well as Basal peat. High K_2O concentrations in the molten surface of crucibles may be attributed to contact with (high-K_2O) fuel ash. This does, however, not explain the high concentrations of MgO and especially Na_2O, nor does it explain why these values occur throughout the crucible and not just at the surface.

A comparison of the chemical data with literature data on West-European plant ashes, however, shows that the compositional data are in line with a significant contribution of halophytic plant ashes in the glassy material of the crucibles (Fig. 10; (Tite et al., 2006; Cílová and Woitsch, 2012). The most likely explanation for this is that the crucibles were constructed from a mixture of silty loam and halophytic plant ashes. During firing, the alkalis from the ashes acted as flux, melting the clay minerals in the fine fraction and forming a glassy phase. The atmosphere was reducing enough, and the temperature high enough, that $Fe(II)$ oxides and - locally - new TiO_2 minerals were formed. We hypothesize that the melting of the clay-ash mixture was incomplete on the inside of the crucibles, where the temperature was lower – although it was still high enough to melt the bronze charge.

After discarding, and especially after burial, any remaining non-fused ashes would have dissolved. The same could have been true for water-soluble and easily weatherable minerals as well; maybe the lath- or needle-shaped cavities in the dross (Fig. 9B, C) are cavities left behind from such dissolution processes. The high Al_2O_3 concentrations of the proto-glass in the inner parts of the crucibles may indicate that the kaolinitic components in the clays may have been the only components of the clay-ash mixture that survived the heating and subsequent dissolution processes in the soil.

The use of halophytic plant ashes as flux is well-known from prehistoric faience and glass: In faience production, heating a mix of fine quartz grains and ash results in a glassy, fused outer surface of an object whereas unmolten quartz grains on the inside are connected with minor glass fragments (Tite, 2007; Tite, 2008). Clays are not used in this type of application. For ceramic glazing, fluxes are only on the surface. In the present study, we seem to have recognized for the first time a combination of these techniques (ceramic and faience) in the form of a mixture of quartz, clay and halophytic plant ashes. This mixture may have been especially made for crucibles.

What could be the reason to use a hybrid ceramic-faience technique for these crucibles? The most likely explanation is that the locally or regionally available clays were not suitable for use in this type of crucible. Crucibles for copper alloy processing in ovens, typically need refractory clays, which are high in Al_2O_3 (c. 25–40%; Martinón-Torres & Rehren, 2014,), i.e. are dominated by kaolinite. Other clays or clay mixtures are not resistant to the high temperatures attained in
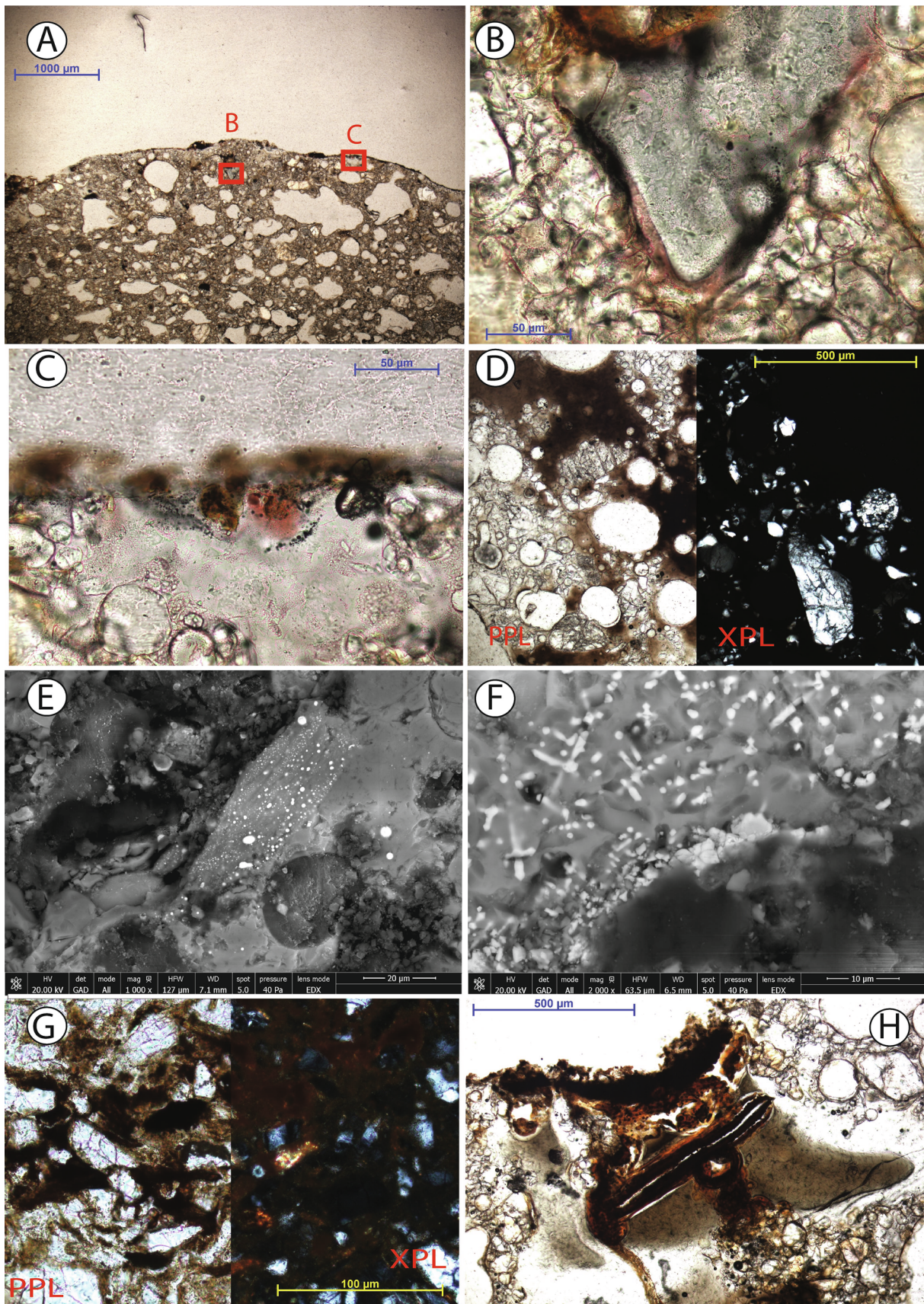
(caption on next page)

Fig. 8. Micrographs (A, B, C, D, G, H, I) and SEM backscatter images (E, F, J, K, L, M, N) of dissolved compounds and secondary minerals. A: Outside surface of crucible 11 (PPL); B and C indicated. B, C: Magnifications of red and purple + red stained areas in 8A. D: Brown stain in glassy material of crucible 13. E: Euhedral iron minerals a brown stain in crucible 13. F: Concentration of iron globules. G: Orange-brown iron staining in brick-orange part of crucible 12. H: Green stained glassy material, with reddish crusts of iron oxides in crucible 11; 8I indicated. I: Magnification of reddish iron oxide crust in 8H. J: Banded iron crusts in crucible 11. K: Platy iron oxides in crucible 13. L: Empty iron globules in crucible 13. M: Banded and somewhat crystalline infill of rounded cavity. N: Euhedral titanium oxide minerals in glassy matrix.
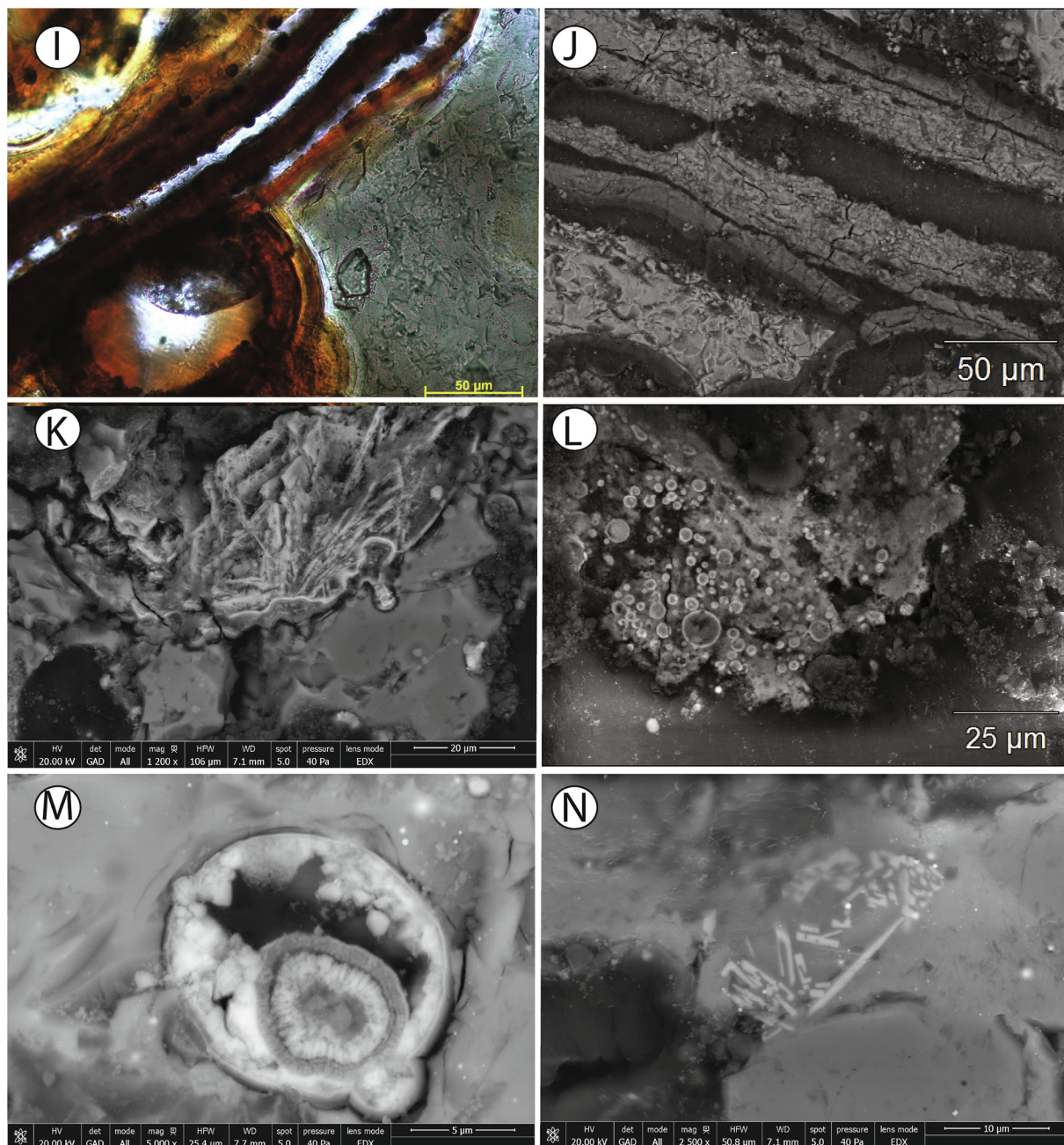

Fig. 8. (*continued*)

metallurgical processes. Crucibles made from unsuitable (low-Al_2O_3) clays are likely to lose their structural stability during heating, unless strongly tempered with coarse material Martinón-Torres & Rehren, 2014).

In North-Western Europe, kaolinitic clays are typically found in Tertiary weathering profiles, e.g. in the Vogelsberg area in Germany, or in weathered or hydrothermally altered granite terrains, e.g. in Cornwall. In the Tilburg region, the local near-surface clays typically are a mixture of illite, smectite and kaolinite, with local occurrences of higher smectite concentrations in the Early Pleistocene deposits (Huisman and Kiden, 1998). This would make them unsuitable for use in metallurgical crucibles.

We propose that the admixture of significant amounts of halophytic plant ash to non-refractory clays would be a way to produce a suitable material for metallurgical crucibles. The alkali-flux in the plant ashes would cause the clay minerals to melt and fuse into glassy material,
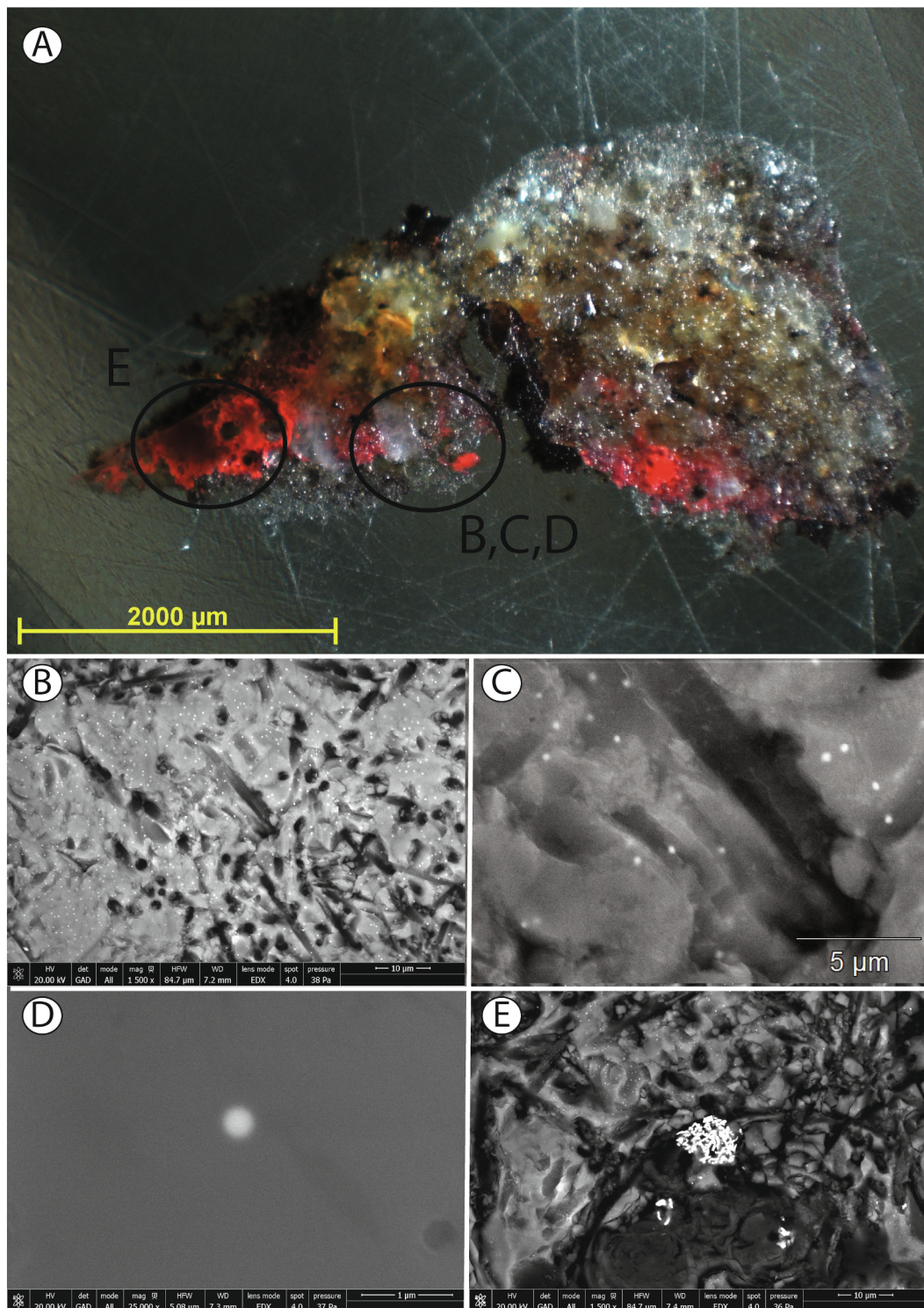
Fig. 9. Fragment of white powdery material. A: Micrograph (oblique incident light) impregnated, cut and polished sample. Note the white and reddish zones. material, and scans, photomicrographs and SEM images of the impregnated and polished sample of this material. General area of image 9B-D are indicated. B: Porous groundmass with lath- or rod-shaped pores. C: Enlargement of B, showing small white round spots. D: One of the spots, identified as metallic copper. E: Cluster of (white) lath-shaped minerals, identified as tin oxide.

especially in the surface parts of the crucible, thus preventing catastrophic failure. This would at the same time make the crucible walls more plastic, which may have further helped prevent cracking under strain. The inside of the crucibles fused only to a limited degree, which prevented too strong deformations.

Koenig et al. (2013) found elevated Ca and Mg concentrations in the mantle of Roman crucibles, and attributed those to the addition of dolomite, marl or plant ash for improving the thermal properties of the clays used. However, they do not find elevated Na concentrations. Modarressi-Tehrani (2004) attributes high Na concentrations in the glassy phase of La Tène crucibles from Hochdorf to the melting of feldspar minerals. Our study is the first to recognize the use of a hybrid
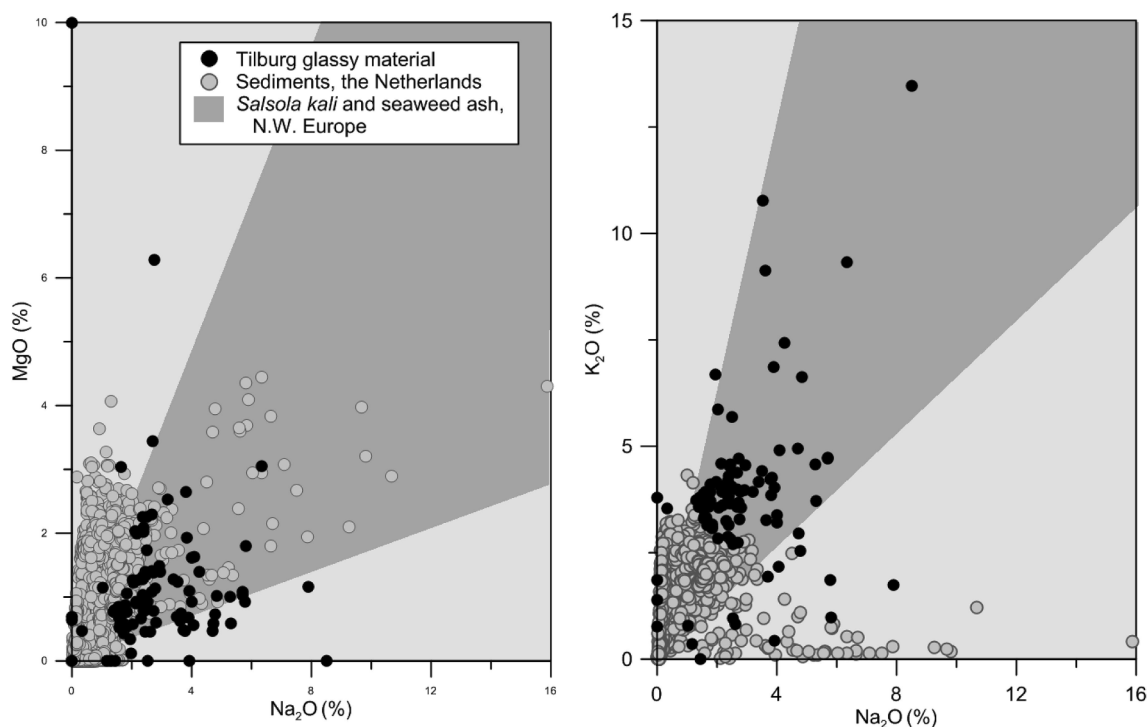
Fig. 10. Scatterplots of Na, K and Mg for the crucible glassy phase (SEM-EDX measurements), Dutch sediment composition (c. 4000 XRF analyses from www.dinoloket.nl) and plant ash composition range from literature (Tite et al., 2006; Cílová and Woitsch, 2012).

material that combines halophytic plants ash and clays for the use in crucibles. Further research would be needed to determine how common the use of this material was during this period.

4.3. The chaîne operatoire

Based on the above, we propose the following *chaîne operatoire* for preparation, making, using and discarding the crucibles (see also Fig. 11):

Preparation: The bronze objects that need to be recycled are cut into small fragments that would fit in a crucible. Plate fragments are folded or rolled up. Raw materials for the crucibles – silty loam, halophytic plant ash and maybe some very fine plant material as temper – are gathered. Charcoal is prepared or obtained. A small oven or firing pit is built.

Crucible making: The raw materials are mixed to a paste. Partially open cradles are made from the paste and dried. Each of the cradles is filled with scrap fragments, after which a mantle is formed around it using the same paste. Where the scrap fragments touch the mantle they may leave impressions. The outside surface is formed into an egg-shape with a hole in the sharp end.

Crucible use: The crucibles are placed into a charcoal-fueled oven with (generally) a reducing atmosphere. Here, the bronze charge melts, while in the crucible walls reduced iron oxides are formed and ilmenite is transformed into iron and titanium oxide minerals. The crucibles are removed while still hot, and the bronze is poured out - some 10–20 cm³ of molten metal from each crucible. The iron tongs used for gripping the crucibles leave impressions on their outer surfaces; some fragments of iron break off due to the heat, and end up in or on the crucible wall. Since the shape made it impossible to put objects into the crucibles after first use, the crucibles could only be used once: After use they must have been discarded.

As no mould fragments or recognizable casting waste have been found on the site (in contrast to e.g. Hochdorf, where e.g. moulds for casting bracelets were found (Modarressi-Tehrani, 2004), we hazard that that at this stage in Tilburg only ingots were cast, e.g. in sand.

5. Conclusions

Middle Iron Age egg-shaped crucibles from Tilburg (The Netherlands) were in use for remelting (and therefore recycling) of bronze scrap. Indentations left on the inside of the crucibles included recognizable imprints from fragments of twisted wire and fibulae. Most remarkable, however, are the fragments of metal plate: They must have originated from objects like buckets and basins, which are rare, and are generally thought to have ended up in burials and wetland depositions.

In order to make crucibles from the local, non-refractory clays, a hitherto unknown ceramic-faience hybrid was used: A combination of clay and halophytic plant ash was mixed with silt into a paste, and this was used to construct the crucible. During firing, the flux would promote melting of the clays and probably prevent catastrophic failure of the crucibles. The resulting glassy groundmass – in which silt grains are embedded and partially dissolved – is rich in Al_2O_3 as well as in Na_2O, K_2O, CaO, MgO and Fe_2O_3.

It is likely that this technique of crucible manufacture was widespread in Late Prehistory in areas where no refractory clays were available.

CRediT authorship contribution statement

D.J. Huisman: Conceptualization, Visualization, Writing - original draft, Writing - review & editing. **A. Bach:** Writing - review & editing. **I. Joosten:** Writing - review & editing. **D.J.M. Ngan-Tillard:** Visualization, Writing - review & editing. **G. van den Eynde:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
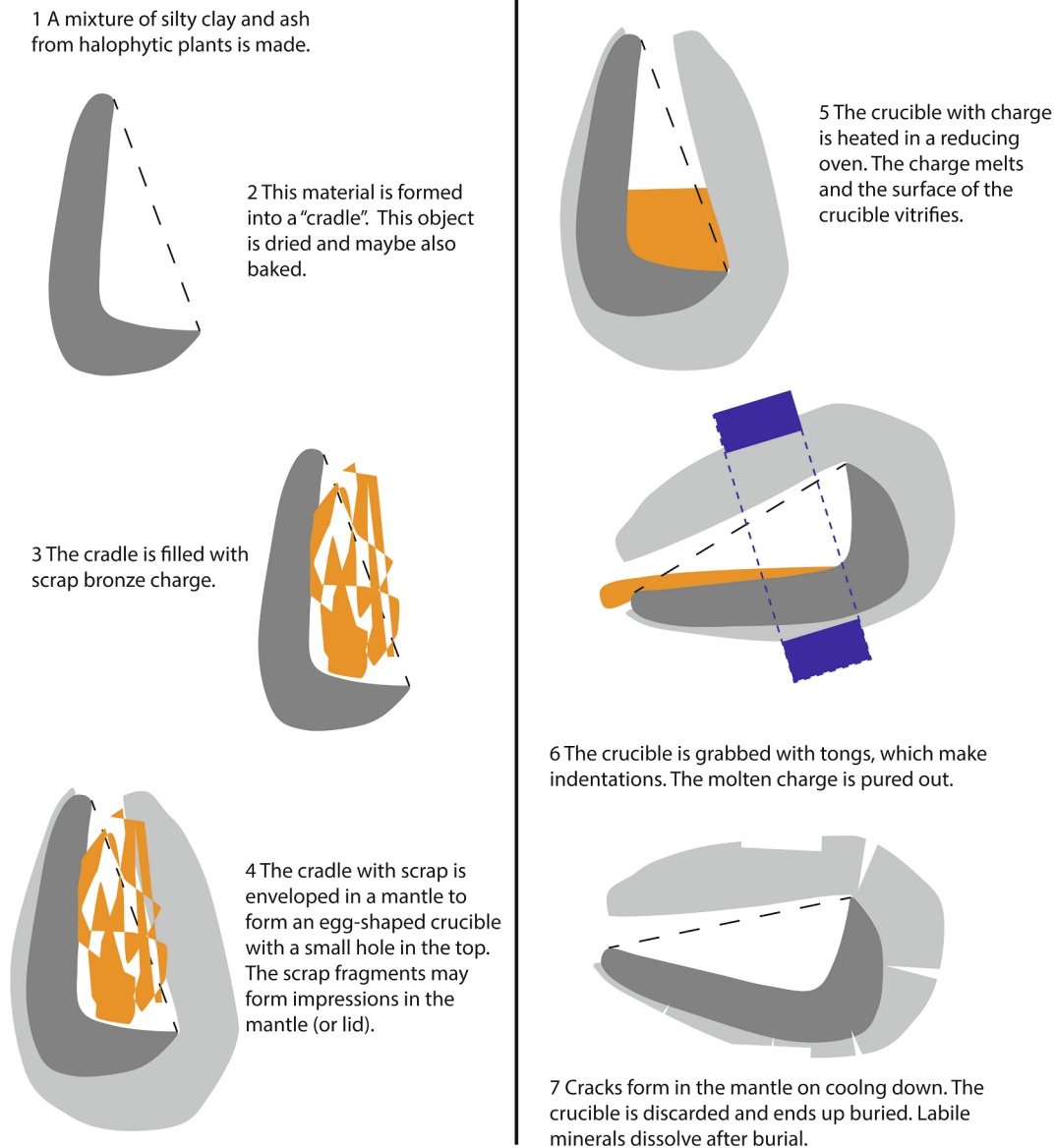
1 A mixture of silty clay and ash from halophytic plants is made.

2 This material is formed into a "cradle". This object is dried and maybe also baked.

3 The cradle is filled with scrap bronze charge.

4 The cradle with scrap is enveloped in a mantle to form an egg-shaped crucible with a small hole in the top. The scrap fragments may form impressions in the mantle (or lid).

5 The crucible with charge is heated in a reducing oven. The charge melts and the surface of the crucible vitrifies.

6 The crucible is grabbed with tongs, which make indentations. The molten charge is pured out.

7 Cracks form in the mantle on coolng down. The crucible is discarded and ends up buried. Labile minerals dissolve after burial.

Fig. 11. Schematic overview of the *chaîne operatoire* for preparation, making, using and discarding egg-shaped crucibles.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2020.102421.

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