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First evidence for alloying practices in the Chalcolithic Southern Levant (4500–3800 BCE) as revealed by metallography

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Abstract

Excavations at the Chalcolithic site Fazael in the central Jordan Valley uncovered a large number of metal items, many of them polymetallic copper alloys cast in the lost wax technique. Metallography and SEM–EDS analysis on a subset of the assemblage confirm previous notions of the lost wax metallurgy in the Chalcolithic Southern Levant but extend them significantly in three aspects: The Fazael metal assemblage is slightly depleted in its arsenic content compared to metal assemblages from other sites, silt-sized quartz inclusions in unalloyed and polymetallic copper items, and the presence of unalloyed copper inclusions. These latter provide the earliest direct evidence for mixing of different metal types in West Asia, potentially alloying or recycling.

Keywords Polymetallic copper alloys, Lost wax casting, Unalloyed copper inclusions, SEM–EDS, Metallography, Fazael, Chalcolithic, Southern Levant, Mixing, Alloying

Introduction

The Chalcolithic Southern Levant (4500–3800 BCE) is known for its intricate lost wax cast copper objects, prominently featured in the Nahal Mishmar Hoard with more than 300 mace heads, standards, crowns and vessels cast in this technique [1, 2]. Almost all of them are made of copper alloys rich in arsenic and antimony [4–6], an alloy not used elsewhere at any time in West Asia [7]. The production process of these objects remains poorly understood due to the lack of production sites. Investigations on the metal objects and mould remains adhering to them show that the metal was smelted from ores in Anatolia or the Southern Caucasus [7] but cast in the Southern Levant [6, 8, 9]. Only recently, a large assemblage of lost wax cast polymetallic copper alloy items was presented [10], mostly fragments of mace heads, standards and crowns, found at Fazael in the central Jordan valley together with several crucible fragments. It is by number the largest metal assemblage in the Southern Levant after the Nahal Mishmar Hoard. Rosenberg et al. [10] suggest that the co-occurrence of lost wax cast metal fragments and crucible fragments indicates the presence of a lost wax casting production site in Fazael. However, immobile metallurgical features such as furnaces are yet to be found. Moreover, the unprecedentedly large number of fragments could be an indicator for the recycling of lost wax cast polymetallic copper alloys [10].

The crucible fragments of Fazael are the first indicators of Chalcolithic metallurgy in the Southern Levant outside the confines of the Northern Negev. There, an unalloyed copper industry thrived at several sites that smelted ore, predominantly mined in Faynan, to unalloyed copper. The unalloyed copper was cast into tool-shaped objects

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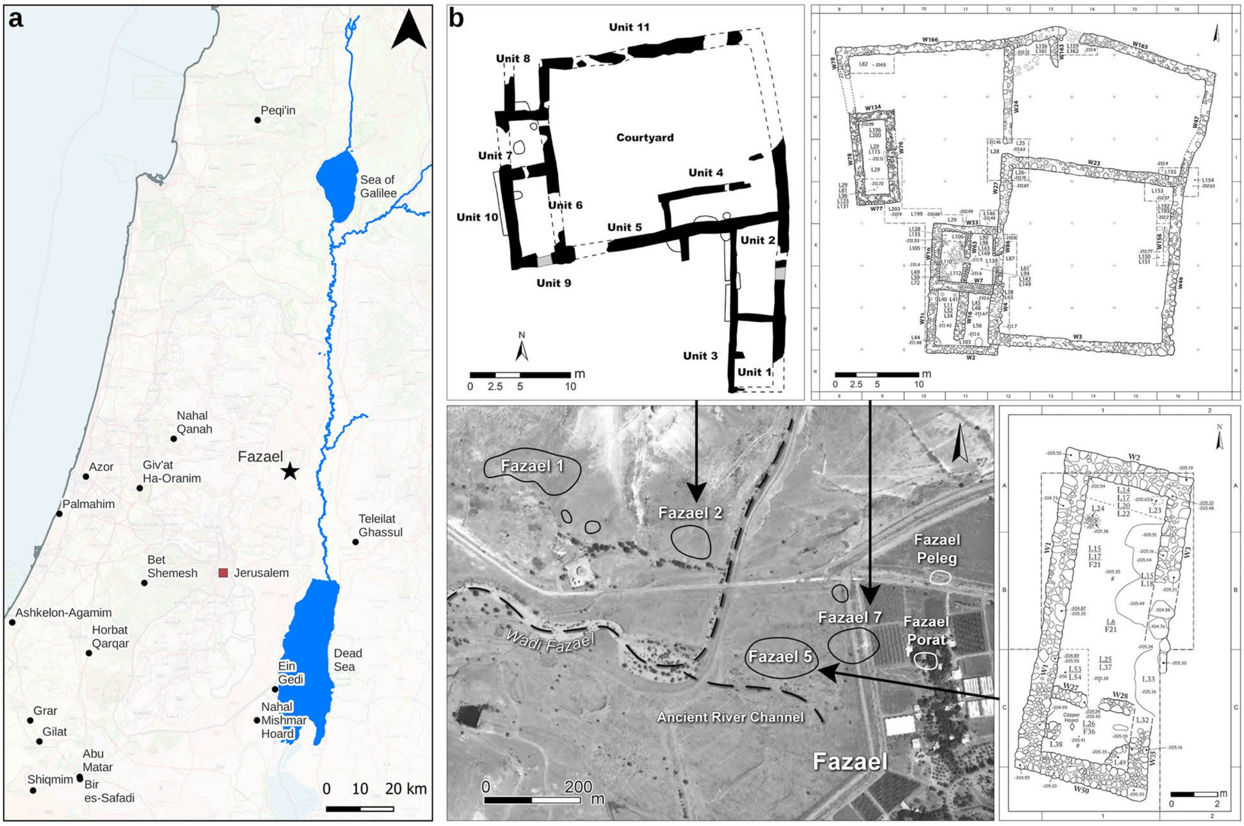

Fig. 1 (**a**) Map with the location of Fazael (basemap: openstreetmap.org) and (**b**) satellite image with the location of the Fazael sub-sites within the site cluster and the plans of the architectural features excavated in Fazael 2, 5, and 7 (Fig. 2 in [10], licensed under CC-BY 4.0)

in open moulds [11–17]. Therefore, the technological study of the Fazael metal items promises to provide new and important insights into the metallurgical process at the site and our understanding of polymetallic copper alloy metallurgy of the Chalcolithic Southern Levant in general.

Thanks to the fragmented state of most of the metal items in Fazael, it was possible to sample 16 for metallographic investigation, including scanning electron microscope-electron dispersive X-ray spectrometry (SEM–EDS) analysis of the metallographic sections. The aim is to compare the metal items found in Fazael to the other polymetallic copper alloy objects with respect to their chemical composition and manufacturing process. The results significantly enhance our understanding of the polymetallic copper metallurgy in the Chalcolithic Southern Levant. Moreover, they add an important aspect to it: the mixing of polymetallic copper alloys with unalloyed copper. While the reasons for this mixing remain unknown, evidence of this practice puts the Chalcolithic Southern Levant among the earliest cultures practising alloying of metals.

Archaeological background of Fazael

The multi-site cluster Fazael extends along the northern riverbank of the Wadi Fazael (Fig. 1). Fazael 1, the site furthest west in the cluster, is the oldest. It is a multi-strata settlement site dating to the Chalcolithic of the Southern Levant [18]. Towards the end of the Chalcolithic, settlement activities shift towards the east with the sub-sites Fazael 2 [19], 5 [20], 7 [21], and Porath 1985 excavation [22]. They all feature a broad room house connected to a courtyard. Fazael 2, 5, and 7 have the same general stratigraphy of three strata and also the same material culture. The main settlement phase is recorded in stratum II, radiometrically dated on charcoal from Fazael 2 between 4000 and 3900 BCE. This date puts settlement activities in this site cluster to the very end of the Chalcolithic [19].

A Chalcolithic broad room house with a courtyard was found in Fazael 2, 5, and 7. The four-roomed building at Fazael 7 is the largest known broad room house of the entire Chalcolithic Southern Levant, but also the houses at the other sites are larger than the usual Chalcolithic houses [21]. Their outer walls and the courtyard walls are made of two rows of large stones (up to 1 m size) and an infilling of gravel and earth. In Fazael 2, remains of clay bricks were found on top of them [19]. Rooms within the houses were created by smaller walls made of smaller pebbles. While a prolonged settlement period is indicated at Fazael 2 by several floors per room, Fazael 7 and Fazael 5 had only one floor per room [19–21].

The material culture of these sites supports the date at the end of the Chalcolithic. It can be characterised as incomplete assemblage of the later phase of the Late Chalcolithic sensu Gilead [23] due to the complete absence of churns and fenestrated bowls and a single find of a cornet tip. It is complemented by several elements that become characteristic of the succeeding Early Bronze Age such as S-shaped bowls, Canaanean Blades and a preference for mortars instead of grinding stones [19–21, 24].

Metal objects were found in all three sites. Fazael 2 yielded most of them (34 items are reported by Rosenberg et al. [10], but excavations are still ongoing and uncovered new items since then), followed by Fazael 7 with 14 items and Fazael 5 with 4 items. This distribution might reflect the extent of the areas excavated at each site with Fazael 5 being only probed, Fazael 7 excavated to some extent and Fazael 2 vastly excavated. Most metal items are fragments of lost wax cast objects and chisels, but some complete chisels were found, as was a mace head placed in a wall at Fazael 7. The metal items at Fazael 5 are a head-shaped standard with a chisel, an awl and a third object shoved into its shaft hole [10, 20, 21]. The metal items in Fazael 2 and 7 are scattered all over the sites without any apparent pattern [10]. Preliminary analyses with pXRF identified several objects with > 0.5 wt.% Pb and one object made of Pb- and Bi-rich copper alongside many Sb- and As-rich polymetallic copper alloys and a couple of unalloyed copper items [10]. Moreover, several crucible fragments were excavated in Fazael 2, as indicated by the metal prills in some of the fragments and bloated rims [10].

Material

Fifteen metal objects of the assemblage presented by Rosenberg et al. [10] were sampled for metallography. The metal samples represent the full range of the reconstructed object types (e.g., crown, axe, potential production remains), and alloy types as identified by pXRF analyses on the (partially) corroded surfaces, and subsites of Fazael (Table 1). Of particular interest is F236. By its shape, it is very likely a casting prill, and pXRF analysis yielded arsenic-nickel copper. In addition to the Chalcolithic finds, an axe from the Early Bronze Age site Fazael 4 was sampled (F4-107, Fig. 2), resulting in a total of 16 sampled items for metallography.

Methods

Metal objects were cut at the indicated positions (Fig. 2, Additional file 1). The standard fragment F203 was sampled in a section perpendicular (F203-m1) and a section parallel (F203-m2) to the shaft hole. Crown fragment F238 was sampled on the rim (F238-m1) and the opposite corner of the fragment (F238-m2). The mace head fragment F220 was sampled in different depths because the corrosion layer was so deep that the first section

Table 1 Key characteristics of the sampled metal items

Sample	Type	Metallographic group	Corrosion	Porosity	Unalloyed Cu	Quartz	Sulphides
F203	Standard (fragment)	polymet. high	Yes	Yes	No	Yes	No
F204	Mace head (fragment)	polymet. low	Yes	Yes	Metal + corrosion	No	Yes
F205	Crown (fragment)	polymet. low	Yes	Yes	Corrosion	No	No
F206	Axe (fragment)	polymet. low	Yes	Yes	Corrosion	No	Yes
F208	Mace head (fragment)	polymet. low	Yes	Yes	Corrosion	No	Yes
F217	Standard (fragment)	unalloyed copper	Yes	Yes	Corrosion	Yes, in some areas	No
F220	Mace head (fragment)	polymet. low	Yes	Yes	No	Yes	Yes
F231	Crown (fragment)	F231	Yes	Yes	Metal + corrosion	No	No
F234	Axe (fragment)	unalloyed copper	Yes	No	No	No	No
F236	Metal chunk	polymet. high	Yes	Yes	Metal + corrosion	No	Yes
F238	Crown (fragment)	polymet. high	Yes	Yes	No	no	yes
F241	Mace head (fragment)	polymet. low	Yes	Yes	No	No	No
F4-107	Axe	Unalloyed copper	Yes	No	No	Yes	No
F502	Axe (fragment)	F502	No	No	No	Yes	No
F703	Fragment	Unalloyed copper	Yes	No	No	Yes	No
F709	Metal chunk	Unalloyed copper	Yes	Yes	No	No	No

"polymet. low" and "polymet. high" denote polymetallic copper alloys with low and high levels of alloying elements, respectively

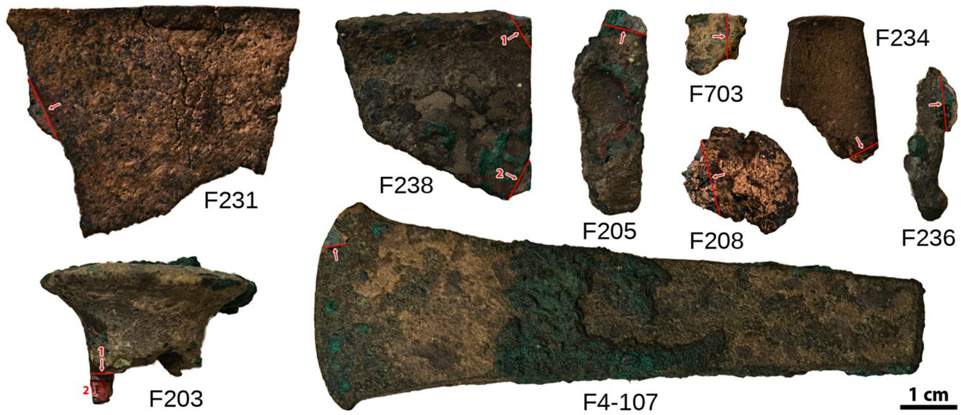

Fig. 2 Selection of sampled metal items with the locations of the sections. The arrow indicates the direction of view in the sections

(F220-c) contained almost no metal and, therefore, will not be included in this study.

All sections were embedded in epoxy resin, ground with silica carbide powder and polished with alumina powder down to 0.3 µm grain size. The polished samples were examined with the metallographic microscope Leica DMI 5000 M, equipped with a Leica MC170HD digital camera. Sections were etched with $FeCl_3$-HCl solution in ethanol for 20 s if mechanical deformation was indicated by deformed pores, preferential orientation of inclusions, and deformed or fractured inclusions. The sections were subsequently coated with carbon and inserted into the SEM Hitachi S-2500 equipped with a Kevex ThermoElectron EDS system at the Metallography Laboratory of the Dipartimento Ingegneria Chimica Materiali Ambiente, Sapienza—Universitá di Roma (Italy) to analyse the chemical composition of the different phases. The SEM was operated at an acceleration voltage of 25 kV and a working distance of 35 mm in high vacuum mode. Life time per EDS analysis ranged between 10 and 30 s with the majority of analyses having life times of 10 or 15 s. Pseudo-bulk compositions were obtained by EDS analysis of representative areas of the sections at as low magnification as possible without including larger areas covered by pores or corrosion. The presence of elements in the spectra was manually determined by the presence/absence of their peaks. Spectra were quantified with the Thermo Electron® NORAN System SIX 1.8 software using the ZAF method. Because the overlap of the Pb Lα and the As Kα lines impedes a reliable quantification of Pb and As by their main peaks, the Pb Mα and As Lα lines were checked to determine whether only one or both elements are present. If peaks could be observed at both lines, they were chosen for quantification. If they indicated the presence of only one element, the Pb Lα or As Kα line was chosen for quantification because of their better peak-to-background ratios. In none of the analyses, As, Pb, and S were present simultaneously, thus the overlap of the peaks at the Pb Lα and S Kα lines was unproblematic.

Results

The key characteristics of each section are summarised in Table 1 and described in detail in the Additional file 1. The microstructure of the sections can be subdivided into three groups: unalloyed copper, polymetallic copper alloys with low levels of alloying elements, and polymetallic copper alloys with high levels of alloying elements. Polymetallic copper alloys with low levels of alloying elements differ from unalloyed copper by being a multi-phase metal and/or showing a heterogeneous copper matrix. Sections were classified as polymetallic copper alloys with high levels of alloying elements when the copper matrix coexists with a network of other phases (Fig. 3a–c). Two sections revealed singular microstructures. F231-m is a polymetallic copper alloy with low levels of alloying elements but clearly differs by the morphology of its phases (Fig. 3d) and thus was not assigned to this group. F502-m has a homogeneous multi-phase microstructure unique among the sections (Fig. 3f). Except for F4-107-m, all sections are affected by corrosion to varying degrees. Cuprite as phase and not as corrosion product is abundant in some sections belonging to the unalloyed copper group (Fig. 3f), and five samples (three unalloyed copper, two polymetallic copper alloys, Table 1) contain abundant angular inclusions of pure silica, most likely silt-sized quartz (Fig. 3e). Sulphide inclusions were observed in the sections of seven samples, all belonging to the polymetallic copper alloy groups. Moreover, sections of seven samples contain distinctive orange-reddish phases, usually with a rougher texture than the surrounding phases. Some are embedded in the

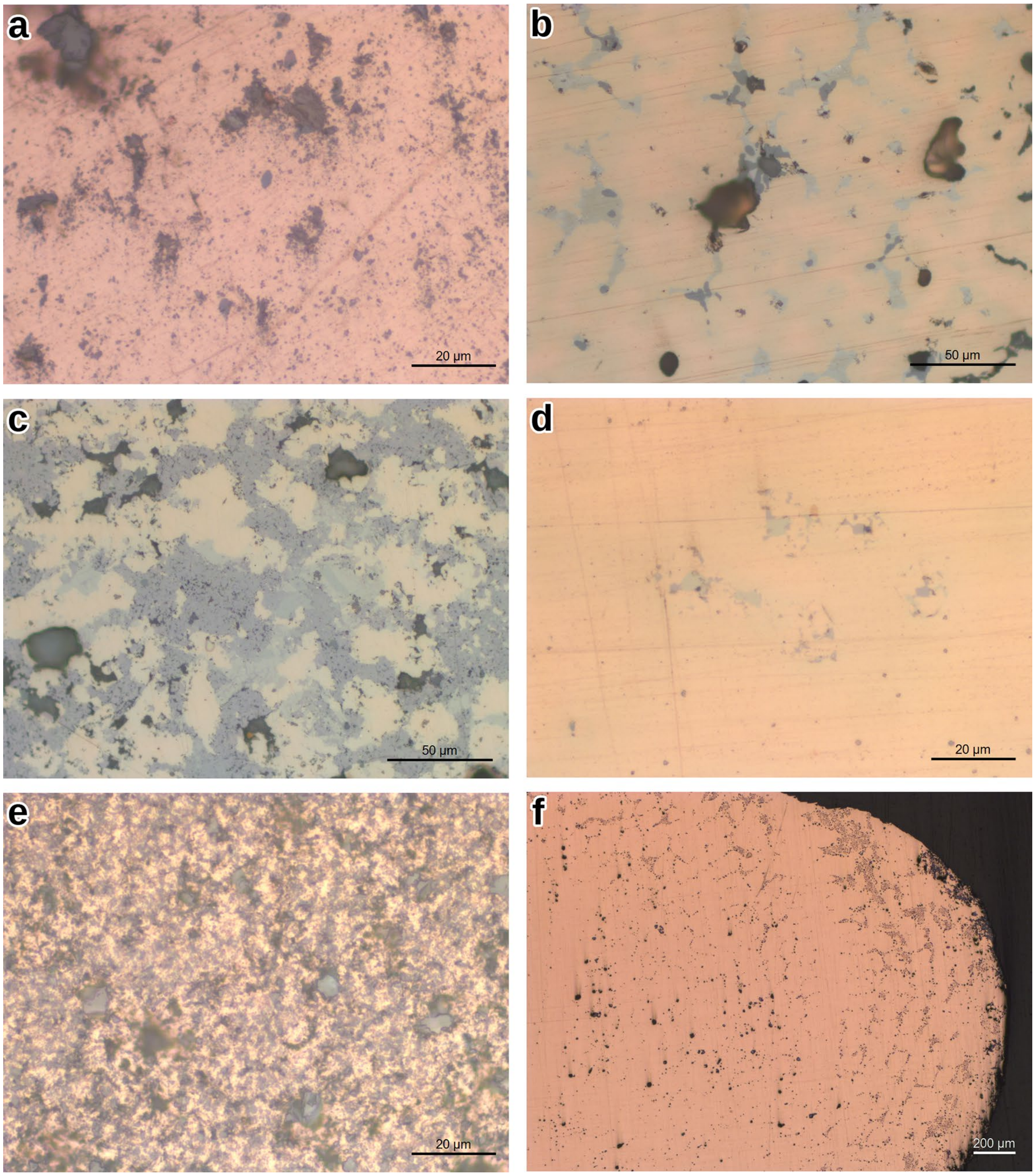

Fig. 3 Typical examples for (**a**) unalloyed copper, section F4-107-m, with quartz inclusions, (**b**) polymetallic copper alloys with low levels of the alloying elements, F206-m, (**c**) polymetallic copper alloys with high levels of alloying elements, F238-m1, (**d**) F231-m, (**e**) F502-m, and (**f**) cuprite phase in unalloyed copper, F234-m

copper matrix; some are in contact with the other metal phases. In several sections, they are also in contact with corrosion phases, some of them have a partly hexagonal shape. In section F236-m, some inclusions consist of at least two phases (Fig. 4). Most of the sections in the polymetallic copper alloy groups show considerable porosity, mostly from the casting process (Table 1).

Only section F234-m, from the rear part of an axe, was etched because a wave-like orientation of its cuprite inclusions indicates potential post-casting treatment. Etching revealed a gradient from up to 800 µm large grains and a granular microstructure in the centre of the section to about 10 µm large grains and a dendritic microstructure close to the surface (Fig. 5). The section

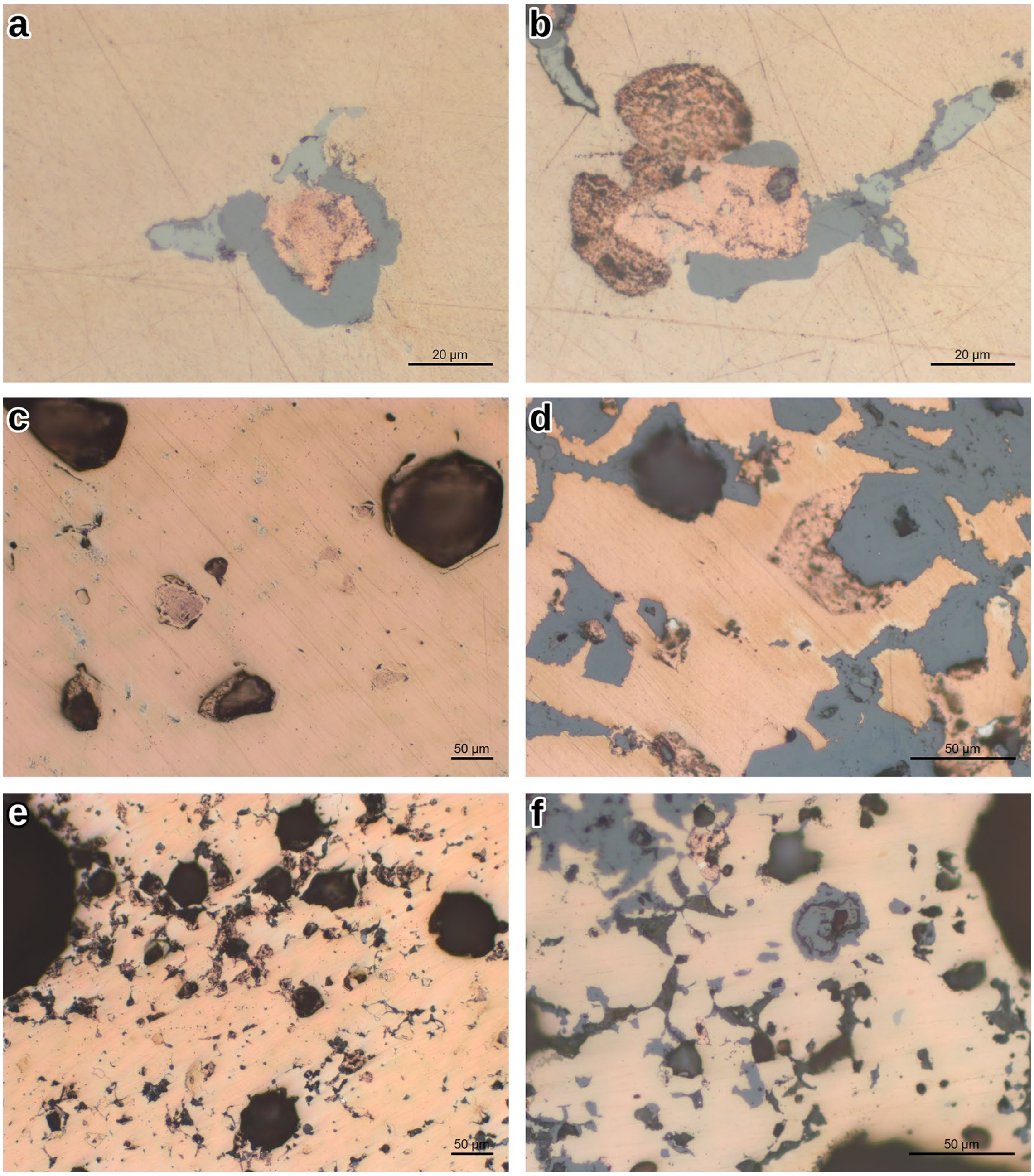

Fig. 4 Examples for copper inclusions: (**a**, **b**) F236-m, inclusions with copper and a whitish phase in direct connection with a sulphide phase, (**c**, **d**) F231-m, (**e**) F205-m, (**f**) F204-m

taken from the blade of F4-107 does not show any traces of deformation or fracture of the abundant quartz inclusions (Fig. 3a).

SEM analyses largely confirm the observations made with the optical microscope. Chlorine concentrations indicate the presence of corrosion phases in several analyses. Unfortunately, it was impossible to differentiate and, therefore, analyse by SEM all phases that were identified under the optical microscope in the sections of polymetallic copper alloys with high levels of alloying elements. Alloying elements are Sb (present in ten samples), Pb (10), As (9), Ni (2), Bi (6), and Ag (4). Ni occurs only in combination with Cu and As and never with Sb, Pb, Bi, and Ag. All obtained pseudo-bulk compositions are provided in Table 2 and single phase compositions in the Additional file 1. Where measured, multiple pseudo-bulk

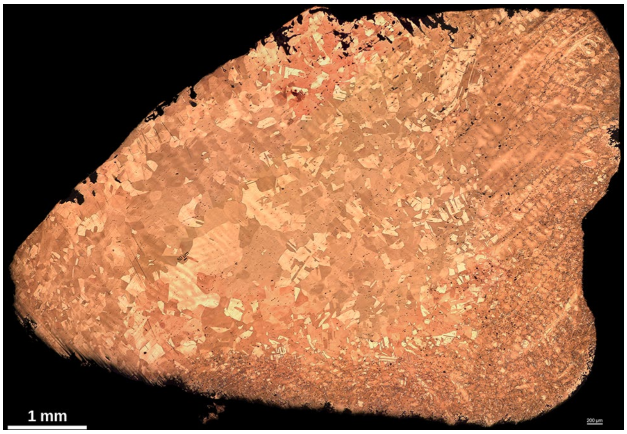

Fig. 5 F234-m, etched with ferrichloride in ethanol for 20 s, composite image

compositions from the same sections gave identical compositions within analytical uncertainties (Table 2). The metallographic groups are consistent with the bulk chemistry of the sections: > 30 wt.% of alloying elements in the polymetallic alloys with high levels of alloying elements, between 9 and 4 wt.% of alloying elements in the polymetallic alloys with low levels of alloying elements, and < 2 wt.% of alloying elements in the unalloyed copper group. Exceptions are F208 and F220. Although pseudo-bulk analyses of these samples indicate the absence of alloying elements, polymetallic phases were observed by the optical microscope and the SEM. Their low abundance makes it likely that the overall amount of these phases is too low for a detectable contribution to their pseudo-bulk composition. In contrast to all other samples, F231 contains Bi-dominated phases in its Cu-Sb matrix, supporting its classification as belonging to its own metallographic group. F502 is an As-Ni copper with > 1 wt.% Ni and about 1 wt.% As. Although no pseudo-bulk analysis could be obtained from F236 due to its extensive porosity, the chemical composition of its phases (Additional file 1) identifies it as the other one of the two As-Ni coppers among the sampled metal items. It confirms its metallographic classification as a polymetallic copper alloy with high levels of alloying elements.

The two sections of F203 and F238 did not show any difference in their microstructure. Nevertheless, the pseudo-bulk composition of F238-m2 has significantly higher concentrations of the alloying elements compared to F238-m1. At the same time, the 3.95 wt.% Cl indicate a significant impact of corrosion in section F238-m2, which might have resulted in the depletion of copper relative to the alloying elements [25]. In addition, some heterogeneity in the chemistry must be expected due to the complex interplay of the alloy's constituents, likely to result in local differences in the phase evolution during cooling.

Table 2 SEM–EDS pseudo-bulk analyses in wt.% for the metal sections

Section	Object	Magnification	Metallographic group	Cu	Sb	Pb	Bi	As	Ni	Ag	SiO_2	Cl	Al_2O_3
F203-m1	Standard (fragment)	1000	High polymet	65.68	17.74	3.49		7.74		1.19	4.15		
F204-m	Mace head (fragment)	150	Low polymet	90.54	5.63	0.11					0.25		3.47
F205-m	Crown (fragment)	500	Low polymet	95.41	1.69	1.56		1.34					
F206-m	Axe (fragment)	700	Low polymet	90.98	6.44	0.62		1.58				0.38	
F208-m	Mace head (fragment)	1000	Low polymet	100.00									
F217-m	Standard (fragment)	1000	Unalloyed copper	98.58							1.42		
F220-c	Mace head (fragment)	1000	Low polymet	97.32	1.27	1.20						0.22	
F220-m	Mace head (fragment)	1200	Low polymet	92.51							7.49		
F220-m	Mace head (fragment)	1200	Low polymet	93.20							6.80		
F231-m	Crown (fragment)	250	F231	98.62	1.38								
F234-m	Axe (fragment)	1300	Unalloyed copper	99.35	0.65								
F238-m1	Crown (fragment)	200	High polymet	65.11	19.83	10.65	0.17	4.25					
F238-m2	Crown (fragment)	1000	High polymet	45.50	18.74	24.70		5.54			1.56	3.95	
F4-107-m	Axe	200	Unalloyed copper	75.58							24.42		
F4-107-m	Axe	200	Unalloyed copper	76.28							23.72		
F502-m	Axe (fragment)	1500	F502	69.94				0.96	1.68		27.42		
F502-m	Axe (fragment)	1500	F502	69.21				1.04	1.36		28.39		
F703-m	Fragment	1500	Unalloyed copper	86.98							13.02		

"polymet. low" and "polymet. high" denote polymetallic copper alloys with low and high levels of alloying elements, respectively. Due to the high porosity of section F204-m, alumina polishing powder could not be completely removed, resulting in the Al_2O_3 signal of this sample. No pseudo-bulk analysis could be obtained for sample F236 because of high porosity

Comparing the metallographic groups with the object types confirms the well-known general separation between tool-shaped unalloyed (pure) copper objects and so-called prestige items made of polymetallic copper alloys [7, 26]. Three exceptions from this pattern can be identified: The axe fragment F206 and the axe F502, which are polymetallic copper alloys, and the standard fragment F217, which was classified as unalloyed copper. All other items in the unalloyed copper group are tool-shaped or, in the case of F703-m, their original shape cannot be reconstructed. Similarly, except F217 all fragments that can be reconstructed as parts of mace heads, standards, or crowns are polymetallic copper alloys. It must remain open whether mace heads fall exclusively in the category of polymetallic copper alloys with low levels of alloying elements or if this is an effect of the small number of investigated items in the other polymetallic copper alloy group (n = 3). In addition, SEM–EDS analysis of the axe fragment F234-m revealed a couple of polymetallic inclusions (Additional file 1). However, it was kept in the metallographic group "unalloyed copper" because the overall appearance of the metal is typical for unalloyed copper.

Discussion

Comparison with previous studies

The polymetallic copper alloys in Fazael adhere to the general characteristics of the Chalcolithic Southern Levantine metallurgy but also show some important deviations. Their pseudo-bulk compositions are within the known range of the main alloying elements Sb, Pb, and As (Fig. 6a). The Ag concentration of F203-m1 is practically identical with the highest Ag concentration reported so far (standard 61–253 of the Nahal Mishmar Hoard with 1.2 wt.% Ag [7]). F238 clearly stands out by its very high Pb content, making this crown fragment one of the most heavily alloyed coppers of the Chalcolithic Southern Levant (Table 2). However, corrosion likely obscured the pseudo-bulk composition of F238-m2 towards the extremely high concentrations. The polymetallic copper alloys in the Fazael assemblage tend to be richer in Sb compared to As than most of the other polymetallic copper alloys (Fig. 6b), and the samples containing Pb and As have much higher Pb/As ratios (Fig. 6c). The two As-Ni coppers (F236, F502) are dominated by Ni, while As is usually the dominating alloying element in the As-Ni coppers in the Chalcolithic Southern Levant (Fig. 7). In summary, the polymetallic copper alloys from Fazael are poorer in As or richer in the other alloying elements than most of the other polymetallic copper alloy assemblages of the Chalcolithic Southern Levant.

As already concluded in previous studies [7, 15, 28], the high concentrations of As and Sb in combination with the presence of sulphide inclusions in six out of the ten polymetallic copper alloys point to fahl ores as the most likely copper ore source. The As-depleted signature could indicate that the Fazael metal items were produced from relatively As-poor fahl ores. Alternatively, As, as the most volatile among the alloying elements, could have become depleted during metallurgical operations. In the latter case, this would imply that the metal of the Fazael objects was subjected to additional or more extensive melting steps than most of the other polymetallic copper alloy items of the Chalcolithic Southern Levant.

No post-cast treatment of the polymetallic copper alloys is observed, confirming results of previous metallographic studies [6, 29, 30]. Other features reported in these studies, such as a dendritic structure, extensive porosity, and a gradient from extensive corrosion at the surface to intergranular corrosion deeper in the metal, were observed in several of the sections (Additional file 1). Information about the enrichment of polymetallic

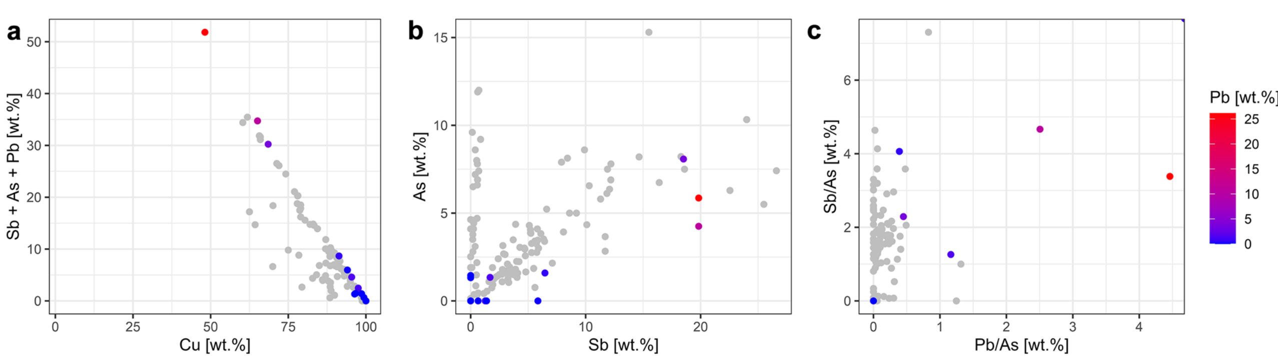

Fig. 6 Pseudo-bulk compositions of the sections, re-normalised to 100 wt.% after exclusion of eventual quartz inclusions and leftovers of polishing powder (Additional file 1 for raw values), colour-coded for their Pb content. In grey chemical compositions of other polymetallic copper alloys of the Chalcolithic Southern Levant [27]. **a** The sum of the main alloying elements plotted against the copper concentration of the samples, (**b**) As against Sb, and (**c**) Sb/As against Pb/As ratios. Concentrations of 0 wt.% denote elements absent in the pseudo-bulk compositions of the sections

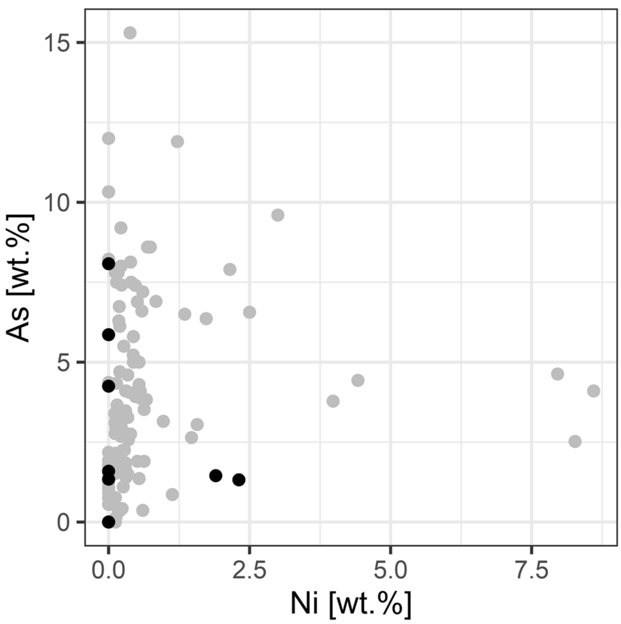

Fig. 7 Pseudo-bulk As and Ni concentrations of the sections (black), re-normalised to 100 wt.% after exclusion of eventual quartz inclusions and leftovers of polishing powder (Additional file 1 for raw values). Other polymetallic copper alloys of the Chalcolithic Southern Levant in grey [27]. Concentrations of 0 wt.% denote elements absent in the pseudo-bulk compositions of the sections

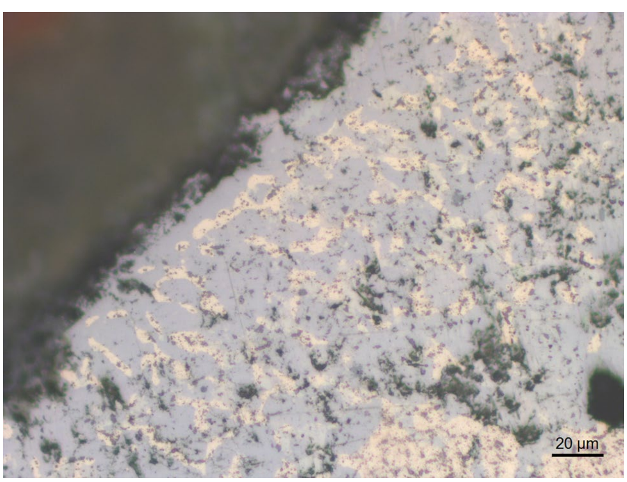

Fig. 8 Photomicrograph of F203-m1 with a corrosion-unaffected surface layer of the Sb-As-rich polymetallic phase

phases on the surface ("inverse segregation") is only provided for the mace head in Shiqmim, where it was not observed [6]. In the sections under study here, F203-m1 shows such an enrichment on the corrosion-unaffected surface (Fig. 8).

The chemical composition of the Ni-As copper axe F502 is similar to chisel 97–3484 of Giv'at HaOranim [5] and 61–147 of the Nahal Mishmar Hoard [4]. Section F502-m was taken from somewhere in the middle of the axe and, based on its microstructure, remained unworked after casting. A more precise reconstruction of its location is impossible because it is shoved into the standard F-501 and the end outside the standard is broken.

In contrast to the polymetallic copper alloys, unalloyed copper items were usually reworked after casting by a combination of hammering and annealing [5, 29, 31–33]. In contrast to these observations, the sampled unalloyed copper items of the Fazael assemblage appear as cast. However, it is important to keep in mind that blades were usually sampled while in the Fazael assemblage, only middle parts or non-orientated fragments of tool-shaped objects were sampled. An exception is the complete Early Bronze Age axe F4-107, sampled at the blade. Neither the abundant quartz nor cuprite inclusions show any deformation or preferred orientation, indicating that the blade was left in an as-cast state.

Section F234-m features the Cu-CuO eutectic towards the surface, similar to copper lump M26 of the Early Bronze Age Camel site [34]. The gradient in grain size of this sample in combination with the very large and well-crystallised grains in the centre and a dendritic microstructure close to the surface indicates casting in an open mould without any significant post-cast treatment of this middle to rear part fragment of an axe. Cu-CuO eutectic is also present between the large copper grains in some areas of F217-m but is mostly overgrown by corrosion in this section.

Only Notis et al. [28] mention silica inclusions, assumed to be quartz, and only for an axe head from Bir es-Safadi. They are restricted to areas close to the surface of the item. Unalloyed copper inclusions in the polymetallic copper objects of the Chalcolithic Southern Levant are a feature not mentioned in any of the previous studies. Both features will be discussed in more detail below.

Phase composition

The phase composition of Sb-rich polymetallic copper alloys is widely unknown. There seems to be only one study that discusses the high alloy phases in the Cu-As-Sb system in some detail [35]. Northover [35] observed that they could be plain after etching with ferric chloride-based solutions or have a banded or needle-like microstructure. Microanalytical investigations of these phases indicate chemical compositions close to $Cu_3(As,Sb)$ and $Cu_2(As,Sb)$, probably as true intermetallic phases Cu_9AsSb_2 and Cu_6As_2Sb. The determination of the chemical composition was complicated by Ni and Ag impurities, with the latter resulting in white needles. No banded or needle-like structure was observed in the Fazael metal items. Still, the high polymetallic phases do consist of multiple phases and several of them are close in their chemistry to the compositions observed by Northover [35] (Additional file 1).

Northover's study [35] is restricted to the Cu-As-Sb system. In addition, only binary phase diagrams are available, leaving insight into the complex interactions of the different alloying elements a desideratum. The binary phase diagrams show that Bi is perfectly soluble in Sb and has a binary phase with Pb, but it is not soluble with the other metals. Likewise, Pb is not soluble in any of the present metals with exception of Sb. However, only F220-m and F234-m have inclusions that could be Sb-Pb prills, i. e., in samples with a very low concentration of alloying elements. In all other sections, Pb seems to be dissolved in the polymetallic phases although Pb prills would be expected based on the phase diagrams. This highlights the complexity of the interactions in the Cu-As-Sb-Pb-Bi(-Ag) system, making it impossible to retrieve any reliable information from projections into the binary systems. In addition, higher cooling speeds shift the phase fields towards lower Cu contents. This followed from general thermodynamic considerations and was quantified for the Cu-As system with shifts > 5 wt.% of the phase boundaries towards the Cu-rich side at high cooling speeds [36]. Consequently, a detailed discussion of the phase composition of the Sb-rich polymetallic copper alloys must await studies on the complex interactions of the alloying elements.

For the As-Ni copper items, the phases could only be analytically resolved for F236-m. Plotting them into the Cu-As phase diagram [36] suggests the presence of α-(Cu,As) and the γ-phase Cu_3As, which is in accordance with previous investigations [36–38].

Unalloyed copper inclusions

Unalloyed copper inclusions in tin bronzes and gun metal were investigated by Bosi et al. [39]. They identified three types of unalloyed copper inclusions: (A) precipitation of copper during corrosion, pseudomorphologically replacing other phases, (B) globular inclusions surrounded by a layer of copper sulphides, which are remains of incompletely reacted and slagged Cu–S phases in the smelting process, and (C) large irregular shaped inclusions with a twinned microstructure.

Type A unalloyed copper inclusions are observed in all sections with unalloyed copper inclusions (Fig. 4d–f). Type B inclusions were exclusively observed in F236-m, where they are not only surrounded by sulphides but also consist of at least one additional whitish phase (Figs. 4a, b, 9c, d). Corrosion products could be observed in the vicinity of many such inclusions. Consisting of at least two phases, it is more likely that corrosion products formed along the phase boundaries rather than the inclusions being a result of corrosion processes. Corrosion-unrelated unalloyed copper inclusions occur in F204-m, F231-m, and F236-m (Figs. 4b, c, 9a, b). In contrast to the other ones, corrosion phases could not be observed close to them, while this was always the case for the Type A inclusions in the same sections. They do not correspond to the type C inclusions of Bosi et al. [39] because they are not large and although their shape could be considered as irregular, it is not as irregularly shaped as the examples in [39]. However, similar unalloyed copper inclusions are reported by Mödlinger & Trebsche [40] from tin bronze tools in Lower Austria. They interpret them as remains from the addition of unalloyed copper to the tin bronze, most likely added as scrap metal during recycling to balance material loss [40].

Such copper inclusions can only exist if the metal melt is not hot enough to melt the metal completely. To gain a rough estimate of the bulk melting temperature per sample, the pseudo-bulk compositions of the polymetallic copper alloys with corrosion-unrelated unalloyed copper inclusions can be projected into the Cu-Sb phase diagram. This provides an upper limit of their melting temperatures (Fig. 10). The true melting temperature is likely to be considerably lower. It can be as low as 600 °C for As-Sb copper [35] and is probably even lower because of the considerably lower eutectic temperatures of Cu-Pb and Cu-Bi with 236 °C and 270.6 °C, respectively [41]. Based on this estimate, it is clear that melted metal sufficiently liquid for casting but with some unmelted parts could be easily obtained at temperatures below the melting point of unalloyed copper (1085 °C). It must also be remembered that even if temperatures beyond the melting point of unalloyed copper were reached, they must be held long enough to melt the unalloyed copper completely.

Similarly, if the metal would have been completely melted, it could be expected that the copper prills in the Type B inclusions are completely melted, leaving rounded sulphide inclusions behind. Therefore, it seems highly likely that these (unalloyed) copper inclusions in the Fazael metal items evidence an incompletely melted state of the metal upon casting.

Quartz inclusions

Notis et al. [28] suggest that the silica inclusions in the axe head from Bir-es Safadi are most likely quartz inclusions originating from the crucible or mould. Silt-sized quartz is abundant in the Fazael crucible fragments [43]. The extensive bloating of the crucible fragments and the heavily heat-affected rim of F219 suggest that part of the crucibles melted. While the clay was slagged and removed (no slag inclusions were found in the metals),

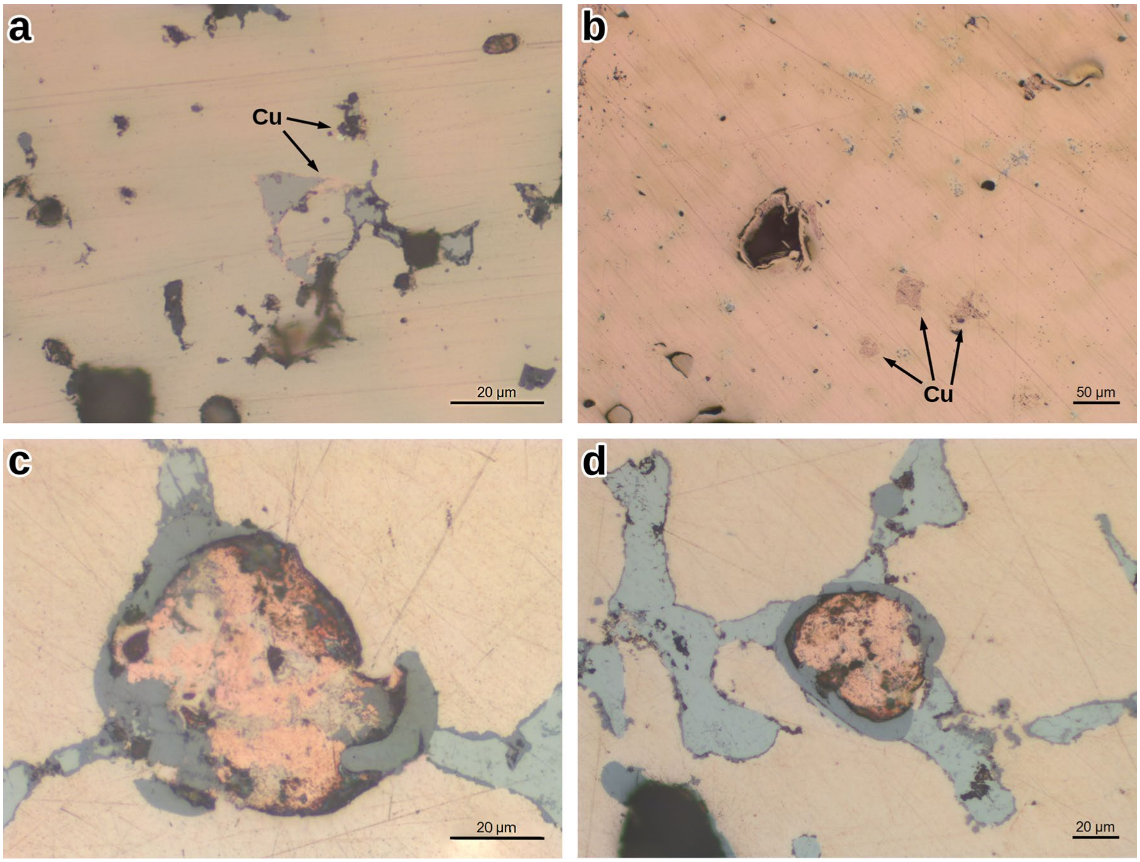

Fig. 9 Examples for copper inclusions unrelated to corrosion: (**a**) F204-m, (**b**) F231-m, and (**c**, **d**) type B copper inclusions after Bosi et al. [39] with more than one phase, F236-m. See also Fig. 4

the quartz could have remained in the melt due to its higher melting temperature.

This interpretation fits well with the quartz inclusions in F217-m, where they are limited to a certain section area, probably one closer to the original surface. However, it must be doubted that it explains the large amount of such inclusions throughout the entire section of, e.g., F703-m (Fig. 11). Following this interpretation, they would indicate substantial melting of the crucible or mould. The admittedly very restricted evidence of crucibles in Fazael does not indicate such an extensive melting, neither do the many fragments found in Abu Matar [44]. In addition, it is unlikely that the quartz grains would have been able to penetrate that deeply into the metal melt when the slag was removed completely at the same time. The mould as a source for the quartz inclusions is even more unlikely because the melt requires heating and stirring after casting to distribute the quartz throughout the metal.

Another possibility would be the addition of the quartz to the metal batch either during or before melting. The shape and size of the inclusions are characteristic of loess, i.e. sediment transported by wind, which might have been trapped between stored metal pieces such as prills or was deliberately added to the metal melt to slag off impurities such as iron. In the latter case, stirring of the melt is expected to reach impurities beyond the surface. In any case, the metals should also contain at least some slag inclusions—a perfect removal of the slagged material is extremely unlikely with the equipment available back then. Additional research is necessary before any definite answers concerning the origin of the quartz inclusions can be provided.

Mixing, alloying or recycling?

While many of the metallurgical features of the Fazael assemblage confirm or enhance our concepts and notions on the metallurgy of the Chalcolithic Southern Levant, the (unalloyed) copper inclusions allow us to gain access to a previously entirely unknown aspect: mixing and alloying practices related to the polymetallic copper alloys.

Smelting sites for the polymetallic copper alloys are yet to be found. They were likely located close to the

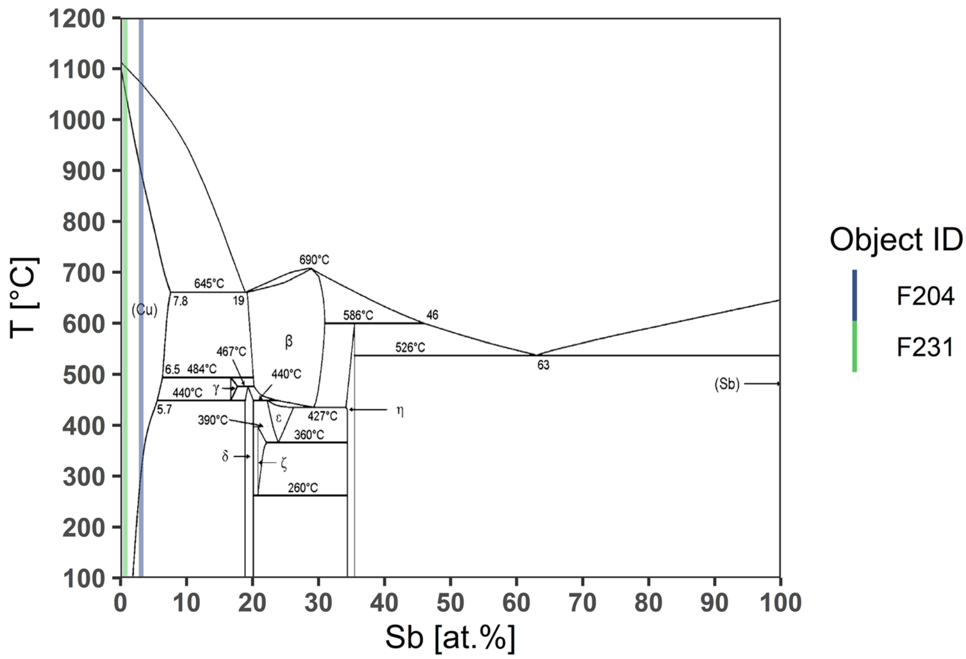

Fig. 10 Cu-Sb phase diagram with the pseudo-bulk compositions of F204-m and F231-m, providing an upper limit of their melting temperatures. Note that the digram gives values in at.% instead of the wt.% reported in Table 2). Values in at.% are provided in the Additional file 1. Phase diagram redrawn from [42]

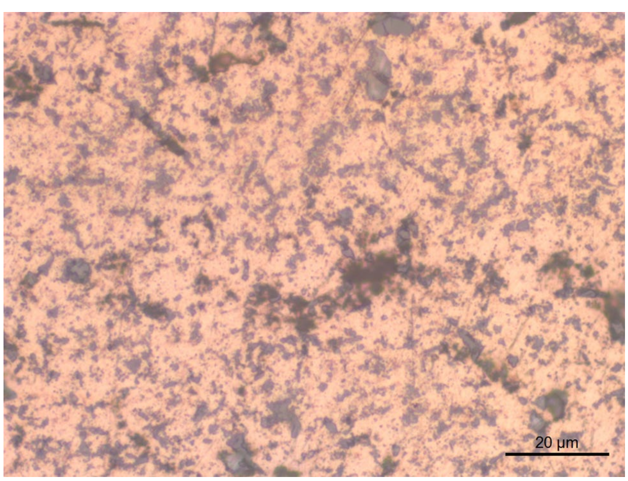

Fig. 11 Photomicrograph of F703-m with many quartz inclusions

fahlore ore deposits exploited for their production, i.e., somewhere in Anatolia or the Southern Caucasus [7]. Archaeometallurgical remains from these regions indicate that smelting operations were carried out in crucibles and yielded metal prills that needed to be mechanically extracted from the slag [45–49]. Mixing the polymetallic copper alloys with unalloyed copper could have happened there, when prills from both metal types were mixed and melted into a larger metal lump. Such prills could even be obtained in the same smelting event [50].

However, the mixing of the metals in the Southern Levant seems to be more likely. Analyses of the polymetallic copper alloys did not reveal any chemical groups (Fig. 6), which could be expected if mixing was carried out in the ore provenance regions to meet certain requirements before exporting the metal. Instead, the prills could have been directly exported. This would save extra effort on the producer side. Probably more important, prills represent a smaller unit for exchange and allow on the consumer side better control over the alloy's properties, such as colour or castability, and the amount of metal per batch. In addition, it is in the Southern Levant, where we now find evidence for processing polymetallic copper alloys such as casting prill F236, while even sites in the ore provenance regions with suitable ore fragments remained devoid of such remains [51].

Assuming that mixing happened in the Southern Levant, the motivation for it was manifold. Increasing the copper content of the Sb-rich polymetallic copper alloys would change their colour and mechanical properties, turning it from silvery into golden or haematite-like colours. Mixing it with local unalloyed copper could also have been a strategy to extend the available amount of the more exclusive imported material. Alternatively, it might be a reaction to a shortage in the supply of polymetallic copper alloys. Such a shortage was suggested as the reason why leaded copper was used in the Chalcolithic Southern Levant [27]. This or even supply disruption could have occurred at the end of the Chalcolithic, when the Kura-Araxes phenomenon spread towards the likely source regions of the polymetallic copper alloys [52]. Radiometric dates from Fazael 2 date the site into this period [19]. Besides these more mundane aspects, reasons for mixing could also be related to symbolic practices such as adding unalloyed copper from local production to make a foreign material local.

The uniquely large number of fragments from polymetallic copper alloys in Fazael could even point towards recycling as a special case of mixing [10]. Unalloyed copper could be added to the melt of recycled polymetallic copper alloys to balance the loss of material, as was suggested for Bronze Age Austria [40]. The motivation for recycling polymetallic copper alloys and metal, in general, might have been similar to the motivations for mixing. In addition, the spiritual connotations of the metals might have limited the possibilities for the disposal of old or damaged metal items and required their recycling. The overall depletion in As of the Fazael metal assemblage seems to support the interpretation of recycling. However, loss of As by repeated melting and casting is only one of three possibilities for obtaining such an As-depleted signature. Keeping the metal longer in a melted state, and a particularly oxidising melting process could also result in the observed As-depletion.

If the (unalloyed) copper inclusions and the As-depleted signature of the Fazael metal assemblage indeed evidence recycling in the Chalcolithic Southern Levant, this could indicate a change from depositing metal items (e.g. in the Nahal Mishmar Hoard) to recycling them, probably in response of a supply shortage at the end of the Chalcolithic, or regional differences in the deposition behaviour of the Chalcolithic Southern Levant. As intriguing as these thoughts may be, more research is needed before any reliable statements about the nature and motivation for the Southern Levantine alloying practices can be made.

Conclusions

Many of the metal items excavated in Fazael are fragments of lost wax cast objects made of polymetallic copper alloys. While their archaeological context was presented by Rosenberg et al. [10], their technological aspects were assessed in this study by metallography and SEM–EDS analysis.

Metallography and chemical compositions allow to subset the samples into three groups: unalloyed copper, polymetallic copper alloys with low levels of alloying elements, and polymetallic copper alloys with high levels of alloying elements. Comparison with the reconstructed object type confirms the general separation of the metallurgical traditions in the Chalcolithic Southern Levant between tool-shaped unalloyed copper items cast in open moulds and lost wax cast polymetallic copper alloy “prestige” items. However, they extend the general notions of the lost wax casting technology and the polymetallic copper alloy metallurgy of the Chalcolithic Southern Levant in three important aspects: (1) the overall chemical composition of the sampled metal items indicates on average a lower arsenic content than in items found in other sites; (2) silt-sized quartz inclusions were observed in several sections from all metallographic groups; (3) the presence of corrosion-unrelated unalloyed copper inclusions and at least in F236-m also multi-phase copper prills in the polymetallic copper alloys.

The (unalloyed) copper inclusions provide the earliest evidence for mixing/alloying in this region and, to our knowledge, the oldest evidence for alloying in general after the copper-rich gold objects in the cemetery Varna I [53]. Unfortunately, the available information is too limited yet to allow any conclusions beyond the fact that polymetallic copper alloys were mixed with unalloyed copper. It seems likely that such mixing happened in the Southern Levant, maybe in an attempt to increase the amount of the limited polymetallic copper alloys by adding local unalloyed copper. Similarly, further research is needed before any conclusions can be drawn about the origin of the silt-sized quartz inclusions.

Further studies on the admittedly limited available material would allow providing important additional information. Studying more of the metal objects and including the newly excavated ones would help to substantiate the conclusions drawn from this subset. Reconstructing the ore provenance of the polymetallic copper alloys and of the (unalloyed) copper inclusions with, e.g., lead isotopes and laser ablation techniques could provide important information about whether the metals came from the same source area or different ones, practically discriminating between mixing in the source region or the Southern Levant. An additional severe limitation to a better understanding of the metallurgical practices of the Chalcolithic Southern Levant is the incomplete knowledge about the behaviour and phase evolution of these alloys. Dedicated studies towards a better understanding of this complex alloying system would allow gaining valuable information about the casting process of these metals. For these reasons, this study can only provide the starting point for an in-depth and multi-directional investigation of the metallurgical assemblage of Fazael.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-023-01030-2.

Additional file 1. Metallographical details, microphotographs and single-point SEM-EDS analyses of the studied material.

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Author contributions

TR: Conceptualization, Formal Analysis, Investigation, Visualisation, Writing—original draft, Writing—review & editing. SN: Resources, Supervision, Writing—review & editing. AB: Investigation, Writing—review & editing. SB: Resources, Writing—review & editing. YG: Conceptualization, Investigation, Funding acquisition, Project administration, Supervision, Writing—review & editing.

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Availability of data and materials

All data generated or analysed during this study are included in this published article and its Additional file information files.

Declarations

Ethics approval and consent to participate

Not applicable.

Competing interests

The authors declare no competing interests.

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