Physicochemical analyses of copper based artefacts from the Late Predynastic site of Maadi (Egypt)

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Abstract:

Maadi (Egypt) is a significant Lower Egyptian Culture site, which is particularly famous for being a crossroads in the connection between Egypt and Southern Levant in Late Predynastic period. The site has also provided a meaningful quantity and diversity of copper artefacts, obtained during many years of archaeological excavations conducted by different international teams, which, together with other imported items from Palestine, may indicate it was also an important junction in the overall copper exchange routes. Some of the materials were under archaeometallurgical examination in the past, primarily by the means of the lead isotope analysis.

In this thesis project, a multi-versatile systematic approach is applied to investigate some copper based artefacts, coming from the Sapienza University excavation at Maadi. In fact, a large number of techniques is used, including Optical Microscopy (OM), Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDS) Energy Dispersive X-ray Diffraction (EDXD), X-ray Diffractometry, ICP-OES/ICP-MS and Strontium Isotope Analysis. Various aspects are under the light of this study, among them, the overall chemical composition and the structure of objects, the corrosion patina nature, the manufacturing techniques, with the final aim of a possible identification of the copper ore. The acquired results are compared with earlier studies performed on the copper samples from Maadi and other similarly dated archaeological sites connected to metallurgical activities in this part of the world.

Of greater importance in this thesis is the presentation of the first successful experiment concerning the application of Strontium Isotope Analysis in the provenance of the copper ore. The $^{87}Sr/^{86}Sr$ values of Maadi samples studied in this work point out Timna copper mines as source of raw material. The Strontium Isotope Analysis is commonly used in studying the other archaeological materials, especially bones and dental enamel for the purpose of tracing migration patterns of human and animal populations in past. In this thesis work, it is showed that this analysis has a great chance to be implemented in the metal studies and become another possible option in tracing the sources of copper ore in ancient times. It might serve as independent or supplementary technique to lead isotope analysis.

Combining the set of above mentioned techniques in adequate systematic way, allows to gain sufficient data, which in turns can contribute to the reconstruction of the overall picture of the copper trade and early metallurgy in Egypt and Near East in Late Chalcolithic and Early Bronze Age I.

Content:

1. Introduction

Maadi is a crucial archaeological site in the history of the so called Lower Egyptian Late Predynastic Culture (existing in the Nile Delta region around 3900-3300 BC). Nowadays, Maadi is an area belonging to the capital city of Cairo (Egypt). The site has a long excavation history including different archaeological missions working in this area: from 1930 and lasting to 1950s from Cairo University directed by M. Amer and O. Menghin, the latter replaced by I. Rizkana in 1938; between 1977-1986 Missione Italiana per le Ricerche Preistoriche in Egitto e Sudan (MIRPES) from the Sapienza University in Rome, together with Geography Department of Cairo University leaded by Puglisi S. M., Caneva I., Frangipane M., Palmieri A.; in 1985-1986 carried by F.A. Badawi from El-Azhar University and 1999-2002 by U. Hartung from the German Archaeological Institute (DAI) together with the Egyptian Supreme Council of Antiquities (SCA) and University of Cairo. During many years of work, different types of copper objects have been discovered, such as: tools, ornaments, ingots, copper ores, copper nodules and droplets. Even though no clear metallurgical installations or crucibles were found on the site, the quantity and diversity of the copper objects indicates that Maadi might have played an essential role in the metal distribution. Moreover, based on strong archaeometric evidence, the copper exchange connections between Maadi and other sites located in Southern Levant was proposed, what will be discussed further in this thesis work.

The thesis project aims to study by chemical and physical investigations some metal objects found during the archaeological works carried out by the Italian mission between 1977-1986 (in total six campaigns). The research work wants also to deepen the study about the provenance of the metallic artefacts using investigations on isotopic decay. The obtained results are compared to the previous analyses conducted on the metal objects from Maadi (Pernicka E., Hauptmann A. 1989; Abdel-Motelib A. et al. 2012; Hauptmann et al. 2012; Hauptmann A. 2017, 145-155) and to the archaeometric data of the similarly dated sites located in Egypt, Sinai and Southern Levant. The extensive investigation aims to shed more light on how the metallurgical activities were performed in Maadi in the past and how they were connected with the metal trade between Egypt and Levant in Late Predynastic period, by using a multi disciplinary research approach. It will be presented how the use of different techniques can improve scientific workshop by complementing the data.

Various analytical methods are applied during the research. In order to characterize the structure and the manufacturing methods of the archaeological methods, Optical Microscopy (OM) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) are used. As for defining the elemental composition, Energy Dispersive X-ray Diffraction (EDXD) analyses are carried out. For a more comprehensive understanding of the corrosion products and of the alteration patina X-ray Diffraction tests are applied. In a last step, ICP-OES/ICP-MS and strontium isotope analyses are used for provenance studies purpose. Knowing the exact composition of the objects (major, minor and trace elements) will help to investigate the origin of raw materials used for manufacturing the metal objects from Maadi. The attempt will be made to verify from which of the main copper ore deposits closer to the site (those in the Eastern Desert, in Sinai or in Southern Levant – Timna and Feinan) the Maadi copper did come. The presence of particular trace elements like arsenic, nickel, antimony and others can yield further information on the provenance of the raw material and technology.

In this thesis work, not only systematic traditional study approach of metal samples is proposed, but also we attempted to apply strontium analysis, which is widely used in archaeology for other kind of materials, most frequently bones and dental enamel of both human and animals. The first successful experiment, performed during this thesis project and presented in this work, shows that strontium isotope analysis has a great chance to become another possible option in tracing the sources of copper ore in ancient times. It can serve as independent or supplementary technique to other isotopic analyses, including the most common used one of lead isotope.

Finding answers to the questions on the metal ore origin and the ways these copper based objects from Maadi were manufactured is essential in reconstructing the overall picture of the early Egyptian metallurgy and trade connected to metals in the Predynastic period. In order to obtain the best possible results, all-encompassing methodology must be applied and the research techniques must be improved.

2. The place of Maadi in Predynastic Egypt

Maadi site, located nowadays in the area belonging to modern city of Cairo, is exceptional for many reasons (Map.2.1). It was the first site where the clear evidence of existence of the Lower Egyptian Culture was recorded. Due to this discovery, primary it was called as Maadi culture and later when similar activity was yielded in Buto, the name was changed to Maadi-Buto culture. With time more sites in Delta region appeared to be bearing traces of this culture. In result, it was proclaimed to use the Lower Egyptian Culture term which admitted the regional reach of this culture. The chronology of the site is much longer then on the other known Predynastic sites and covers the whole period of Lower Egyptian Culture existence (the other only known case is Buto) (Hartung U. 2013 b, 186). The site started to be inhabited in the second half of Nagada I and it lasts until the beginning of the second half of Nagada II period, which means shortly before the Nagada culture expansion into Lower Egypt area started (Map.2.2).

The other essential aspect is that Maadi settlement was extensively excavated. In most of Predynastic settlement sites located in Delta region, reaching the older layers possibly connected to Lower Egyptian Culture activity is impossible due to high water level. The information coming from the settlement excavations are essential in understanding the Lower Egyptian Culture, it's characteristics, development and contacts with different cultures. Mainly, evidences concerning this culture comes from its necropolis which do not say much even about material culture since funeral inventory is rather poor and also do not represent the daily aspects of living (Bajeot J. 2017, 13).

The settlement appears to bear features of simple village inhabited by numerous families living in self sustained households without any apparent evidence of the surplus production which could indicate the existence of the exchange market. There are only some vague evidence which suggest that some specialized workshops might be located in the area of the settlement, like the places of processing the food, manufacturing the pottery, flint tools and possibly copper objects. Due to new data it has been proposed that at least some of the people inhabiting the village were living in semi-mobile way. They combined the seasonal activities connected to mobile animal breeding with sedentary agricultural cultivation connected to village.

Nevertheless, among the archaeological material discovered on the settlement site were numerous imports which testify for maintaining contacts between Delta region with Upper Egypt as well Southern Levant in aforementioned period. Among them, which is particularly most interesting in the context of this work, are early metal objects findings but also other commodities – organic (in the form of food and cedar wood) and inorganic materials (pottery, precious stones, pigments etc). The greatest known quantity of copper objects, copper ore and tabular scrapers which have been ever found in the Lower Egyptian Culture settlement context, come from Maadi. The other link between Maadi with southern Levant are subterranean structures which are known from the Beersheva Valley region (Israel). This is only Predynastic site in Egypt were such constructions were detected so far. It seems that maybe some of the Maadi inhabitants might be incomers from the Near East area and they brought and applied some of their traditions into the local conditions. The levantine imports as well the local imitations of the levantine pottery match to this theory. Moreover, the oldest remains of donkey were discovered in Maadi which might indicate the use of those animals in the exchange process between Egypt and Southern Levant (Bajeot J. 2017, 172-174).

Fig. 2.1. The location of Maadi settlement site (Google Maps).

Recently, basing on the archaeological material found in Maadi as well on other Southern Levantine sites it was possible to make a link between particular sites and define the ways used for the trade purposes. In case of the site H in Wadi Ghazzeh probably was used the route along the northern part of Sinai Peninsula which in later periods was known as “Way of Horus”. It seems that marine route along the Mediterranean Sea coast could be another choice since in Atlit near Haifa (Israel) ovoid jar with a small flat base and everted rim was discovered, containing shells of Chambardia rubens arcuata, which indicates Egyptian provenance. In Maadi cedar wood was yielded which also could be brought to Egypt from Near East by naval navigation. Moreover, the Red Sea marine route can also be taken into consideration since there were found connections between Maadi and Tell Hujayrat al-Ghuzlan (Jordan) in the Aqaba Gulf region.

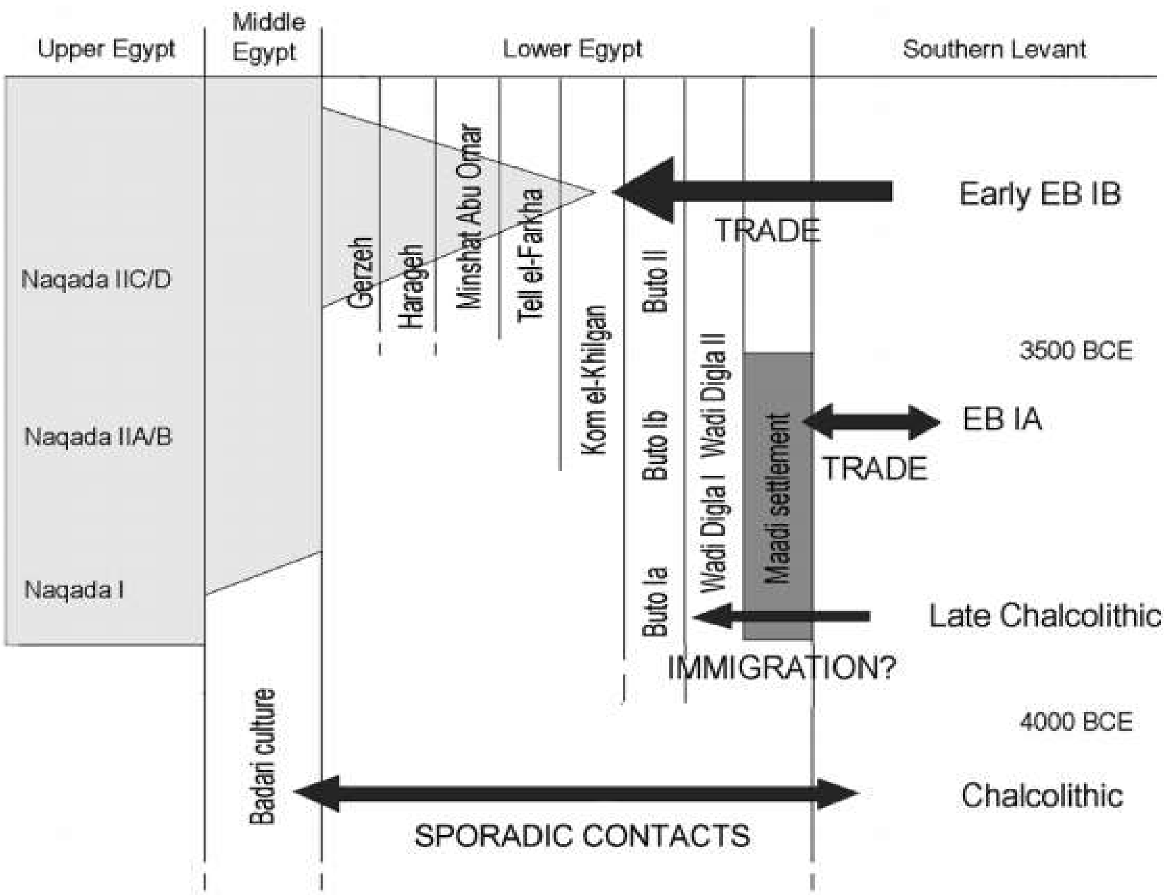


Fig.2.2. The chronological table, which indicates the types of the relations between Lower Egypt and Southern Levant in the particular periods (Hartung U. 2013, 180, fig. 4; Buchez N., Midant-Reynes B. 2007, 54, fig.9).

Of the greater importance are findings of moulds discovered in Tell Hujayrat al-Ghuzlan which corresponds to copper ingots known from Maadi. Also copper ore discovered on both sites appears to have very similar chemical composition and petrographical features and seems to have its origin is in the Feinan copper district (Jordan). In this case, we can as well assume that the routes going through central and southern Sinai Peninsula could serve as alternative path. The issue of Maadi maintaining contacts with Levantine sites will be presented in more details in the following chapters of this thesis.

Even though the extensive excavation were performed on Maadi settlement, many data is still missing which could be helpful in reconstructing in more details the connections and its frequencies between this site with the area of Southern Levant in Predynastic period. Mainly, this data gap is caused by the methodology and the way of documentation applied in the past excavations done in 1930s. The other thing is missing material which partially have been looted or stored in disorganized way. Many of information had been lost also due to destruction of site caused by the uncontrolled sudden modern urbanization process of the area.

3. The origins and developments of early metallurgy in Egypt and Near East

The issue of the beginning of metallurgy in Egypt and Near East was always a vividly disputed subject in academia which still faces some unsolved questions. The difficulties in studying this matter are partially caused by the scarcity of metallurgical material in Egypt as well in Sinai and Levant. It seems that since ancient times the reusing of copper was a common practice. Copper was considered a very precious good since its availability was quite limited. The lack of material can be also explained by the fact that copper could be processed even far from the settlements area.

The origin of metallurgy seemed to evolve earlier in the area of Near East. Initially, at Natufian culture time, copper ore was used as a pigment as well as material for realization of small ornament pieces, like beads and pendants (Shugar A. N. 2000, 75). Nevertheless, the beginning of the true metallurgical branch can be associated with Ghassulian culture (around 4500-3800 p.n.e.). One of the earliest discoveries were the Nahal Mishmar treasure and the copper awl from Tel Tsaf (5100-4600 p.n.e.) (Garfinkel Y., Klimscha F., Shalev S., Rosenberg D. 2014, 1-4). In Chalcolithic period most of the metallurgical production seemed to be mainly concentrated in the Southern Levant, along the Beersheva Valley until lower Nahal Besor. The most essential metallurgical sites were Tell Abu Matar (Perrot J. 1955, 167-189; Shugar A. N. 2000) Bir es-Safadi and Shiqmim (Golden J., Levy T., Hauptmann A. 2001, 951-963). Some scholars want to associate the sudden emergence of this craftsmanship with the incoming of new groups of people. On the other hand some search for local background explanation of this phenomenon (Shugar A. N. 2000, 69).

In the ancient Egypt the dissemination of metal processing occurred during Nagada II period. During Badarian and Nagada I cultures, only the use of the copper objects and tools was recorded (Teeter E. 2011, 167). No traces of metallurgical production were noted so far. Similar situation appeared on many archaeological sites connected to Lower Egyptian culture: Maadi, Tell el-Farcha, Buto, Minshat Abu Omar, Heliopolis and Wadi Digla (Mączyńska A. 2013, 167-170). Whereas, on sites dated to Nagada II and III the quantity of metallurgical evidences are in bigger number. In this time, probably due to the establishment of regular long-range trade contacts with Near East, the process of borrowing of some technological news might appeared as well. Presumably, facing with the Levantine metallurgical production which had a much longer tradition, gave an impulse for the development this branch in Egypt.

According to so far gathered data it is possible to point out few common general features of the early metallurgy in Egypt and Southern Levant (Hauptmann A., Wagner I. 2007, 67; Levy T.E., Shalev S. 1989, 352-372). One of them is copper smelting in the vicinity of the raw material extraction place and further metal processing in the area of settlements. However, the latter one is currently doubted since in the light of recent studies some scholars proposed that on some sites like Tell Abu Matar, Shiqmim and Ashqelon-Afridar might have taken place the practice of copper smelting (Hauptmann A., Wagner I. 2007, 68). Another characteristics of early metallurgy is the occurrence of high amount of slag which can be explained by still insufficient knowledge of early metallurgists. In both areas the access to copper ore sources and fuel needed for smelting process was highly restricted.

Basing on the archaeological data and Egyptian iconography, the particular stages in metallurgical production can be distinguish. Among the most important images are those dated to little bit later times like from tombs of Meresankh III (IV dynasty, Giza), Teti (V dynasty, Saqqara), Mereruke (VI dynasty, Saqqara) or Rekhmire (XVIII dynasty, Thebes). They are of great importance in attempting to reconstruct the stages of metallurgical production.

In Egypt, the raw material was obtained by open cast and underground mining. Prior to the extraction process, the selected raw material needed to be recognized by Egyptian specialists – mineralogists. Then copper ore was extracted by miners, subsequently was comminuted and sieved in order to separate undesirable components from correct material (Lucas A., Harris J.R. 1962, 210-211; Scheel B. 1989, 14). The main copper deposits were exploited in the area of Wadi Arabah, especially in Timna (Israel), Feinan (Jordan) and Sinai as well in Eastern Desert (Abdel-Motelib, A. et ali. 2012, 3) (Fig.3.1). The Anatolian provenance of some of material can not be excluded. The existence of circulation of copper along the Mediterranean coast from the area of contemporary Turkey to southern Levant sites might be indicated by example of unusual set of copper objects containing arsenic and antimony from Nahal Mishmar and Kfar Monash treasures (Wengrow D. 2006, 32).

The studies of trade routes connected to circulation of copper in the area of Egypt and Near East are supported by archaeological data as well by isotope analyses (Rothenberg B., 1970-1971, 4-29). Undoubtedly, since 4th millennium BC the way going through Northern Sinai area had already been used. The copper ore originating in Feinan has been found on sites of En Besor (EB IB) (Hauptmann A. 2007, 272) and Ashqelon-Afridar (EB IA) (Segal I., Halicz L., Kamenski A. 2004) located along thee mentioned route and it is supposed that those places might be used as point for caravans. A large group of experts link it to the famous ancient Egyptian fortified overland route called the Way of Horus

(Abdel-Motelib, A. et ali. 2012, 7). The alternative northern path around oases could be the way of Shur going between Ismailiya and Nizana. The other possibly used routes went through central Sinai – known as "Darb el-Hajj" or "Kings Highway" which connected Aqaba and Suez regions (Rothenberg B. 1979, Abdel-Motelib A. 2006). The maritime way along Sinai coasts cannot be excluded, since many harbour sites like Ras Butran or Ain Soukhna were located there (Hauptmann A., Begemann F., et al. 1992, 7). The archaeological evidence and isotopic studies made on copper material from such sites as Maadi, Tell Hujayrat al-Ghzulan and Timna indicate the trade connection between them and probable use of the above mentioned routes.

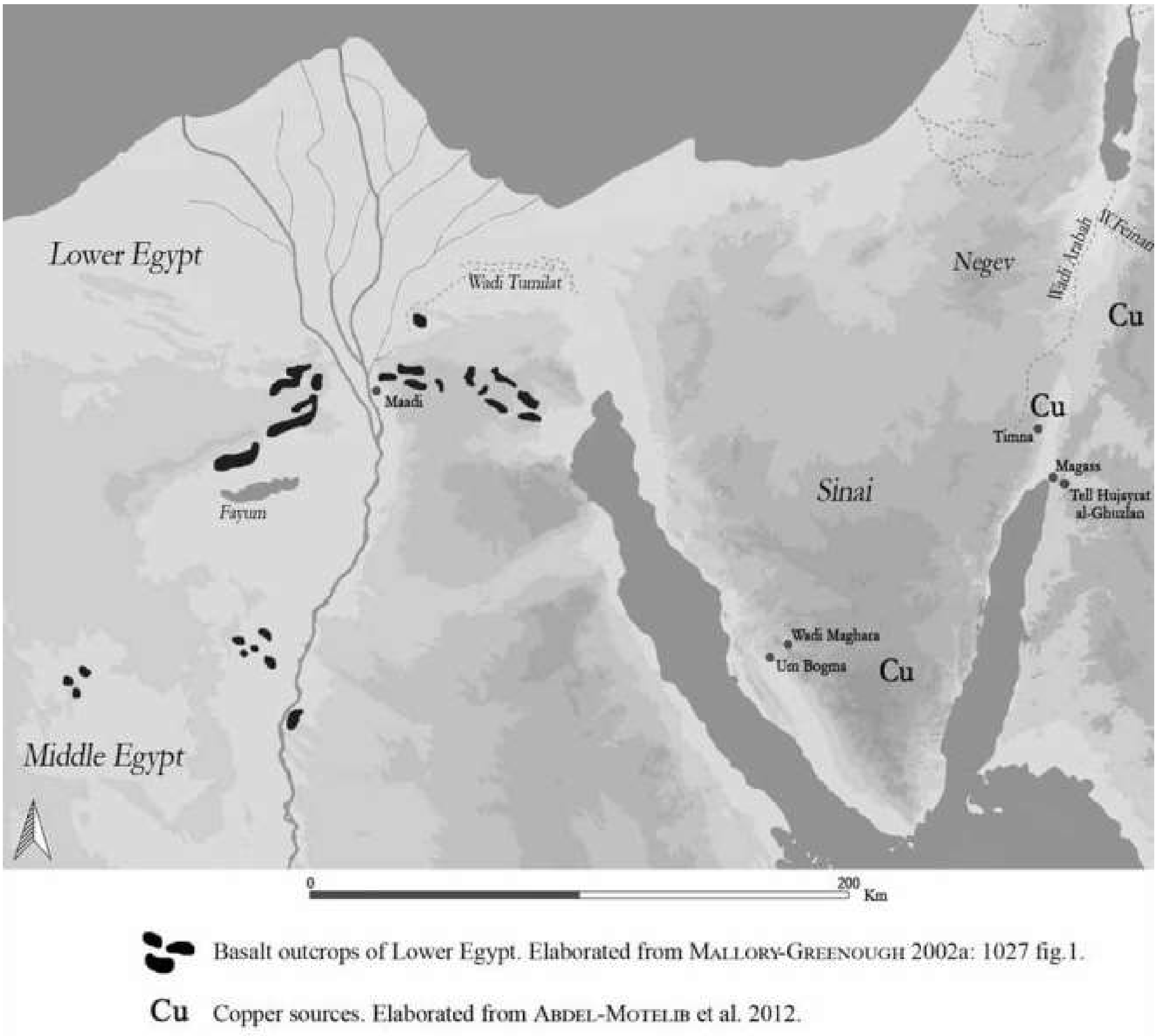


Fig.3.1. The map of the basalt outcrops and the main copper deposits used in 4th millennium BC in Egypt and Southern Levant (Bajeot J. 2017, 26).

In the area of Egypt, Sinai and Southern Levant the isotopic studies are much restricted due to the fact that copper ore from this region is characterized by the elemental composition poor in trace elements like arsenic, lead, nickel, bismuth, cobalt or antimony. This make the provenance studies difficult to conduct. Wadi Tar is an exception since copper ore contains high amount of arsenic. Nevertheless, in some cases this kind of analysis found its way. A great example is famous Nahal Mishmar treasure dated to Chalcolithic period (Bar Adon 1980) (Fig.3.2). The metal objects appeared to be made from copper alloy very rich in arsenic, antimony and partially in nickel which helped to ascertain its non Sinai or Eastern Desert origin (Abdel-Motelib, A. et ali. 2012, 36).

Fig.3.2. Nahal Mishmar treasure at the moment of the discovery (Bar-Adon P. 1980, 15)

After being extracted, copper ore went through smelting process. At the beginning, the primitive pit-furnaces for copper smelting were in use or copper was smelted directly on the ground surface. Such installations are well known from Timna (Tylecote R. F. 1992, 9-10) and Asqelon-Barnea (Golani A. 2014, 119-124). In order to facilitate setting of fire, usually they were founded on hills, with convenient exposition to direction of blowing winds. They were just regular pits which were dug into ground. During the process of smelting, a mixture of the crushed malachite and charcoal was heated and its size was reduced to shape of little bricks rich in copper ore embedded in the slag. Those bricks were extracted by crushing the slag and then melting together in order to create copper bars (Lipińska J., Koźiński W., 152).

In the simple wind powered furnace the temperature could only reach the value around 700-800° (Lucas A., Harris J.R. 1989, 211). The melting temperature of copper is 1083°C so usually copper ore needed to be divided into small portions and the smelting process had to be repeated several times to acquire bigger quantity of copper (Lipińska J., Koźiński W., 152). The problem was resolved during the Ramesside period when shaft furnace appeared which allowed to reach the temperature of around 1200°C (Scheel B. 1989, 15).

By using proper tools it was possible to reach higher temperature in fireplace. Bellows made of reed and clay cap were widespread tools. In Egypt the archaeological evidence is known for Old and Middle Kingdom (Scheel B. 1989, 23) but from the southern Levant comes the oldest finding of bellows found in Chalcolithic site of Tel Abu Matar (Shugar A. N. 2000, 245). The possible use of fans in the earlier times cannot be as well excluded.

Due to archaeological evidences and iconographical representations it is possible to assume that extraction and circulation of raw material had to be controlled by elites. The presence of copper objects in richer graves like Tell el-Farcha, Minshat Abu Omar or Abydos may indicate it. On the other hand the aforementioned depictions testify that certainly in later times extracted material was stored in warehouses which had belonged to the temples and palaces. The supplies were redistributed and controlled by qualified officials who weighted metal in order to prevent against embezzlement practice (Scheel B. 1989, 21-24).

One of the first metal processing techniques were hammering and annealing where the copper objects were made directly from sheet metal (Wengrow D. 2006, p. 38-39). Maybe, at the beginning the lack of appropriate tools allowing to hold heated metal might be a reason for not adapting hot working (Lucas A., Harris J. R. 1989, 212).

During the work, craftsmen used simple tools, including two kinds of stone hammers: with flat surface intended to smooth the metal and rounded one essential in hammering. Metal objects were processed on stone anvils, made from basalt, diorite and granite (Scheel B. 1989, 28). The techniques of polishing and creating elements of decoration on surface by scratching might also be applied to some objects.

Another most common early method of manufacturing was the casting into moulds. Simple forms of moulds/open cast moulds had already appeared during the Early Dynastic period. In Old Kingdom the composite types/piece moulds have been introduced in Egypt.

In the Early Bronze Age the metal started to be circulated as ingots cast in shallow moulds or in form of standardised pieces of sheet (Rehren et al. 1997; Golden 2002). The findings of Kfar Monash treasure (Israel) (Tadmor 2002, 240) or artefacts from Maadi and Tell Hujayrat al-Ghuzlan support this theory.

The knowledge of casting and lost wax method techniques were already known by the Sumerians around 3500 – 3200 BC and in the area of Southern Levant during Chalcolithic period. As a great evidence serves the Nahal Mishmar treasure. In ancient Egypt the traces of using the lost wax method are only evident for Old and Middle Kingdom (Scheel B. 1989, 34-44).

In Nahal Mishmar (Bar-Adon P. 1980) case the unique set of objects made by lost wax technique has been discovered. Those prestige objects in form of the “crowns”, sceptres, weapons and many others, were produced from copper ore rich in arsenic, nickel and antimony. In Egypt since reign of I dynasty, the production of objects based on arsenic bronze became a common practice. The matter of consciously adding arsenic or using copper with high content of this element is highly debated in academia. For deliberately adding arsenic to copper and not using ore rich in it, speaks the fact of the rare occurrence of ingots characterized by such chemical composition (Tylecote R. F. 1992, 11-20). Probably, that time the craftsmen could be aware of benefits coming from addition of extra elements. Among the profits coming from the addition of different elements, we may mention the increasing of the hardness of the material, a better aesthetic effect (arsenic helps copper to get silvery hue), a decrease of the melting point and an impressive positive effect on casting properties. Commonly, it was believed that lack of production waste in settlement area indicate that those types of objects might be produced in different places but recent studies at Tell Abu Matar revealed that arsenic bronze artefacts might be manufactured there (Shugar A. N. 2000, 218).

A general picture of metallurgical production can be reconstructed by using the data provided by the researches conducted at Aszkelon-Barnea (Golani A. 2014, 124-125) (Fig.3.3) and at Tell Abu Matar (Tylecote R. F. 1992, 21-22). On both sites simple pit-furnaces filled with stones and surrounded above by mudbrick wall were found. The crucible in the form of clay pot filled with copper ore was placed inside the pit. At this stage of production the copper ore inside the crucible was heated, then it was refined from contaminants and finally the best quality material was extracted, ready for further processing steps.

Aszkelon-Barnea and Tell Abu Matar sites give a clear evidence for the changes in metallurgical manufacture taking place in Chalcolithic and Early Bronze Age. Complex metallurgical installations discovered at Ashkelon-Barnea suggest a sudden intensification of the production scale in

Early Bronze Age. It seems that in Egypt as well in southern Levant the hypothesis of the transition from Chalcolithic small scale production to Early Bronze "industrial" one is also true for metallurgical branch. The aforementioned transition is not only marked by an increased production in Near Eastern metallurgical centres but also by the occurrence of greater amount of copper objects in Egypt.

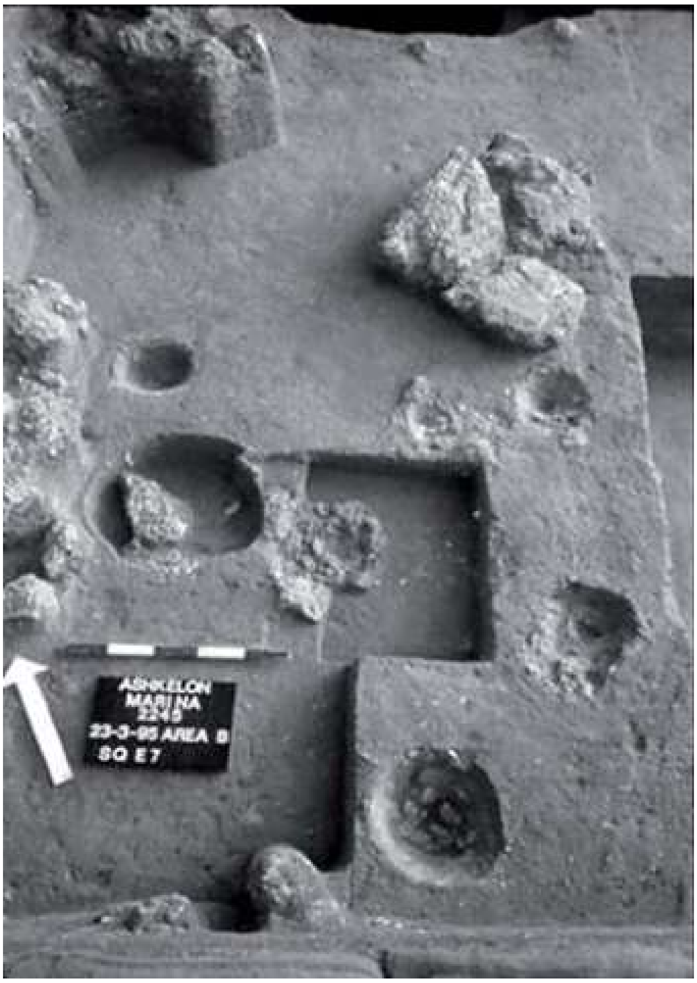


Fig.3.3. Asquelon-Barnea: Pit - furnace associated with metallurgical production (Golani A. 2014, 124).

4. Maadi – the history of excavations

Maadi settlement site is located on desert ridge oriented on E-W axis which constitute of the strip around 1 km long and 100-200 m wide. Today mentioned area belongs to the southern outskirt of modern Cairo city (Hartung U. 2013 b, 178). The site was erected on elevated area (37-43 above sea level) which is common practice in the Predynastic period since it prevented the settlement from annual flooding of the Nile river (Bajeot J. 2017, 24). The site has a very long history of the excavations during which a large quantity of various artifacts were obtained (Fig.4.1). Many of them appeared to bring key information about the Lower Egyptian Culture as well it's contacts with Upper Egypt and especially with Southern Levant in the 4th millennium BC.

The history of Maadi started with its discovery made by P. Bovier-Lapierre in the beginning of the XX century. It was yielded during the project aiming to recognize Predynastic sites along the Memphite region. That time it was marked as Station 10 (Bovier-Lapierre P. 1926, 298-308). In 1928 J. Lucas paid a visit to Maadi and in his notes he included short description of site and the visible on surface material. He distinguished 3 separate sites which later, in truth appeared to be the different parts of the same settlement (Bajeot J. 2017, 18).

The first excavation were conducted by M. Amer and O. Menghin from Cairo University in 1930 and lasted to 1950s. Wherein in 1938 the second one had been replaced by I. Rizkana (Rizkana I., Seeher J. 1987, 1988, 1989, 1990; Seeher J.1990). Three types of dwellings were recognized: oval, rectangular and subterranean. The first kind represents the simple oval structures which remains mainly constitute of rows of postholes. Presumably, the average dimensions were around 4×2.5 m. Those dwellings were built probably from the light organic materials which has not been preserved. The buildings were founded along W-E axis and were accessible from the southern side. Inside the dwellings was discovered the domestic material in the form of hearths, storage vessels, mortars and others (Rizkana I., Seeher J. 1989, 39-43, figs. 8-21; Mączyńska A. 2013, 80-81). The second type of building construction found in Maadi is thought to rather serve as place for keeping the animals since no typical domestic material and installments like hearths and vessels occurred there. Two variants of those rectangular structures were detected: shallow pits (interpreted as semi-subterranean by Seeher J. 1989, 45) and the ones which outline is formed by the shallow and narrow furrows. Only some pits and holes of undefined function were located inside of those rectangular structures. As in the first case, here also all the structures are composed of organic materials. Most of semi-subterranean structures were

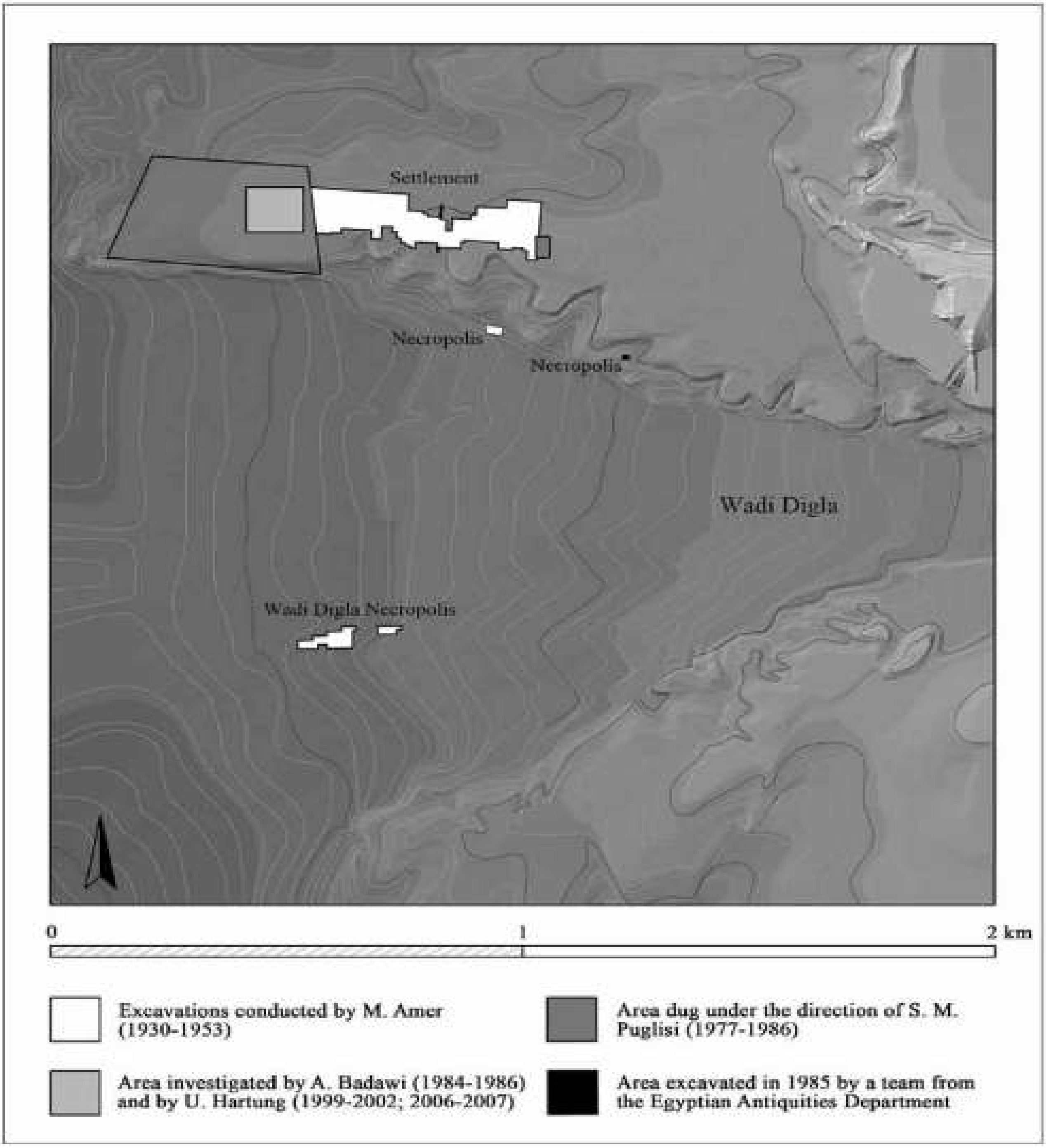


Fig. 4.1. The map presenting the Maadi settlement excavation areas of particular archaeological missions (Bajeot J. 2017, 19)

raised on NS axis with entrance in the southern or northern wall. (Rizkana I., Seeher J. 1989, 45; Mączyńska A. 2013, 81). The most of interest is the third kind of residential structures which was discovered in the northern part of excavation area. Subterranean dwellings (Fig.4.2) reached the deep of 2-3 m and their diameter varied between 3 and 4.8 m. The entrance was located on the end of corridor from southern side of the building. Inside, sometimes the walls were supported by stones or dried mudbricks. Many holes and post which constituted the part of roofing construction were detected inside the dwellings. In every building hearth found to be located in the middle of room and as well other archaeological material appeared in the form of the vessels, ceramics, animal bones and flint tools (Rizkana I., Seeher J. 1989, 49-55; Mączyńska A. 2013, 81). Maadi subterranean dwellings are similar to Late Chalcolithic constructions known from Beersheba Valley in southern Levant. Lately, Early Bronze I chronology was even proposed (Braun E., van den Brink E.C.M. 2008, 649-650). Except residential structures also many signs of possible fence constructions were discovered around the settlement which were clearly associated with dwellings. In the same domestic context as well postholes, storage pits, vessels, hearths and other archaeological artifacts like copper objects, ceramics, flint tools, animal bones, stone material were yielded (Rizkana I., Seeher J. 1989). Essential group of pottery constitute Levantine imports recognized and discussed by N. Porat (Porat N., Seeher J. 1988, 215-228). Among other imports noted in Maadi were tabular scrapers, sickle blades (Rizkana I., Seeher J. 1985, figs. 7, 10), cedar wood (Rizkana I., Seeher J. 1989, 25), turquoise bead (Rizkana I., Seeher J. 1988, 109), nine bone spatulas in cache (Rizkana I., Seeher J. 1989, 22, pl. 8), copper objects (Rizkana I., Seeher J. 1989, pls. 3-4), giant shells of *Tridacna maxima* and *Tridacna squamos* (Rizkana I., Seeher J. 1989, 21) as well basalt V-shaped bowls and discs (Rizkana I., Seeher J. 1985, fig. 11, Rizkana I., Seeher J. 1988, pl. 95; Porat N., Seeher J. 1988, 215-228).

In Maadi not only installments typical to settlements area occurred. Few graves belonging to adults, children and infants appeared as well (Rizkana I., Seeher J. 1989; Bajeot J. 2017). It is worth to bear in mind that in Lower Egyptian Culture it was common to bury adult members of society in the specially designated areas – cemeteries. There existed strong division between area for living and dead. Surprisingly, in Maadi few cases of adults buried inside the settlement area occurred even though that the cemetery was located 180 m into the southern direction and most of Maadi inhabitants were resting there after the death (Mączyńska A. 2013, 92). Those burials are represented by simple shallow pits. In one case the body of adult woman lied on left side, with the head facing the southeast direction and face oriented towards the southwest. In the other known shallow pit burial, the poorly preserved remains of adult of unidentified sex were found. The body of dead was position on the back which is uncommon for Lower Egyptian Culture customs. The same few exceptions appeared on Maadi cemetery located nearby the settlement area. Another particular finding in Maadi settlement area was a skull deposited inside the hearth which probably might be connected with some unknown ritual ceremonies (Rizkana I., Seeher J. 1989, 66). The inventory of dead was rather poor, with only few artifacts like examples of pottery, flint tools, animal bones and others. As for child cases, the inventory was usually much more poorer than comparing to adults. In Maadi around 56 graves belonged to children, infants or fetus. Usually they were deposited in vessels or in pits. The custom of bearing children in the areas of settlements it is know from many cultures, not only from Lower Egyptian Culture. It is believed that it might be connected to attempt to maintain the relation with dead children and another reason might be their "incomplete" social status which did not allow them to access regular burial place designated for other members of the community (Mączyńska A. 2013, 83).

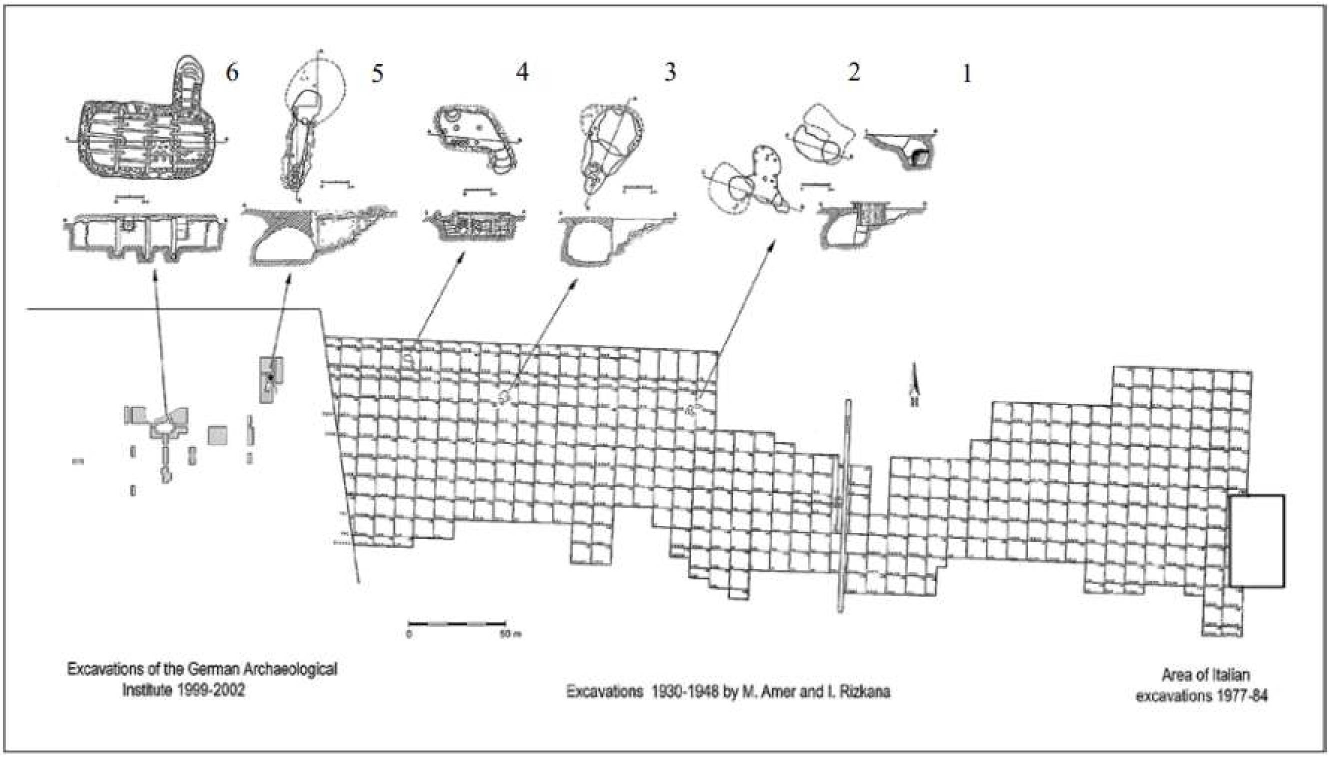


Fig.4.2. Plan of excavation areas done by various missions, indicating the location of subterranean and semi-subterranean structures (Hartung U. 2013, 179, fig.3).

The another research was done by Missione Italiana per le Ricerche Preistoriche in Egitto e Sudan (MIRPES) from the Sapienza University in Rome, together with Geography Department of Cairo University. The excavations were under the leadership of Puglisi S. M., Caneva I., Frangipane M., Palmieri A. (1986a, 1986b, 1987; Caneva I., Marcolongo B., Palmieri A. 1995; Bajeot J. 2017). The six campaigns between time span of 1977-1986 took place in the eastern part of the settlement, close to the area exposed in studies carried in 1930s and 1940s. The main goal was to pay more attention to stratigraphy than in the previous research done on the site, which could help to better understand the chronology and the changes appeared during the existence of the site. Sometimes it was difficult to distinguish particular cultural layers because of the geological features of the area. Mainly, the sand occurs and only virgin soil appears to be more firm. This is the reason why most of the discovered huts were evident in the second one. The burnt and clay compacted layers in some cases helped to recognized the habitation places. Also such features as postholes, storage pits, fireplaces and in situ vessels were very useful in identifying the households. Usually the organic material yielded on site, was also strongly connected to households areas. The Italian mission obtained many different kinds of material including: pottery (local and imports), flint tools, bone objects, copper ores and finished artifacts, beads, palettes, organic materials (mats, reeds and skin), fibers, botanical remains, wood and others (Bajeot J. 2017, 30-32). No subterranean structures known from previous excavations done in the other parts of settlement site were noted in eastern part. Only two infant burials were discovered on the site. The bodies were lied in the fetal position into small simple pits without any funeral inventory. Only in one case, the remains of organic mat/cloth were discovered. Probably the body of infant was wrapped with it.

The eastern settlement area excavated by Italian mission presented the picture of simple village inhabited by families living in the self sustained households. Due to the overall plan of the village, frequently occurring abandonment layers and shifting in the occupation areas of the settlement, the Italian archaeologists proposed the possible semi-mobile way of living of Maadi inhabitants. Probably, at least some members of the society were involved in seasonal mobile animal herding as well periodic sedentary agricultural activities (Bajeot J. 2017, 44).

In 1985-1986 the excavation in the eastern part of Maadi settlement were carried by F.A. Badawi from El-Azhar University (Badawi F. A. 2003, Watrin L. 2000, 163-184). Another rectangular subterranean structure made of stones, emerged during the works (Fig.4.3). The building dimension were 8.5×4 m and it reached the 2 m depth. The entrance was situated from the northern side of the dwelling. The corners of the structure were rounded and the walls built from stones were plastered with mud. Inside 3 postholes were located which constituted a part of roofing system made from perishable organic materials. Those subterranean building are similar to residential structures known from Southern Levant Early Bronze I sites of Asqelon-Afridar F (Israel), site H in Wadi Ghazzeh and Sidon-Dekerman (Lebanon) (Watrin L. 2000, 163-184; Braun E., Gophna R. 2004, 191-199, 227; Mączyńska A. 2013, 81-82; Hartung U. 2013 b, 184).

Fig.4.3. The semi-subterranean structure discovered by F. A. Badawi (Hartung U. 2003, 8).

Lately, the studies were performed in the western part of settlement between 1999-2002 by the German Archaeological Institute (DAI) (Hartung 2003, 2004, 2013, 2014, Hartung et al. 2003) together with the Egyptian Supreme Council of Antiquities (SCA) and University of Cairo. The main aim of project was to document the archaeological features which had not been yet destroyed by quickly spreading modern urbanization activities which greatly affected the settlement site (Hartung U. 2013 b, 178). German team uncovered different kind of subterranean structures similar to those known from previous excavations. The dwelling here had an oval shape and was directly dug into the ground without any support. The construction had dimensions of 5×4 m and its height was estimated to be around 2-2.5 m (Hartung U. 2004, 343-350). Inside the postholes also appeared which testifies for existence of roof made from perishable materials. The entrance led through 5.5 m long and 1-1.5 m wide corridor. The walls were lined with stones and mud served as plaster media. The exploration of dwelling interior provided with a large quantity of various archaeological materials connected to household activities. Among them were levantine pottery imports, fish bones and bigger flint tools (Mączyńska A. 2013, 82). Hartung U. noticed association between subterranean structures discovered by German team with those known from previous excavation done by Egyptian scientists. He noticed the existence of pattern in the development of architecture in Maadi settlement and connected it with the increasing craftsmen knowledge and skills in using new stone material in building those subterranean dwellings. According to him all those structures have strong association with residential constructions known from Southern Levant and most of them have their origin in Beersheva Valley while subterranean example discovered by Badawi F.A. is related to structures known from northern sites like En Shadud or Yiftahel (Hartung U. 2004, 352-353; 2013 b, 179-180; Mączyńska A. 2013, 82; Perrot J. 1984).

In 2002 the Maadi warehouses were suddenly looted and around 70 objects appeared to be missing. After two years some of those artifacts started to be displayed in auction houses. Thanks to the archaeologists who recognized objects, it was possible to retrieve back some of them (Bajeot J. 2017, 22).

After so many years of archaeological research it was possible to confirm the village character of the settlement without any particular space arrangement. The inhabitants spent their time mainly on agricultural activities, breeding and fishing. They cultivated emmer, barley, pulse and flax. Most common animals kept were goat, sheep, pig and cattle (Bökönyi S., 1985; Van Zeist W., de Roller G. J. 1993; Bajeot J. 2017, 149-165). Also locals were involved in the production of pottery, flint tools, bone objects and maybe copper. The imports that were found on site indicate the involvement into the trade activities (Hartung U. 2013 b, 179-180). It has been proposed that Maadi maintained the trade contacts with several settlements in the Southern Levant, among them are site H in Wadi Ghazzeh (Nahal Besor), Taur Ikhbeineh, Tel Halif and Nizzanim (Hartung 2001, 354-361; Abdel-Motelib A. et al. 2012, 6). Probably, the representative of "Canaanite" population inhabiting Maadi at least for some short period which is attested by material findings as well by subterranean structures, were involved in the trade activities. As well it might be truth for Lower Egyptians living in the area of the Southern Levant where the traces of their presence is also visible by the mudbrick structures and other artifacts (Seeher J. 1990, 153). Probably those people who inhabited both regions were involved in trade and maybe they acted as middlemen in the transactions (Hartung U. 2013 b, 185). Based on archaeological material the EB1 and maybe as well EB1A2 periods were the peak time of the trade exchange of Maadi settlement with sites located in Levant (Yekutieli Y. 2001, 679). The main used route went through the northern Sinai Peninsula and it is confirmed by the camps located along the way (Oren E. D. 1973; 1989; Oren E., Gilead I. 1981; Oren E., Yekutieli Y. 1992; Caneva I. 1993). The marine routes and one passing through central and southern Sinai cannot be excluded as well (Gophna R., Liphschitz N. 1996; Gophna R. 2002; Abdel-Motelib A. et al. 2012, Bajeot J. 2017, 28).

5. Archeometallurgical investigations of Maadi

One of the reasons making Maadi a unique site is the quantity as well the diversity of copper based objects discovered there through many years of research carried out by different archaeological teams. Certainly, this site is outstanding in this matter when compared with other contemporary sites located in the Lower Egypt. The quantity and types of copper objects widely exceed what is known from other locations. The excavation work at Maadi settlement yielded an array of various objects, among them: fishing hooks, awls, needles, chisels, 3 ingots, 3-4 axes and adzes (Rizkana, Seeher J. 1989, 13ff.; Mączyńska A. 2013, 169) (Fig.5.1). Moreover, a rare types of findings were noticed like a spatula possibly used for pigment preparation, or around 15 kg of copper-manganese ore, which is thought to be used as pigment for cosmetic purpose such as an eye paint (Rizkana, Seeher J. 1989, 17f.; Abdel-Motelib A. et al. 2012, 6). It seems that Maadi might played a crucial role in the distribution of copper in 4th millennium BC.

The traces of burning materials and the presence of possible by products of the copper processing were also unearthed like copper ore, droplets and nodules. Nevertheless, no clear evidences proving the existence of the metallurgical installations, like parts of furnace or crucibles, were discovered. Up to now, it is not possible to admit that the copper was smelted or just processed in the settlement's area. It is highly probable that it was easier for the Maadi inhabitants to import semi-processed material in the form of ingots, ready for further treatments (Mączyńska A. 2013, 168-169). Maadi is located in the area devoid of natural copper resources, so it was needed to acquire material from different places. The physicochemical analyses of the metal samples from Maadi indicate that the metal ore could be imported from different areas at the same time. Most of the chemical analyses show high similarity to the main copper districts located in Wadi Arabah – Timna and Feinan, as the main regions of copper ore provenance. The other candidate is Sinai Peninsula, where few cases appeared to come from the different mining districts located there. Surprisingly, the chemical composition of one of the axes includes very high content of nickel and the only matching source of this element is located in south-east Anatolia (Abdel-Motelib A. et al. 2012, 6). None of the analyzed objects showed the relations by the chemical means with the copper deposits in Eastern Desert.

Nevertheless, the fact that copper ore was obtained outside the Maadi, it seems that the tools and other objects needed to be manufactured somewhere in the settlement area. This assumption can be made on the quantity and the unique form of objects. Some of the researchers consider Maadi as the key distribution center, before EB IB when the representatives of Nagada culture took control. The presence of Egyptians in the area of southern Levant and southern Sinai is well attested by the findings of pottery and building structures (Abdel-Motelib A. et al. 2012, 7). In past due to Menghin O, Amer M. (1936, 48) statement concerning huge quantities of copper material discovered in Maadi in first seasons of excavations, new assumptions were made by other researchers. Baumgartel E. J. (1955, 122) proposed to concern Maadi settlement as an important stop for the caravans traveling between Southern Levant and Upper Egypt. Copper was considered to be one of the exchanged goods traded between those regions. Nonetheless, according to Mączyńska A. (2013, 188) in the light of recent studies Baumgartel E. J. interpretation should be view with great caution. She highlights that copper artifacts occur rarely in the context of Predynastic sites in Lower as well in Upper Egypt areas. If there would be existing long range copper exchange between Upper Egypt and Near East, bigger quantity of copper material should appear in the south of Egypt so in this case, she proposes to exclude the possibility of copper trade. She supports her theory with Hoffman M. A. (1979, 207-208) observations made on copper artifacts from Delta and Upper Egyptian sites in the mentioned period. There exists strong difference in production technology of metal objects. In Badarian and Nagada I cultures the objects are hammered from nearby available natural copper and in case of Maadi the smelting from ore was common practice.

In recent time some analogies were made between archaeological materials coming from different distant sites: Maadi (Rizkana I., Seeher J. 1989), Tell Hujayrat al-Ghuzlan (Eichmann R., Khalil L., Schmidt K. 2009, 17-78; Pfeiffer K. 2009) and Tell Magass (Khalil L. 2009, 5-16). This proofs the existence of some cultural interactions between Nile Delta and Southern Levant (especially Aqaba region) in this time. The ingots and casting moulds, which show the great similarity in terms of form and dimensions, have been discovered on the aforementioned sites (Fig.5.2). Perhaps, the regional standardization connected to the trade exchange was already established. The copper found at Maadi has similar chemical composition to Tell Hujayrat al-Ghuzlan one, which on the other hand is connected to Timna. It is very probable, that actually the copper ore from Maadi could be coming from Timna and Tell Hujayrat al-Ghuzlan settlement could play the role of trading agent since the Egyptian artifacts and other types of findings were found there. Unfortunately, no chemical analyses were done on Maadi ingots as well on copper-manganese ore (with possible cosmetic use) since all of these objects were looted from the site warehouses in 2002 (Abdel-Motelib A. et al. 2012, 52).

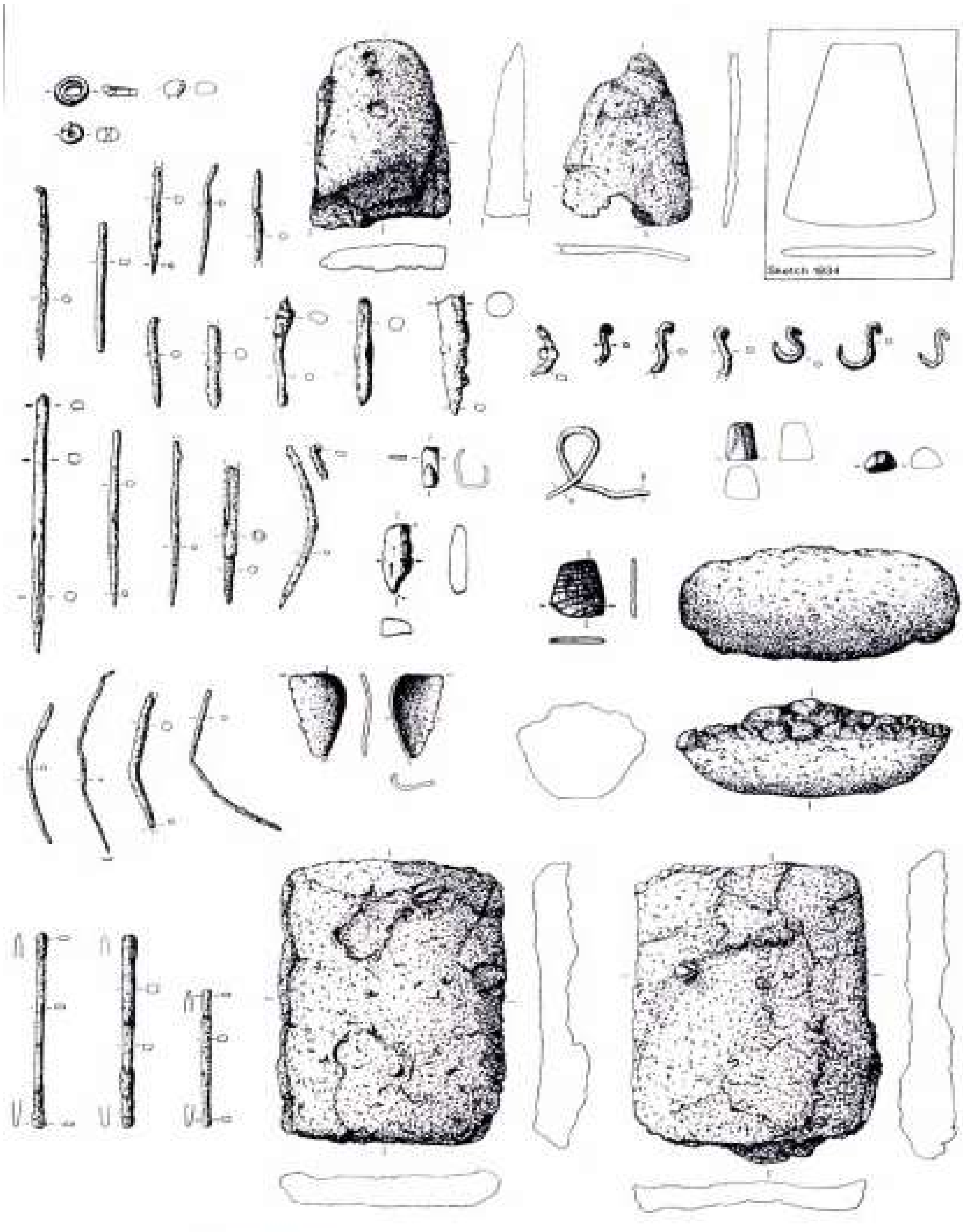


Fig.5.1. Metal objects discovered in Maadi (Rizkana I., Seeher J. 1989, plates 3-4; Hartung U. 2013 a, 23).

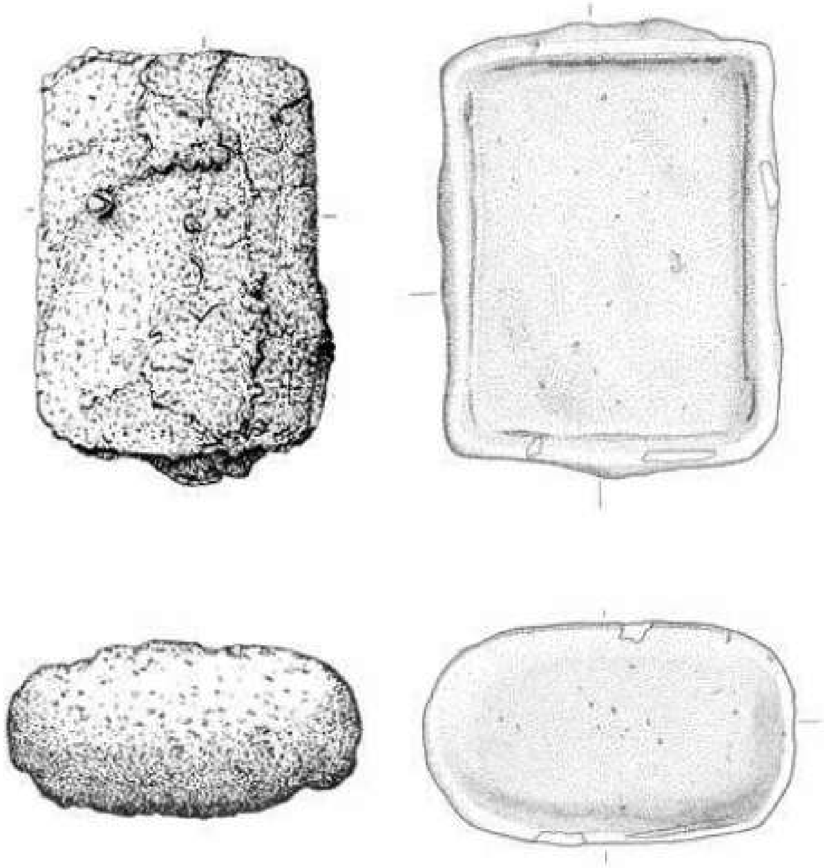


Fig.5.2. On the left side Maadi ingots and on the right, matching moulds- Tell Hujayrat al-Ghuzlan (Pfeiffer K. 2009, 30)

Itt seems that Maadi maintained contacts not only with the southern Levant area but also with the nomadic tribes in Sinai Peninsula, which had access to the local copper ore deposits. The lead isotope analysis of few Maadi metal samples confirms this hypothesis (Eichmann R., Khalil L., Schmidt K. 2009, 46-52). This relation between sites can be seen as an evidence of use of the trade route going from Lower Egypt, through northern Sinai until it reaches the southern part of Levant. Many of scholars associate it with the famous "Way of Horus" well known for later periods in Egypt (Abdel-Motelib A. et al. 2012, 47). In the Sinai Peninsula and Southern Levant many artifacts of Egyptian provenance dated to fourth millennium BC have been recorded. They occurred on sites, which very likely were located along the main ancient trade routes. The copper samples from site „H" in Wadi Ghazzeh (Nahal Besor) were studied by lead isotope analysis as well and the obtained results revealed that the copper ore were imported from Feinan to the area of northern Sinai in the Chalcolithic period and Early Bronze Age IA. Similar results were acquired for at least two samples from Maadi (Abdel-Motelib A. et al. 2012, 47), confirming that it maintained trade contacts with this site and with other sites located in southern Levant such as Taur Ikhbeineh, Tel Halif, Nizzanim and more (Hartung U. 2001; Bajeot J. 2017, 145). In Maadi case the use of marine route cannot be excluded but the current state of research cannot prove this theory (Mączyńska A. 2013*,* 44-45).

The first archaeometric analyses of Maadi metal samples coming from Cairo University excavations were conducted by Pernicka E. and Hauptmann A. (1989). The studies aimed at defining the petrographic features of samples and their chemical composition by the means of neutron activation analysis (NAA). Five metal objects and two copper ores were chosen. The authors made the first provenance analysis of Maadi objects and the obtained results mainly corresponds to copper sources located in Feinan in Jordan (Hauptmann A. 2017, 145). Nonetheless, they did not exclude other possibilities about the copper ore origin like Timna or Sinai deposits. In latter case, they suggested that it can be true especially for the manganese ores but it is important to remember that those kind of ores as well exist in Eastern Desert and they are located just around 100 km away from Maadi (Abdel-Motelib A. et al. 2012, 7). One copper fragment of possible axe appeared to contain an extraordinary quantity of nickel (about 2,5 %). For that time it was not possible for authors to point out the provenance area of material but recently the Anatolian copper deposits were proposed (Pernicka E., Hauptmann A. 1989, 137 ff.; Abdel-Motelib A. et al. 2012, 6). Pernicka E. and Hauptmann A. (1989) suggested the relation between copper ores and metal objects from Maadi rather indicate that the first one was used as pigment and the other one was imported together with it. But lately it has been doubt the cosmetic use of ores since the mix of copper minerals recognized did not allow to obtain any specific colour, neither green nor black (Hauptmann A. 2017, 145-155).

The latter studies were done on another 5 copper samples by Hauptmann et al. (2012) as well on 6 ores and 2 metal artifacts by Abdel-Motelib et al. (2012) as the part of the bigger project which also included the two expeditions in 2006 and 2008 to the archeometallurgical areas located in south-western Sinai, including Um Bogma and Serabit el-Khadim, and northern area of the Eastern Desert in Egypt. The aim was to obtain archeometallurgical material for the provenance analysis in order to define the connections between Lower Egypt and raw material deposits in the Southern Levant. These Maadi samples came from the archaeological excavations conducted by German team. The physicochemical analysis was based on lead isotope studies of the samples using Multicollector-ICP-Mass Spectrometer and Thermal Ionization Mass Spectrometer. Also attention was paid to the mineralogy of the ores and metals which were studies by Optical Microscopy and X-ray Diffractometry. Similarly to previous petrographic investigation (Pernicka E. and Hauptmann A. 1989), quartz grains associated with copper minerals were found which stand for the close intergrowths of chrysocolla, manganese rich-shales and arcosic sandstone (Hauptmann A. 2017, 145-155). The lead isotope ratios of at least three Maadi samples match with Feinan and as well Timna deposits. As authors stated Feinan provenance of those samples is more probable since their petrographic features are typical to this ore deposits, which do not occur in the deposits of Timna and Sinai. The Feinan ore has arkosic composition with distinctive quartz grains in the blue-green range of colours. Nevertheless, some of Maadi metal objects correspond to the composition of samples coming from Northern Sinai site "H" in Wadi Ghazzeh (Hauptmann A. 1989) and in turn they both revealed the high similarity with Feinan deposits. The existence on the northern Sinai way originating in Feinan and reaching Nile Delta (Maadi) was proposed. On the other hand the possible origin of some copper material from Eastern Desert in Egypt has been excluded by authors (Abdel-Motelib et al. 2012, 47). The most possible provenance of the Maadi copper ores and objects is Timna copper district. It is indicated by the lead isotope ratios but also mineralogical properties. The authors as well suggested Maadi's very close relation to sites in Aqaba region, located very close to Timna, Tell Hujayrat al-Ghuzlan and Tell al-Magass (Fig.5.3). Those tight contacts between sites occur not only in similar composition of ores and metal objects corresponding to Timna deposits but also the matching ingots and moulds findings (Pfeiffer K. 2009) and other Egyptian artifacts discovered on aforementioned Aqabian sites which constitute the strong evidence for maintaining the copper trade exchange between Lower Egypt and Southern Levant in this period. Some of the Maadi samples could also come from sites located in Sinai Peninsula – like Um Bogma.

The latest research were performed by Hauptmann A. et al. on twelve copper ores and objects from the Italian excavations (MIRPES) (Hauptmann A. 2017, 145-155). The chemical analyses based on High Resolution Inductively-Coupled Plasma Mass Spectrometer (HR-ICP-MS/Element XR, Thermo Scientific) were done on all the aforementioned samples. Four metal objects and three copper ores were subjected to further lead isotope analysis by the means of Multicollector-ICP-Mass Spectrometer (Neptune, Thermo Scientific). The chemical composition of ores and metals appeared to be missing the trace elements. Only one ore sample and one metal prill contained higher concentrations of arsenic, nickel, cobalt and in first case also uranium. The authors noticed that the metal objects from Maadi do not match to the metal distribution pattern during the Chalcolithic period and Early Bronze Age I where arsenical copper played the first role. As for provenance of the raw material it was proposed to exclude the Eastern Desert in Egypt and Nubian copper deposits due to lack of gold and also Sinai Peninsula because of missing of the manganese. Most of the copper samples have very low sulphur content so non-sulphidic origin was proposed and very likely they come from sedimentary environment with oxidic ores. Interesting results were also obtained through lead isotope studies which indicated once again Feinan and Timna as possible place of origin of Maadi copper ore. Of great interest is the matching footprints of some samples to the ores coming from different mining sites in the Sinai Peninsula, among them Sheikh Mukhsen, Bir Nasib, Wadi Ba'Ba and other. The authors discussed the issue of lead evolution trend of uranogenic ores and metals and how it might affected the lead isotope results. The problem was as well mentioned previously by other scientists (Abdel-Motelib A. 2012; Rehrem T., Pernicka E. 2014).

In the present research an another set of copper ores and objects obtained during Italian mission excavation is examined according to a detailed physicochemical protocol. Twenty six samples are available, ten of which has been primarily chosen and analyzed. Advanced techniques have been coupled with conventional chemical analyses with the aim of expanding the knowledge of the objects available in this study. The obtained results have been also compared to previous studies made on Maadi samples as well to data coming from different works of objects coming from sites in Egypt, Sinai Peninsula and Southern Levant.

6. Experimental Analyses and Methodologies

One of the main ideas of this project was to use an array of various techniques, non-invasive and destructive as well, aimed at studying the archaeological material and showing at the same time the advantages and disadvantages of the methods. Moreover, it was intended to compare the results coming from different techniques and to stress the need and importance of using multidisciplinary approach in studying ancient artefacts. In previous works Maadi copper objects were studied mainly by destructive techniques, especially by ICP-MS and lead isotope analyses for provenance studies. The use of such techniques is very restricted and strongly debated in the academia, since many factors can affect the results coming from these analyses.

The present project is focused on the objects coming from the excavation conducted by the Italian missions in 70s and 80s. The materials considered in this work aroused new interest, since other copper artefacts, in number of 12, coming from the aforementioned excavations have already been studied by Hauptmann A. et al. and published in the Italian excavation final report (Bajeot J. 2017). Among the 26 available samples, only 10 were chosen for further examination (Tab.6.1) while a complete catalogue has been prepared as integral part of the thesis project and accomplished with the results of other artefacts studied by Hauptmann A. The catalogue can be found at the end of this thesis work. Due to time and instrument access restrictions the number of object needed to be reduced. The samples were chosen basing on their classification: type, function, state of preservation and also according to stratification layers. The approach was to create a sequence of objects coming from different layers covering all the phases of existence of settlement in its eastern part and try to determine if there exist some change pattern of the metal objects.

The project has been divided into several steps. The first act was the observation of the samples and the organization of the complete catalogue, which includes details about the general features of copper samples and also the main information obtained by particular method in order to provide the readers with the access to all the results and the methodology of the research. The next step was the study of the artefacts, using non destructive techniques, namely: Optical Microscopy (OM), Scanning Electron Microscope with Energy Dispersive Spectrometry (SEM-EDS), Energy Dispersive X-Ray Diffraction (EDXD) and X-ray Diffraction (XRD). As the last step, we moved to destructive techniques as FTIR (Fourier-Transform Infrared Spectroscopy) and ICP-OES/ICP-MS (Inductively Coupled Plasma Optical Emission Spectrometry/Induced Coupled Plasma Mass Spectrometry) using part of the archaeological samples. Finally, we took advantage of the collaboration of researches at Sapienza who shared their experience in the use of the Strontium isotopic analysis for provenance studies of copper artefacts. The particular techniques and the strategy of their use will be presented in the following sub-chapters in the right order showing the overall approached of analysing the Maadi copper objects.

1	Square: VI L, US: L, Phase:-, Date: 26.03.1978, Type: copper object
2	Square: IV W, US: 2c α, Phase: Ia, Date: 26.04.1977, Type: Pin
3	Square: IV E, US: 2c, Phase: Ia, Date: 25.04.1977, Type: Two matching pieces of chisel?
4	Square: II, US: 3c, Phase: Ia, Date: 3.02.1986, Type: ‘plaque’
5	Square: I, US: 5c β, Phase: Ia, Date: 27.03.1978, Type: two copper ore pieces
6	Square: 39, US: 4, Phase: Ia, Date: 3.02.1986, Type: chisel fragment?
7	Square: 46, US: 2d, Phase: III, Date: 21.05.1984, Type: copper ore
8	Square: IV S, US: 5a, Phase: Ia, Date: 25.03.1978, Type: ‘slag’

Tab.6.1. The list of artefacts chosen for further analysis in this thesis work. US – Stratification Unit (Bajeot J. 2017) (the complete catalogue with detailed information on all of the copper objects discovered by Italian mission in Maadi is attached at the end of this work).

6.1. Optical Microscopy (OM) Analyses

The Optical Microscopy technique was used as initial analysis for a preliminary classification of the objects and the identification of their general features. Basing on this, the selection was made between artefacts and some of them have been designed for further analyses. The observations were performed with the stereo-microscope Nikon SMZ-π, oculars 10x, objective 1x and magnification range of 0.67x-5x with Toup View software.

Ten artefacts were studied under the optical microscope. All of them appeared to be highly corroded and in most of the cases the visual examination could not allow to recognize the type and the function of the object. Only the function of pin object is confirmed and in two other cases it is supposed that they might served as chisels. Some of the objects were classified as copper ores. Different corrosion structures have been identified on the particular artefacts. In most situations severe cracking and detaching of the surface layers appeared (Fig.6.1.1).

Most of the samples were covered with thick crust of sand particles, varying in size and shape (including both rounded and angular shapes). Sometimes the sand was aggregated in specific spot on the object. The sand grains differ much in colour, ranging from white, yellow, orange to red and brown. Some areas had been affected by the green colour of the copper mineralisations (Fig.6.1.2).

Some carbon based compounds have been detected on the surface of the objects. Charcoal was the most common compound which was further studied by SEM-EDS technique. The identification of the wood species was not possible due to really small size and scanty preservation of the structure. The remains of fiber have been found on the "plaque" objects which corresponds to other flux fibers materials previously discovered in Maadi (Gleba M. 2017, 166-170) (Fig.6.1.3).

Except, the surface studies of the all objects, Optical Microscopy was used for studying the cross sections details of the two of them („palque" and chisel), which were chosen for further analysis by the means of other techniques like SEM-EDS, EDXD, FTIR, ICP-OES and Strontium Isotope Analysis. They appear to consists of the different kind of the corrosion layers, which completely vary in colour and structure (Fig.6.1.4).

One object completely differs from the rest of the artefacts. It has glassy structure with visible bubbles and an organic fiber embedded underneath its surface. Probably, it is silicate by-product of the smelting process (slag) (Fig.6.1.5).

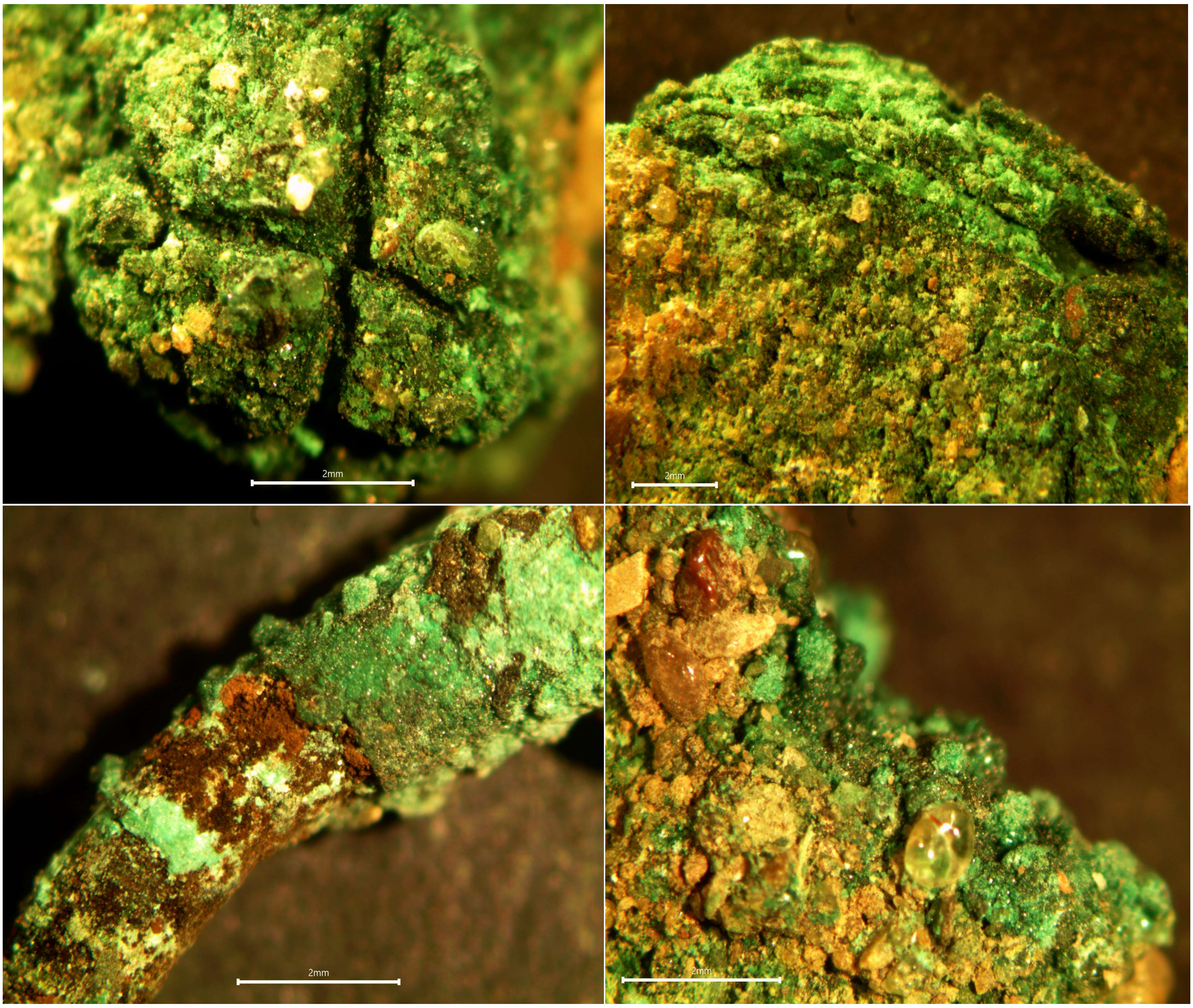


Fig.6.1.1. Various corrosion formations. Upper left: cracked globular area (chisel: Sq. 39, US: 4). Upper right: detaching of the surface layers (chisel: Sq. 39, US: 4). Lower left: detaching of the surface particles (pin). Lower right: globular copper mineralisations ("plaque").

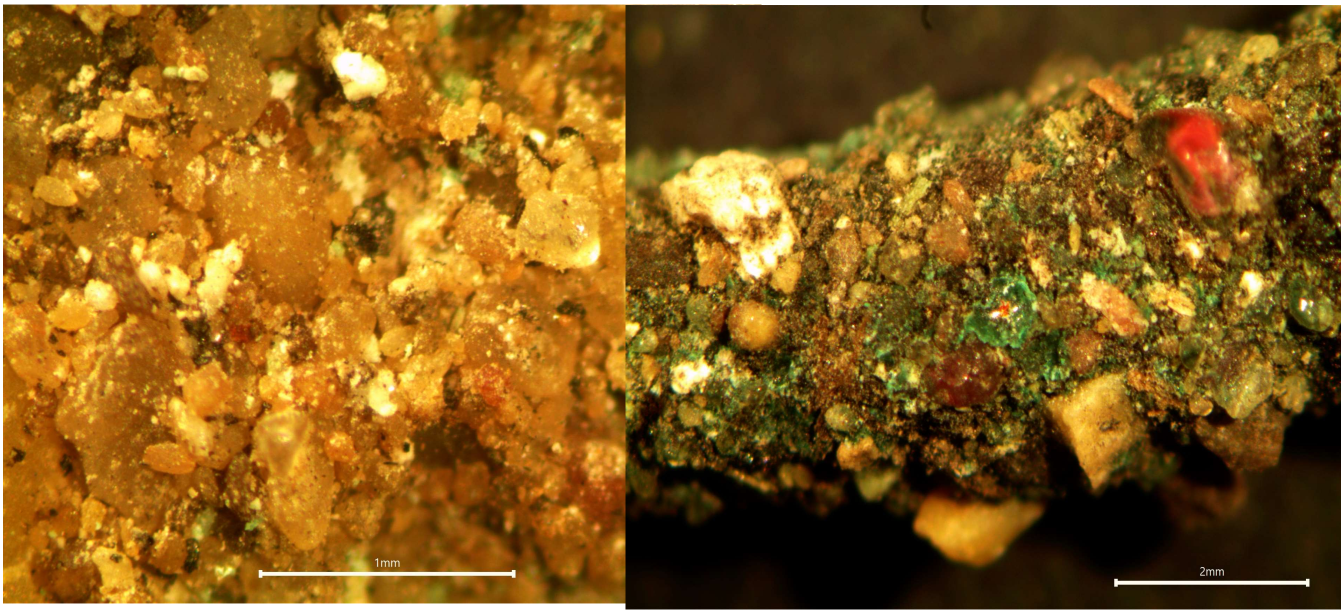


Fig.6.1.2. The sand crust formations: chisel (Sq. 39, US: 4) on the left and pin on the right.

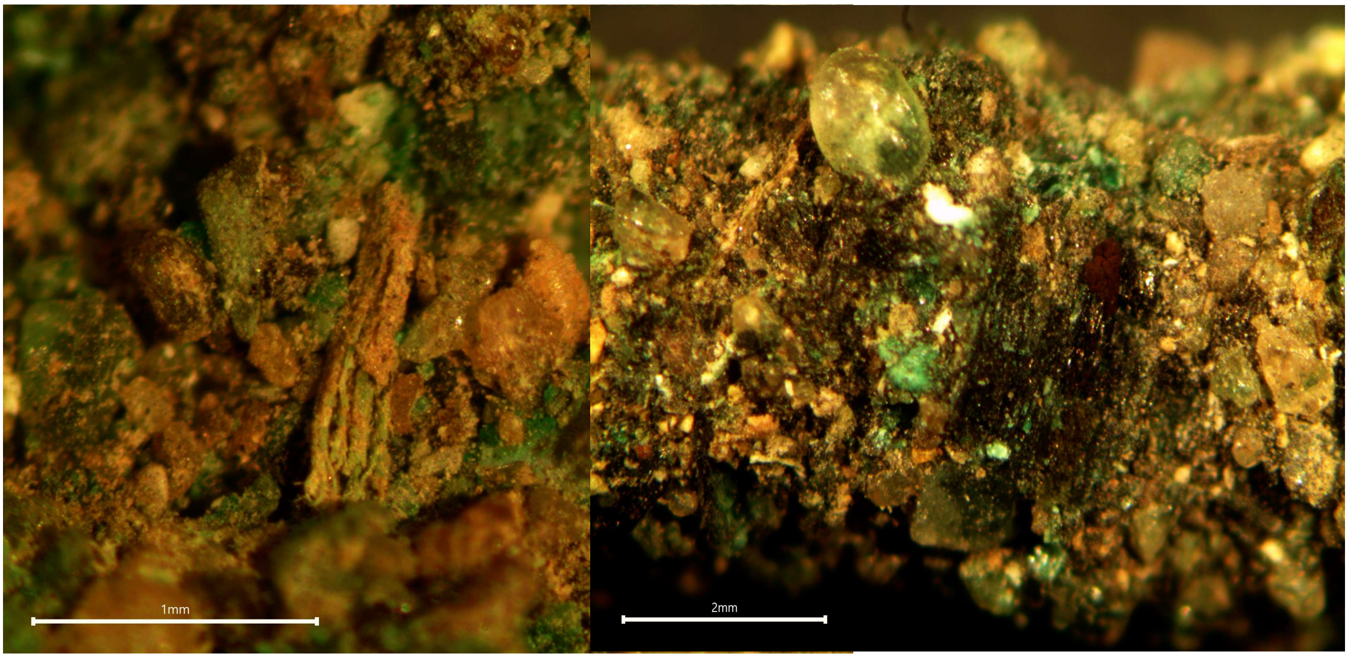


Fig.6.1.3. The organic remains. On the left: fiber ("plaque"). On the right: charcoal (pin).

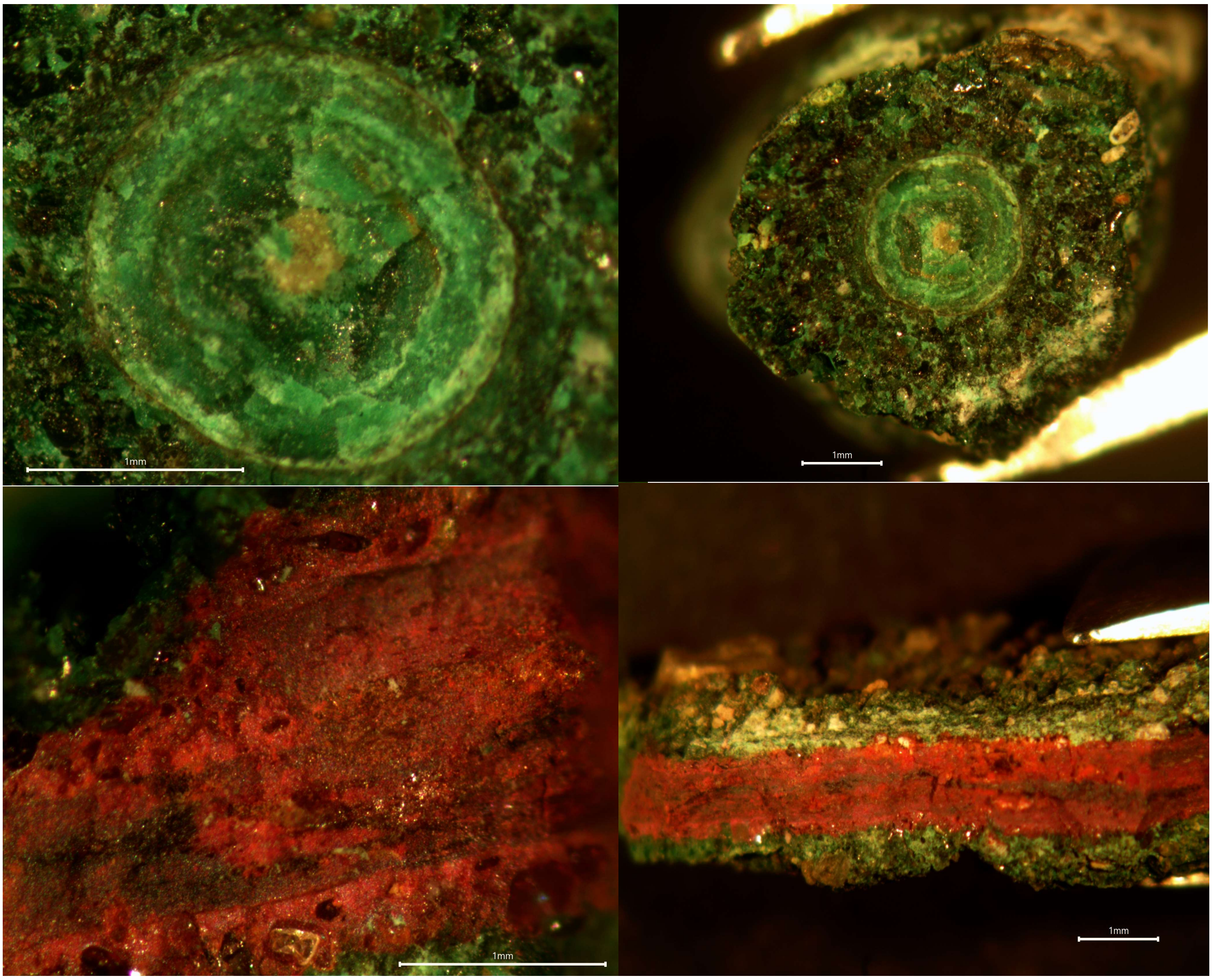


Fig.6.1.4. Upper left and right: the cross section of the chisel (Sq. IV E, US: 2c). Lower left and right: the cross section of the "plaque".

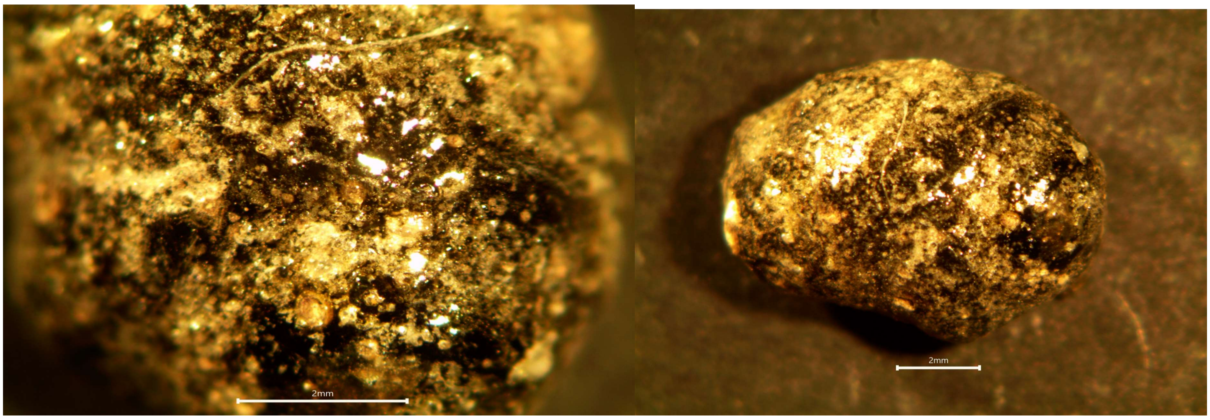


Fig.6.1.5. The silicate by-product of the smelting process.

6.2. Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) Analyses

The surface analysis of ten objects was performed using the Field Emission Scanning Electron Microscope, Auriga Zeiss model, equipped with microanalysis EDS – 123 Mn Kα eV (Bruker) at Research Centre for Nanotechnologies Applied to Engineering of Sapienza (CNIS).

The aim of this research was to identify the corrosion products and their structural relation with the original parts of the objects. Another goal was to define the elemental distribution on the surface of the object and recognize the overall morphological features of the samples.

No sample preparation was needed so the samples were not coated by any means. The samples were analysed in the same sample holder and properly tilted assuring an homogenous observation of the objects.

The instrument was set to 20 KV and both, 3D-backscattered electrons and secondary electrons modes were selected depending on the area under study and the kind of data needed to be acquired.

According to the sample's particular surface features, the energy dispersive spectrometry was conducted. Few spots were taken on each sample to obtain more comparable data on chemical composition of the objects. The multi-spot analysis was done with the use of the same filament voltage employed in scanning electron microscopy analysis.

Copper (Cu) is the main component of most of the samples, with the exception of one object, which appears to be principally based of silica ('slag': Sq. IV S, US: 5a, Phase: Ia, Date: 25.03.1978) (6.2.1). In most cases chlorine (Cl) and oxygen (O) appear to be dominant in creating the corrosion patina (Fig.6.2.2). The forth commonly found element is carbon (C). Only occasionally the presence of sulphur (S) and sodium (Na) are detected. Calcium (Ca) and potassium (K) seem to be the main compounds of the crust. The presence of these elements comes from the burial environment covering the majority of the studied artifacts (Fig.6.2.3). Sometimes also aluminum (Al) and magnesium (Mg) have been detected. Depending on the particular objects observed, some minor elements appear like Ni, Ag, Au, Pb, Sb, Zn, Hg, Ti and Zr (Fig.6.2.4).

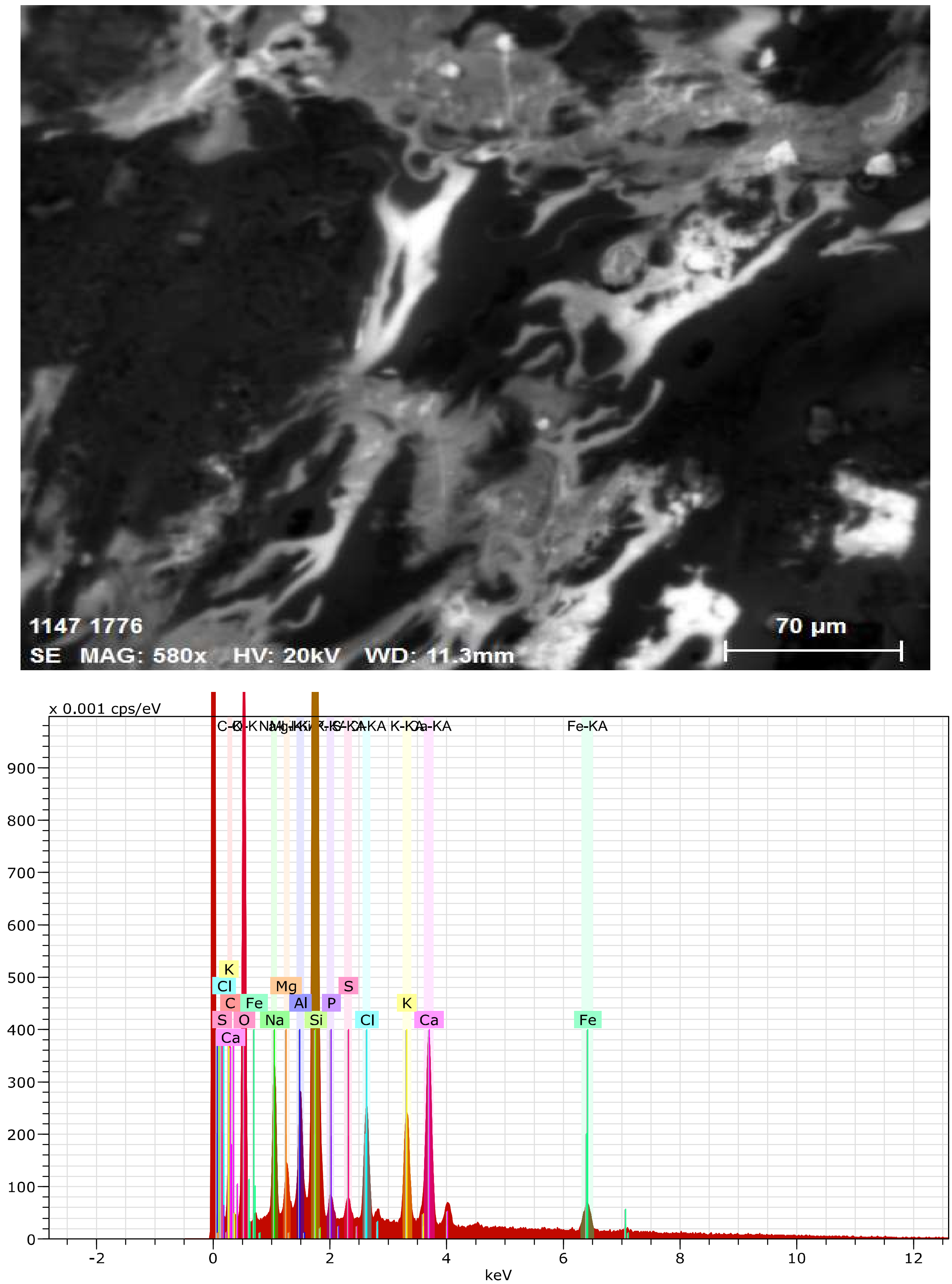
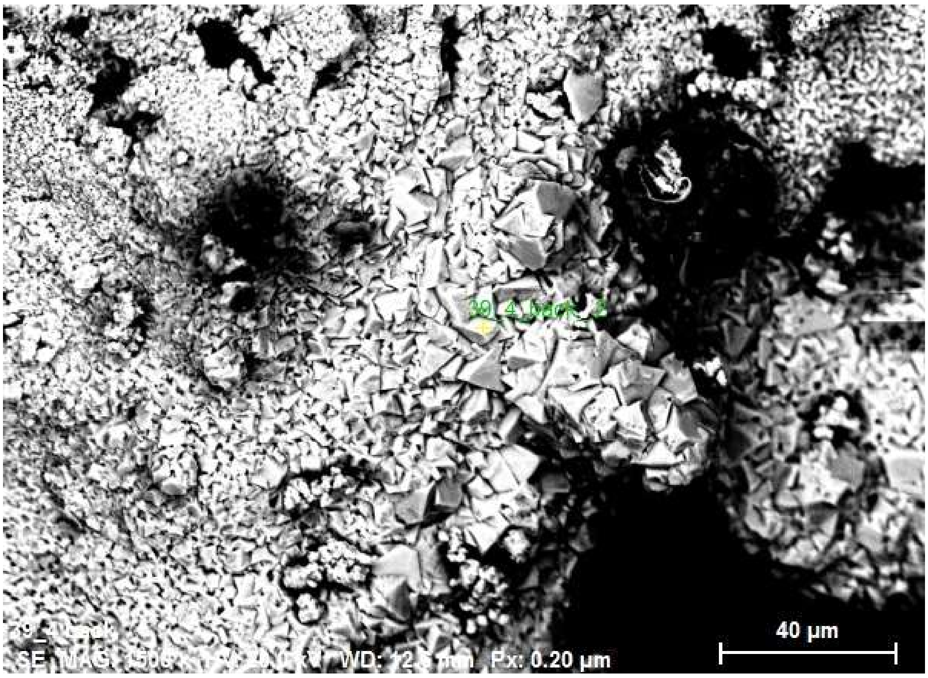
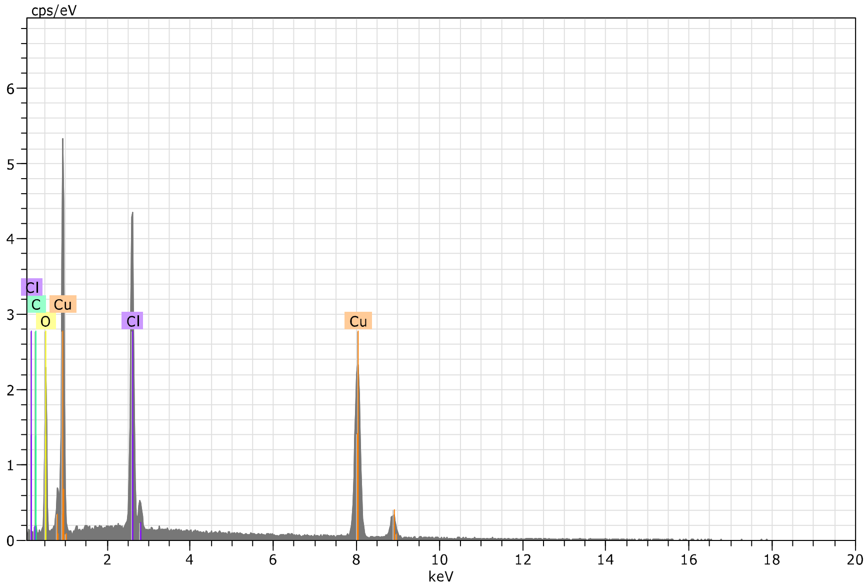


Fig.6.2.1. The surface of silicate smelting by-product and its X-ray spectra.

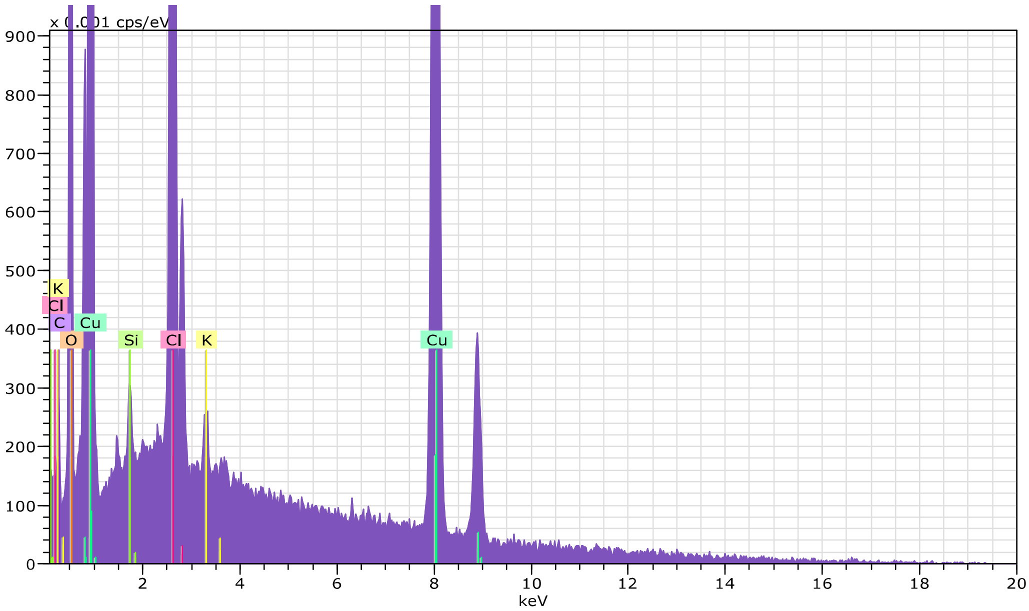




Spectrum: 39_4_back_ 2

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	18.76	20.48	40.90	3.13
Cu	29	K-series	52.67	57.51	28.92	1.53
C	6	K-series	5.38	5.88	15.64	1.80
Cl	17	K-series	14.77	16.13	14.54	0.55
		Total:	91.59	100.00	100.00	

Fig.6.2.2. The cubic structure of the chisel's (Sq.39, US:4) detaching bands area. Cl and O are main corrosion compounds of most of the studied objects in this thesis work.



Spectrum: sharp tip_ 7

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	18.56	20.53	41.46	2.70
Cu	29	K-series	51.84	57.33	29.15	1.45
Cl	17	K-series	14.61	16.16	14.73	0.53
C	6	K-series	4.65	5.14	13.82	1.26
Si	14	K-series	0.41	0.45	0.52	0.05
K	19	K-series	0.35	0.39	0.32	0.04
		Total:	90.43	100.00	100.00	

Fig.6.2.3. X-Ray spectra and elemental mass ratio of the spot located in the sharp tip area of the pin. It represents the main elemental compounds occurring in most of studied objects in this work.

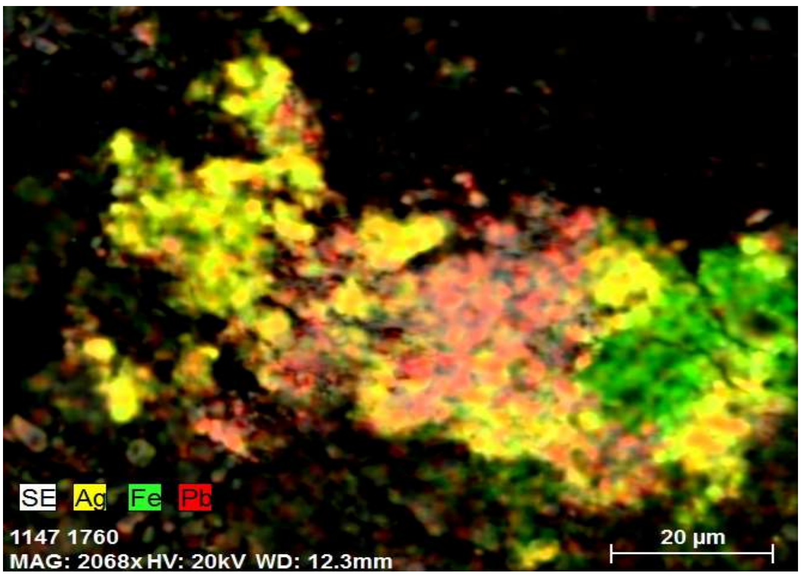


Fig.6.2.4. Elemental-mapping of Ag, Fe and Pb in the red region of the broken part of the plaque.

Several different nanostructures have been found even on the same object. Among them some structures have been detected showing spherical, rod-shaped, cubic, wire, spike and tree-like forms (Fig.6.2.4).

In three objects: pin (Sq. IV W, US: 2c α, Phase: Ia), plaque (Sq. II, US: 3c, Phase: Ia) and chisel (Sq. IV E, US: 2c, Phase: Ia), lead segregation has been identified in form of spots located on their surfaces (Fig.6.2.5; Fig.6.2.6).

The "organic materials", previously detected by Optical Microscopy analyses, have been verified by SEM-EDS tests. In particular, the plaques' fiber and the charcoal on all the samples have been thoroughly studied but, due to their very tiny sizes, it was impossible to recognize the structure and the nature of plant the fibers some from. We suppose that the fiber found on a metal artefact consists of linen as previously observed on textile findings from Maadi (Fig.6.2.7) (Gleba M. 2017, 166-170).

Some recent contaminations have been noticed on few objects. Inn the case of the chisel (Sq. 39, US: 4, Phase: Ia) some microorganisms have been recognized on the surface, which might be due to the interaction with environment after the object being found and exposed to the air.

All the main features of the objects, detected by SEM-EDS, are added to the catalogue included at the end of this thesis work.

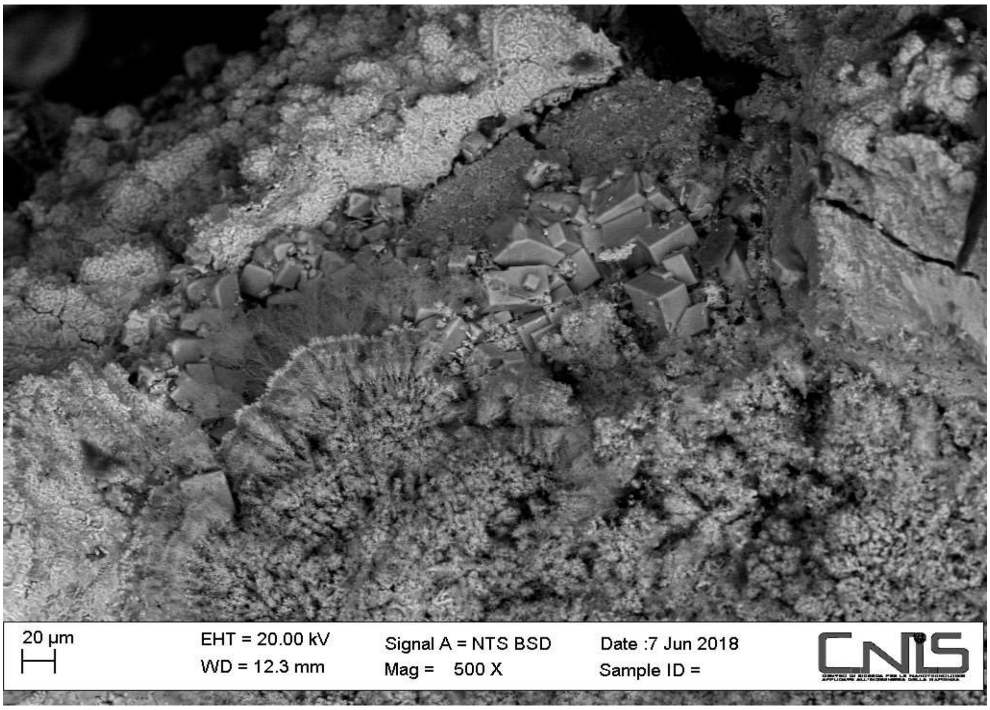


Fig.6.2.5. Different types of nanostructures: globular, cubic and tree-like, detected on the middle part of the pin.

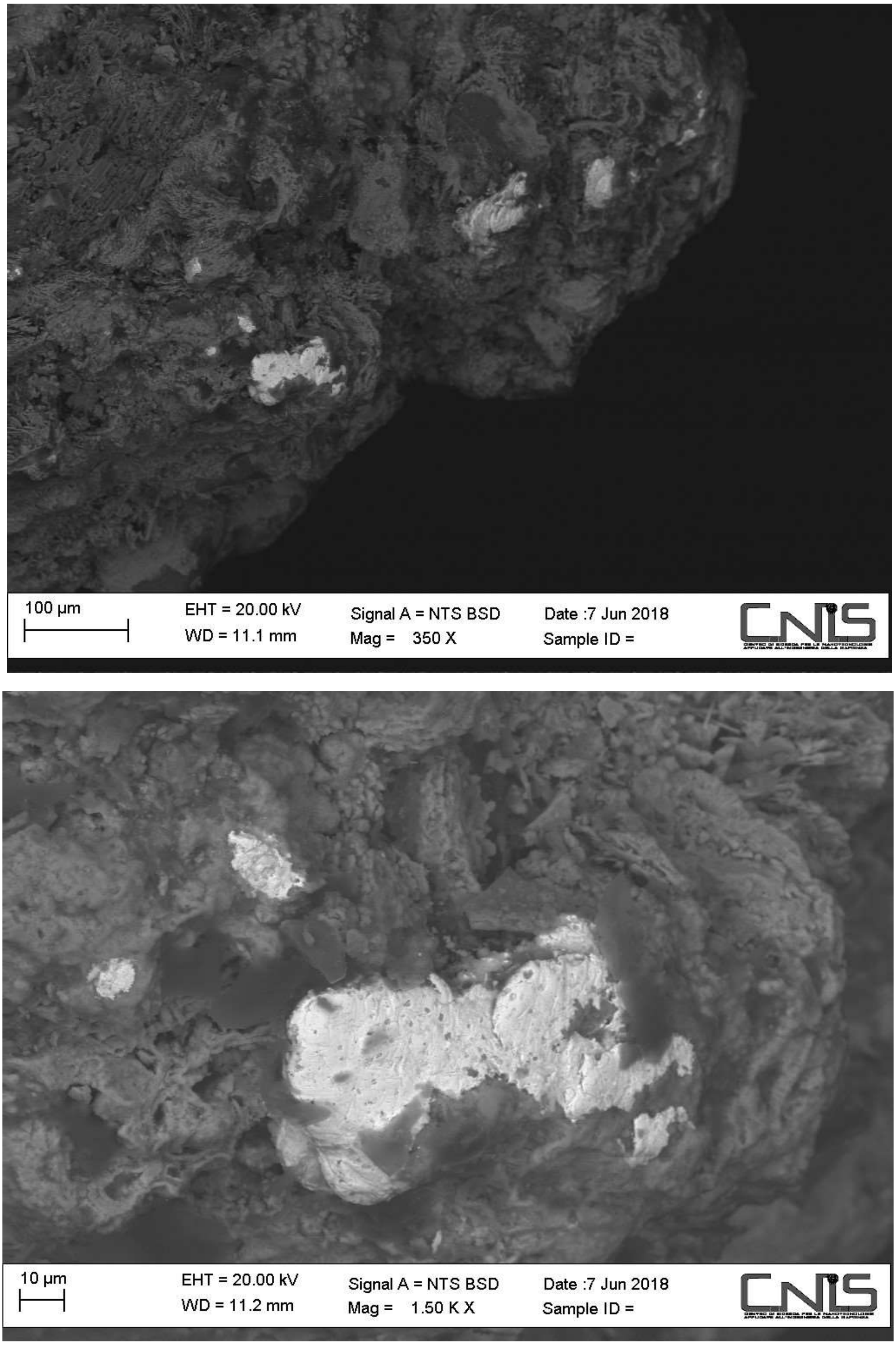
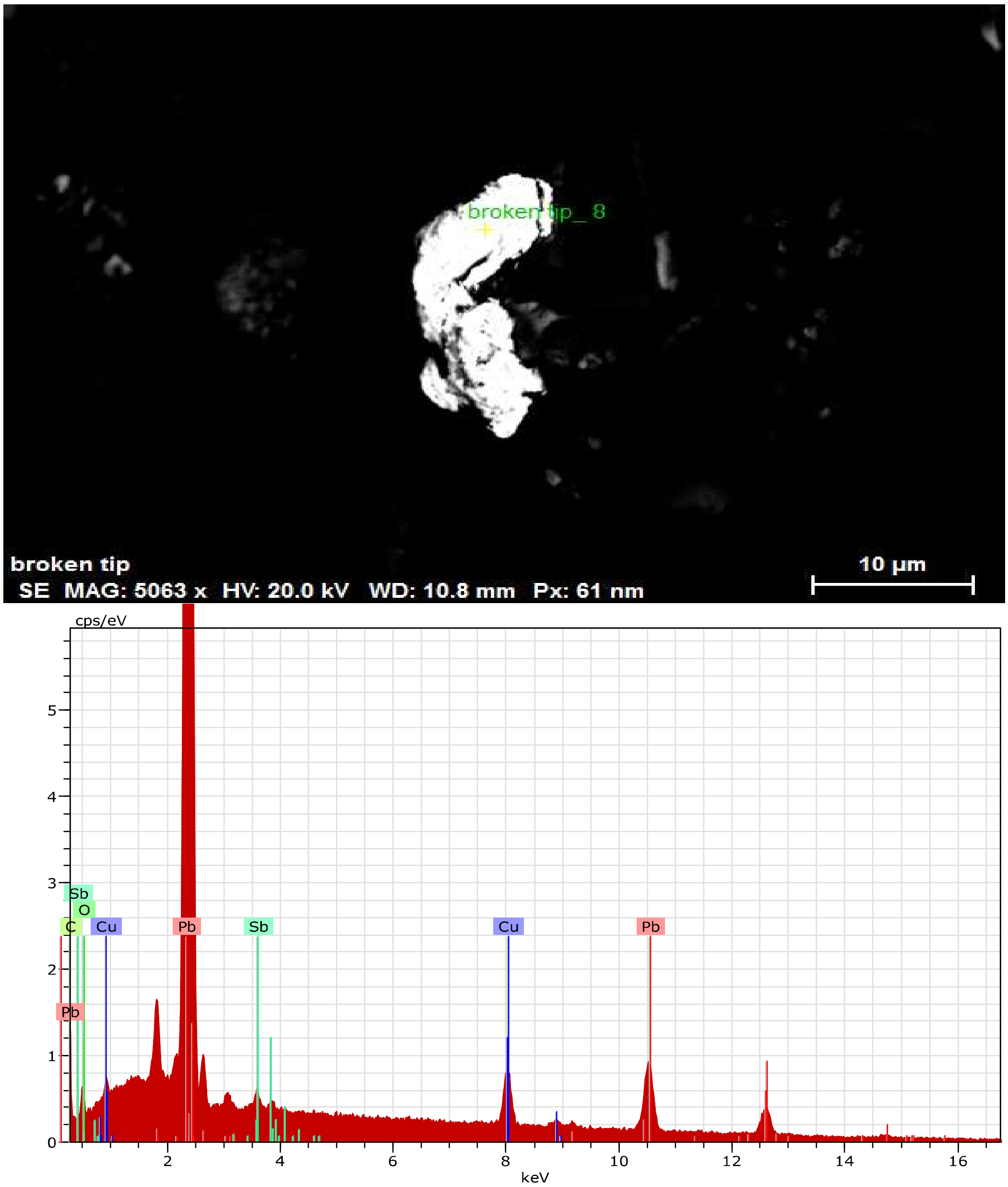


Fig.6.2.6. Lead segregation identified on the sharp tip of the pin.

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Spectrum: broken tip_ 8

El AN  Series   unn. C norm. C Atom. C Error (1
Sigma)
                  [wt.%]   [wt.%]   [at.%]          [wt.
%]
-----------------------------------------------------
-
C   6  K-series   7.88     9.36    52.00
1.28
Pb 82  L-series  65.01    77.18    24.86
2.07
```

Fig.6.2.6. On the top the picture lead spot detected on the broken tip area of the pin. Underneath, the X-ray spectra of the Pb spot and its elemental mass ratio.

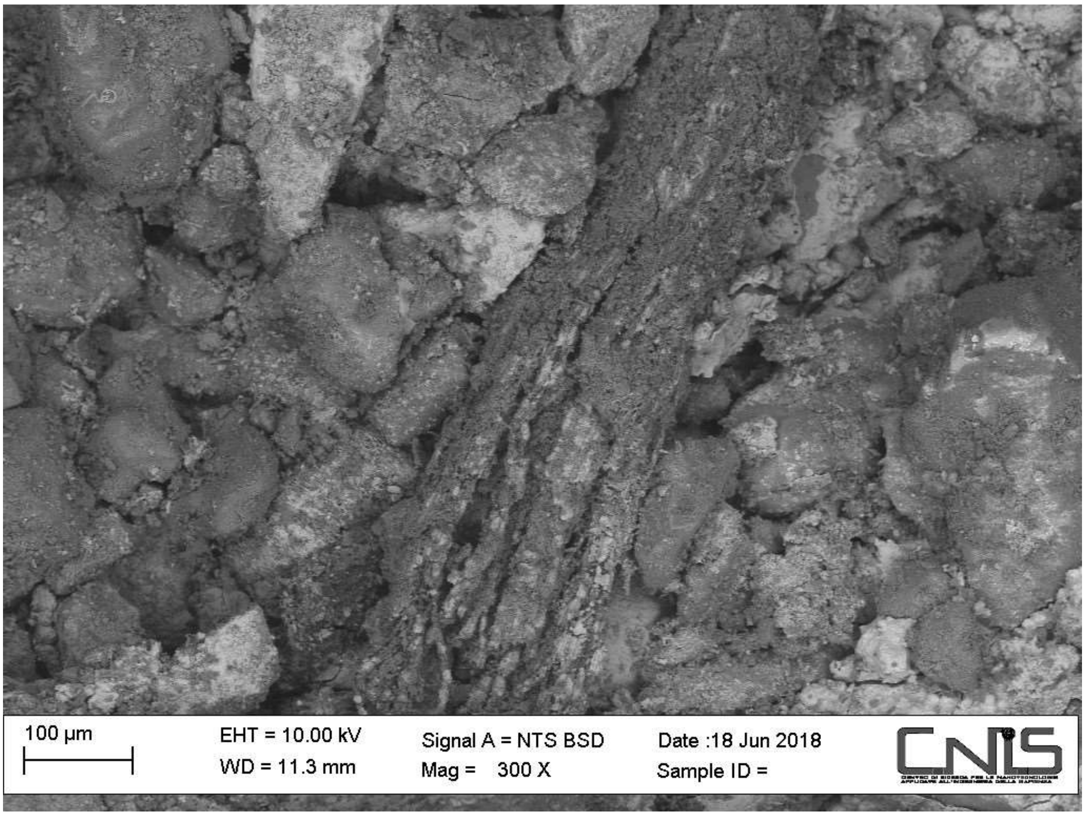


Fig.6.2.7. Fiber which was identified on the plaque’s surface (to compare with OM go to Fig.6.1.3.).

6.3. Energy Dispersive X-ray Diffraction (EDXD)

Three object were studied by the means of EDXD, which in non commercial instrument constructed by prof. R. Camminiti and his research team at Research Centre for Nanotechnologies Applied to Engineering of Sapienza (CNIS) (Caminiti R. 2006). The mapping of both sides of the objects were performed on the fixed angles: 28 and 30 degrees in theta. The parameters of the instrument are as follows: tungsten as a source set to 50 kV and 40 mA and hyper-pure germanium crystal detector from Amptek. The technique is completely non-invasive and does not require any particular sample preparation. The artefacts were mounted to the sample holder by the scotch tape.

No particular shifts of energy in fluorescence peaks were detected between those obtained at 28 and 30 degrees in theta. All of the measurements depicts the samples as primarily consisting of pure copper (Cu). Among other commonly detected minor elements are iron (Fe), strontium (Sr), calcium (Ca) and potassium (K). Generally, the samples appear to have rather homogeneous distribution of elements of both their faces, with only few exceptions. In some cases the peaks of Ca and K were overlapping and impossible to be resolute so the mass ratio concentration of both of the peaks is presented together as Ca/K wt.%. As well in some cases some trace element occurred: silver (Ag), antimony (Sb), barium (Ba), chromium (Cr) and bromium (Br). Due to their really low quantity their mass ratio concentrations are presented all together in table as one category “Other wt.%”. In order to confirm the occurrence of particular minor elements of interest, the detection sensibility of the instrument was tested by measuring the chemical substances, among them: $SrBr·H_2O$, copper nanoparticles 99.8%, lead metal powder and silver nitrate.

Due to time and instrument access restrictions only few samples were chosen for further analysis by the means of EDXD. The choice was based on the type, function, value of the objects and their state of preservation. Among the studied in this way artefacts was “plaque” (Fig.6.3.1) on which in total 12 measurement points were taken, six per each of the sides (Tab.6.3.1). Most of the measurements are corresponding to each other. Copper appears to be the main component of the artefact while other elements are iron, calcium/potassium and strontium. The minor elements quantity differs greatly in particular spots. Of particular interest is the almost complete lack of the strontium in exposed, broken part of the artefact and it high content even reaching around 2,5 % in the other areas.

Similarly, in case of Fe content varies from 0.22% to 5.11% and Ca/K from 0.34% to 3.12% (Fig.6.3.2).

Fig.6.3.1. The points measured by the means of EDXD on the "plaque". Also in the central part of the objects the points were taken from both sides: II3C28 (Fig.6.3.2), II3C30 (Face 1) and II3D28, II3D30 (Face 2).

Point	Cu wt.%	Fe wt.%	Ca/K wt.%	Sr wt.%	Other wt.%
II3AL28	99.32	0.24	0.42		0.02
II3AL30	99.29	0.22	0.34	0.03	0,12
II3ALB28	93.79	3.82	1.63	0.76	
II3ALB30	93.15	4.31	1.86	0.68	
II3ALBS28	92.38	4.36	0.93	2.33	
II3ALBS30	89.99	4.27	3.12	2.56	0.06
II3ALBD28	91.44	3.81	2.24	2.51	
II3ALBD30	93.86	3.47	2.12	0.3	0.25
II3C28	92.03	5.11	1.3	1.56	
II3C30	92.52	4.78	0.94	1.61	0.15
II3D28	76.98	5.08	1.56	15.78*	0.6
II3D30	84.8	4.39	0.86	9.95*	

Tab.6.3.1. Table with points taken by EDXD on the both sides of the "plaque" (Sq. II, US 3c).
*the strontium signal was tested and enhanced by adding SrBr· H_2O.

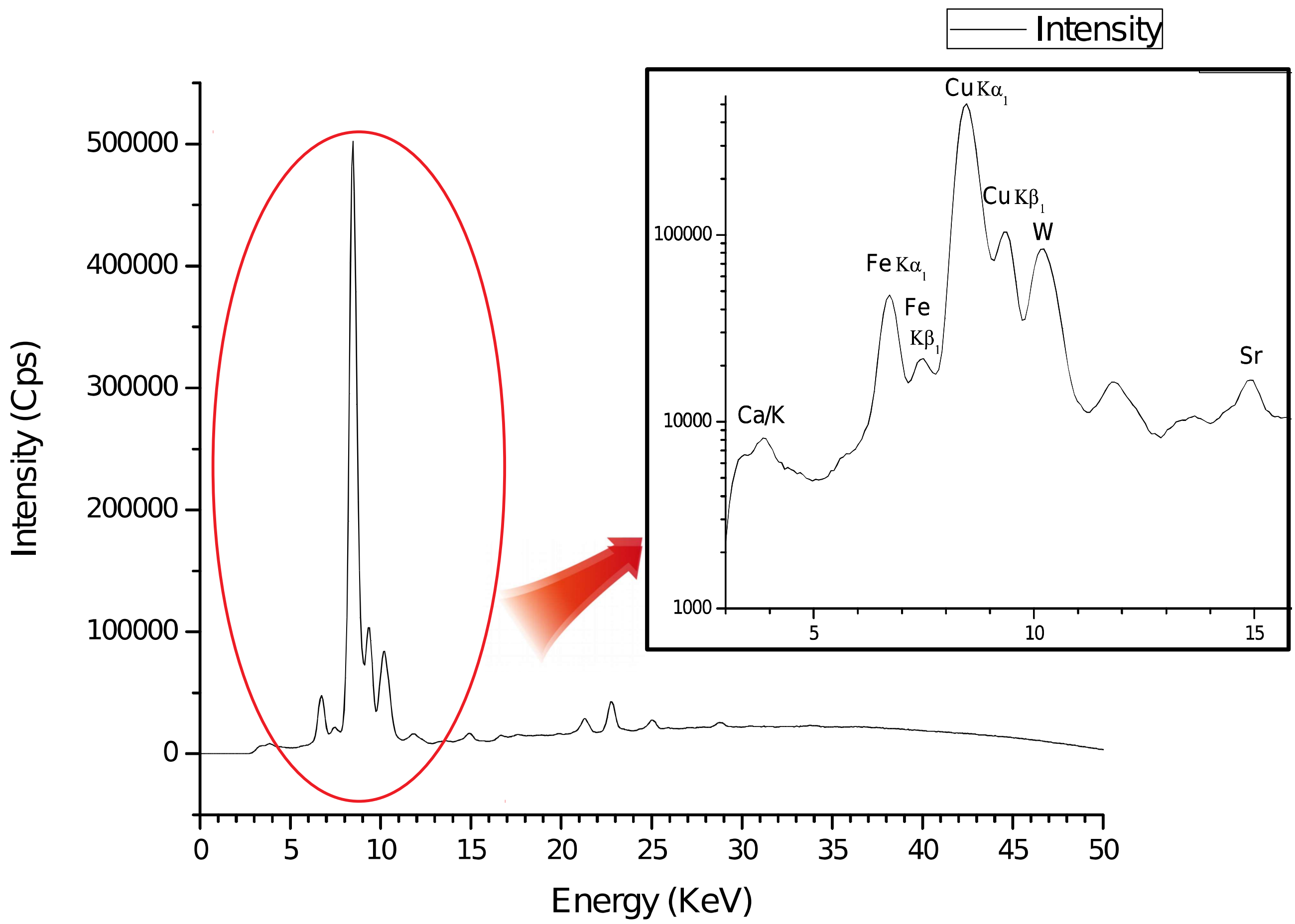


Fig.6.3.2. EDXD spectra of plaque point II3C28 with visible peaks of Ca/K, Fe, Cu, Sr and W (from the source). The peaks appearing between the range of 11-13 keV are the result of the diffraction process, which is connected to the specific feature of the instrument.

The pin (Fig.6.3.3) was the most important artefact due to its state of preservation and known function. Most of the surface is covered by the thick crust made of sand particles. Nevertheless, some of the areas were deprived from the crust and fairly exposed in the middle and at the ends of the pin. In this case the object seems to be produced from very pure copper (Cu) from around 94% where covered with crust to even 96-98%` in the area without sand cover. In the crust regions the Ca/K reaches 1.66% to around 2,7%. Also the difference appears in the strontium content, in the crust it reaches around 0,4-0,7 % while in the exposed area it is occurrence is much lower 0.02-0.11 %. In total 6 point were measured on the object in the more thicker areas which were more accessible for the instrument (Tab.6.3.2; Fig.6.3.4).

Fig.6.3.3. The points measured by the means of EDXD on the pin.

Point	Cu wt.%	Fe wt.%	Ca/K wt.%	Ca wt.%	Sr wt.%	Other wt.%
IV2CM28	98.05	1.47	0.37		0.11	
IV2CM30	96.29	3.05	0.64		0.02	
IV2GR28	93.74	3.06	1.65		0.44	1.11
IV2GR30	94.21	2.92	2.06		0.58	0.23
IV2PU28	94.68	1.88	2.7		0.71	0.03
IV2PU30	94.65	2.08		2.67	0.59	0.005

Tab.6.3.2. Table with points taken by EDXD on the both sides of the pin (Sq. IV W, US 2c).

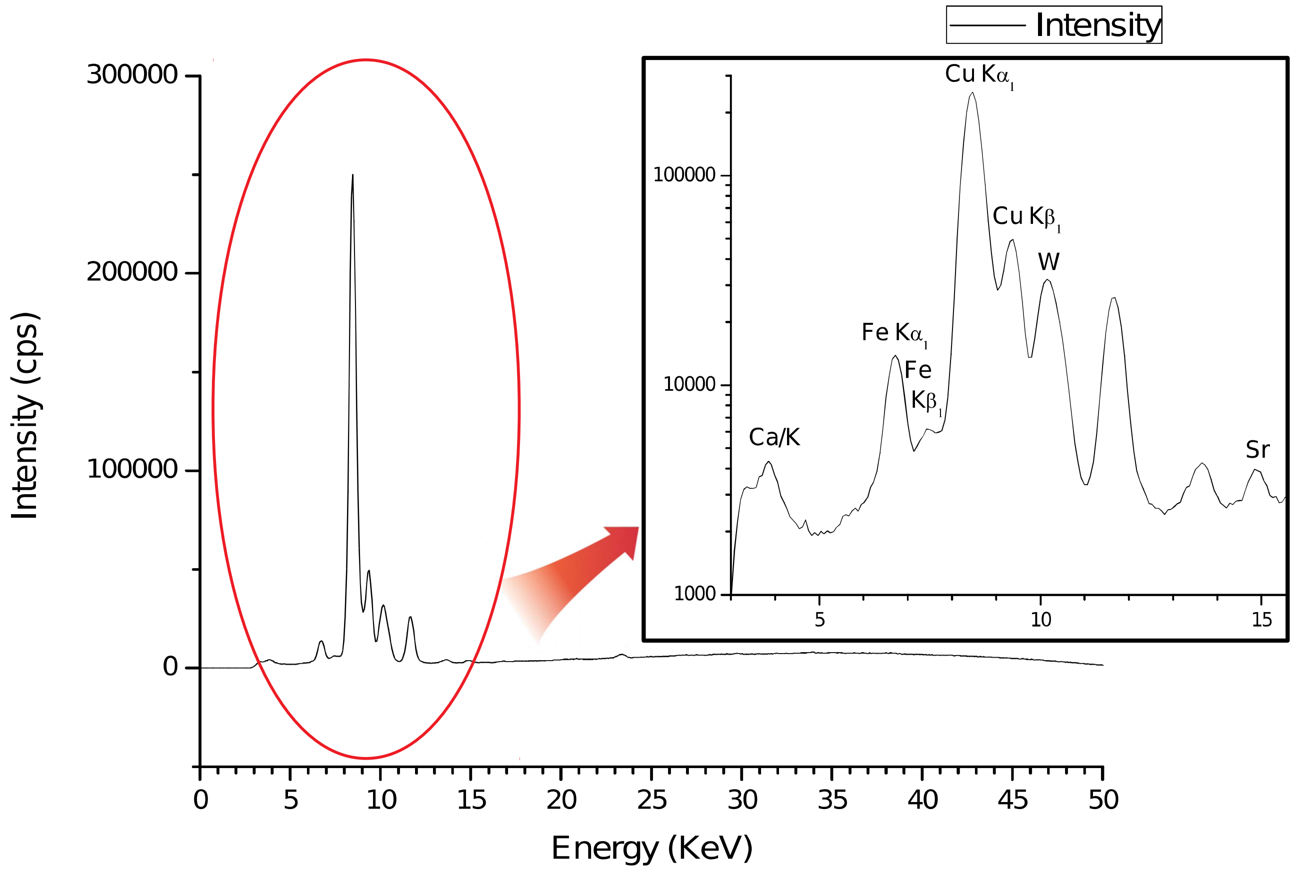


Fig.6.3.4. EDXD spectra of pin point IW2GR28 with visible peaks of Ca/K, Fe, Cu, Sr, W (from the source). The peaks appearing between the range of 11-13 keV are the result of the diffraction process, which is connected to the specific feature of the instrument.

The another sample is object which might played in a past a role of the chisel (Fig.6.3.5). It consists of two parts: bigger (G) and smaller (P) in size. The mapping of both pieces were performed and the results are similar in both cases. 11 spots were taken on bigger part and 6 on smaller one. The area slightly differ in the distribution of the particular elements but composition of copper (Cu) usually comprise 96-97%, iron (Fe) 1.5-2% (in some cases reaching even more then 4%); calcium/potassium (Ca/K) 1-2 % and strontium (Sr) more or less 0.5 %. Nothing particular was noticed in the case of the trace elements (Tab.6.3.3; Fig.6.3.6).

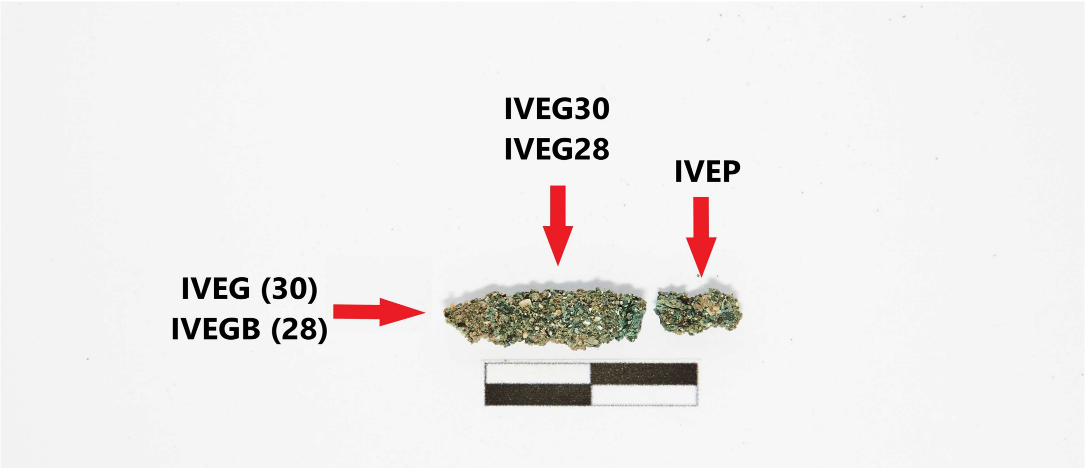


Fig.6.3.5. Some of the points measured by the means of EDXD on the chisel. Also the same procedure was repeated for the other site of the artefact.

Point	Cu wt.%	Fe wt.%	Ca/K wt.%	Ca wt.%	Sr wt.%	Other wt.%
IVEG – 30	96.12	2.2		1.04	0.5	0.14
IVEG2 -30	96.36	1.84		1.12	0.48	0.2
IVEGB-28	95.1	2.5	1.77		0.58	0.05
IVEG28A	96.43	1.51	1.92			0.07
IVEG28B	96.94	1.73		0.97	0.37	0.01
IVEG28C	94.99	3.51	0.95		0.51	0.04
IVEG30	96.13	2.56		1.06	0.18	0.07
IVEG30A	96.45	1.95		1.59	0.01	
IVEG30B	97.36	1.52		0.91	0.19	0.02
IVEG30C	94.24	4.29		1.11	0.32	0.04
IVEGB	96.86	1.85		0.84	0.37	0.09
IVENP	97.94	1.39		0.48	0.18	0.01
IVENPB	97.05	1.68	1.04		0.23	
IVENPB1	96.33	0.76	2.28		0.29	0.34
IVENPB2	96.02	1.55	2.1		0.1	0.23
IVEPA	97.39	1.54	0.87		0.2	
IVEPB	97.45	1.49	0.76		0.3	

Tab.6.3.3. Table with points taken by EDXD on the both sides of the “chisel” (Sq. IVE, US 2c) (G – bigger piece; P – smaller piece).

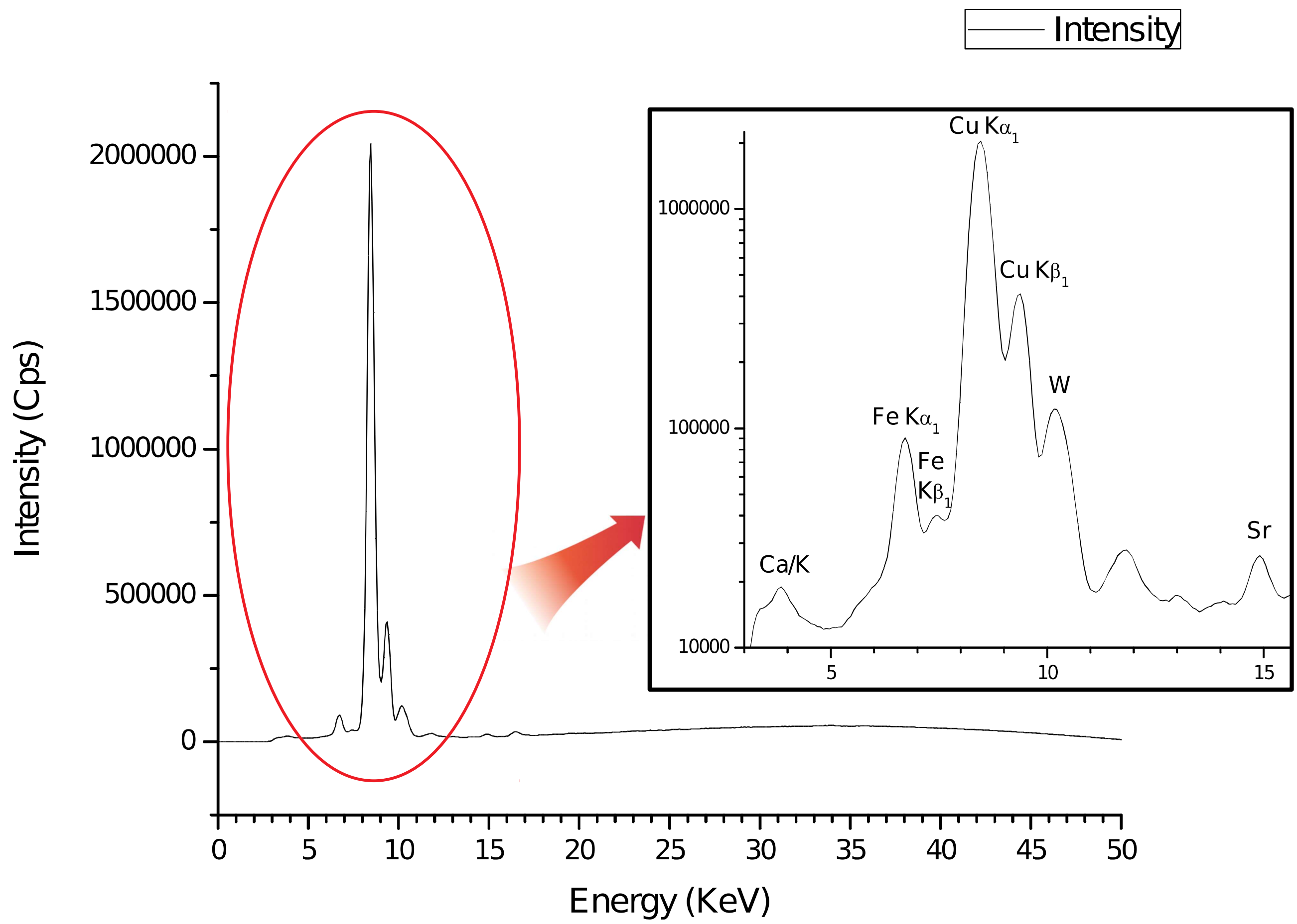


Fig.6.3.6. EDXD spectra of chisel point IVEG28 with visible peaks of Ca/K, Cu, Fe, Sr, W (from the source). The peaks appearing between the range of 11-13 keV are the result of the diffraction process, which is connected to the specific feature of the instrument.

6.4. X-ray Diffraction (XRD)

XRD analysis was applied for identification of the minerals, coming from the environment where the artefacts were deposited as well as for recognizing the particular products and the phases of the corrosion. The instrument used for the analysis was a Rigaku D-max Ultima+Xray Diffractometer which employs Cu Kα. radiation. The starting angle was 20 degrees and terminating 90 degrees. Working condition was set to 50 keV and 24mA. The total scanning time per sample was 70 min.

The obtained spectra was processed in a data processing software and identification of the peaks was supported by QualX2, Maud and FindIt software with the use of free POW_COD database for inorganic components. For the recognition of the peaks were used rruff.info online database as well articles, touching the issue of the copper based archaeological material studies (Chmielov á M., Seidlerov a J., Weiss Z. 2003, 883–889; Lau D., Kappen P., Strohschnieder M., Brack N., Pigram P. J. 2008, 1283-1289; Di Carlo G., Giuliani C., Riccucci C., Pascucci M., Messina E., Fierro G., Lavorgna M., Ingo G.M. 2017, 120–127; Knotkova D., Kreislova K. 2007, 107-142; Wells A. F. 1949, 175-180).

Two artifacts were chosen for the XRD analysis: “plaque” and “chisel”. The pin was skipped due to its importance and fine state of the preservation. In order to better understand the structure and chemical composition relation of the object, the decision was made to separate and prepare individual powder samples for both crust and core. The measurements of the all samples were performed by implementing two different sample holders: cylindrical and regular one. Better results were obtained by employing the latter, which spectra are presented here in this chapter.

The XRD analysis of “plaque” parts revealed the results which were expected due to previously conducted Optical Microscopy and Scanning Electron Microscopy of the cross-section of the sample (Fig.). The crust of the object seems to be mainly composed of grains of quartz (SiO_2) and calcite ($CaCO_3$) (Fig.6.4.1), which are typical for the dry desert environment where sample was deposited. Meanwhile, the core is made of cuprite (CuO_2) which is specific to dry, anaerobic deposit conditions (Fig.6.4.2).

In case of the chisel, the interpretation of the XRD results appeared to be more complicated. The Optical Microscopy and SEM analyses of the object’s inter section show that the artefact is composed of several corrosion layers and only tiny remain of the original core. The chisel crust seems to be composed of similar components as plaque: quartz (SiO_2) and calcite ($CaCO_3$) but here with the prevailing form of aragonite (Fig.6.4.3). Also some K feldspar peaks were detected. With XRD analysis $Cu_2Cl(OH)_3$ composition was confirmed but it was difficult to distinguish atacamite from clinoatacamite. Their crystalline structures are very similar (Di Carlo G., Giuliani C., Riccucci C., Pascucci M., Messina E., Fierro G., Lavorgna M., Ingo G.M. 2017, 123). In this case, also the analysis is affected by the fact that it was impossible to seperate all inner corrosion layers of the object due to its really small size and hardness (Fig.7.3.). The XRD analysis needs to be supported by the FTIR evaluation of the chisel core.

Quite interesting is the clear difference between the cores of plaque (cuprite) and chisel (atacamite/clinoatacamite), which were deposited in the same environment in the areas not far from each other. The desert conditions are more favourable for cuprite emergence. The appearance of the atacamite/clinoatacamite corrosion products seem to be more surprising in this case. The atacamite/clinoatacamite are connected to direct access to salty water environment (mainly marine). Here, it can be explained by the sporadic unpredictable geological processes which can be connected to water precipitation, the oxygen access, the movement of the water table of river and also the loose, not compacted composition of sand which support the transport of chemical substances within the soil (Quaranta M. 2009, 12-13).

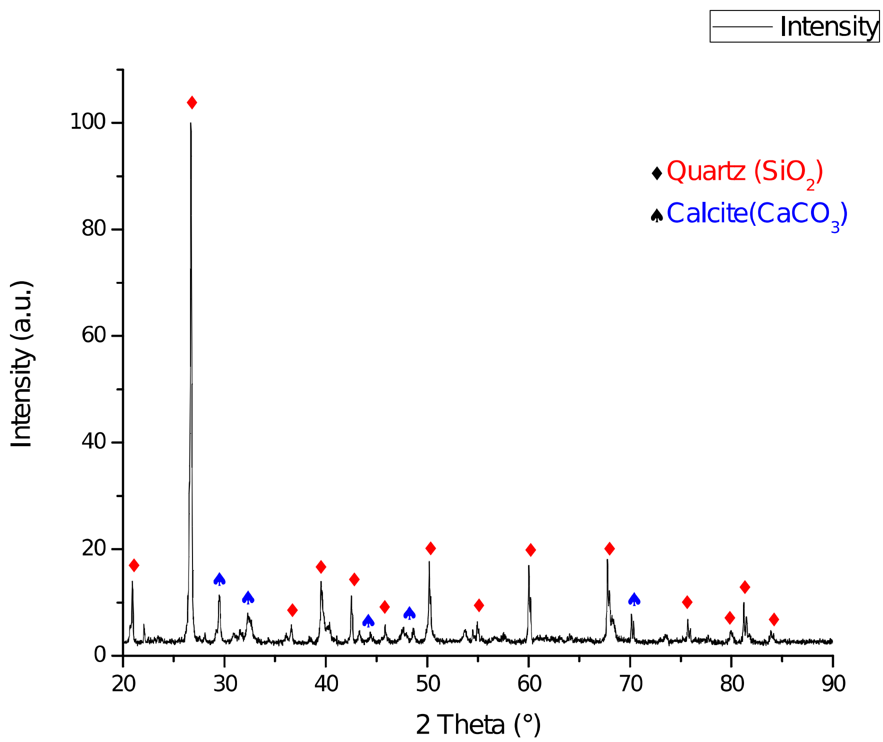


Fig.6.4.1. The XRD spectra of "plaque" crust.

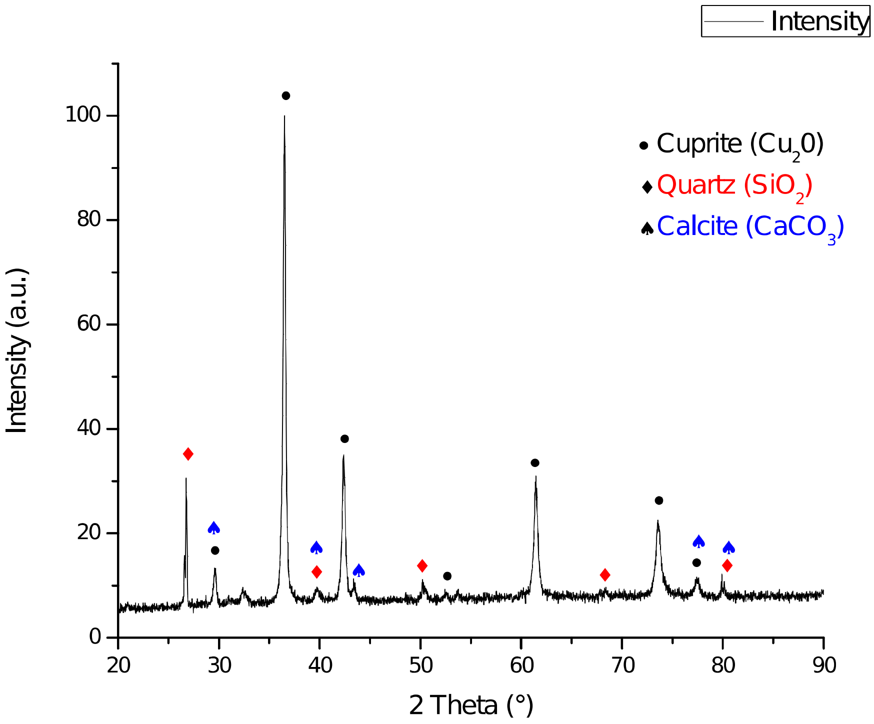


Fig.6.4.2. The XRD spectra of “plaque” core.

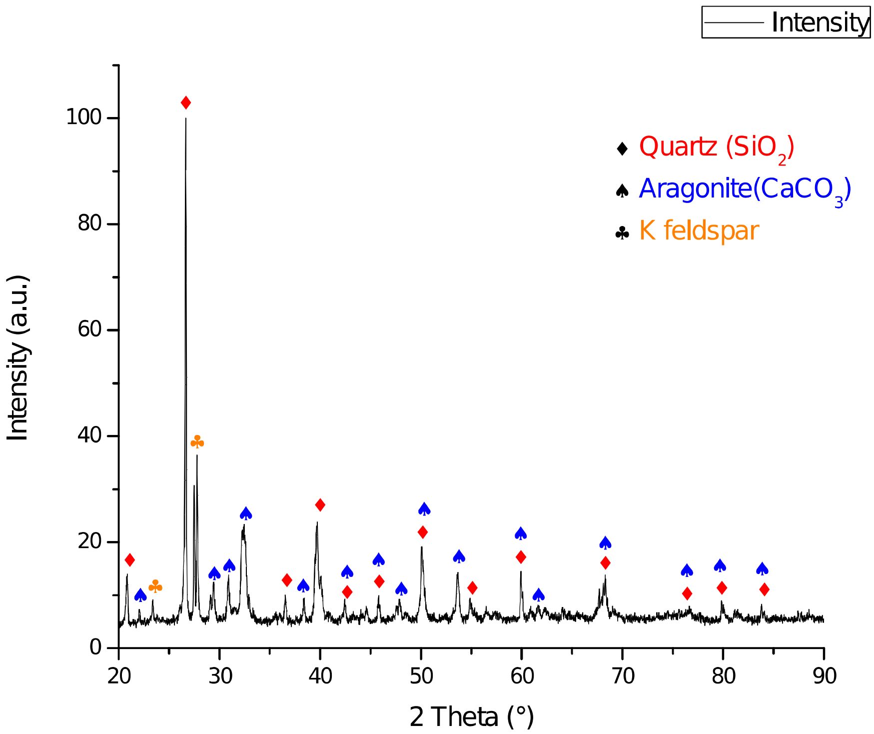


Fig.6.4.3. The XRD spectra of “chisel” crust.

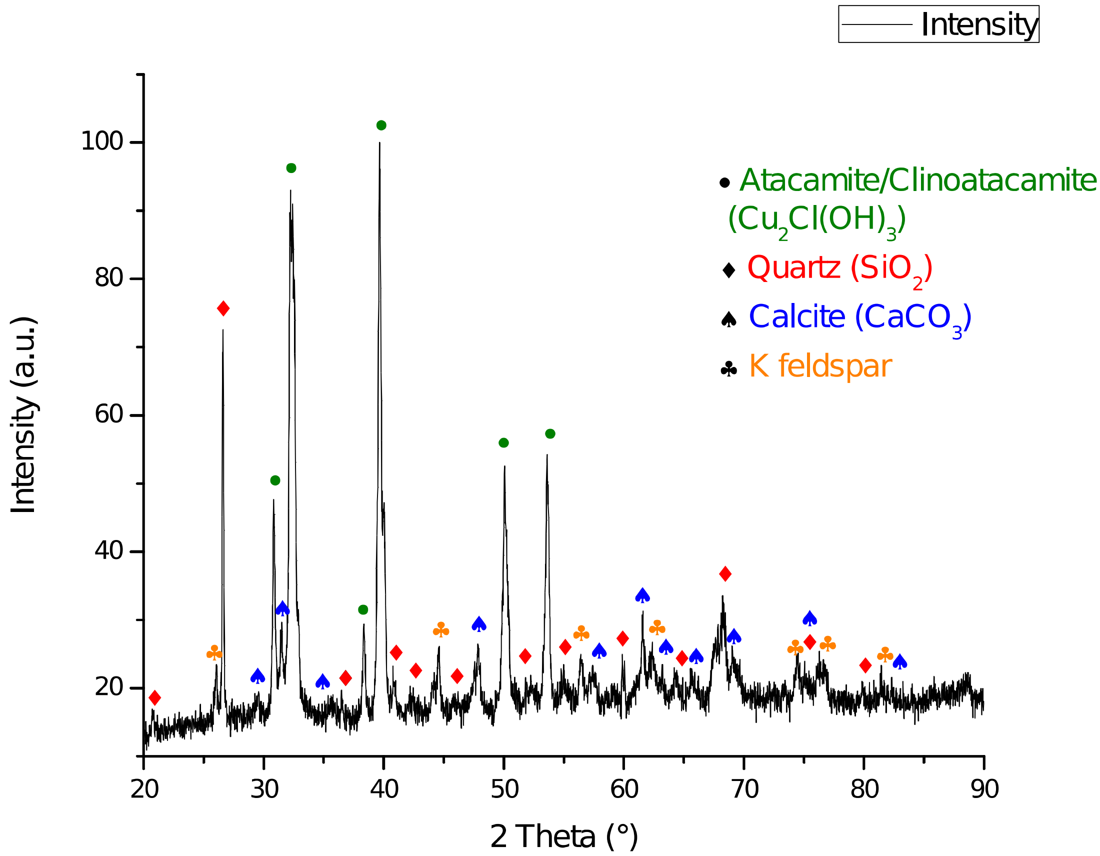


Fig.6.4.4. The XRD spectra of "chisel" core.

6.5. Fourier-Transform Infrared Spectroscopy (FTIR)

Two samples were studied by ALPHA FTIR Spectrometer from Bruker with OPUS 7.0 software. The surface material were collected from pin and chisel samples and subsequently was turned into powder. Afterwards, KBr pellets were prepared and further the samples were analysed.

The aim was to perform additional test for the analysis of the corrosion patina and identify possible organic compounds located on the surface of the objects, which presence was indicated by previously conducted Optical Microscopy and SEM-EDS analyses.

Of the great importance was to try to distinguish between different copper hydroxichlorides polymorphs: atacamite and clinoatacamite, which are expected to compose separate layers in very close relation in the chisel object. This theory is based on the data obtained through Optical Microscopy and SEM-EDS observations. XRD was also performed but it was not possible to distinguish the particular polymorphs because of their diffractograms similarity.

All the spectra here are presented in the absorbance mode. Because of the complexity of the obtained spectra, the general view (Fig.6.5.1a) is presented as first and then closer look on spectra at ranges 4000-2000 cm^{-1} (Fig.6.5.1b) and 2000-400 cm^{-1} (Fig.6.5.1c). The identification of the peaks was supported by the literature of similar nature: Di Carlo G., Giuliani C., Riccucci C., Pascucci M., Messina E., Fierro G., Lavorgna M., Ingo G.M. 2017, 120–127; Martens W., Frost R. L.,Williams P. A. 2003, 197-215; Quaranta M. 2009, 49-52; Socrates G. 2001.

The obtained results for both, pin and chisel, show great similarity. For this reason the both spectra were put together for better comparison (Fig.6.5.1a, b, c). The same corrosion products were detected in pin and chisel: atacamite, clinoatacamite and malachite. Clinoatacamite peaks prevail and are followed by atacamite. Some of the peaks were associated with malachite. As for the crust components, the peaks of calcite, quartz and aluminosilicates were recognized. Except that, O-H stretching appeared as broad peaks around 4000-3600 cm^{-1} and KBr associated with pellet occurred around 2350 cm^{-1}.

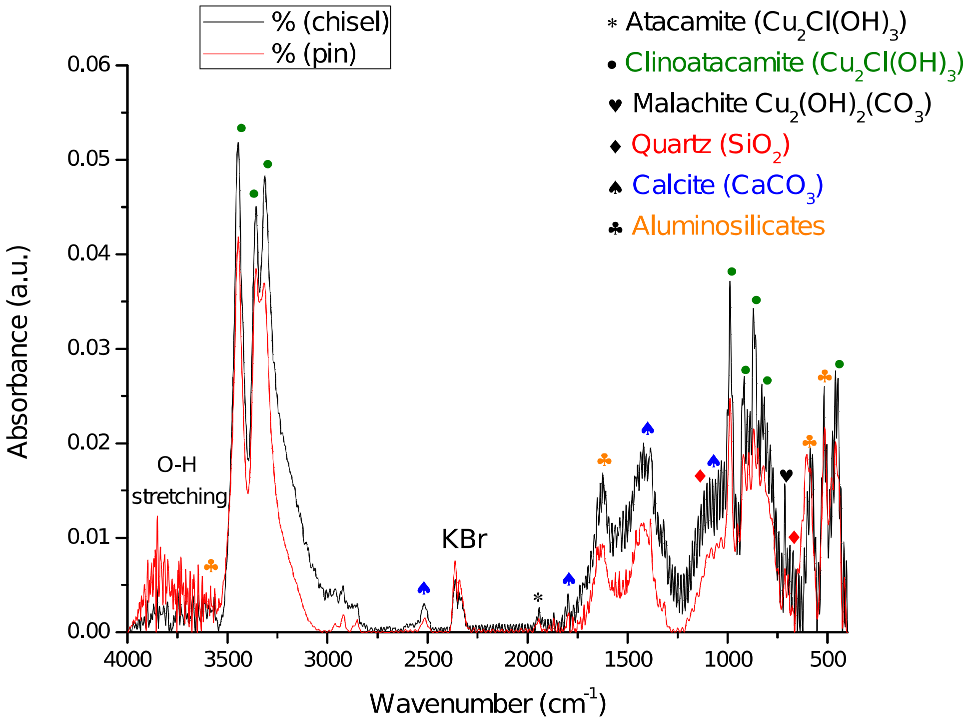


Fig.6.5.1a.

Comparison of the general FTIR absorbance spectra of chisel and pin.

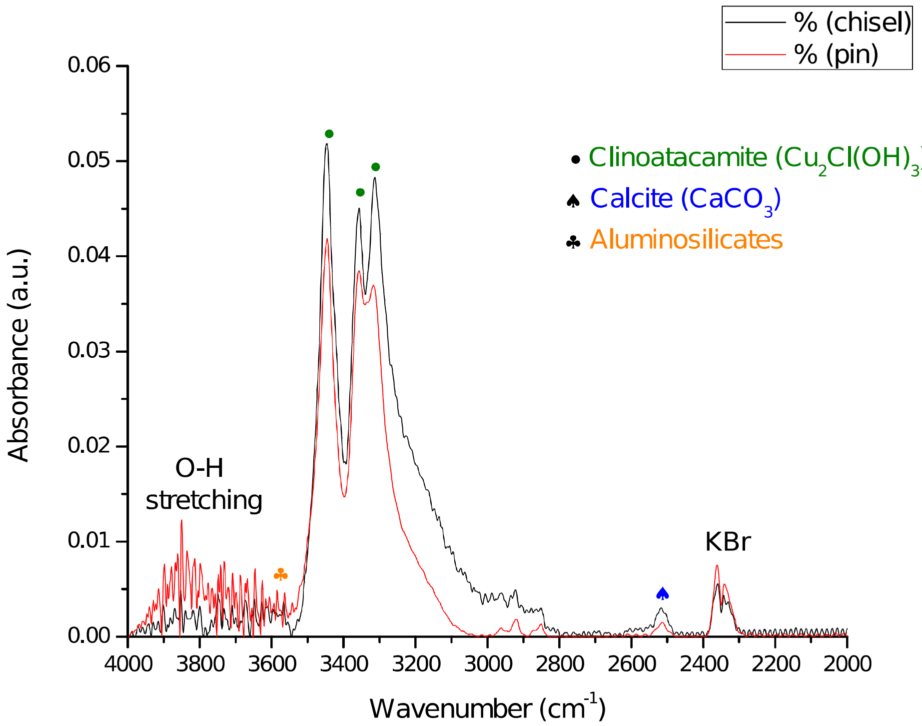


Fig.6.5.1b. Comparison of FTIR absorbance spectra of chisel and pin at the range of 4000-2000 cm^{-1}.

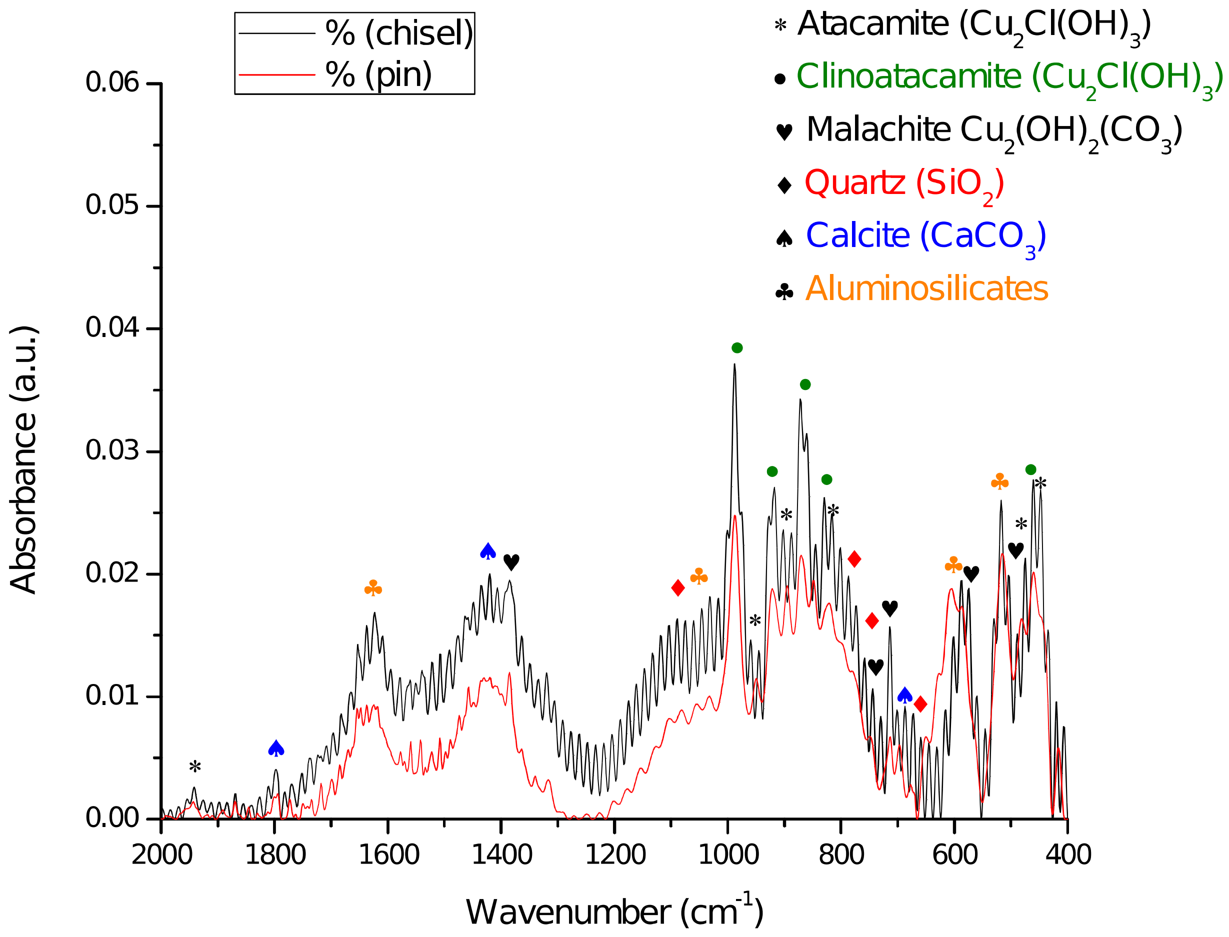


Fig.6.5.1c. Comparison of the general FTIR absorbance spectra of chisel and pin. Closer look on spectra in the range of 2000-400 cm-1.

6.6. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively coupled plasma mass spectrometry (ICP-MS)

For the determination of the trace elements composition of the objects, an inductively coupled plasma optical emission spectrometer (ICP–OES; Vista MPX CCD Simultaneous; Varian, Victoria, Mulgrave, Australia) using axial view mode and equipped with cyclonic spray chamber was used. For the recognizing the Ag and Au components, an inductively coupled plasma mass spectrometry (ICP-MS; 820-MS; Bruker, Bremen, Germany) equipped with a glass nebulizer (0.4 mL min^{-1}; MicroMistTM; Analytik Jena AG, Jena, Germany) was chosen (Tab.6.6.1).

The knowledge of trace element content is essential in the provenance studies of the raw materials. Some details about the exact elemental composition of metal objects can serve as a footprint, which can help in identyfying the geological source from where copper ore comes.

The same two artefacts (plaque and chisel) which have been previously examined by XRD analysis, were further studied by ICP-OES/ICP-MS and Strontium Isotope Analysis. The latter will be described in the following chapter. It was decided to follow the idea to examine separetly the core and the crust parts of the objects so in total four powder samples were performed.

In the same way were prepared the samples for both, the chemical composition by ICP-OES/ICP-MS and for strontium isotope analysis. It was decided to apply the same sample preparation due to better comparison reliability/possibilities of the obtained data by both methods.

A microwave digestion (with Ethos 1 – Advanced Microwave Digestion System) was performed in 6 mL of HNO_3/H_2O_2 (in ratio 2:1; concentrated and with use of the suprapur reagents) of the four solid samples (powders). 50 mg of each solid sample was taken in order to obtain the final volume of 50 mL, from which 5mL of digest was intended for ICP-OES/ICP-MS analysis and 40 mL for Strontium Isotope Analysis. Remaining 5 mL of solution was expected to be lost during the filtration process. The samples were left inside the microwave for 1 h and 10 min. In the first 5 minutes the temperature inside reached 50° and then gradually was increasing until it reached the maximum of 180°. Afterwards, the samples were filtrated with the use of nitrocellulose filters of 0.45 μm porosity.

Blanks were subjected to a similar sample preparation and analytical procedure were deducted from all measurements. Limits of detection (LODs) and limits of quantification (LOQs) were set at three and ten times the standard deviation (SD) of the replicate blank determinations, respectively.

For the ICP-OES analysis the following standards were chosen:

- EXAXOL ITALIA, ICP STANDARD MULTIELEMENTO; 1µg/ml: Al, As, Ba, Be, Bi, Cd, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Te, Ti, U, V, W, Zr; matrix: 5% HNO_3/0.2% HF.
- EXAXOL ITALIA, ICP STANDARD MULTIELEMENTO; 1µg/ml: 10 Fe, Zn – 50 B, P, Si, Sr- 500K, Mg, Na – 1000 Ca; matrix: 5% HNO_3.
- EXAXOL ITALIA, ICP STANDARD MULTIELEMENTO; 1µg/ml: 1 Tl – 5B, Ce, Co, Sr; matrix: 2% HNO_3.

Sample	Al 237,312*	As 188,980*	B 249,772*	Ba 233,527*	Be 313,042*	Ca 315,887*	Cd 214,439*	Ce 407,347*
plaque core	773	<LOD	<LOD	<LOD	0.31	12755	0.4	19
plaque crust	2189	<LOD	<LOD	<LOD	<LOD	39751	0.4	17
chisel core	1032	<LOD	<LOD	<LOD	0.30	8405	0.4	12
chisel crust	2995	<LOD	<LOD	<LOD	0.30	48649	0.3	15
LOD	34	67	28	46	0.2	2959	0.3	10
LOQ	100	200	294	495	2	30824	3	102

Sample	Co 228,615*	Cr 267,716*	Cu 324, 754*	Fe 238, 204*	Ga 417,204*	K 766,491*	La 333,749*	Li 670,783*
plaque core	3	19	85770	1127	<LOD	7749	4	<LOD
plaque crust	3	91	41709	4073	<LOD	5132	12	<LOD
chisel core	<LOD	8	56251	1365	<LOD	1652	3	<LOD
chisel crust	3	22	29526	4880	16	3650	15	<LOD
LOD	3	0.3	13	34	13	32	3	3
LOQ	31	3	129	100	40	334	10	10

Sample	Mg 279,800*	Mn 257,610*	Mo 202,032*	Na 589,592*	Ni 231,604*	P 185,878*	Pb 220,353*	S 180,669*
plaque core	541	20	<LOD	801	25	198	127	4183
plaque crust	1637	74	<LOD	2159	16	551	160	21525
chisel core	650	37	<LOD	623	185	403	<LOD	8768
chisel crust	1862	141	<LOD	1231	23	1021	<LOD	50143
LOD	19	3	7	38	7	167	13	527
LOQ	201	10	20	408	20	500	40	5668

Sample	Sb 206,834*	Se 196,026*	Si 251,611*	Sn 189,927*	Sr 407,771*	Te 214,282*	Ti 334,941*	U 263,553*
plaque core	60	<LOD	1949	<LOD	152	109	80	<LOD
plaque crust	14	<LOD	2136	<LOD	611	19	251	<LOD
chisel core	11	<LOD	2338	2	118	34	144	<LOD
chisel crust	<LOD	<LOD	705	<LOD	399	<LOD	379	<LOD
LOD	5	33	17	1	2	12	20	81
LOQ	50	100	182	11	27	123	203	837

Sample	V 268,796*	W 209,475*	Zn 206,200*	Zr 339,198*	Ag107 **	Au197 **
plaque core	4	28	<LOD	<LOD	123	1
plaque crust	15	10	<LOD	14	15	5
chisel core	4	21	<LOD	<LOD	7	0.5
chisel crust	13	7	<LOD	16	2	0.2
LOD	2	2	40	7	0.004	0.03
LOQ	19	21	420	20	0.04	0.3

Tab.6.6.1. Chemical composition of plaque and chisel. All the results are presented in mg/Kg. LODs – Limits of detection and LOQs – limits of quantification; *Near the element the wavelength chosen for the analysis is reported, **Near the element isotope chosen for the analysis is reported.

6.7. Strontium Isotope Analysis

The clear presence of significant quantities of Sr in the studied samples, was confirmed by the means of EDXD, gained a great interest during this thesis work. Respectively, it was agreed to try to understand its provenance and mass ratio distribution among the samples with the help of other techniques. As first, the SEM-EDS surface analysis of plaque and chisel, both core and crust parts, was performed and the Sr was detected in the plaque object but it was not possible to clearly confirm its presence since it appeared to be at the detection limit. Subsequently, the chemical composition of both samples was measured with ICP-OES and ICP-MS and considerable amounts were noticed in crusts as well in cores of the samples (to see results go to chapter 6.6).

Due to promising results obtained with aforementioned instrumentation, it was decided to perform the Sr isotope analysis. This kind of analysis is well known in archaeological world for its application in studying the human and animal migration and mobility processes (Slovak N. M., Paytan A. 2011, 743-768; Buzon M. R., Simonetti A., Creaser R. A. 2007, 1391–1401). Commonly, the best results are acquired by studying bones, teeth and pottery but recently it has started to be used also for other kind of materials like glass (Henderson J., Evans J., Nikita K. 2010, 1-24), wood (Hajj F., Poszwa A., Bouchez J., Guérolda F. 2017, 24-49), textiles (Benson L.V., Hattori E. M., Taylor H. E. et al. 2006, 1588–1599), building elements (Gale N. H., Einfalt H. C., Hubberten H. W. et al. 1988, 57–72) or food products (Castorina F., Masi U. 2011, 41-48). Whereas, none of the publications, known to author, mention the implementation of this method in studying the provenance of copper based materials. For this reason, it was tempting to try to find the answer if it is possible to apply Sr technique in investigating copper objects and do it on unique example of Maadi artefacts.

In this thesis work the strontium concentration was determined by Varian ICP-AES (Vista MXP Rad) in total four samples, which has been previously thoroughly studied by other methods (Tab.6.7.1.). The same sample preparation was applied for Sr isotope analysis as in the case of chemical composition analysis by ICP-OES and ICP-MS (for more details see chapter 6.6).

Tab.6.7.1. Table with obtained values of $^{87}Sr/^{86}Sr$.

Sample	$^{87}Sr/^{86}Sr \pm 2se$
plaque core	0.707905 ±0.000035
plaque crust	0.707813 ±0.000014
chisel core	0.707833 ±0.000024
chisel crust	0.707810 ±0.000027

7. Results and Discussion

All ten artefacts chosen as study object of this thesis, were examined by Optical Microscopy and SEM-EDS. The obtained results by both techniques are complementary to each other. Most of samples appeared to be made of pure copper and only really small quantities of other elements, which could act as alloying part, were detected. The same picture is supported by EDXD and ICP-OES/ICP-MS results. This corresponds to previously made studies on other Maadi metal material (Pernicka E. and Hauptmann A. 1989; Hauptmann et al. 2012; Abdel-Motelib A. et al. 2012, 3-59; Bajeot J. 2017, 145-155). As was noted by Hauptmann A. this makes Maadi samples outstanding from overall pattern of arsenical copper, especially common for Predynastic and Early Dynastic periods metal objects in Egypt and chronologically corresponding Late Chalcolithic and Early Bronze Age I in Southern Levant.

Due to very advanced corrosion processes, which have greatly affected the studied samples, the recognition of the type of the objects was impossible in most of the cases. Only the pin was certain. Many cracks, holes, perforation, detaching of object's parts or deformations on surface were possible to be identified even with naked eye in many cases. Most of the samples were covered by thick crust of the sand particles, which were differentiated by colour, size and shape. One sample ('slag': Sq. IV S, US: 5a, Phase: Ia, Date: 25.03.1978) appeared to be non copper based object. Due to its glassy structure, it was assumed that it might constitute the silicate by-product of the smelting process. The assumption was confirmed with SEM-EDS analysis (for more information check chapters 6.1 and 6.2).

In some cases, the organic material was recognized, initially by Optical Microscopy and respectively, confirmed by SEM-EDS evaluation. Charcoal was the most frequent but due to its really small sizes and scarce structure preservation it was impossible to identify at the specie level. The remains of fiber was detected on the surface of the "plaque", which was identified as flux. This is in the agreement with other Maadi findings of flux fiber materials (Gleba M. 2017, 166-170) (see chapters 6.1. and 6.2).

SEM-EDS evaluation of the studied objects revealed copper (Cu) as main compound while chlorine (Cl), oxygen (O), carbon (C) prevail in corrosion patina (Fig.6.2.2). To a lesser extent, sulphur (S) and sodium (Na) as well occur but only in few cases. Crust appeared to be mainly made of calcite (Ca) and potassium (K) but also in smaller quantity from aluminum (Al) and magnesium (Mg). Some trace elements were found in particular objects, among them: Ni, Ag, Au, Pb, Sb, Zn, Hg, Ti and Zr.

Thanks to this technique various nanostructures were identified: spherical, rod-shaped, cubic, wire, spike and tree-like forms. Some of them occur even on the same artefact and do not present any differences in the elemental composition (more information in chapter 6.2).

Moreover, SEM-EDS technique allowed the lead segregation to be detected on the surface of three objects: pin (Sq. IV W, US: 2c α, Phase: Ia), plaque (Sq. II, US: 3c, Phase: Ia) and chisel (Sq. IV E, US: 2c, Phase: Ia). It was accumulated in spots located in the exposed surface area, devoid of crust (go to chapter 6.2., Fig.6.2.5; Fig.6.2.6). This might serve as clear evidence of applying casting method in production of aforementioned objects.

The same three objects: pin, plaque and chisel were subjected to EDXD analysis. The elemental mapping of the objects were performed in order to acquire the spatial distribution of elements. The obtained results match to the elemental mass ratios previously defined by SEM-EDS. All of the three artefacts seem to be made of very pure copper, sometimes even reaching 99 wt. % at certain points. Subsequently, quite big amounts of Fe, Ca and K were noted, which constitute the crust layer. The most surprising is the considerable high Sr peaks, occurring in all the points. The EDXD technique allowed only to detect few trace elements like Ag, Sb, Ba, Cr and Br. Probably, it is connected to higher X-ray penetration possibilities of EDXD, comparing to SEM-EDS surface analysis (for more details go to chapter 6.3).

Two artefacts, plaque and chisel, were chosen for further detailed studies by the means of other non-invasive and also destructive techniques. Starting with SEM-EDS the prepared cross section of both objects were thoroughly analysed. The cores of objects appeared to completely differ in terms of colour, structure and composition. The plaque core (Fig.7.1) has a red colour but also some blackish bands occur. No relation exist between the colour and elemental composition. Both red and blackish areas of the core consist mainly of Cu, O, C but also Al, Si, Sr and around 0.5% Ni (Fig.7.2). Some minor inclusions of Pb, Ag, Au and Sn were detected inside the core. On the other hand, chisel present completely different picture (Fig.7.3.). Its cross section revealed the entirely crystallized structure of green colour. Chisel's core consists of several well consistent layers and remains of original core localized just right in the center of the object. The main components are Cu, Cl, O and C and their ratios differs according to particular layer (Fig.7.4). The original core part appears to contain more Cu and Cl in comparison to rest of the core structure as well as is far less oxidized and poorer in C. Moreover, it is surrounded by K, which appears in the middle part of the core in bigger quantity, even reaching more than 12% of mass ratio. It seems that the corrosion process was initiated in the center of the object and gradually spread to outer layers. Beside the elemental mass ratio differences, all the layers vary in shades of green colour and porosity of their structure (to compare with OM picture of both cross sections go to chapter 6.1., Fig.6.1.4.).

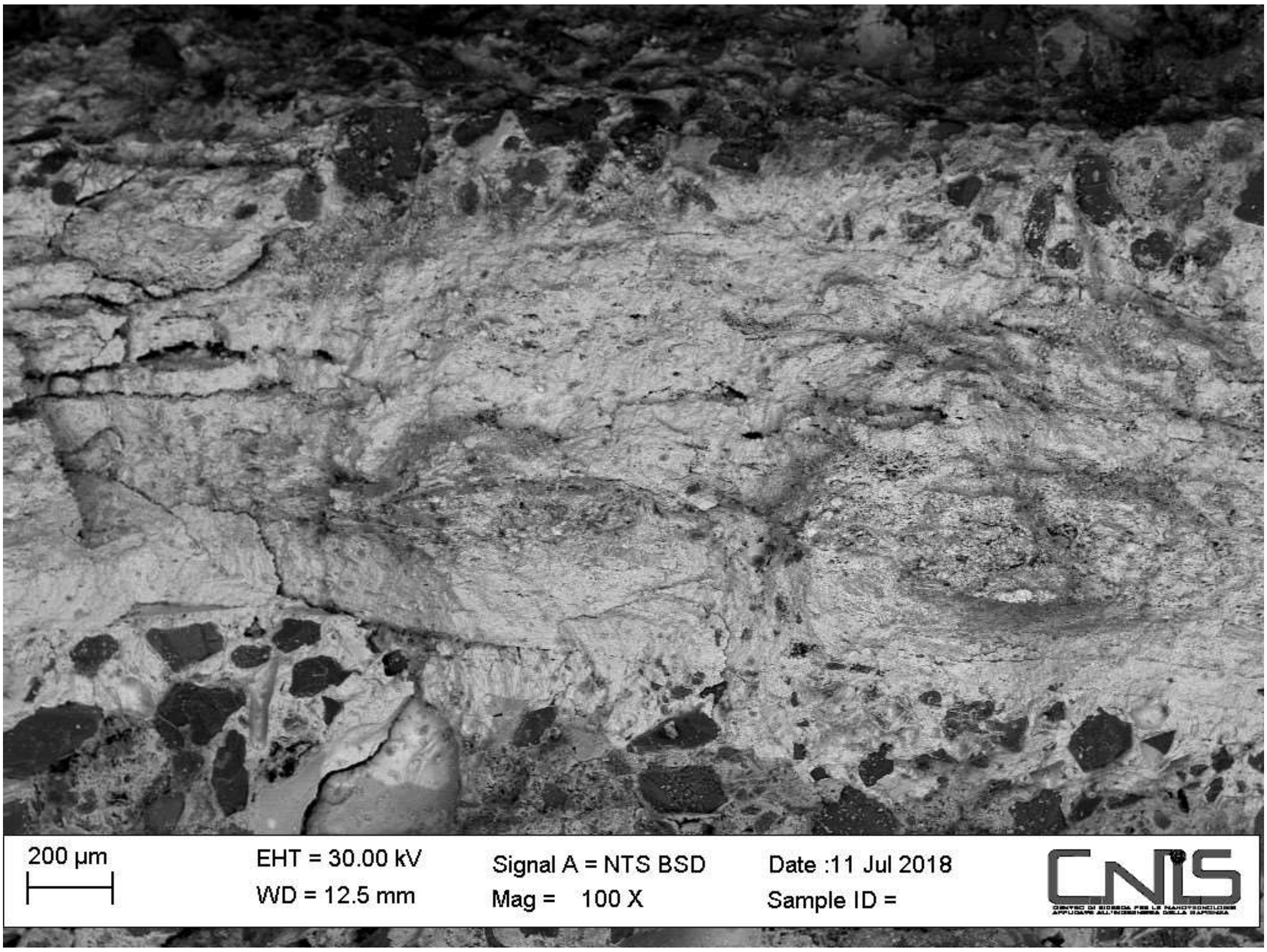
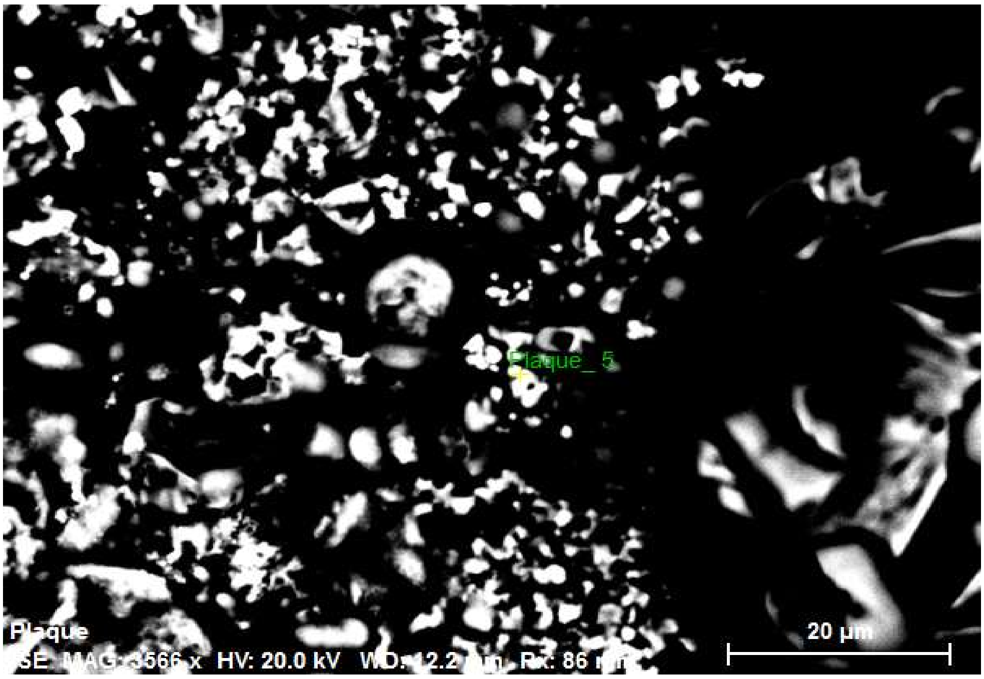
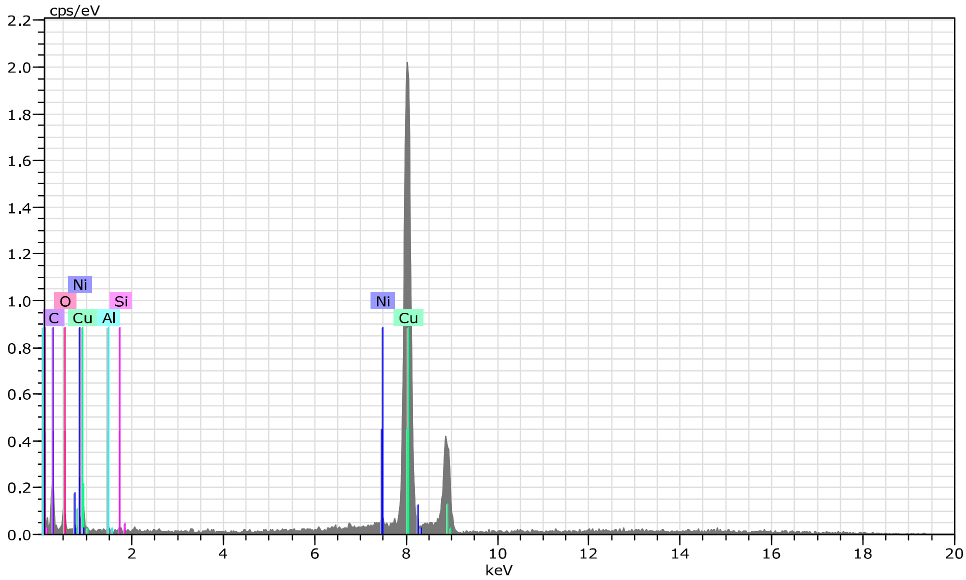


Fig.7.1. The cross section of the plaque.

For better understanding the corrosion products the XRD analysis was applied for both of the samples. The results obtained for the "plaque" were corresponding to previously acquired data from Optical Microscopy and Scanning Electron Microscopy of the cross-section of the sample (Fig.7.1). The crust and the core of the object reflects the desert environmental conditions. The quartz (SiO_2) and the calcite ($CaCO_3$) appeared to be the main components of the crust, while the core is made of cuprite (CuO_2).





Spectrum: Plaque_ 5

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Cu	29	K-series	73.03	86.83	58.99	2.13
C	6	K-series	7.92	9.42	33.85	2.44
O	8	K-series	1.33	1.59	4.28	0.55
Al	13	K-series	0.69	0.82	1.32	0.16
Si	14	K-series	0.60	0.72	1.10	0.14
Ni	28	K-series	0.53	0.63	0.46	0.09
		Total:	84.11	100.00	100.00	

Fig.7.2. The red core area of the plaque, which contains also Ni.

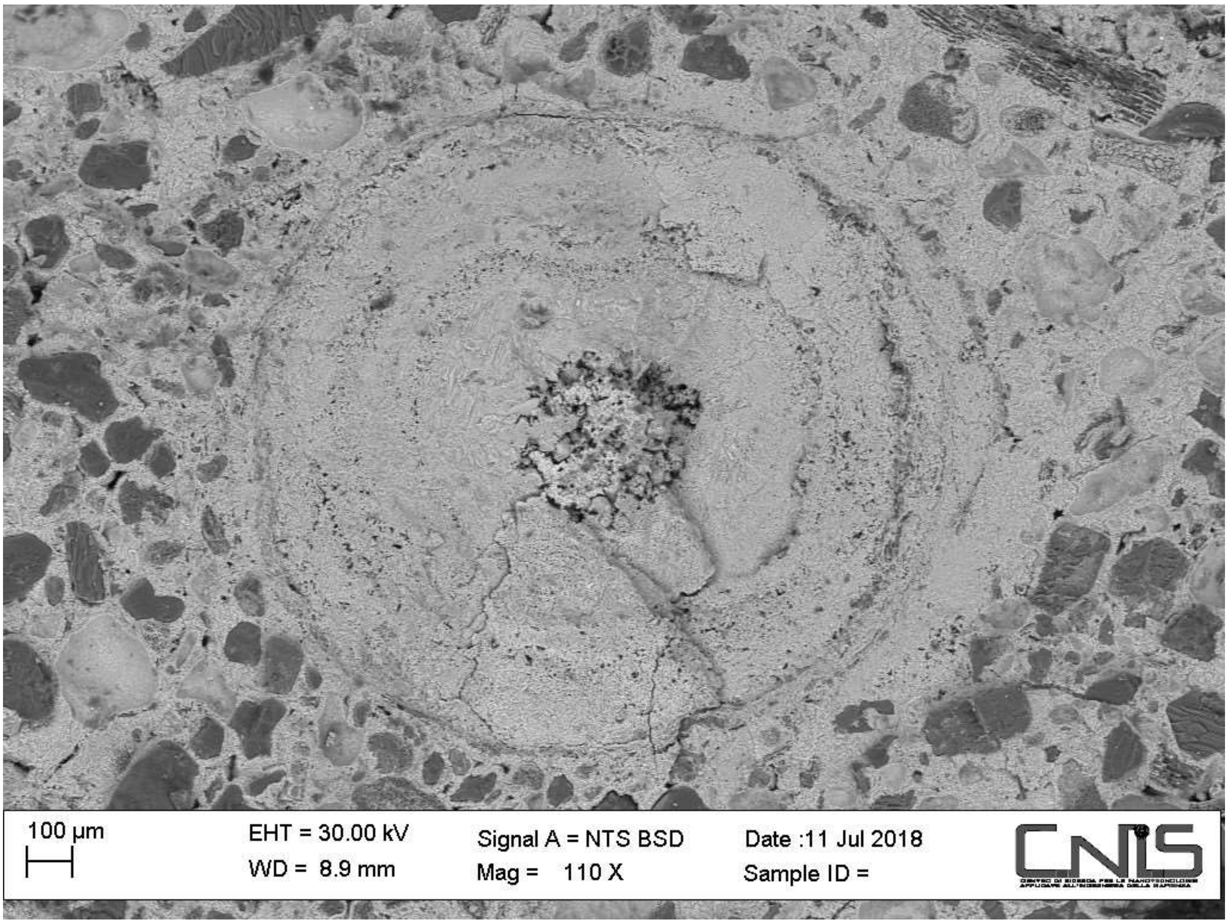


Fig.7.3. The cross section of the chisel.

Spectrum: chisel section 2_15 keV_25 KX_60 um_ 63 335

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Cu	29	K-series	57.21	56.62	32.14	1.43
Cl	17	K-series	26.32	26.05	26.50	0.93
O	8	K-series	11.48	11.36	25.61	1.46
C	6	K-series	4.94	4.89	14.67	0.85
K	19	K-series	0.42	0.42	0.39	0.04
Ca	20	K-series	0.39	0.38	0.34	0.04
Si	14	K-series	0.15	0.15	0.19	0.03
Al	13	K-series	0.10	0.10	0.13	0.03
Fe	26	K-series	0.03	0.03	0.02	0.03
		Total:	101.05	100.00	100.00	

Fig.7.4. The elemental composition of the chisel's central core part.

The XRD analysis of the chisel confirmed $Cu_2Cl(OH)_3$ composition of the core but it was not neither possible to distinguish particular polymorphs nor subject it to specific core layer. Atacamite and clinoatacamite crystalline structures show great similarity, which are not possible to be recognized with the certainty by the means of XRD. This makes chisel completely different from plaque. The atacamite/ clinoatacamite emergence is more connected to salty water environment than desert. In this case, it can be associated with unpredictable geological and environmental events. On the other hand, the crust appeared to be similar to plaque's one. Mainly consists of quartz (SiO_2) and calcite ($CaCO_3$) (here dominate the aragonite form). Moreover, some of the peaks have been associated with K feldspars (for more information considering XRD analysis go to chapter 6.4.).

In order to try to recognize particular corrosion products of chisel, the FTIR was performed to support so far obtained results by OM, SEM-EDS and XRD. Thanks to FTIR it was possible to distinguish peaks of atacamite, clinoatacamite and malachite. Clinoatacamite has appeared to be dominant but also several peaks of atacamite were identified as well as few peaks were attributed to malachite. The crust components, recognized with FTIR were identical as XRD ones: calcite, quartz and aluminosilicates. Additionally, FTIR analysis was performed on powder sample collected from the pin surface layer, which brought very similar results as chisel (for details go to chapter 6.5).

Respectively, plaque and chisel were chosen for ICP-OES and ICP-MS analyses (go to chapter 6.6, Tab.6.6.1). Preparation of the samples was made in the way that cores and crusts of the artefacts were separated and tested individually. As in the previous methods, the attempt was made to understand the elemental compositions existing between the crust and the core. The crust is considered to reflect the geological conditions where artefact was deposited, while the core might represent the original raw material from which the object was manufactured. The results of ICP-OES and ICP-MS analyses are consistent with the chemical compositions obtained by previously discussed techniques in this thesis work. The main component is copper and the trace elements occur in very low quantity so the deliberate adding the alloying element in this case can be excluded. Since arsenic and antimony are here mostly below the detection limits it can be assumed that none of them have been produced from fahlores, from which famous Nahal Mishmar treasure was created. As well other element as cobalt, tin, zinc, nickel or lead are in significant amounts to classify them as added alloying agents. Trace elements are very important in the finding the origin of the copper ore. In case of plaque and chisel the possibility that the ore came from Eastern Desert (Egypt) and Nubia can be ruled out since the gold and silver content is scarce. The manganese concentration in the samples is also limited so the possibility that the copper ore could come from Bir Nasib or Um Bogma district in the Sinai Peninsula or Eastern Desert in Egypt can be rejected. The sulphur content is notably low, especially when compared with dominating chloride content defined by other techniques so the sulphidic origin of copper ores used for production of these object can be dismissed. The analysis of the crusts of the artefacts yielded the same composition, which was expected from prior examinations. Mostly, it consists of Ca, Si, Al, Fe, Mg, K and also Na. Considerable, for the next planned analysis of strontium isotope, was to confirm the possible content of Sr in both parts of the objects, crusts and cores. The presence of Sr in the aforementioned samples as well pin was detected by EDXD. With the ICP-OES analysis the Sr content was revealed in both cases. The much higher amounts were noticed in crusts parts in relation to the cores.

Nevertheless, the ICP technique is well known to meet great restrictions while applying it to provenance studies of archaeological metal artefacts. Many factors can affect the trace elements composition of the artefact and even can be responsible for it complete disappearance. Among them are smelting process (its duration, applied reducing or oxidizing conditions), the temperature in particular parts of furnace, oxygen supply, type of fuel and flux, and others. Notably, some elements as zinc or arsenic can completely vanish as volatile oxides meanwhile the roasting process of sulfide ores just before being smelted (Scott D. A., Podany J. 1990, 31-32). This kind of difficulties might be resolved by other elemental composition studies or by examination of lead isotope ratios but even those meet some limits. This is the reason why provenance studies are vividly debated lately by scientists and some of them expressed skepticism towards those techniques. As Paul Craddock stated: "real problems lie... fundamentally in the almost total lack of information on the chemical processes and composition changes between the ore source and the finished metal of the analyzed artifact which can only be bridged by often untenable assumptions" (Meyers P. 1990, 241).

Even though, ICP faces so many obstacles, still it can bring essential data to studies. Of great importance is to improve the method and find the way to resolve the main problems. In this thesis work the experimental measurement of $^{87}Sr/^{86}Sr$ for provenance of Maadi copper based artifacts was successfully performed. The isotopic values of the crusts and cores of the objects were proved to be homogeneous and they are as follows: plaque core: 0.707905 ±0.000035, plaque crust: 0.707813 ±0.000014, chisel core: 0.707833 ±0.000024 and chisel crust: 0.707810 ±0.000027 (for details check chapter 6.7, Tab.6.7.1).

The obtained results of Sr isotope analysis seems to be close matching to Wadi Arabah region where average bioavailable $^{87}Sr/^{86}Sr$ values are equal to 0.70781-070798 (Fig.7.5). Meanwhile, the other geological features which might affect the values of the local food chain are as follows: cretaceous sediments from western slope of Wadi Araba: 0.707436, alluvial deposits 0.708597 and groundwater 0.70747 ± 0.0004 (2σ) (Perry M. A. et al. 2016, 953). The highland regions to the east and west of Wadi Araba have $^{87}Sr/^{86}Sr$ of 0.7079–0.70883 (Perry M. A. et al. 2008; Perry M. A. et al. 2016, 957). The ocean water is thought to be around 0.709178 and the process of the seawater source precipitation can also contribute to the differentiation of local geological $^{87}Sr/^{86}Sr$ signature (Perry M. A. et al. 2016, 953).

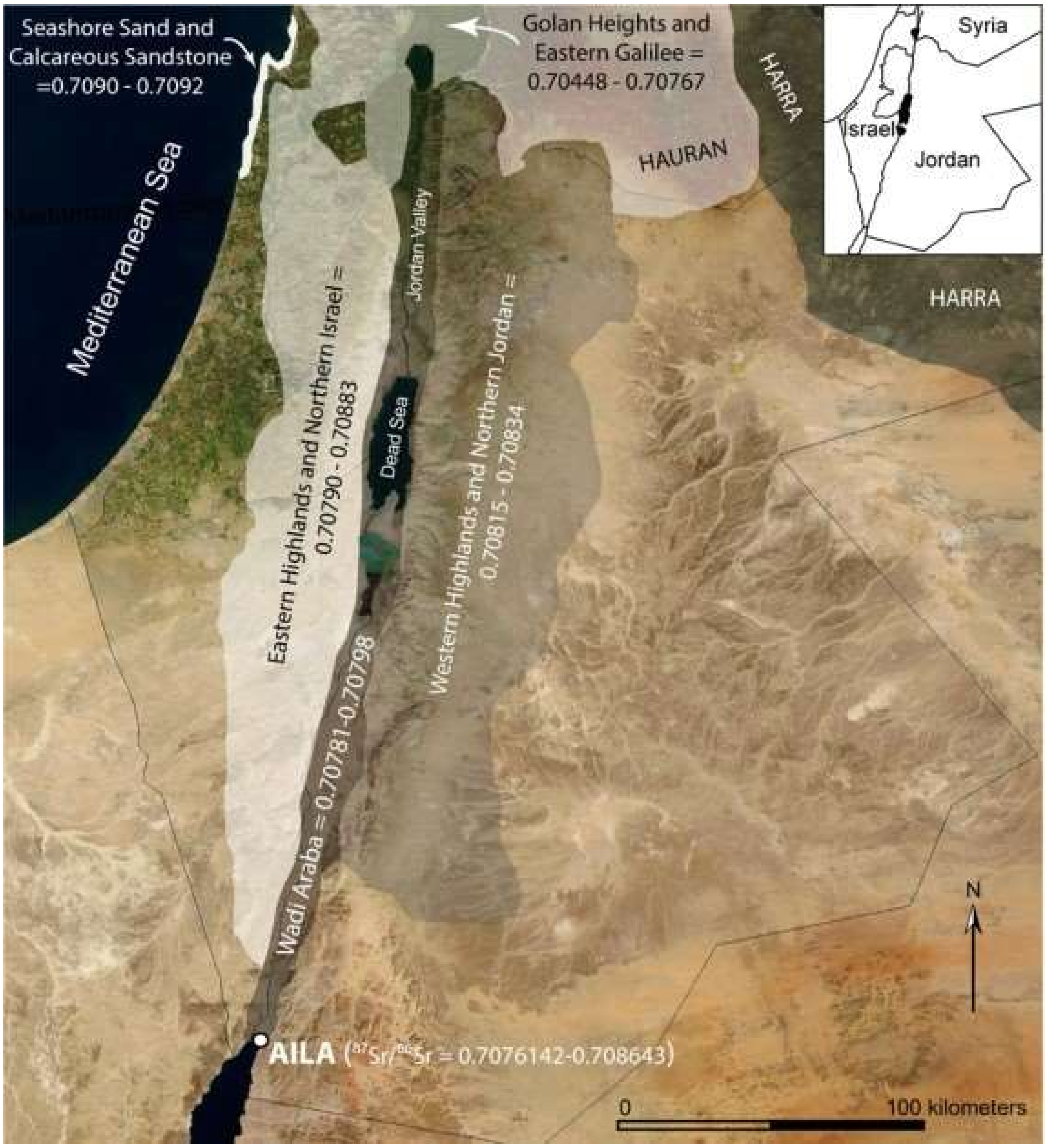


Fig.7.5. Map of Levant presenting the regional differentiation of bioavailable strontium isotope values (Perry M. A. et al. 2017, 946).

The regions of interested, where ancient copper mines of Timna (Israel) and Feinan (Jordan) are located, are divided into two geological complexes of Aqaba and Arabah. They are separated by a regional unconformity overlain by the Saramuj Conglomerate, which is dated to happen at about 600 Ma (Jarrar et al., 1993) and it is thought to mark the beginning of an extensional tectonic phase, which lasted to around 545 Ma. The Aqaba and Araba complexes are subdivided into several suites, which $^{87}Sr/^{86}Sr$ signatures vary. The Arabah complex (600-545 Ma; bimodal igneous activity and rift-related intermontane molasse sediments) comprises among the others from Humrat-Faynan Suite (A-type granitoids) and Araba Mafic-Intermediate Suite with $^{87}Sr/^{86}Sr$ of 0.7043-0.7057. Whereas, Precambrian rocks of Aqaba area $^{87}Sr/^{86}Sr$ are 0.70793-0.70813. The Aqaba complex formed around 800-600 Ma, consists of Metamorphic rocks – 800-750 Ma, Horneblendic Suite – 640?-610 Ma, Calc-Alkaline Granitoids – 625-600 Ma and have several suites Rumman Suite ($^{87}Sr/^{86}Sr$: 0.7059-0.7099), Yutum Suite ($^{87}Sr/^{86}Sr$: 0.7059-0.7278), Urfu Suite ($^{87}Sr/^{86}Sr$: 0.7055-0.7077 but a few 0.7137-0.7299), Darba Suite ($^{87}Sr/^{86}Sr$: 0.7058-0.7077), Rahma Suite ($^{87}Sr/^{86}Sr$: 0.7046-0.7076) and Horneblendic Suite (Jarrar et al., 2003, Table 1, 298; Table 3, 309-310).

It seems most likely that Timna copper mines located in western part of Wadi Arabah are the origin area of studied copper based objects from Maadi. This would be in accordance with the theory about Maadi relations with Tell Hujayrat al-Ghuzlan and Tell al-Magass sites, located in Aqaba region (Abdel-Motelib A. et al. 2012; Hauptmann A. 2017, 145-155). In Timna, the Lower Cambrian-Precambrian mafic-felsic volcanic dikes of the igneous basement of the Arabian-Nubian Shield, formed mainly by granites and granodiorites of I-type and low Initial Sr Ratios 0.7032-0.7046, are the prevailing source of copper in the sediment-hosted Cu deposits. At the time, around 570 Ma those rocks have been intruded by diorites and dikes. The presence of Cu mineralisations is bound to quartz veins of andesitic volcanic rocks and low-grade metamorphics. The creation of an epigenetic type ore deposit such as the stratiform-stratabound sedimentary-hosted deposits of Timna, but also Sinai and Feinan, characterized by highly variable ratios of non-radiogenic to radiogenic Pb differences in their composition was caused by complex processes of erosion of these volcanic rocks at time of the Lower Cambrian as well as multiple remobilization and migration of copper in uranium-containing sedimentary environments during and after the Cambrian (Abdel-Motelib A. et al. 2012, 43-47).

The other possible explanation of Maadi's samples $^{87}Sr/^{86}Sr$ values is the influence of Nile river activity. The Nile river sediments $^{87}Sr/^{86}Sr$ since 6000 BP varies between 0.7088 and 0.7073 and are affected by the frequency and differentiation of inputs coming from the main river sources, which are located in Ethiopia and Uganda (Krom M. D. et al. 2002; Perry M. A. et al. 2016, 957). The strontium analysis performed on human dental enamel coming from ancient cities of Memphis and Thebes, located in the vicinity of the Nile river, yielded 0.70777 ± 0.00027 of bioavailable strontium, which corresponds to the soils strontium values (Buzon and Simonetti 2013; Perry M. A. et al. 2016, 957).

8. Conclusions

In this thesis work ten copper based artefacts from Late Predynastic site of Maadi (Egypt) have been studied using archaeometric methods. An advanced physico-chemical approach has been proposed with the aim to improve information coming from the artefacts and to confirm the results obtained from previous studies on similar metal samples coming from the aforementioned site (Pernicka E., Hauptmann A. 1989; Abdel-Motelib A. et al. 2012; Hauptmann A. 2017). The objects discussed here comes from the excavations carried by the Italian mission (MIRPES) from Sapienza University in Rome between 1977-1986. Another important aim of this thesis project was the realization of an open catalogue of the all metal artefacts discovered in Maadi by the Italian team. The objects from the Italian excavations previously studied by Hauptmann A. (2017) were also included into the catalogue, attached at the end part of the presented thesis work.

During the project the systematic approach was implemented, using various advanced instrumentations. The samples were thoroughly characterized according to clearly defined steps. Idea was to emphasize the possibilities of multi-versatile approach in archeometric reconstructing of ‘the past life’ of the artefacts including their production and processing method, origin, corrosion and its relation with the environment. The used methods (including Optical Microscopy, SEM-EDS, EDXD, XRD, FTIR, ICP-OES/ICP-MS and strontium isotope analysis) complement each other. Thanks to them it was possible to effectively understand variable sort of data, to fill the missing gaps in knowledge acquiring in this way much better idea about the specific nature of the objects.

The objects under evaluation appear to be made of almost pure copper with very scarce trace element content. The chemical composition of the artefacts and the stratigraphy of the settlement site are not bound but any specific relation. This is consistent with the previously analysed objects from Maadi and confirms the unusual trend among the metals from this site, which do not follow the copper arsenical findings pattern of objects from other contemporaneous sites in Egypt and Levant. The overall chemical composition and the evidence of lead segregation detected on some objects suggests that probably they were directly produced from the copper ingot by applying simple metal processing methods like hammering and annealing. The findings of copper ingots are acknowledged in Maadi. Recently, it was proposed that Maadi might have maintained tight copper trade contacts with the metallurgical production sites of Tell Hujayrat al-Ghuzlan and Tell al-Magass in Aqaba region. The matching moulds were discovered there and the copper ore has similar chemical composition and features, which suggests that all of the aforementioned sites imported the copper ore from the same source – most certain, from Timna copper mines.

The artefacts analysed in this work are characterized by the presence of advanced corrosion patina, where chloride appeared to be the dominant corrosive agent. To a lesser extent, sulphur and sodium based compounds are responsible for the degradation of the studied metals. The surface alterations are strictly connected to the dry environment, in which objects were found. Different forms of corrosion have been identified, which do not manifest any major differences in the chemical composition. The thick crust of sand particles covers most of the samples. Its main components are quartz, calcite and aluminosilicates. Several carbon based materials have been detected on the surface of the objects. Most common is charcoal but also other examples were noted, like fiber.

The essential point of this thesis project was the attempt to use the strontium isotope analysis to define the provenance of the Maadi copper based materials. The experiment was performed on two objects, plaque and chisel, in which the core parts and crusts were separated and analysed individually in order to compare and present the relations between the strontium content and its $^{87}Sr/^{86}Sr$ isotopic values. In this sense, both parts of the objects appeared to be homogeneous in terms of Sr distribution. The $^{87}Sr/^{86}Sr$ isotopic values best match with the Wadi Arabah region, where Timna copper mines are located. This result reinforces the hypothesis that Timna was the main raw material source for Maadi population and in turn, it links to its trade relations with Tell Hujayrat al-Ghuzlan and Tell al-Magass. Moreover, we believe that the strontium isotope analysis can become another useful tool in the provenance studies of archaeological metals, where the lead isotope technique is the most commonly used by academia. The restrictions of lead isotope method are widely known to scientists. In this case, the strontium analysis could be supplementary or even self-sufficient method in the origin studies to the aforementioned one. The first trial results proved to be successfully performed but still much more additional experiments are needed to be done for a reliable data assemblage. Further strontium isotope analysis on the other Maadi metal samples is planned to be carry out in the nearest future.

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Catalogue of objects

Square	US	Phase	Context	Object	Year	Weight (g)
IV S	5a	Ia		glassy object	25.03.1978	0,1082
V W	1b-2a	Ia/II		copper droplet	21.04.1977	0,1338
VI	L		from the cleaning	metal object	26.03.1978	0,1544
XIII	?			copper droplet	10.12.1985	0,2155
XIII-XVII			Cl.gebel	many copper pieces	22.12.1985	1,4491 (total)
XVII	1b	III		copper fragment	7.04.1980	0,0450
IV E	4a	Ia		copper droplet	30.04.1977	0,0590
IV N	5a	Ia		metal fragment	24.03.1978	0,1077
IV N	5cd?	Ia		metal fragments	28.03.1978	1,309 (total)
V	4a	Ia		copper nodule	2.04.1978	0,2459
X	2c	Ia		metal object	3.04.1978	1,3755
X	2g	Ia		metal object	5.04.1978	0,1226
X	2a	Ia		metal object	1978	0,8705
balk VI-IX	2a			copper droplet	20.04.1977	0,1413
I	5c β	Ia		two metal objects	27.03.1978	1,2727 (total)
I	7b	Ia		metal object	6.04.1978	0,2078
I W	3b α	Ia	zona sconvolta?	metal object	27.04.1977	0,2655
II	3c	Ia		“plaque”	3.02.1986	2,1536
IV W	2c α	Ia	62, 17	pin	26.04.1977	1,6656
IV E	2c	Ia	61, 16	a chisel fragment	25.04.1977	0,7445 (total)
46	3b	II		copper nodule	11.06.1984	0,6099
46	2d	III		copper ore	21.05.1984	3,2750
46	2f	III	N.inv.: 104/170	metal fragment	5.06.1984	0,0535
44	3c	Ia		copper droplet	28.05.1984	0,4102
40	4	Ia		metal object	3.02.1986	0,5690
39	4	Ia		chisel fragment	3.02.1986	2,9089
V-VIII	3c	Ia	Inv. no. Bochum: ET-5/9	copper ore		0.063
XIII-XVIII	virgin soil		Inv. no. Bochum: ET-5/10	two copper ores		0.11
IV	2a	Ia	Inv. no. Bochum: ET-5/11	copper prill		0.039
II	3c	II	Inv. no. Bochum: ET-5/12	rectangular “plaque”		0.068
V	1b α	II	Inv. no. Bochum: ET-5/13	copper nodule (ore)		0.06
XVII	1b	III	Inv. no. Bochum: ET-5/14	two copper ores		0.003
40	4	Ia	Inv. no. Bochum: ET-5/15	copper prill		0.024
			Inv. no. Bochum: ET-5/16	not sampled?		
IV E	2c	Ia	Inv. no. Bochum: ET-5/17	pin		
46	2e	III	Inv. no. Bochum: ET-5/18	awl		0.03
IV W	2c α	Ia	Inv. no. Bochum: ET-5/19	awl		0,0450
IX W	2b	II	Inv. no. Bochum: ET-5/20	copper ore		
XXV S	3a		Inv. no. Bochum: ET-5/21	awl		

Square	US	Length (cm)	Width (cm)	Thickness(cm)	Cross section	Notes
IV S	5a	0,8	0,6			
V W	1b-2a	0,4	0,4			
VI	L	1,3	0,5 and 0,9	0,3-0,5	irregular flat	
XIII	?	0,5	0,5			
XIII-XVII		0,1-1,0				
XVII	1b	0,4	0,3			
IV E	4a	0,4	0,4			
IV N	5a	0,6	0,5			
IV N	5cd					Two copper objects: irregular-shaped one 1,1x0,6-0,9 cm (0,8615g)
V	4a	0,8	0,6			and droplet 0,5x0,5cm (0,1439g); glassy object 0,3x0,3cm (0,0264g)
X	2c	1,6	0,5-0,7			
X	2g	0,6	0,4			
X	2a	1,9	0,6-0,8	0,4	flat rectangular	
balk VI-IX	2a	0,5	0,4			
I	5c β					Two copper fragments with irregular shape 1,2x0,9 cm (0,9658 g)
I	7b	1	0,4	0,3	flat rectangular	and 0,7x0,7 cm (0,3070 g)
I W	3b α	0,9	0,6	0,4		
II	3c	1,7	1,6	0,4	rectangular	
IV W	2c α	5 (diagonal), 6,1 cm	0,1-0,4	0,1-0,3	round	
IV E	2c			0,3 and 0,5	rectangular	Two parts of object: bigger one 1,9x0,5 cm and 0,5 cm thickness,
46	3b	1,1	0,9	0,6		0,6108 g; smaller one 0,7x0,4 cm and 0,3cm thickness, 0,1338 g
46	2d	1,6	1,3	1,1		
46	2f	0,5	0,4	0,3		
44	3c	0,6	0,6	0,5		
40	4	0,8	0,7	0,6		
39	4	2	0,8-1	0,5-0,7	rectangular	
V-VIII	3c					
XIII-XVIII	virgin soil					
IV	2a					
II	3c	1,5	1,5			
V	1b α					
XVII	1b					
40	4					
IV E	2c					
46	2e	7,6				
IV W	2c α	8,0				
IX W	2b					
XXV S	3a					

Samples studied in details in this thesis work:

Sample	**Optical Microscopy**	**FTIR**
Sq. IV W	One of the pin ends is broken	Mainly: clinoatacamite
US: 2c α	Pin ends are devoid of sand grains	Also atacamite and malachite
Phase: Ia	Crust layer is detached in the central part of the pin	Crust: quartz, calcite and K feldspar
Inv.62, 17 Date :26.04.1977	Sand grains vary in colour (usually orange – brown), shape (rounded) and size Different colours of copper mineralisations: red, green and white	 **EDXD**
Copper pin	Remains of charcoal and other vegetal parts (straws)	Mainly: Cu
 General description	 **SEM-EDS**	Minor: Fe, Ca/K, Sr and other trace elements
Weight: 1,6656 g	Mainly: Cu, Cl, O, Ca, C, Si, K, Al, S, Fe, Na, P, Mg	**XRD**
Length: 5 (diagonal), 6,1 cm	Minor: Ni, Pb, Sb, Ag, Au, Zn, Hg, Ti, Zr	none
Width: 0,1-0,4 cm	Main corrosion compounds: Cl and O but also S and a little bit of Na	
Thickness: 0,1-0,3 cm	Different composition and colours of corrosion patina layers :green, reddish and white	**ICP-OES and ICP-MS**
Cross section: round	Spherical, rod-shaped, cubic, spike and tree-like nanostructures	none
	Lead segregation on the surface in the broken tip area, which is devoid of crust The surface is rather porous and also some more compacted area occurs	 **Sr isotope analysis**
	Many cracks and holes are located on the surface	none
	Quartz sand particles attached to the surface of the object Crust is made of Si, Ca, K, O, Al, Mg	
	Organic remains: charcoal	

Sample	**Optical Microscopy**	**FTIR**
Sq. IV E	Some charcoal remains detected	Mainly: clinoatacamite
US: 2c	The whole object is covered with thick crust of sand particles	Also atacamite and malachite
Phase: Ia	Green discolorations spots caused by copper mineralisations	Crust: quartz, calcite and K feldspar
Inv. 61, 16	Sand grains vary in colour (usually orange), shape (rounded) and size	
Date: 25.04.1977	Cracks located on the end sides of the object	**EDXD**
copper chisel/awl		Mainly: Cu
B – big piece	**SEM-EDS**	Minor: Fe, Ca/K, Sr and other trace elements
S – small piece	Mainly: Cu, O, Cl, C, S, Ca, C, Si, K, Al, S, Fe, P, Mg; Minor: Pb, Bi	
	Main corrosion compounds: Cl and O but also S	**XRD**
General description	Different composition and colours of surface corrosion patina layers: green, red and white	Core: atacamite/paratacamite ($Cu_2Cl(OH)_3$)
0,7445 (total); B 0,6108g; S 0,1338g	Spherical, rod-shaped, cubic, wire, spike and tree-like nanostructures	Crust: quartz (SiO_2) and aragonite ($CaCO_3$)
Length: B 1,9x0,5cm, S 0,7x0,4cm	Lead segregation on the surface in the both end areas, which is devoid of crust	
Thickness: B 0,5 and S 0,3cm Cross section: rectangular	The surface is rather porous and also sporadically more compacted area occurs Many cracks and holes are located on the surface	**Sr isotope analysis** Core – 0.707833 ±0.000024
	Quartz sand particles attached to the surface of the object	Crust - 0.707810 ±0.000027
	Crust is made of Si, Ca, K, O, Al, Mg Organic remains: charcoal detected on the surface	
	Cross section: chisel consists of several different green layers of corrosion	
	Only very tiny part of the original core survived inside	
	The main components inside the chisel are Cu, Cl, O and C	
	Only very small piece of the original core remained and it’s seems to be less oxidized	
	The corrosion process started in central part of the object, which contains more Cu and Cl	
	The center core part is poorer in C and it is surrounded by K	
	ICP-OES and ICP-MS	
	Core-main: Cu, Fe, Ca, K, Al, Sr, Mg, Na, P, Ni, Si, S, Sr, Ti	
	Core-other: As, B, Ba, Be, Cd, Ce, Co, Cr, Ga, La, Li, Mn, Mo, Pb, Sb, Se, Sn, Te, U, V, W, Zn, Zr, Ag, Au	
	Crust-main: Cu, Fe, Ca, K, Al, Sr, Mg, Mn Na, P, S, Si, Sr, Ti	
	Crust-other: As, B, Ba, Be, Cd, Ce, Co, Cr, Ga, La, Li, Mo, Ni, Pb, Sb, Se, Sn, Te, U, V, W, Zn, Zr, Ag, Au	

Sample	Optical Microscopy	FTIR
Sq. II	One side of the “plaque” is broken	none
US: 3c	Broken (cross section) area: red core and green outer layer	
Phase: Ia	The object is covered by homogenous crust	**EDXD**
3.02.1986	Only two bigger stones are attached from one side	Mainly: Cu
“plaque”	Orange and yellow are prevailing colour of the sand	Minor: Fe, Ca/K, Sr
	.Remains of charcoal, straws and fiber	Some trace elements
General description		
Weight: 2,1536 g	**SEM-EDS**	**XRD**
Length: 1,7 cm	Mainly: Cu, Cl, O, Ca, C, Si, K, Al, Na, S, Fe, P, Mg	Core: cuprite (CuO_2)
Width: 1,6 cm	Minor: Ni, Pb, Ag, Au, Cr, Sr, Sn, Zr, Ti	Crust: quartz (SiO_2) and calcite ($CaCO_3$)
Thickness: 0,4 cm	The core of the plaque is mostly made of Cu, O, C and some Al, Si, Sr, 0.5% Ni occur	
Cross section: rectangular	Some minor inclusions of Pb, Ag, Au and Sn were detected inside the core	**Sr isotope analysis**
	The colour of core is mainly red but some black bands occur	Core **–** 0.707905 ±0.000035
	Main corrosion compounds: Cl and O but also S and a little bit of Na	Crust **–** 0.707813 ±0.000014
	Different composition and colours of corrosion patina layers: green, reddish and white	
	Spherical, rod-shaped, cubic, spike and tree-like nanostructures	
	Lead segregation on the surface near the broken area	
	The surface is rather porous and also some more compacted area occurs	
	Many cracks and holes are located on the surface	
	Quartz sand particles attached to the surface of the object	
	Crust is made of Si, Ca, K, O, Al, Mg, Fe	
	Organic remains: charcoal and fiber	
	ICP-OES and ICP-MS	
	Core-main: Cu, Fe, Ca, K, Al, Sr, Mg, Na, P, Pb, S, Si, Sr, Te, Ag	
	Core-other: As, B, Ba, Be, Cd, Ce, Co, Cr, Ga, La, Li, Mn, Mo, Ni, Sb, Se, Sn, Ti, U,	
	V, W, Zn, Zr, Au	
	Crust-main: Cu, Fe, Ca, K, Al, Sr, Mg, Na, P, Si, S, Mn, Pb, Sr, Ti	
	Crust-other: As, B, Ba, Be, Cd, Ce, Co, Cr, Ga, La, Li, Mo, Ni, Sb, Se, Sn, Te,	
	U, V, W, Zn, Zr, Ag, Au	

Sample	Optical Microscopy	FTIR
Sq. VI	No organic remains detected	none
US: L (from cleaning)	The object differs in structure from others	
Phase:	Very fine sand grains are attached to surface but do not create particular crust	**EDXD**
Date: 26.03.1978	Many perforations and scratches appears on its surface (due to erosion process)	none
Copper object	Light green and whitish copper mineralisations appear on the surface of the object	
Irregular-shaped		**XRD**
	SEM-EDS	none
General description	Mainly: Cu, Cl, O, C, Na, Ca, C, Si, Al	
Weight: 0,1544 g	Minor: K, S, Fe, P, Mg	**ICP-OES and ICP-MS**
Length: 1,3 cm	Main corrosion compounds: Cl, Na, O and S	none
Width: 0,5 and 0,9 cm	Green and white are the colours of corrosion patina layers	
Thickness: 0,3-0,5 cm	Spike nanostructures	**Sr isotope analysis**
Cross section: irregular flat	The surface is very porous and have many scratches and perforations	none
	No organic remains detected	

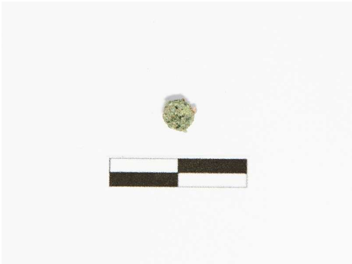
Sample	Optical Microscopy	FTIR
Sq. IV S	Completely differs from the rest of the artefacts	none
US: 5a	It has black and white colours	
Phase: Ia	Probably, it is the silicate by-product of the smelting process	**EDXD**
Date: 25.03.1978	It has glassy structure with visible bubbles and sand grains under the surface	none
Glassy object – slag?	An organic fiber is embedded underneath its surface	
	It looks similar to droplet from Sq.V W, US: 1b-2a, 21.04.1977	**XRD**
		none
General description	**SEM-EDS**	
Weight: 0,1082 g	Mainly: O, C, Si, Ca,	**ICP-OES and ICP-MS**
Length: 0,8 cm	Minor: Cl, S, Al, Mg, K, Na, P, Fe	none
Width: 0,6 cm	Visible glassy surface and many bubbles are underneath the surface	
Shape: rounded nodule	Organic, fiber-like material is embedded inside the object’s structure	**Sr isotope analysis**
	Many cracks located on surface, which are probably caused by sudden cooling process	none

Sample	Optical Microscopy	FTIR
Sq. 39	Detaching of the surface layers in the form of light and dark green bands	none
US: 4	Heavily cracked globular areas	
Phase: Ia	In many places the flat surfaces is heavily cracked	**EDXD**
3.02.1986	Sand grains vary in colour (usually orange), shape (rounded) and size	none
a chisel fragment	The bigger aggregation of sand in one spot and the rest dispersed on the object's surface	
	Remains of charcoal, straws and fiber (probably modern)	**XRD**
		none
General description	**SEM-EDS**	
Weight: 2,9089 g	Mainly: Cu, Cl, O, Ca, C, Si, K, Al, S, Fe, Na, P, Mg	**ICP-OES and ICP-MS**
Length: 2 cm	Minor: Ni	none
Width: 0,8-1 cm	Main corrosion compounds: Cl and O but also S and a little bit of Na	
Thickness: 0,5-0,7 cm	Green and white colours of corrosion patina layers	**Sr isotope analysis**
Cross section: rectangular	Spherical, rod-shaped, cubic, spike and tree-like nanostructures	none
Rectangular shape	The surface is rather porous and also some more compacted area occurs	
	Many cracks and holes are located on the surface	
	Quartz sand particles attached to the surface of the object	
	Crust is made of Si, Ca, K, O, Al, Mg	
	Organic remains: charcoal and fiber (modern)	
	Microorganisms connected to corrosion process	

Sample	Optical Microscopy	FTIR
Sq. 46	The whole object is covered with thick crust of sand particles	none
US: 2d	Sand grains vary in colour (usually orange – brown), shape (rounded) and size	
Phase: III	Cracks appear on the object's surface	**EDXD**
Date: 21.05.1984	Light green and whitish mineralisations on the surface	none
Copper object (ore)	Sand particles are affected by green colour of mineralisations	
	Some remains of charcoal and straws	**XRD**
		none
General description	**SEM-EDS**	
Weight: 3,2750 g	Mainly: Cu, Cl, O, Ca, C, Si, S, K, Al, Fe, P, Mg	**ICP-OES and ICP-MS**
Length: 1,6 cm	Minor: Ti, Mn	none
Width: 1,3 cm	Main corrosion compounds: Cl and O	
Thickness: 1,1 cm	Green and white colours of corrosion patina layers	**Sr isotope analysis**
Irregular shape	Spherical and rod-shaped nanostructures	none
	The surface is very porous	
	Many cracks are located on the surface	
	Quartz sand particles attached to the surface of the object	
	Crust is made of Si, Ca, K, O, Al, Mg	
	Organic remains: charcoal	

Sample	Optical Microscopy	FTIR
Sq. I	Some remains of roots and fibers (modern) detected on both pieces	none
US: 5c β	Sand grains vary in colour (usually orange – brown), shape (rounded) and size	
Phase: Ia	B: covered with the homogeneous thick crust of sand and copper mineralisations	**EDXD**
Date: 27.03.1978	B: big sand particles attached to the object	none
Two metal objects (ores?)	S: it has rounded surface covered with sand particles	
B – bigger piece	S: in some spots on the surface copper drops are visible	**XRD**
S – smaller piece		none
	SEM-EDS	
General description	B – mainly: Cu, Cl, O, Ca, C, Si, K, Al, Fe, P, Mg	**ICP-OES and ICP-MS**
Weight: 1,2727 g (total);	B – minor: Na, S, Sr, Ba, Ti	none
B: 0,9658 g; S:0,3070 g	S – Cu, Cl, O, Ca, C, S, Si, K, Al, Fe, P, Mg	
B: 1,2 x 0,9 cm; S: 0,7 x 0,7 cm	Main corrosion compounds: Cl and O	**Sr isotope analysis**
Both objects have irregular shape	Green and white colours of corrosion patina layers	none
	Spherical and rod-shaped nanostructures	
	The surface is very porous	
	Many cracks are located on the surface	
	Quartz sand particles attached to the surface of the object	
	Crust is made of Si, Ca, K, O, Al, Mg	
	Organic remains: charcoal and straws	

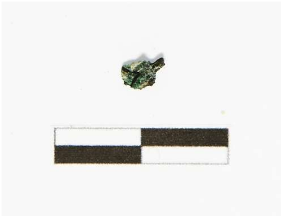
Photos of the objects

Sample	Photo
Sq. IVS, US: 5a	
Sq. V W, US: 1b-2a	
Sq. VI, US: L	 
Sq. XIII, US:?	

Sq. XIII-XVII, Cl. gebel	
Sq. XVII, US: 1b	
Sq. IV E, US: 4a	
Sq. IV N, US: 5a	
Sq. IV N, US: 5cd	
Sq. V, US: 4a	

Sq. X, US: 2c	 
Sq. X, US: 2g	
Sq. X, US: 2a	 
Sq. balk VI- IX, US: 2a	
Sq. I, US: 5c β	 
Sq. I, US: 7b	

Sq. I W, US: 3b α	
Sq. II, US: 3c	 
Sq. IV W, US: 2c α	
Sq. IV E, US: 2c	
Sq. 46, US: 3b	 

Sq. 46, US: 2d	 
Sq. 46, US: 2f	
Sq. 44, US: 3c	
Sq. 40, US: 4	 
Sq. 39, US: 4	 

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