Nails from a 2,400 Year Old Shipwreck: A Study of Copper in a Marine Archaeological Environment

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The metal nails that fastened the wooden components of a 2,400 year old ship found along the coast of kibbutz Ma'agan Mikhael, Israel, were made of unalloyed copper that was intensively hammered. A lead isotope analysis of one nail indicates with high probability that it was made of copper from Cyprus. The copper of the nails in the wood was replaced entirely by copper sulfide mineral, displaying the occurrence of deep anaerobic conditions in a breaker zone under a shallow cover of sand. The slow decay of the cellulose and hemicellulose in the wood is a possible explanation for the specific necessary environmental conditions.

Nails from a 2,400 Year Old Shipwreck: A Study of Copper in a Marine Archaeological Environment

S. Shalev, Y. Kahanov, and C. Doherty

Figure 1. The ship's freshly exposed bow.[1]

INTRODUCTION

There are rare cases in archaeology when finds are encapsulated within extreme and well-defined environmental conditions in a relatively known time scale. Such cases may serve as a unique laboratory for studying chemical processes through time and for reconstructing the micro-environmental conditions that dictated the choice of material and might have caused observed alterations in chemical and mechanical properties. Such is the case of metal nails that were made and used to fasten the wooden components of the structure of a ship that sank to the bottom of the Mediterranean Sea some 2,400 years ago.

In the fall of 1985, while diving in shallow water less than 2 m in depth along the coast of kibbutz Ma'agan Mikhael, some 30 km south of Haifa, Israel, a member of the kibbutz noticed the remains of wood and broken pottery shards covered by a large pile of stones that were not from local provenance. He alerted Elisha Linder from Haifa University, who, with the help of Jay Rosloff from the Institute of Nautical Archaeology at the University of Texas A&M, excavated the site.[1] It took six pairs of divers (shown on the cover of this issue) and an additional five auxiliary expedition members on the shore working in one and a half hour shifts for 32 net days to clear 1.5 m of sand that covered the entire shipwreck and its contents. The ship timbers were dismantled underwater and conserved with polyethylene glycol at the Center for Maritime Studies' conservation laboratory for seven years. The conserved timbers are now being reassembled at the University of Haifa.[1]

Pottery analyses and radiocarbon methods have dated the ship to about 400 B.C., during the Persian Period. The ship was a small merchantman estimated to have been about 13.5 m long and 4.1 m amidships with a displacement of 20 tonnes. It may have sunk only a short time after its launching.

Among the archaeological findings at the site were 13 tonnes of stones and rocks; five different lithic types were identified. The largest amount of stones found is of a Blueschist type from around Euboea (Evia), Greece. Another type, Gabro rocks, were identified as originating at the Kouris River in southern Cyprus.

Seventy ceramic items were retrieved, including a pithos, basket handle jars, mortiers, a cooking pot, jugs, juglets,

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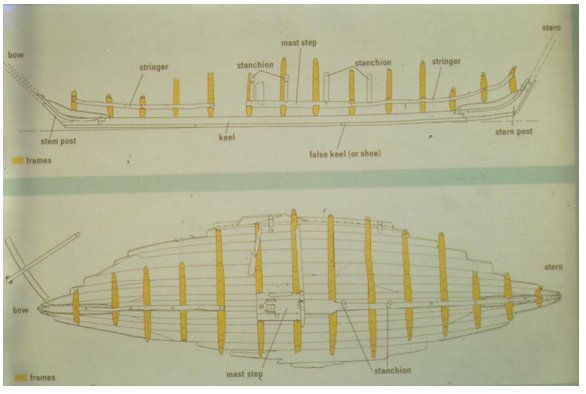


Figure 2. A plan of the hull remains of the ship.[1]

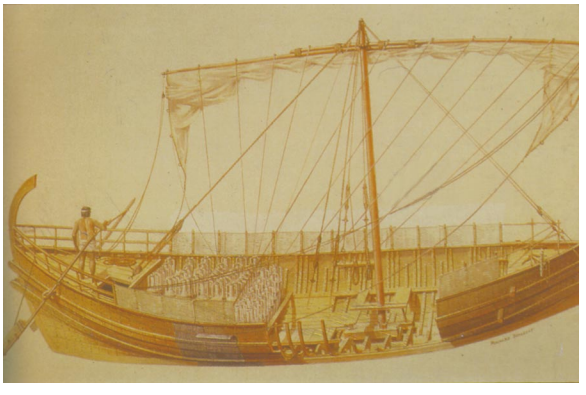


Figure 3. An artist's reconstruction of the Kyrenia ship.[1]

Over the last 30 years, there has been a discernible increase in the number of scholars who have focused their research on early industrial organizations, a field of study that has come to be known as **Archaeotechnology**. Archaeologists have conducted fieldwork geared to the study of ancient technologies in a cultural context and have drawn on the laboratory analyses developed by materials scientists as one portion of their interpretive program. Papers for this bimonthly department are solicited and reviewed by **Robert M. Ehrenreich** of the National Materials Advisory Board of the National Research Council.

Shalev *(Continued from page 14.)*
bowls, and black-glazed vessels. Most of them can be attributed to Cyprus, although some were identified as originating in Greece. Some remnants of food were found; most were common to all of the Mediterranean, but some have been identified as originating in what is now southwest Turkey or the nearby Aegean Islands. Other findings included ropes, lead ingot, carpenter tools, a grinder stone, decorative wooden boxes, and a one-armed wooden anchor.

THE SHIP

Most of the original wooden structure of the ship is preserved in superb condition (Figure 1). It measures 11.15 m long, 3.35 m wide, and 1.5 m high (Figure 2). Most of the structural components of the hull are of pine, including the keel, the stem and stern posts, the frames, and the planks. Only the false-keel, tenons, and tapered pegs are of oak.

The entire lower portion of the hull was preserved. The pine keel (8.25 m length) was found intact. The oak false keel was found complete as well as the lower stem and stern posts. The port side was preserved to the seventh strake, while the starboard side was found intact to just above the level of the wale. The strakes, made of pine, were composed of two planks scarfed together. Their typical dimensions were 20 cm wide and 4 cm thick. Sections of 14 frames were preserved. The frames were full frames, widely spaced, composed of floor timbers and futtocks. Also surviving were two knees, the mast-step, stringer, lateral beams, and stanchions.

The Ma'agan Mikhael ship met its fate some 95 or 100 years before the Kyrenia ship, another shipwreck that has many important similarities (Figure 3). Both were originally about 14 m long and were built by the "shell-first" method in which the planks of the hull are joined first by mortise and tenon joints; only later are the frames added. The Ma'agan Mikhael ship frames were attached to the planks by metal nails (Figure 4) thought to be made of iron and inserted through wooden pegs.[2–4]

THE METAL NAILS

An analysis of the composition and microstructure of the metal nails from the Ma'agan Mikhael ship have identified the original material and reconstructed the process the nails have undergone from the day of their sinking to the day they were uncovered by marine archaeologists.

The metal nails were found in three separate archaeological contexts. First, the majority of the findings consist of nail concretions in their original location, still attached to the wooden structure of the ship (Figure 5a). Second, several nail concretions were found detached, but in close proximity to the wreck. In one of these nails, remains of the original metal were found (Figure 5b). Third, four well-preserved metal nails were found with no concretion in the vicinity of the wreck (Figure 5c).

Figure 4. A metal nail still attached to a floor timber after removing the futtock.

Twenty samples were selected from different locations, cold mounted, and polished for metallographic and metallurgical analysis. Optical metallography was conducted primarily with an Olympus PME 3 inverted metallurgical microscope and hardness was measured by a Shimadzu microhardness tester HMV-2000, both in the Weizmann Institute of Science, Israel. Qualitative and quantitative chemical analyses were performed with an electron-probe x-ray microanalyzer on a Camebax SX50 scanning electron micro-probe in the Department of Materials at Oxford University, with the help of Chris Salter, using a wavelength dispersive spectrometer. The operating conditions and the detection limits for the various elements, detailed in Shalev 1995,[5] are in the region of 100–200 ppm for the relevant elements.

The metal nails (17–30 cm) were originally made of copper and were inserted straight into the wood structure from the outer side of the planks and double clenched into the inner face of the frame (Figure 4). Their head profile is concave on top (up to 0.42 cm thick) (Figure 5) and round (2.06 cm in diameter); the shaft section is square (up to 0.66 cm). The concretion thickness varied between 0.3–0.7 cm around the corroded nail.

Following the sinking of the ship, most of the wreck was buried deep enough in the sand to be isolated from the circulation of the oxidizing seawater (up to 9 mg oxygen per liter). In these deep anaerobic conditions with a redox potential (Eh) of at least –250 mV, the entire copper structure of the nail and the en-

a b c

Figure 5. (a) A section of an upper part of a nail from the wooden structure, (b) a section of an upper part of a nail found in close proximity to the wooden structure, and (c) a copper nail from the vicinity of the wreck.

THE PERSIAN PERIOD

The conquest of Babylonia by the Persians in 539 B.C. proved a decisive turning point for the whole of the ancient Near East. A new epoch began in the region, a period of imperial Persian domination after which the local Persian Period is named. Until 332 B.C., when the whole of the Near East was conquered by Alexander the Great, the Persians continued to rule this region.

The Persian Empire was the largest known to the ancient world, and its borders stretched from northern Africa to southern Russia and from Asia Minor to India. In the administrative sphere, the Persian Empire inherited the system of internal subdivision employed by the Assyrians and Babylonians. In addition to Syria, Phoenicia, and Cyprus, Samaria and Judah were included in the fifth satrapy of the empire—Abar-Nahara or "the land beyond the (Euphrates) river." In this period, coins began to come into use for the first time in this area. The coins in circulation included examples from Greece and the Phoenician cities as well as locally minted coins.

From an archaeological viewpoint, this period was, until recently, one of the most obscure in the history of Israel, and only because of recent excavations is a clearer picture beginning to emerge. Some continuity of tradition from the preceding period can be traced in the material culture of the inner parts of the country. In contrast, a new material culture appeared in the coastal area and Galilee, characterized mainly by objects imported from Greece, Cyprus, Egypt, Persia, and the Phoenician cities.[15,16]

THE KYRENIA SHIPWRECK

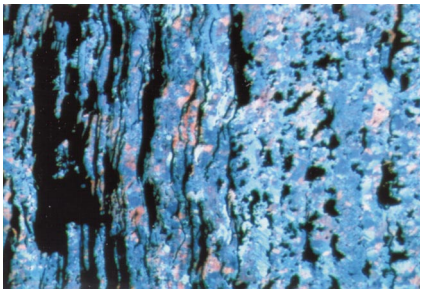
Authors' Note: For more information on the Kyrenia shipwreck, refer to the following references: "The Kyrenia Ship: An Interim Report on its Hull Construction," by J.R. Steffy, *American Journal of Archaeology 89*, 1985, pp. 71–101 and *Wooden Ship Building and the Interpretation of Shipwrecks*, by J.R. Steffy, published by Texas A&M University Press, 1994.

The Kyrenia shipwreck was found in 1967 by a sponge diver one kilometer off the northern coast of Cyprus, close to the town of Kyrenia, at a depth of 30 m. The ship was dated to the end of the fourth century B.C. It was a small merchantman with an estimated length of slightly less than 14 m. In the site were found 404 amphoras, ceramic vessels (some of which belonged to the crew), mill stones, almonds, working tools, coins, and arrow heads. A significant part of the hull survived.

The ship was shell-first constructed by a close set of mortise and tenon joints. The framing system was composed of alternating floor timbers and half frames that were attached to the hull by copper nails. The excavation of the ship was directed by M. Katzev. The waterlogged wooden elements were dismantled underwater and retrieved from the sea bottom to the surface, where they were conserved with polyethylene glycol. Today, the reassembled wooden elements are exhibited in the Kyrenia castle.

The ship's relevance to the Ma'agan Mikhael ship is due to several factors. First, the Ma'agan Mikhael ship sunk only about 100 years earlier than the Kyrenia ship. The construction method of the two ships is similar as is the size, general shape, longitudinal silhouette, and the lateral section. The same wood types were used in both ships for the same elements. A few additional construction elements are very similar: the planking pattern; the plank scarfs; the oak false keel; the oak tenons and tapered pegs; and the general shape of the mast step.

There are, of course, a few different elements, such as the framing system and the lead sheathing that was evident in the Kyrenia ship. Still, although the Kyrenia ship is slightly younger than the Ma'agan Mikhael ship and has some characteristics similar to the later Roman shipbuilding tradition, she is one of the closest parallels to the Ma'agan Mikhael ship.



180 μm

Figure 6. Small covellite crystals that replaced the original copper body of the nail.

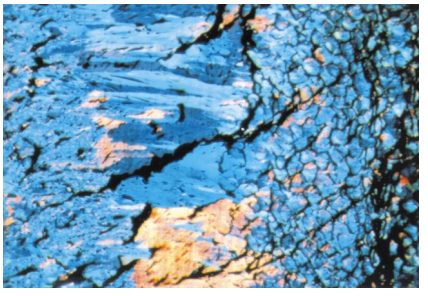


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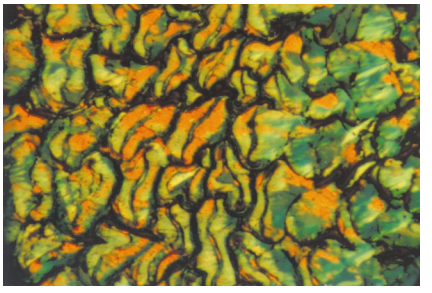
Figure 7. Large covellite crystals between replaced nail (left) and replaced wood (right).



45 μm

Figure 8. The outer covellite zone preserving the cellular structure of the wood.

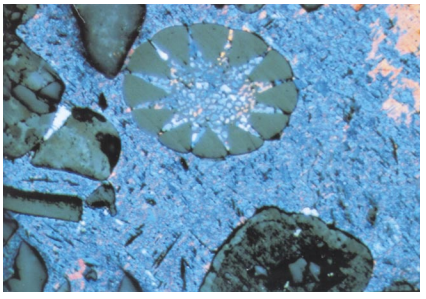


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Figure 9. Imbedded sand and shell fragments in a covellite grain supported framework above the nail's head.

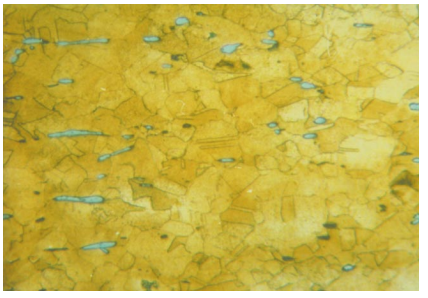

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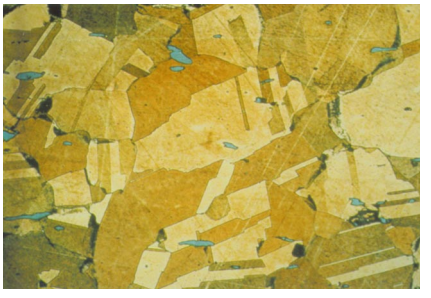
Figure 10. Elongated CuS inclusions representing intensive hammering. (Photographed by A. Pasternak.)



45 μm

Figure 11. Equiaxed small grains and twins representing cycles of hammering and annealing.

closed wood tissue (Figure 5a) was replaced by copper-sulfide mineral covellite (about 67% copper and 33% sulfur). The square-section shape of the original nail was replaced by small crystals of covellite typically aligned along the relic texture of the original hammered copper (Figure 6). Behind this was a zone of large covellite crystals (Figure 7) which had developed at right angles to the long axis of the nail. The outer covellite zone was of replaced wood (Figure 8), preserving the original cellular structures. The outer zone above the head of the nail was comprised of a grain-supported framework of quartz sand and shell fragments (Figure 9) in a covellite matrix. X-ray diffraction analysis of two corroded nail fragments at the Technion, Haifa, and the Geological Institute, Jerusalem, identified the brittle black-blue mineral of the nail corrosion as covellite and the blue concretion with white inclusions on the nail's head as covellite matrix with quartz and calcium-carbonate inclusions.

Copper in the aerobic environment of seawater is oxidized quite rapidly[6] on a scale of a few tens of micrometers of paratacamite, often with a mixture of cupric hydroxide and basic cupric carbonate, per year. This corrosion layer is toxic to micro-organisms and protects the copper from sulfides. Therefore, the sulfidization of the copper nails could have occurred only if they had reached deep anaerobic conditions when they were still relatively new. This assumption fits quite well with the state of the wood (Figure 1) with no signs of teredo (ship-worm infestation) or wood wear from recurrent sailing.

The formation of copper-sulfide layers through the bacterial reduction of sulfates in marine environments is well known,[7,8] although it is hard to imagine how deep anaerobic conditions, necessary for the bacterial reduction of sulfates, may occur in a breaker zone under 1.5 m of sand. The slow decay of the cellulose and hemicellulose in the wood may create a micro-environment of deep anaerobic conditions around the copper nails in the wood simply by absorbing most of the scarce available oxygen in the immediate vicinity of the wreck.

In order to check the validity of this model, additional nails that were exposed to oxidizing conditions in an underwater environment were sought. As might be expected, four intact nails (Figure 5c) covered in thin patina and similar in shape and size to the covellite cores in the nails concretions were found in the sand near the wreck.

(Continued on page 20.)

Shalev *(Continued from page 17.)*

Metallographic and chemical analyses of preserved metal remains (groups two and three) enabled us to identify the original properties of the metal and to ascertain the means of production and utilization of these nails. The bulk composition is copper with impurities of less than 0.7% Fe, 0.5% S, 0.4% As, 0.08% Ag, and 0.04% Sb/Pb/Au. The nails were intensively hammered up to 70–80 percent total reduction, as shown in the elongated CuS inclusions (Figure 10) and the equiaxed small grains of about 30 µm (Figure 11). This mechanical treatment dramatically improved the hardness of the metal, up to 125 Hv close to the edge and 100 Hv in the center. That is about the maximum hardness for unalloyed copper, identical to Early Bronze Age dagger blades,[9] more than twice the value of as-cast copper, and half the hardness of hammered tin bronze.

Several metal nails from the Kyrenia shipwreck were previously analyzed. An x-ray fluorescence spectrometry analysis of four objects showed that they were also made of 99% copper with less than 1% lead.[10] The metallographic analysis of the copper remains of one nail[11] was identical in microstructure and metal properties to the Ma'agan Mikhael nails.

One nail fragment was submitted for lead-isotope analysis in the Isotrace Laboratory, Department of Physics, University of Oxford. The procedures used are specified in Stos-Gale et al.[12] The results were 2.07321 for $^{208}Pb/^{206}Pb$, 0.84161 for $^{207}Pb/^{206}Pb$, and 18.493 for $^{206}Pb/^{204}Pb$. This composition is identical to a group of sulfide-copper ores from the mines of Apliki and Mavrovoni in the Morphou Bay, Cyprus.[13,14]

CONCLUSIONS

The lead-isotope evidence indicates with high probability that the analyzed nail from the Ma'agan Mikhael wreck was made of copper that was mined in northwest Cyprus. It was concluded that these nails were directly inserted into the wood without any wooden plug treenails. They were deliberately made of copper instead of bronze or iron, widely known and used during the Persian period, to be strong enough to fasten the frames to the ship's hull while not being too brittle and resisting the cutting pressures on the structure in motion.

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