HUNGARIAN ARCHAEOLOGY
E-JOURNAL • 2013 WINTER
www.hungarianarchaeology.hu

PROOF OF THE METEORITIC ORIGIN OF MANKIND'S EARLIEST IRON ARTEFACTS THROUGH NEUTRON AND X-RAY ANALYSIS

László Rosta[1], Tamás Belgya[2], György Káli[1], Zsolt Kasztovszky[2], Zoltán Kis[2], Imre Kovács[3], Boglárka Maróti[2], László Szentmiklósi[2], Zoltán Szőkefalvi-Nagy[3], Albert Jambon[4], Thilo Rehren[5]

In August of 2013 the publication of a new study in the Journal of Archaeological Science appeared which reveals that 5000 year old Egyptian iron beads have been found to be made from hammered pieces of meteorites.[6] The nature and origin of humankind's earliest iron artefacts has been a matter of debate for over a century. This discovery not only demonstrates a successful nuclear analytical methodology to uncover trace elements after complete corrosion, but also proves that already in the fourth millennium BC metalworkers had mastered the smithing of meteoritic iron, an iron-nickel alloy much harder and more brittle than the more commonly worked copper.

This study focuses on the earliest known iron artefacts – nine small beads positively dated to circa 3200 BC, from two burials at Gerzeh in northern Egypt. The iron beads were strung onto a necklace together with other exotic minerals such as lapis lazuli, gold and carnelian, revealing the status of meteoritic iron as a special material on a par with precious metal and gem stones. The experimental study of three iron beads was performed at the Budapest Neutron Centre. Neutron and proton beam techniques were applied: Prompt gamma activation analysis, time-of-flight neutron diffraction and particle induced X-ray emission spectroscopy have resulted in compositional data showing that the beads were made from meteoritic iron. Neutron tomography has revealed the inner topology of the finds; they were formed from thin sheets of presumably hammered metal rolled into cylindrical beads. No actual metal survives in any of the beads studied, but their corrosion products and preserved shape clearly point to their manufacture from hammered and rolled meteoritic iron sheets.

The nature and origin of mankind's earliest iron artefacts have remained a matter of uncertainty and dispute ever since their excavation in 1911, from a pre-dynastic cemetery near the village of el-Gerzeh in Lower Egypt. A total of nine tubular iron beads were retrieved from the cemetery, all from two closed archaeological contexts, and so can be dated with certainty. Four beads were found in their original order as strung into a necklace with tubular lapis lazuli, carnelian, agate, and gold beads;[7] this tomb also contained three more iron beads, a limestone mace-head, a copper harpoon, a small ivory vessel, a mudstone fish-shaped palette, an ivory spoon, a flint bladelet, two stone vessels and twelve ceramic vessels. Two more beads were from another tomb, which contained the most diverse materials in the entire cemetery: lapis lazuli, obsidian, gold, carnelian, calcite, chalcedony, steatite, faience, garnet and serpentine (*Fig. 1*). Both the material diversity and the opulence of the goods from these two tombs indicate the distinguished roles, status and wealth

1 Wigner Research Centre for Physics, Hungarian Academy of Sciences, Institute for Solid State Physics and Optics
2 Centre for Energy Research, Hungarian Academy of Sciences
3 Wigner Research Centre for Physics, Hungarian Academy of Sciences, Institute for Particle and Nuclear Physics
4 Université Pierre et Marie Curie, Paris
5 University College London, Qatar, a UCL department at Hamad bin Khalifa University, Doha

6 Rehren, Thilo – Belgya, Tamás – Jambon, Albert – Káli, György – Kasztovszky, Zsolt – Kis, Zoltán – Kovács, Imre – Maróti, Boglárka – Martinón-Torres, Marcos – Miniaci, Gianluca – Pigott, Vincent C. – Radivojevi, Miljana – Rosta, László – Szentmiklósi, László – Szőkefalvi-Nagy, Zoltán: 5,000 Years Old Egyptian Iron Beads Made from Hammered Meteoritic Iron. *Journal of Archaeological Science* 40 (2013)/12, 4785–4792, http://dx.doi.org/10.1016/j.jas.2013.06.002

7 Petrie, William M.F. – Wainwright, Gerald A. – Mackay, Ernest J.H.: *The Labyrinth, Gerzeh and Mazghuneh* (London: British School of Archaeology in Egypt, University College, 1912).

of the deceased from a social and economic aspect, as well as perhaps a specific link to some particular role in specialized networks of trade relations.[8] As such, the el-Gerzeh beads support the idea that the initial use of a metal (e.g., iron, copper, gold) is impelled by "the desire for new materials to serve as aesthetic visual displays of identity, whether of a social, cultural or ideological nature".[9]

Fig. 1: Collection of stone and faience beads from Tomb 67 – modern re-stringing, without the iron beads

Since both tombs are securely dated to Naqada IIC-IIIA, c. 3400–3100 BC, the beads predate the emergence of iron smelting by nearly 2,000 years, and other known meteoritic iron artefacts by more than 1,000 years, giving them an exceptional position in the history of metal use. Their early date makes it reasonable to assume that they were made from meteoritic iron; while the tombs were undisturbed, the intrusion into the tomb of man-made iron through taphonomic processes or contamination during excavation cannot be excluded entirely. Here we present positive proof of a meteoritic origin of these beads, strengthening the argument that these are indeed the earliest known examples of iron metal worked by humans.

Meteoritic iron has several characteristics that distinguish it from smelted iron. Most prominent are the large crystal grain size and Widmannstaetten pattern, elevated bulk concentrations of nickel (1 to 10 wt%), cobalt (1000 to 10,000 ppm) and germanium (mostly 200 to 400 ppm), and the presence of mineral phases such as schreibersite ([Fe,Ni]3P), troilite [FeS] and sphalerite [ZnS]. Some of these characteristics, however, are not diagnostic. While germanium has not been found in smelted iron above c 10 ppm, nickel and cobalt are common alloying elements in modern steel, and have been found in similar concentrations in some ancient smelted iron. Elevated phosphorus and sulphur concentrations are also found in smelted iron. The chemical and micro-structural characteristics of meteoritic iron may also be distorted or lost through extended working of the metal or corrosion during burial.

We analysed the three beads currently held at the UCL Petrie Museum of Egyptology in London, UK for their composition and surviving structure using non-invasive methods (*Fig. 2*). Earlier analysis by pXRF indicated an elevated nickel content on the surface of the beads in the order of a few per cent, and their magnetic properties suggested that iron metal may be present in their body. Following this, prompt-gamma activation analysis (PGAA), particle-induced X-ray emission (PIXE), neutron radiography (NR), and time-of-flight neutron diffraction (ToF-ND) were used[10] to characterise surface and body of the beads, at the laboratories of the Budapest Neutron Centre.[11]

By ToF-ND testing for grain size and crystal lattice structure of any metallic phases present in the beads, no metallic form of iron was found. No definite Bragg peaks were observed, consequently they should consist of a larger number of low symmetry crystalline phases (probably with non-uniform chemical compositions, as oxides), imperfectly crystallized or amorphous compounds (these occur typically at hydroxides) and/or

[8] Stevenson, Alice: *The Predynastic Egyptian Cemetery of el-Gerzeh: Social Identities and Mortuary Practices*. Orientalia Lovaniensia Analecta 186 (Leuven – Paris – Walpole: Peeters, 2009), 192–199.

[9] Roberts, Benjamin W. – Thornton, Christopher P. – Pigott, Vincent C.: Development of Metallurgy in Eurasia. *Antiquity* 83 (2009)/322, 1019.

[10] Kasztovszky, Zsolt – Rosta, László: How can Neutrons Contribute to Cultural Heritage Research? *Neutron News* 23 (2012), 25–29.

[11] Rosta László: A neutronkutatások nyolcvan éve és mai társadalmi haszna (Eighty years of neutron research and its use to present-day society). *Magyar Tudomány* (Hungarian Science), 2013/4, 488–497.

Fig. 2: Photographs of three of the nine original iron beads from Gerzeh, Lower Egypt (from left UC10738, UC10739 and UC10740)

hydrogen in any other form. This is considered typical for the corrosion products of iron.

Neutron radiography revealed the original shapes and bulk morphology of the artefacts and details of their manufacture. All three artefacts have a central hole along their long axis that was not visible during visual inspection due to corrosion. These images demonstrate that the beads were made from rolled iron sheets, with areas of overlapping metal visible at the centre of the seam and V-shaped tapering at one end of bead UC10740 (*Fig. 3*). This would have required repeated hammering with intermittent annealing, a technique also documented for pre-Columbian Hopewellian meteoritic iron beads.[12]

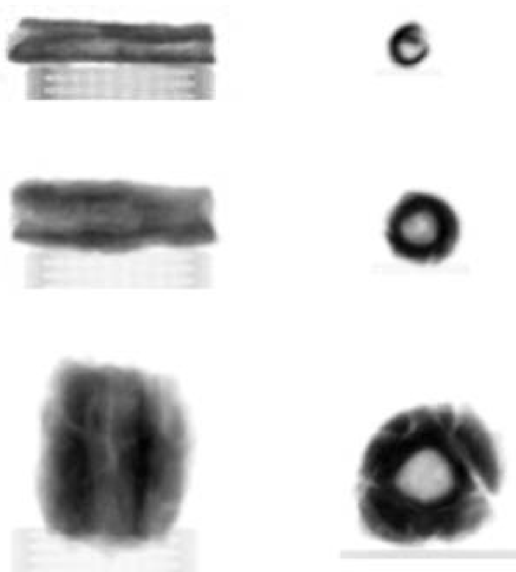

Fig. 3: Neutron radiographs of the three beads 10740, 10739, 10738 (from top), side view and longitudinally

PGAA showed that the beads consist predominantly of iron and oxygen in broadly similar amounts, which is consistent with their corroded state. Of more interest, the beads contain between 2.8 and 4.1 wt% nickel, 0.6 to 1.0 wt% phosphorus, and 1700 to 2400 ppm cobalt. Small amounts of light elements (hydrogen to manganese) are thought to represent corrosion and soil particles incorporated from the burial environment. PIXE analysis of the beads' surfaces (*Fig. 4*) confirmed the presence of iron as the main element, followed by nickel at an estimated 5 wt%. Individual areas have different concentrations of copper, lead, arsenic, zinc and manganese, reaching several hundreds of ppm. (The X-rays from lighter elements were filtered out to avoid disturbing pile-up peaks.) Two of the three beads showed areas with germanium above the detection limit estimated to be at c 30 ppm, and reaching up to c 100 ppm in individual areas. Due to the elevated detection limit of 1000 ppm for germanium caused by the germanium content of the detector used in the PGAA measurements it was not possible to detect this element by PGAA in such low concentrations.

The most surprising finding of the neutron radiography images was the wrapped sheet-like internal structure, which was preserved in spite of the complete corrosion of the beads. The bulk content of the beads in iron, nickel, cobalt, and phosphorus are consistent with meteoritic iron. Germanium levels as found by PIXE in selected areas on the surface of two of the beads reach about half the level common for meteorites,

[12] McCoy, Timothy J. – Marquardt, A. E. – Vicenzi, Edward P. – Ash, Richard D. – Wasson, John T.: Meteoritic Metal Beads from the Havana, Illinois, Hopewell Mounds: A Source in Minnesota and Implications for Trade and Manufacture. *39th Lunar and Planetary Science Conference* (2008), Abstract #1984.

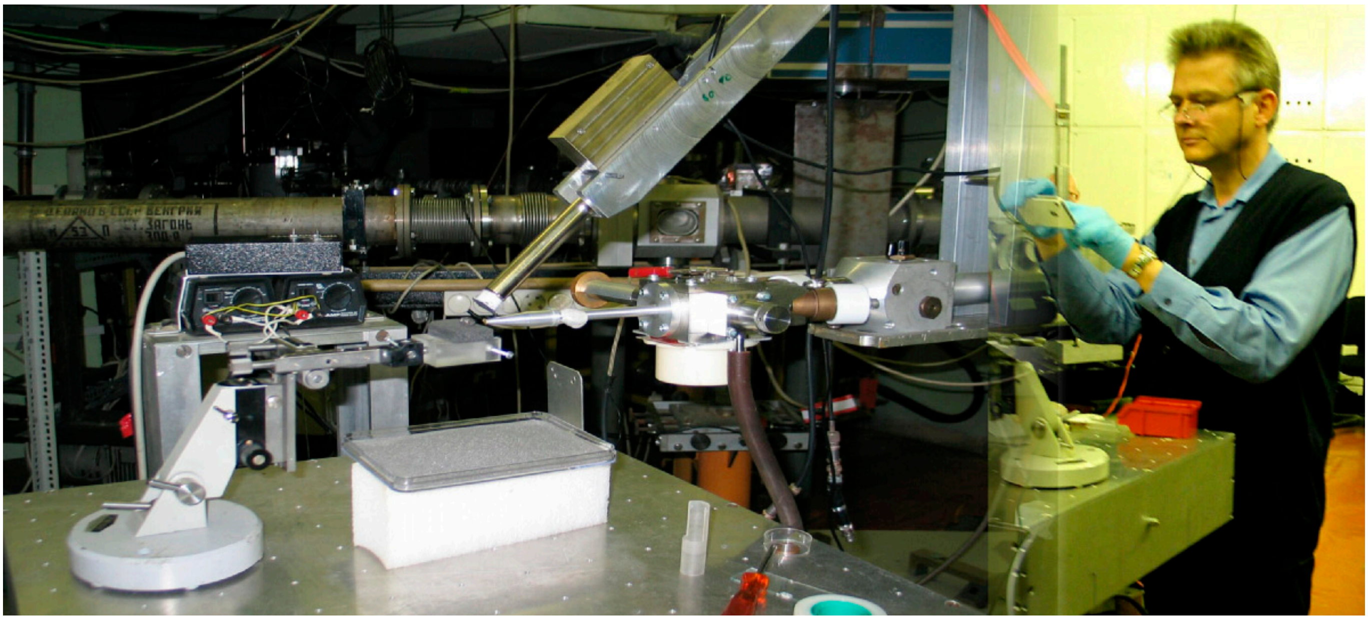

Fig.4: Prof. Thilo Rehnen (University College London) checking the placement of one of the beads at the PIXE facility of the proton accelerator (Wigner Research Centre)

much higher than levels detected in smelted iron. We can explain the relatively lower level of germanium compared to fresh meteoritic iron by the selective oxidation and subsequent loss of germanium during smithing. Repeated heating and hammering would also have broken up any coarse-grained Widmannstaetten texture into irregular small ferrite grains, and destroyed the schreibersite crystals, partially homogenising the phosphorus content across the worked metal.[13] The diagnostic textural properties of meteoritic iron were therefore most likely already lost prior to the corrosion of the metal.

Copper, zinc, arsenic and lead are not present in meteoritic iron at levels similar to those found on the surfaces of the archaeological beads, but can all occur in smelted iron. PIXE found significant amounts of these elements, whereas PGAA did not detect them because it has higher detection limits. We assume that the presence of these elements on the surface is a consequence of environmental contamination and electrochemical precipitation onto the corroding iron beads. Copper, arsenic and possibly lead are presumed to have come from the large copper harpoon found in the same tomb. Alternatively, they could originate from contamination by copper tools used in the manufacture of the beads, such as tongs or rods for rolling the metal around to shape the tubes. An environmental origin is assumed for boron and chlorine, both common in the saline soils of Egypt's desert into which the tombs were dug. The zinc content is inconclusive; it can either be due to environmental contamination or stem from zinc sulphide present in the original meteoritic metal.

Following our results on the Petrie Museum's beads, a recent study was published by a Manchester group which concerns another piece of the same Gerzeh excavation held at the Manchester Museum.[14] Although the research group from Manchester used X-ray techniques, completely different methods than ours during their investigation, they achieved very similar results. We should add, however, that X-ray analytical methods presented by them are suitable only for surface or near-surface analysis of the artefacts. In contrast, we were able to carry out absolutely non-destructive neutron analyses providing bulk compositional information on the entire objects. In fact, the similar results of the measurements performed in varying methods on different pieces of the same group of beads complement one another, supporting the conclusions to this scientific question from two directions.

---

[13] Ibid.

[14] Johnson, Diane – Tyldesley, Joyce – Lowe, Tristan – Withers, Philip J. – Grady, Monica M.: Analysis of a Prehistoric Egyptian iron Bead with Implications for the Use and Perception of Meteorite Iron in Ancient Egypt. *Meteoritics & Planetary Science* 48 (2013)/6, 997–1006, doi: 10.1111/maps.12120

In conclusion, the composition of the beads is consistent with meteoritic origin of the metal. The germanium content is the strongest proof for this, despite the irregular and relatively low concentrations found. The presence of elements not consistent with a meteoritic origin is explained by environmental contamination, particularly from the corrosion of a large copper artefact near-by. The shape of the beads was obtained by smithing and rolling, probably involving multiple cycles of hammering and annealing, not by stone-working techniques such as carving or drilling used for the other tubular beads from this tomb. No metallic structure was identified by the non-invasive methods used, due to the complete corrosion of the beads. It is assumed that recrystallization and homogenisation during the hammering and annealing of the original meteoritic iron into sheet metal would have removed much of the original structure even prior to corrosion. Cycles of hammering and annealing were used previously for producing similar beads made of soft copper during the Neolithic and Early Bronze Age. However, the beads we have studied are the earliest smithed iron artefacts known, and were made from a material that was much more difficult to work. Their composition and method of manufacture rule out a more recent origin of the beads, confirming that they are not later intrusions into Gerzeh tombs 67 and 133, but indeed humankind's oldest known iron artefacts.

Recommended literature

Kasztovszky, Zsolt – Rosta, László
How can Neutrons Contribute to Cultural Heritage Research? *Neutron News* 23 (2012), 25–29.

Rehren, Thilo – Belgya, Tamás – Jambon, Albert – Káli, György – Kasztovszky, Zsolt – Kis, Zoltán – Kovács, Imre – Maróti, Boglárka – Martinón-Torres, Marcos – Miniaci, Gianluca – Pigott, Vincent C. – Radivojevi, Miljana – Rosta, László – Szentmiklósi, László – Szőkefalvi-Nagy, Zoltán
5,000 Years Old Egyptian Iron Beads Made from Hammered Meteoritic Iron. *Journal of Archaeological Science* 40 (2013)/12, 4785–4792.

Roberts, Benjamin W. – Thornton, Christopher P. – Pigott, Vincent C.
Development of Metallurgy in Eurasia. *Antiquity* 83 (2009)/322, 1012–1022.