Scientific Studies on Gold Objects

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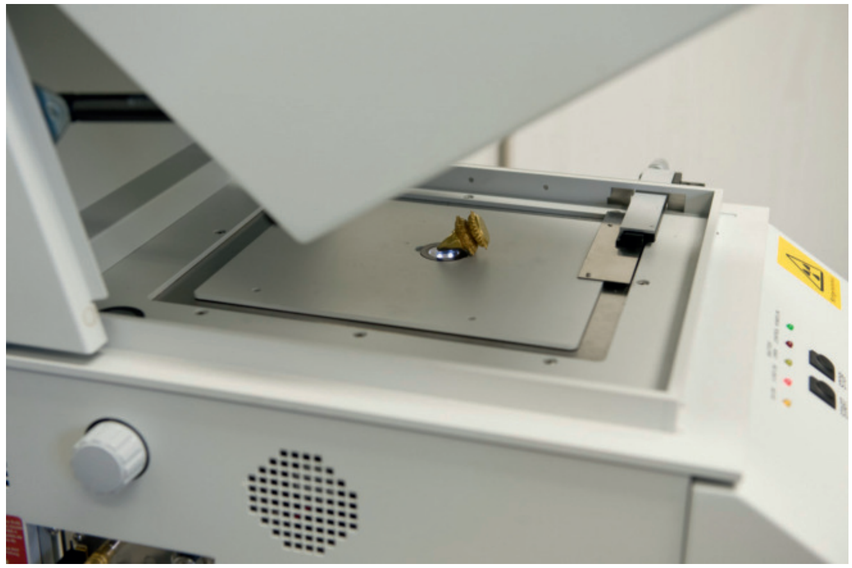
Gold is an extremely rare metal, whose special attraction is based on its colour and its high resistance to corrosion. Gold therefore has an unique status in the history of mankind, as it has always been a symbol of rank, prestige and power. Gold jewellery in particular served as a medium to express social, ethnic and religious affiliations. While iron, e.g., was associated with the god of war Mars in classical antiquity and thus rather negatively regarded, gold represented the sun, light, purity, fertility and immortality. Since gold is resistant to almost any chemical attack, it occurs predominantly in its elemental form on earth and is therefore one of the earliest metals used by humans. However, native gold is always a natural alloy of gold with sometimes up to forty percent silver. In the past it could not be purified, i.e. separated from the silver, until a method called cementation was developed. Pure gold has a very high plastic deformability (ductility) and could very early be turned into thin foils, which were used for the gilding of other materials. Due to the close connection to the rank and status of the owner and due to the mostly very good state of preservation, gold objects have always been of great interest for archaeological and art historical research. At the Curt-Engelhorn-Centre Archaeometry (CEZA) in Mannheim, archaeological and historical gold objects from various eras and cultures have been scientifically researched for many years.

Material Analysis

It is not surprising that the first chemical analyses of archaeological gold objects were performed as early as the middle of the 19th century. However, analyses of gold objects from Southeast Asia were first conducted in the 1980s. In archaeometallurgy, the characterisation of chemically similar groups of materials and their chronological, geographical and typological comparison with other artefacts or groups of artefacts is the most important working basis for revealing economic links and trade relations and for researching technological developments. As great as the research interest in gold has always been, it has long been difficult to analyse it. The

Fig. 1: Energy-dispersive X-ray fluorescence spectrometer for a non-destructive analysis of alloys by X-rays.



reason for this is that objects made of gold are generally given a higher value than objects made of other materials and therefore, material sampling was rejected. In recent decades, however, there has been significant progress in the applied methods, which have become more and more effective and are now almost completely non-destructive.

The X-ray fluorescence analysis (XRF) is a completely non-destructive method, by which the chemical composition of the object's surface can be determined (Figs. 1 and 2). An X-ray beam excites electrons of the material to be analysed (sample or object), i.e. they are briefly raised to a higher energy level. Once they drop back to a lower energy level, they emit a fluorescence radiation in the X-ray range characteristic of the respective element. This can be measured by a detector. This way, it is possible to determine, which alloy the object is made of and whether all parts of the object are made of the same metal. (Pre-)historical gold objects usually consist of alloys, which, in addition to gold, contain various portions of silver and copper. Other elements are usually only present in such a low concentration in gold that they cannot be detected by X-ray fluorescence analysis.

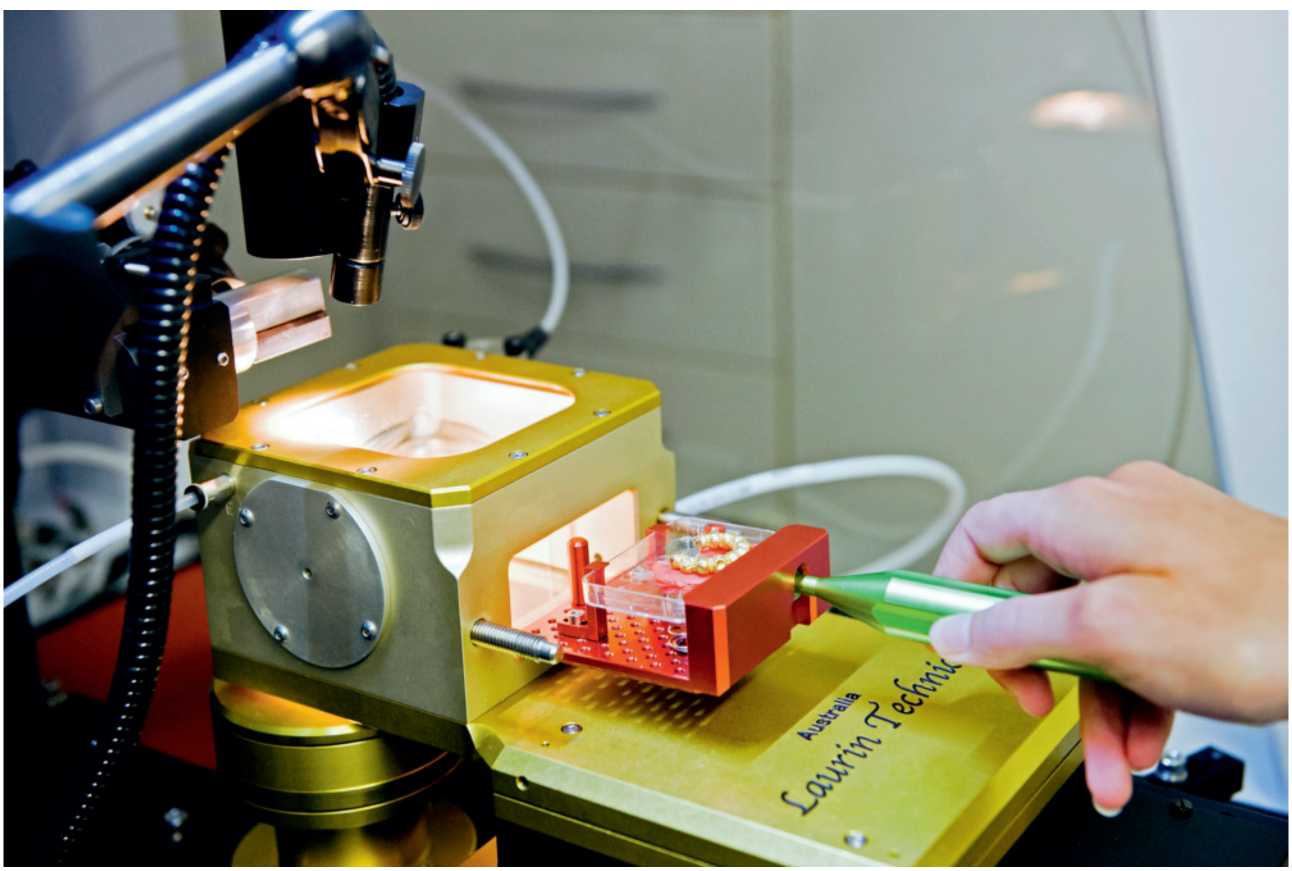
Modern analysis equipment, sometimes with the aid of a camera, provides a precise examination, whereby solder joints or other unusual spots on an object can be specifically analysed. This allows many insights into the manufacturing techniques used for the objects, including modern repairs. However, the information depth of this method is relatively low at only approx. 10 μm (0.01 mm), i.e. gilded objects, e.g., cannot always be detected. Other surface effects, such as changed surfaces due to ground storage, can also significantly falsify the analysis result. During soil storage, e.g., copper and silver may be dissolved from the upper layers by soil water. In comparison to the object's unchanged material, the gold grades measured at the surface are therefore too high.

Fig. 2: Portable energy-dispersive X-ray fluorescence spectrometer for a non-destructive analysis of alloys of a gold bowl. A portable instrument can also be used for bigger objects.

For this reason, it is advisable to analyse the gold with another method, depending on the state of preservation and the question regarding the objects. One method that has established itself over the last ten years is mass spectrometry (ICP-MS), which is coupled with a laser for sampling (Fig. 3). The focused laser beam has a high energy density, which enables it to remove tiny amounts of material when it hits the sample or object. The sample then passes through a helium gas stream into the mass spectrometer. The crater created by the laser is only a few micrometers big and hardly visible to the naked eye.

The actual analyser, the mass spectrometer, is very effective, which means that considerably more elements can be analysed than with the X-ray fluorescence analysis. This provides new possibilities for material classification. The elements of the platinum group are relatively robust to the various metallurgical procedures and also to the prehistoric gold purification procedures. Additionally, they provide important pointers for the identification of workshops or the different raw material forms such as ingots. With certain restrictions, it is also possible to make assumptions about the origin of individual objects, even if a direct proof of origin or deposit proof is usually not possible. The different geological conditions as well as the changes in the metal resulting from the manufacturing process like washed minerals from the river, accidental impurities caused

Fig. 3: Cell for laser ablation. Here, samples or smaller objects can be tested directly with a laser. The ablated material is then transfered into an analyser by a helium gas stream.



by metallurgical processes or specifically produced alloys with other metals are too great for this. Due to the particularly good detection sensitivity of this method, it also helps to detect counterfeits. For example, cadmium, a metal that was only discovered in the 19th century and was then increasingly used for solder alloys, can be well identified. On the other hand, metals of unusual purity can be detected, as they could only be produced in the 20th century.

Technological Analyses

For gold objects, especially jewellery, the method of production is of particular importance, as certain technologies, such as the way the wire is made, the connection techniques or the use of certain tools, can be specific to a particular time, region or culture. Here, conventional optical microscopy with stereomicroscopes is mainly used by standard for analyses. For the documentation of goldsmith techniques, however, the depth of field of conventional light microscopes decreases considerably with increasing magnification, which is why only one part of a measuring object with a pronounced topography can be focused at a time.

A digital confocal microscope is used to create images of objects with large differences in height by focusing a composite image from the highest to the lowest point in sequence (Figs. 4 and 5). Various image correction functions ensure that strong colour contrasts and differently reflecting areas are correctly displayed.

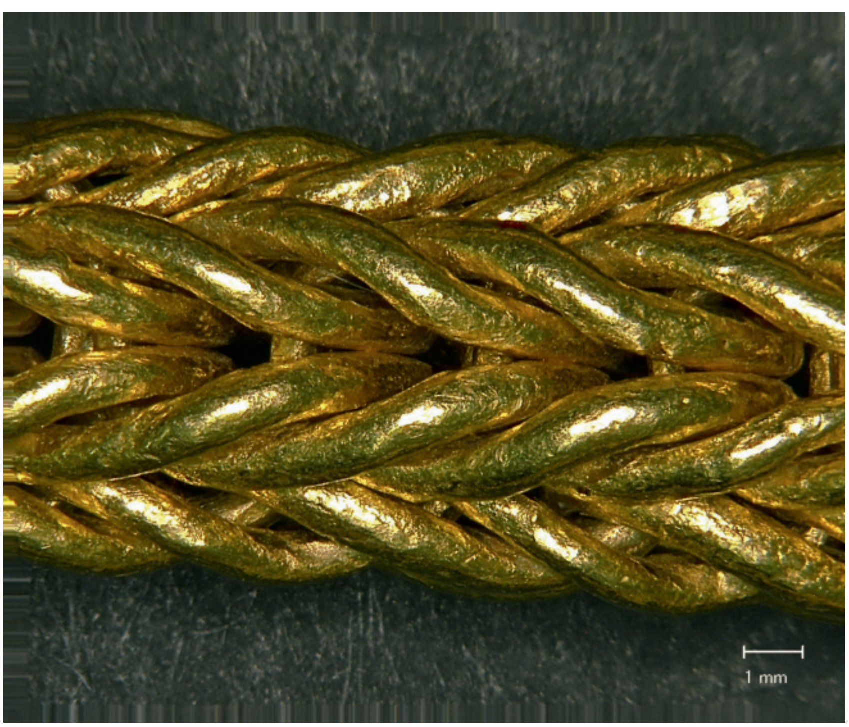


Fig. 4: Zoom of a braided gold chain (Inv. Nr. 07909).

Scanning electron microscopy is used for detailed surface research. This is a versatile method, which provides morphological images with a high depth of field and numerous analytical information through the interaction of an electron beam with the surface. Depending on the sample signal, a topographic or material-specific contrast is generated, in which the chemical composition of the sample part can be determined by the resulting X-ray radiation. For gilded or soldered objects, the applied technique can often not be clarified by non-destructive examinations, which is why sometimes a tiny sample is taken for a metallographic examination. A cross section perpendicular to the related surface must be created from this, containing all relevant information. This can then be examined with a light or scanning electron microscope.

Dating

For objects of cultural-historical significance, the question of age determination is often the main focus. In the case of organic materials, such as paintings or wood sculptures, age is usually determined by radiometric methods such as radiocarbon dating, and today it is done routinely. The term age dating is usually used to refer to the determination of the time of origin of an object, but the extent to which dating determines the age of the object's manufacture must be clarified depending on the method used. Many methods only date the age of the material the object was made of. The age of a wood sculpture, e.g., is dated, but not when the wood was actually processed. Dating a sculpture that is carved today from an old log would reveal the age of the wood, but not the age of the sculpture, and dating a modern painting on an old canvas would reveal only the age of the canvas. Age dating distinguishes between the direct determination of the object's age and indirect dating, which is always applied when a material itself cannot be dated, but is temporally related to another datable material.

Metals and especially gold often elude direct dating as conventional methods such as the radiocarbon method cannot be used because metals normally do not contain carbon.

Some objects of the Javagold exhibition are partially covered with reddish adhesions. Studies have shown that these „red spots“ may contain carbon and could therefore theoretically be dated using the radiocarbon method. However, the dating of these „red spots“ faces major technical obstacles, since conventional dating with a modern accelerator mass spectrometer (AMS) requires one milligram of pure carbon, the spots, however, contain considerably less carbon. But after the costly removal of dirt and other contaminations, the material could be dated with the help of a specially developed extraction and purification plant by CEZA for very small amounts of carbon (≈0,01 milligram carbon). After the technical challenge, a major difficulty now lies in the interpretation of the data obtained, since it involves indirect dating; first of all, it must be clarified whether and to what extent the age of the „red spots" is related to the age of the respective objects, where the carbon in the spots comes from and when it has deposited on the gold objects. Only the formation of carbon is dated and not the time of deposition on the objects.

Direct dating of objects is always superior to indirect dating, since the correlation between the measured age and its significance for the object is usually evident and does not have to be explained indirectly. This is why CEZA has been developing a method for dating gold directly for about five years.

When natural gold is formed, trace elements, such as uranium and thorium are always incorporated in addition to the most common elements in gold, such as silver, copper or palladium. Their long-lived unstable isotopes (^{238}U, ^{235}U, and ^{232}Th) decay in several steps into lead and release alpha particles. One alpha particle is the nucleus of a ^{4}He atom. If two electrons are combined with an alpha particle, a ^{4}He atom is formed. Due to the dense crystal structure of gold, a formed ^{4}He atom remains in the gold, as does a much more long-lived isotope of the element samarium (^{147}Sm). It could be demonstrated that up to a temperature of approx. 500 °C, the diffusion rate of helium into gold is negligibly small, i.e. it remains in gold up to this temperature. However, if gold is gradually heated to a temperature just below the melting point, the structure of gold expands so that helium can be extracted from the gold structure, especially in high vacuum.

This reaction was used for the first time by a Russian team to extract helium from the gold of archaeological objects thermally (approx. 50–100 °C below the melting point) in a high vacuum. The released helium can then be quantitatively determined directly in a highly sensitive helium mass spectrometer. The degassed gold sample from the helium mass spectrometer is then analysed for uranium, thorium and samarium. From the quantity of parent nuclides, i.e. the nuclides of uranium, thorium and samarium, it is then possible to calculate the time required to produce the specific quantity of helium as a daughter nuclide up to the time of the helium analysis.

The fundamental idea for dating archaeological gold objects is that the metal is melted to produce a gold object, all the helium contained in the gold escapes and the „U-Th-He clock" is set to zero. Once the metal has cooled down, new helium is formed as a result of the radioactive decay and remains trapped in the – now dense – gold structure. The time span mentioned above thus describes the age of a gold object as long as it was melted and therefore liquid at the time of manufacture.

Fig. 5: Zoom of a granulation work of a chain (Inv. Nr. 01208).

Measuring ^{4}He atoms is generally unproblematic, but the extremely small amounts of the expected ^{4}He atoms (50,000–100,000 ^{4}He atoms) complicate the analysis, which is why a new helium mass spectrometer was designed. Currently, the procedure for archaeological objects is not yet safe for use, but the potential is very promising.

Historical Gold in Southeast Asia

There are gold finds from many world-famous archaeological contexts whose tradition is secured, such as Troy or Mycenaeus. The same applies to historical contexts, such as imperial crowns or sacred works of art. In comparison, there are only a few archaeological gold objects from modern excavations in Southeast Asia and hardly any whose tradition is historically proven.

The majority of the objects shown in the exhibition were analysed using the methods described here, on the one hand to investigate the goldsmithing techniques of the Hindu and Buddhist kingdoms of classical Java, but on the other hand also to identify possible forgeries on the basis of material composition and processing techniques. This is an important addition to the art-historical and typological approach, which can fall back on the iconography of artworks made of other materials (copper alloys, stone, wood, etc.). Modern forgeries can be reliably identified in materials science analyses if modern materials have been used. However, it must be pointed out that, on the other hand, proof of authenticity, i.e. of the presumed age from art-historical considerations, cannot be provided, since there is (still) no scientific dating method for gold. It is therefore only possible to conclude that there is no clear evidence of production in modern times.

There is generally a grey area between authentic and counterfeit, since the variety of objects offered on the art market is huge. Original objects are often supplemented or repaired with modern materials, which can lead to confusion in both material analysis and stylistic observation. At the same time, new objects are occasionally created in old style in modern times from real, but art-historically less meaningful old material. In Southeast Asia, in particular, there is the additional problem that there are very few comparable objects from the classical period of Java that originate from documented archaeological excavations and can serve as reference material.

Therefore, it is important to do both the art-historical as well as the material-scientific test, which are based on completely different methods. If both methods result in doubts, there is a high probability that it is not a real object. If both approaches do not provide any conspicuous features, the probability of authenticity increases accordingly and it is possible to use the objects for supra-regional comparisons.

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Catalogue

KN001
Inv.-Nr. 03976
CYLINDRICAL OBJECT

Java, 7th–15th centuries
662 g, h: 117mm
The cylindrical object stands on a pedestal surrounded by two rows of lotus flowers. The rounded top has a small finish, which is also decorated with two rows of lotus flowers. A connecting piece and a slot in the inner part connect attachment and platform with each other. The cylinder is decorated with a ribbon of foliage, pearly garlands and four-layer floral motifs. The purpose of this cylindrical object is unknown, but similar objects made of bronze from the Metropolitan Museum of Art in New York were interpreted as Linga, the phallic symbol of the Hindu god Shiva.

KN002
Inv.-Nr. 01151
STANDING DEITY, PRESUMABLY SHIVA

Java, 7th–15th centuries
359.9 g, h: 134 mm
The deity stands in an upright position on a lotus pedestal. The open and generously decorated frame adds a graceful and elegant posture to the deity. The open hand pointing downwards symbolizes the granting of grace. If the attribute in the left hand is interpreted as a trident, the richly decorated figure represents Shiva. However, it may also be a blue lotus, an attribute of the gods.

KN003
Inv.-Nr. GG124
NAGA KING

Sumatra, approx. 9th century
H: 68 mm, w: 55 mm,
d: 53 mm
This large pendant is decorated with the pearled snake deity, the Naga king. He sits in a meditation pose on a double lotus pedestal. His main pair of hands lies on his knees, while the other hands on the left and right each embrace a snake.
He has a grim face with protruding eyes and big fangs.