2.6. The Challenge of Gold
XRF Analysis for large objects

The "relics of the Magi" were originally situated at Constantinople, but brought to Milan by Eustorgius I, the city's bishop, in 344 AD. The relics of the Magi were taken 1162 from Milan by Holy Roman Emperor Fredrick Barbarossa and given to the Archbishop of Cologne, Rainald von Dassel in 1164 AD. The Three Kings have since attracted a constant stream of pilgrims to Cologne. Parts of the shrine were designed by the famous medieval goldsmith Nicholas of Verdun, who began work on it in 1180 AD or 1181AD. The shrine shows elaborate gold sculptures of the prophets and apostles, and scenes from the life of Christ. The shrine was completed circa 1225AD.
Gold Forgeries

The Greek half-and-half necklace

Hellenistic Greek

19th century Italian
Alessandro Castellani
Observational Evidence

19th century Italian  Hellenistic Greek
Authenticity check for ship wreck coins
Nuestra Senora de Atocha
Tragedy at Sea
Finding the Atocha Treasure
Treasures from the Atocha
The Atocha treasure in auction
Doubts about the authenticity of some of the “Atocha Escudos” on the market.
Suspect coin has considerably higher Au content and less Ag content than Spanish Escudo
Detecting Gold Forgeries by Dating Techniques

Determining gold forgeries is extremely difficult because the lack of patina or any other chemical aging characteristics! Also the difference in impurities is small (Au-Hg-Cu-Sb-Pd-Pt-Os) and x-ray analysis does not provide answers without calibration materials. It is therefore relatively easy to produce fake antique gold objects by just matching antique style characteristics!

Gold contains heavy long-lived radioactive impurities such as Uranium and Thorium which decay by emission of alpha particles ($^4$He) through the so-called natural decay chains. The $^4$He remains trapped and is only released when gold is heated to its melting point of 1064°C. This provides a tool to determine the time period between the production of the gold object and its analysis by measuring the amount of released $^4$He gas and determining the amount of uranium, thorium impurities.

Three examples for age determination of gold

Determination of U, Th, Sm content in gold
Extraction and measurement of $^4$He content

- Gold Torc (Hallstatt/La Tène transition period, 500 BC) ~2500 years old
- Granulated Gold Figurine (Iran or Central Asia, 11$^{th}$ or 12$^{th}$ century AD) ~900 years old
- Signet ring of a Merovingian King - Childebert I (496-558 AD) or Childebert II (570-595 AD) ~1450 years old
Instrumentation for extraction

Release of $^4\text{He}$ from a small 10-20 mg sample taken from the object – a not completely non-destructive approach. Sample is slowly heated in evaporated chamber to ~1200°C well above Au melting point so that $^4\text{He}$ is released and analyzed in a magnetic spectrometer and counted in a detector in the focal plane of spectrometer. $^4\text{He}$ release from ancient gold peaks around 800°C, for younger gold samples the release temperature is near 1000 °C. The amount of the released $^4\text{He}$ corresponds to the age of the sample depending on the U, Th concentration.

U, Th content in Au is being measured independently for each sample using mass spectroscopy with an sensitivity of 0.01-0.1ppm. PIXE for comparison provides a sensitivity of 0.5-5 ppm.
Age determination

Number of radioactive atoms $N$ that decay over time $t$ and produce $^4\text{He}$ atoms to be stored and later released:

$$N = N_0 - N_t \quad N_t = N_0 \cdot e^{-\lambda \cdot t} \quad N_0 = N_t \cdot e^{\lambda \cdot t}$$

$$N = N_0 - N_t = N_t \cdot \left(e^{\lambda \cdot t} - 1\right)$$

for $T_{1/2} = \ln 2/\lambda \gg > t$

$$N = N_t \cdot \lambda \cdot t \quad t = \frac{N}{\lambda \cdot N_t}$$

$\lambda (^{238}\text{U}) = 1.55 \cdot 10^{-10} \text{ y}^{-1}$ 8 $^4\text{He}$ particles

$\lambda (^{235}\text{U}) = 9.85 \cdot 10^{-10} \text{ y}^{-1}$ 7 $^4\text{He}$ particles

$\lambda (^{232}\text{Th}) = 4.95 \cdot 10^{-11} \text{ y}^{-1}$ 6 $^4\text{He}$ particles

$\lambda (^{147}\text{Sm}) = 6.54 \cdot 10^{-12} \text{ y}^{-1}$ 1 $^4\text{He}$ particle.

Example: 1mg of Au contains 15ppb U, 45 ppb Th and 300 ppb Sm, How many $^4\text{He}$ atoms are produced per year?
Example

A piece of 1mg of Au contains:

Elemental fraction $f_{el}$: 15 ppb U, 45 ppb Th and 300 ppb Sm

Isotope fraction $f_{is}$: 99.3% $^{238}$U, 0.72% $^{235}$U, 100% $^{232}$Th, 15.0% $^{147}$Sm

\[ N = N_t \cdot \lambda \cdot t \]
\[ N_t = N(Au) \cdot f_{el} \cdot f_{is} \]
\[ N(Au) = \frac{6.022 \cdot 10^{23}}{197 \cdot 1000} \quad 1\text{mg} \text{ Au} = 197 \]
\[ N(Au) = 3.06 \cdot 10^{18} \]
\[ N(^{238}U) = 3.06 \cdot 10^{18} \cdot 15 \cdot 10^{-9} \cdot 0.993 = 4.55 \cdot 10^{10} \]
\[ N(^{235}U) = 3.06 \cdot 10^{18} \cdot 15 \cdot 10^{-9} \cdot 00072 = 3.30 \cdot 10^{8} \]
\[ N(^4He) = N(^{238}U) \cdot 1.55 \cdot 10^{-10} \text{ y}^{-1} \cdot 1 \text{ y} \cdot 8 = 7.1 \cdot 8 \approx 57 \]
\[ N(^4He) = N(^{235}U) \cdot 9.85 \cdot 10^{-10} \text{ y}^{-1} \cdot 1 \text{ y} \cdot 7 = 0.3 \cdot 7 \approx 2 \]

A total of about 60 $^4$He atoms are being produced and trapped annually. A 2000 year old piece of 1 mg gold would release 120,000 $^4$He atoms.
Final Results

Simplified formula: \[ t = \frac{N}{\lambda \cdot N_t} \]

<table>
<thead>
<tr>
<th>Object and origin (sample Nr.)</th>
<th>Obtained from</th>
<th>Reported century</th>
<th>$^4\text{He}$ \text{atoms/mg}</th>
<th>$^\text{U}$ \text{ppb}</th>
<th>$^\text{Th}$ \text{ppb}</th>
<th>Estimated ( \text{U, Th - } ^4\text{He} \text{ age (years)} )</th>
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</thead>
<tbody>
<tr>
<td>Signet ring of Merovingian King</td>
<td>1</td>
<td>6th AD</td>
<td>10.7</td>
<td>3.4$^9$</td>
<td>79$^9$</td>
<td>1460 $\pm$ 400</td>
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<td>France (MR 1)</td>
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<tr>
<td>Celtic torc, Southern Germany (CT</td>
<td>2</td>
<td>5th BC</td>
<td>18.5</td>
<td>15$^{10}$</td>
<td>45$^{10}$</td>
<td>2200 $\pm$ 1100</td>
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<td>1)</td>
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<tr>
<td>Golden figurine, Islamic (IG 1)</td>
<td>7</td>
<td>11-12th AD</td>
<td>0.85</td>
<td>0.9$^{14}$</td>
<td>0.8$^{14}$</td>
<td>1800 $\pm$ 1000</td>
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<tr>
<td>Golden figurine, Islamic (IG 2)</td>
<td>7</td>
<td>11-12th AD</td>
<td>2.0</td>
<td>6.2$^{12}$</td>
<td>126$^{12}$</td>
<td>170 $\pm$ 100</td>
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The time $t$ is in years, the abundance $[^4\text{He}]$ in atoms/g and $[^\text{U}]$, $[^\text{Th}]$, and $[^\text{Sm}]$ in ppm.