The Role of Analytical Science

- increasing our knowledge and understanding of cultural heritage objects
  - age, composition
  - provenance, authenticity
- assembling information including physical evidence, in order to add cultural value to the heritage
  - composition
  - production processes
- helping to define the conditions, limits, risks, and potential for sustainable conservation and management of human heritage
The Potential of Isotope Research

- age
- provenance
- authenticity
- production processes

- glass and ceramics
- pigments
- metals
- wood and paper
• Isotopes: Atoms of the same element with different mass
  
  – due to the different number of neutrons in the nucleus
  
  – have the same chemical properties

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>Mass number</th>
<th>Nuclear number</th>
<th>Isotope ratio</th>
<th>Relative natural abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARBON</td>
<td>12</td>
<td>6</td>
<td>0.011122</td>
<td>98.90%</td>
</tr>
<tr>
<td>C</td>
<td>13</td>
<td>6</td>
<td></td>
<td>1.10%</td>
</tr>
</tbody>
</table>

Isotope ratio: e.g. $^{13}\text{C}/^{12}\text{C} = 0.011122$
Natural variation of isotopic systems

- Natural chemical processes
  - Radioactive decay (e.g. U, Pb, Sr)
  - Redox reactions (e.g. Fe, Mo, Sb)
  - Photoreactions (e.g. Hg)

- Natural physical processes
  - Diffusion (e.g. C, H, O)
  - Precipitation (e.g. H, O)
  - Temperature (e.g. O)

- Natural biochemical processes
  - Microbial, enzymatic activities (e.g. S, N)
  - Plant activities (e.g. C, Fe, Si)
  - Calcification processes (e.g. Ca, Sr)
### Isotopes with natural variation

<table>
<thead>
<tr>
<th>Element</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>isotopes with natural variation</td>
</tr>
<tr>
<td>Li</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Be</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Na</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Mg</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>K</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Ca</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Sc</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Ti</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>V</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Cr</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Mn</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Fe</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Co</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Ni</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Cu</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Zn</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Ga</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Ge</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>As</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Se</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Br</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Kr</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Rb</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Sr</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Y</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Zr</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Nb</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Mo</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Tc</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Ru</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Rh</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Pd</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Ag</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Cd</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>In</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Sn</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>Sb</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Te</td>
<td>element with only 1 stable isotope</td>
</tr>
<tr>
<td>I</td>
<td>element with &gt;1 stable isotope</td>
</tr>
<tr>
<td>Xe</td>
<td>element with only 1 stable isotope</td>
</tr>
</tbody>
</table>

\[ X^\text{§} \] elements for which natural isotopic variation has been reported using ICP-MS

\[ X \] element with only non stable isotopes
Sr isotopic system

Rubidium

\[ {}^{87}\text{Rb} \rightarrow {}^{87}\text{Sr} + \beta^- + \bar{\nu} + Q \]

\( T_{1/2} \text{ ... half life (} T_{1/2} = 48.8 \times 10^9 \text{ a) } \)

Strontium

\[ {}^{88}\text{Sr} \quad 82.58\% \]

\[ {}^{86}\text{Sr} \quad 9.86\% \]

\[ {}^{84}\text{Sr} \quad 0.56\% \]

variation of \( {}^{87}\text{Sr}/{}^{86}\text{Sr} \) with geological provenance

- geochemical composition
- geological age
Pb isotopic system

variation of Pb isotope ratios
- geological sources
- anthropogenic sources
Isotopes as Tracers of the Past

- provenance
- authenticity
- production processes

isotopic fingerprint tool

<< fingerprint method >>
Isotopic Systems applied in Archaeometry

isotopic systems used in forensics/archaeometry

isotopes with natural variation

element with >1 stable isotope

element with only 1 stable isotope

isotopic systems only used in nuclear or environmental forensics

elements for which natural isotopic variation has been reported using ICP-MS

element with only non stable isotopes
Isotopic Systems applied in Archaeometry

C 49%

N 9.1%

O 15%

S 1.2%

Sr 6.0%

Pb 12%

Nd 0.06%

U 3.0%

H 4.2%

B 0.60%

Mg, Ar, Cu, Ru, Ag, Cd, Sn 0.20%

Os, Sb, Nd, Hg, Pu, Am

'Non traditional isotopes'
Analysis of glass, ceramics and pigments

- isotopic systems used in forensics/archaeometry
- isotopes with natural variation
- element with >1 stable isotope
- element with only 1 stable isotope

- elements for which natural isotopic variation has been reported using ICP-MS
- element with only non stable isotopes

- isotopic systems used in glass analysis

Periodic Table:

- H
- He
- Li
- Be
- B
- C
- N
- O
- F
- Ne
- Na
- Mg
- Al
- Si
- P
- S
- Cl
- Ar
- K
- Ca
- Sc
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn
- Ga
- Ge
- As
- Se
- Br
- Kr
- Rb
- Sr
- Y
- Zr
- Nb
- Mo
- Tc
- Ru
- Rh
- Pd
- Ag
- Cd
- In
- Sn
- Sb
- Te
- I
- Xe
- Cs
- Ba
- La
- Hf
- Ta
- W
- Re
- Os
- Ir
- Pt
- Au
- Hg
- Tl
- Pb
- Bi
- Po
- At
- Rn
- Fr
- Ra
- Ac
- Rf
- Db
- Sg
- Bh
- Hs
- Mt
- Ds
- Rg
- Cn
- Uut
- Fl
- Uup
- Lv
- Uus
- Uuo

- Ce
- Pr
- Nd
- Pm
- Sm
- Eu
- Gd
- Tb
- Dy
- Ho
- Er
- Tm
- Yb
- Lu

- Th
- Pa
- U
- Np
- Pu
- Am
- Cm
- Bk
- Cf
- Es
- Fm
- Md
- No
- Lr
Fig. 3 $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\varepsilon$Nd plot glass analyzed in this study. The typical composition of primary glass from the Syro-Palestine and Egypt is indicated.\textsuperscript{16}
One ensemble?
Identifikation von Keramikfiguren Andrea della Robbia (1435 – 1525, Florenz)

Error: \( U (k = 2) \);
Nouveau Art objects (Louis Comfort Tiffany, 1848 – 1933)

Collaboration with the Academy of Fine Arts

- Pb crystal glasses (~25% Pb)
- different layers

Schultheis, Prohaska, Stingeder, Dietrich, Jembrih-Simbürger, Schreiner – JAAS, 19, 2004
Investigation of cultural objects by LA-ICP-MS

- micro destructive
- highly sensitive
- multielement information
- isotopic information
Laser ablation

camera

laser

ion source

aerosol formation

carrier gas (Ar)

laser cell (x, y, z moveable)

Inductively coupled plasma (ICP)
NouveauArt objects
(Louis Comfort Tiffany, 1848 – 1933)

\[ \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \]

blue layer

yellow layer

error bars: \( U (k = 2); \)

\[ \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \]

\[ \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \]

Schultheis, Prohaska, Stingeder, Dietrich, Jembrih-Simbürger, Schreiner – JAAS, 19, 2004
Evidence for glass ‘recycling’ using Pb and Sr isotopic ratios and Sr-mixing lines: the case of early Byzantine Sagalassos

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Isotopic analysis of antimony using multi-collector ICP-mass spectrometry for provenance determination of Roman glass†

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cDepartment of Engineering and Applied Science, Cranfield University, Shrivenham, Swindon, SN6 8LA, UK
Pb isotopic composition in pigments

Old Masters’ lead white pigments: investigations of paintings from the 16th to the 17th century using high precision lead isotope abundance ratios

G. Fortunato,\textsuperscript{a} A. Ritter\textsuperscript{a} and D. Fabian\textsuperscript{b}

Received 16th December 2004, Accepted 8th March 2005
First published as an Advance Article on the web 15th April 2005
DOI: 10.1039/b418105k
Pb isotopic composition in pigments

Fortunato et al., The Analyst, 2005
Sulfur isotope analysis of cinnabar from Roman wall paintings by elemental analysis/isotope ratio mass spectrometry – tracking the origin of archaeological red pigments and their authenticity

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\textsuperscript{3}Department of Geosciences, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland
S isotopes in pigments of Roman paintings

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aventicum</td>
<td>(n = 12)</td>
</tr>
<tr>
<td>Cosa</td>
<td>(n = 3)</td>
</tr>
<tr>
<td>Almadén</td>
<td>(n = 47)</td>
</tr>
<tr>
<td>Idria</td>
<td>(n = 187)</td>
</tr>
<tr>
<td>Monte Amiata</td>
<td>(n = 10)</td>
</tr>
<tr>
<td>Moschellandsberg</td>
<td>(n = 2)</td>
</tr>
<tr>
<td>Genepy</td>
<td>(n = 2)</td>
</tr>
<tr>
<td>Izmir</td>
<td>(n = 4)</td>
</tr>
</tbody>
</table>

**Figure 3.** Box plot of $\delta^{34}$S values for the cinnabar from the Roman paintings at Aventicum (Switzerland) and Cosa (Italy)$^{13}$ and European Hg deposits, displaying the ranges, 25th (1st quartile, Q1) and 75th (3rd quartile, Q3) percentiles, median, and outliers.
# Metal analysis in archaeometry

The image presents a periodic table highlighting isotopic systems used in forensics/archaeometry and metal analysis. The table categorizes elements based on isotopic variation and stability.

- **Isotopic systems used in forensics/archaeometry**
  - Isotopes with natural variation
  - Element with >1 stable isotope
  - Element with only 1 stable isotope

- **Isotopic systems used in metal analysis**
  - Elements for which natural isotopic variation has been reported using ICP-MS
  - Element with only non-stable isotopes

The periodic table includes elements from hydrogen (H) to lawrencium (Lr), with annotations indicating the specific isotopes and their stability conditions.
Bronze fibulae: Pb isotopes by LA-ICP-MS
Bronze fibulae: Pb isotopes by LA-ICP-MS

- Grave 23: 0.03% Pb
- Grave 8: 0.51% Pb
- Grave 10: 0.98% Pb

Error bar: $U (k = 2)$
**Ag, Cu, Pb multi isotopic fingerprint**

**Isotopi 16th-1**

Anne-Marie Desautel

*Ecole Normale Sup, UMR 5276, 69364 E

Desautel et al., PNAS 108, 2011
AN ASSESSMENT OF OSMIUM ISOTOPE RATIOS AS A NEW TOOL TO DETERMINE THE PROVENANCE OF GOLD WITH PLATINUM-GROUP METAL INCLUSIONS

S. A. JUNK† and E. PERNICKA

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TIN ISOTOPE—A NEW METHOD FOR SOLVING OLD QUESTIONS

M. HAUSTEIN¹, C. GILLIS² and E. PERNICKA³

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Towards a strontium isoscape for the determination of provenance of wooden artefacts

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³ Natural History Museum Vienna, Department of Prehistory, Vienna, Austria
⁴ BLT Wieselburg, Lehr- und Forschungseinrichtung Francisco-Josephinum, Wieselburg, Austria
Motivation and Background

Hallstatt – UNESCO world heritage site
- salt mining history of minimum 3500 years
- high content of salt permitted the preservation of organic material

archaeological questions
- origin of wooden findings
  - timber for construction
  - tools
- conclusions on trade routes, infrastructure, organization of prehistoric mining
Project Outline: ISOwood (FWF P23647)

- archaeology
- Sr isotopes
- dendro-chronology
- C, O, H isotopes

NHM Dept. of Prehistory
BOKU Inst. of Wood Science
BOKU VIRIS lab
Francisco-Josephinum Wieselburg
**Experimental protocol**

### samples

- **prehistoric wood** (drill cores, chips)
  - removal of salt using ultrasound assisted leaching
  - microwave assisted digestion
    - \( \text{HNO}_3/\text{H}_2\text{O}_2 \)

- **recent wood** (drill cores)

- **mine repository material** ('Heidengebirge')
  - extraction
    - 1 M \( \text{NH}_4\text{NO}_3 \)

---

**Sr/matrix separation** (EICHROM Sr-Resin)

**Sr isotope ratio measurement** via
- MC-ICP-MS (Nu Plasma HR)
Identification and selection of sampling areas:
1. knowledge of archaeological settlements
2. tree growth regions
3. geological differences on a local scale
Reference values – sampling strategy

Sampling scope:
- 8 regions in Austria
- 1 – 5 geological sub-regions (total 26)
Sampling scope:
- 8 regions in Austria
  - 1 – 5 geological sub-regions (total 26)
- 4 tree species (upon availability)
  - beech (*Fagus sylvatica*)
  - oak (*Quercus sp.*)
  - spruce (*Picea abies*)
  - fir (*Abies alba*)
- total number of trees sampled in duplicate by drilling: 1080
  - one drill core per location and species separated into 2-4 pieces
Results – possible regions of origin

Sr isotope ratios in modern wood (4 tree species) and in one prehistoric tool shaft
Results – possible regions of origin
Results – possible regions of origin

Terrain map of Austria (source: Google Maps)

Combination with $\delta^{15}$N; $\delta^{18}$O; dendrochronology