3.5. Isotope Separation & Analysis
Isotope Distribution, Isoscapes

\[ \delta^{2}H = \frac{H_{2}}{H_{1}}_{\text{sample}} - 1 \cdot 1000\% \]

\[ \delta^{13}C = \frac{C^{13}_{\text{sample}}}{C^{12}_{\text{sample}}} - 1 \cdot 1000\% \]

\[ \delta^{18}O = \frac{O^{18}_{\text{sample}}}{O^{16}_{\text{sample}}} - 1 \cdot 1000\% \]
Isotopic ratios

Isotope ratios for specific elements can change locally due to geological, climatological, biological, chemical and physical processes during the history of the earth.

The analysis of isotope ratios is a unique tool for provenance studies as seen in previous examples.

Typical isotope ratios used for provenance studies:

\[
\delta^{204}Pb = \left( \frac{Pb^{204}}{Pb^{208}} \right)_{\text{sample}} \cdot \left( \frac{Pb^{204}}{Pb^{208}} \right)_{\text{standard}} - 1 \cdot 1000 \%
\]

Example: isotope distribution in different Greek quarries
Determination of the Pb isotope ratio

Neutron activation technique on $^{204}\text{Pb}$ or $^{208}\text{Pb}$?

$^{204}\text{Pb}(n,\gamma)^{205}\text{Pb}; \quad ^{208}\text{Pb}(n,\gamma)^{209}\text{Pb};$

Not possible since the cross section is extremely weak and $^{205}\text{Pb}$ and $^{209}\text{Pb}$ have no characteristic $\gamma$ decay radiation!

Alternative method: isotope analysis by mass separation techniques!

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Stable $^{204}\text{Pb}$ 1.40%  203.97302
Radiogenic $^{206}\text{Pb}$ 24.10%  205.97444
Radiogenic $^{207}\text{Pb}$ 22.10%  206.97588
Radiogenic $^{208}\text{Pb}$ 52.40%  207.97663
Cosmogenic $^{210}\text{Pb}$ t½=22.6yrs
Separation in magnetic fields

\[ \frac{m}{q} = \frac{B \cdot R}{v} ; \quad m = \left( \frac{q \cdot B}{v} \right) \cdot R \]

Particles with velocity \( v \) are separated by \( m/q \) for a fixed magnetic field \( B \) and a spectrometer radius \( R \).
Example: Separation of $^{204}\text{Pb}$ and $^{208}\text{Pb}$

\[
m = \frac{m}{q} \cdot \frac{B \cdot R}{v}; \quad m = \left( \frac{q \cdot B}{v} \right) \cdot R
\]

\[
m_1 = \left( \frac{q \cdot B}{v} \right) \cdot \frac{R_1}{R_2} = \frac{R_1}{R_2}
\]

\[
m_2 = \left( \frac{q \cdot B}{v} \right)
\]

\[
\frac{204}{208} = \frac{R_1}{R_2} \quad \text{for} \quad R_2 = 1 \text{ m};
\]

\[
R_1 = \frac{204}{208} \quad m = 0.98 \text{ m}
\]

Separated $^{204}\text{Pb}$, $^{208}\text{Pb}$ beams
Mass spectrum in focal plane detector
Isotope Analyzer

Small sample of material with mass <μg is ionized by sputter technique, accelerated and mass separated by sequence of magnetic and electrical fields.
The Hittite empire developed a significant metallurgy and mining industry during the bronze age, between 1500-1300 BC, which initiated the iron age.
Hittite Mining Site determination by lead (Pb) isotope analysis

Control over the mining sites was important for Hittite empire trade

Origin of metal in artifact is determined by their $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratio

Metal contain tin, copper, nickel and lead!

Volcanic origin (earthquake prone region); limestone mountains, lower layers show lava, basalt, soft tuft pillars produced by volcanic eruption and subsequent erosion.

Sizable tin, copper, iron, zinc, lead composition in deeper layers; polymetallic composition with abundance variations.

The Geology of Taurus
The importance of lead isotopes

40% Fe as hematite, magnetite
10-20% Pb with high Zn content
6-8% Zn (~1/2 Pb)
1-2% Cu in some cases 6-7%
3% Co
1.5% Sn in quartz veins

Layered sediments in caves and cavities of limestone mass.

1-100 ppm Au
100-1000 ppm Ag

Isotope composition of Pb deposits changes with the environment; this provides a unique tool for the analysis of antique mining and trading patterns!
There are 4 stable lead isotopes: $^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$, $^{208}\text{Pb}$

Lead isotope distribution is not necessarily constant but may change if significant Uranium & Plutonium abundance exist in the ore material. Natural decay of these a unstable isotopes feed the Pb isotopes.
Natural decay chains & the feeding of Pb isotopes

<table>
<thead>
<tr>
<th>Decay Chain</th>
<th>Isotope</th>
<th>Half-Life</th>
<th>Parent</th>
<th>Daughter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>THORIUM-232</strong></td>
<td>Pb-208</td>
<td>stable</td>
<td>Po-212</td>
<td>0.3 μs</td>
</tr>
<tr>
<td>Ti-208</td>
<td>Bi-212</td>
<td>3.1 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-212</td>
<td>Po-216</td>
<td>10.6 h</td>
<td>Rn-220</td>
<td>55.6 s</td>
</tr>
<tr>
<td><strong>URANIUM-235</strong></td>
<td>Th-231</td>
<td>20.6 h</td>
<td>Rn-219</td>
<td>3.9 s</td>
</tr>
<tr>
<td>Pb-211</td>
<td>Po-215</td>
<td>18.1 μs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-207</td>
<td>Bi-211</td>
<td>4.8 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-207</td>
<td>stable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>URANIUM-238</strong></td>
<td>Th-234</td>
<td>24.1 d</td>
<td>Rn-222</td>
<td>3.8 d</td>
</tr>
<tr>
<td>Pb-214</td>
<td>Po-218</td>
<td>26.8 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi-214</td>
<td>Po-214</td>
<td>19.8 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-210</td>
<td>Po-210</td>
<td>22.3 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-206</td>
<td>stable</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Pb isotopic ratio

Depending on chemical history and water content of ore material significant differences exist in abundances of long-lived “mother” U, Np, Pt elements in the ore material. This eventually leads to build-up of significant differences in lead “daughter” isotopic abundances, which often is characteristic for the mine site.

Present day lead = primeval lead + radiogenic lead

Simple evolution model:

\[ \frac{^{206}\text{Pb}}{^{204}\text{Pb}}(t) = \frac{^{206}\text{Pb}}{^{204}\text{Pb}}(t_p) + \mu \cdot (e^{\lambda_{238} t_p} - e^{-\lambda_{238} t}) \]

\[ \frac{^{207}\text{Pb}}{^{204}\text{Pb}}(t) = \frac{^{207}\text{Pb}}{^{204}\text{Pb}}(t_p) + \frac{\mu}{137.8} \cdot (e^{\lambda_{235} t_p} - e^{-\lambda_{235} t}) \]

\[ \frac{^{208}\text{Pb}}{^{204}\text{Pb}}(t) = \frac{^{208}\text{Pb}}{^{204}\text{Pb}}(t_p) + W \cdot (e^{\lambda_{232} t_p} - e^{-\lambda_{232} t}) \]

Where:
- \( t_p \): time between origin of earth and last geological active period
- \( \lambda_{238} \): decay constant of \(^{238}\text{U} \)
- \( \lambda_{235} \): decay constant of \(^{235}\text{U} \)
- \( \lambda_{232} \): decay constant of \(^{232}\text{Th} \)
- \( \mu \)
- \( W \)
Evolution model applied for US mines

Certain lead isotope ratios help to identify the original mines, the analysis of the lead isotope ratio reveals ancient trading routes.

Present isotope ratio parameters:

$$\mu = \frac{^{238}U}{^{204}Pb}$$

$$W = \frac{^{232}Th}{^{204}Pb}$$
Ancient ship trade ca 1500 BC

Central Mediterranean Mycenaean Greeks colonized parts of southern Italy and sailed around Sicily. There, a Bronze Age Canaanite statuette vetted from the sea hints at Near Eastern sailors in the same region.

Ancient trade route Canaanite and Cypriot pottery recently discovered at Kommos on Crete and Mycenaean and Cypriot pottery found at Mersa Matruh in Egypt suggest that the two ports lay on a counterclockwise loop around the Mediterranean Sea.

Hittites Controlling most of Asia Minor, the warlike Hittites, led by their powerful king Shuppiluliumash, gained control of Syria from Egypt about 1550 B.C.

Arzawa This fiercely independent kingdom of eastern Asia Minor often recoiled against Hittite control. Arzawa’s exact location remains unknown; its capital may have been at Kaš in Turkey.

Early traders brought tin from an unknown eastern source—possibly Afghanistan—through the towns of Eshnunna and Mari to Ugarit. Tin ore was recently found at Bolkardag in Turkey and may have been smelted in Bronze Age furnaces.

Ivory Ancient texts describe elephant hunts by Egyptian royalty in Syria. Excavated skeletons suggest that hippopotamuses also grazed in swamps along the coast.

Colored artifacts indicate probable sources of goods like those in the Ulu Burun cargo. Silhouettes indicate other finds of similar trade goods.

Possible route of Ulu Burun ship
Selected trade route (water)
Selected trade route (land)
Shipwreck
Egyptian trading vessel at Uluburun Kas

Difficulty of Underwater Archaeology
Copper and tin ingots

Tin ingot

Copper ingots
Origin of metals?

Cyprus, Laurion (mainland Greece), and Cappadocia (Taurus Mountains) were antique mining centers, did the Uluburun transport metals from Laurion eastwards or from Cyprus or Cappadocia westwards? The Pb isotope composition from Cyprus and Laurion metals matches most closely the isotope composition of group 4 from the Taurus mines! But differences show up when comparing different Pb isotope ratios!
Origin and destination?
Did the ship sail west or east

Origin of copper and tin can be tested on the mine specific lead isotope ratio in the ingots.

Typical lead ratio of Taurus mines

Typical lead ratio of ship ingots

Lead concentration in copper and tin