3.9. Thermoluminescence

Thermoluminescence (TL) dating is a technique that is based on the analysis of light release when heating crystalline material. TL-dating is used in mineralogy and geology, but is also increasingly being applied for dating of anthropological and archaeological samples.

chlorophane mineral

cool state

heated state
Applicability of TL dating

TL dating is mainly applicable for material with mineral or crystalline structure or with spurious crystalline contents. It is only usable for insulating material not for metallic artifacts.

In archaeology TL is mainly used for pottery analysis.

In anthropology the main use of TL is the dating of flint stone as early tool material for mankind.
The glow curve

Typical phenomenon of thermoluminescence, when sample is heated above 200 °C, light emission in blue range is observed up to 400 °C. At higher temperature, material emits a red glow. For second heating no blue light emission is observed, only the red glow curve remains at the higher temperature range.
Origin of thermoluminescence

Thermoluminescence (TL) originates from the temperature induced release of energy, stored in the lattice structure of the crystal following long-term internal and external exposure to nuclear radiation from natural sources.

TL accumulates in the material with time depending on the radiation (and light) exposure. The TL is released by heating. The dating clock starts with the initial firing of the material, when originally accumulated TL is being driven out.
Age determination

the amount of accumulated TL is proportional to the age of the sample and inverse proportional to the nuclear radiation exposure of the sample.

\[ \text{Age} = \frac{\text{Archaeological TL}}{(\text{Annual Dose}) \cdot (\text{TL/unit dose})} \]

Annual Dose: \( \frac{D}{t} = \frac{E}{m \cdot t} \)

Amount of energy \( E \) deposited by radiation exposure into sample of mass \( m \) within one year. It depends on the content of radioactive nuclei in the sample material and on the exposure to external radioactivity.
reminder from Chapter 1.2:

Dose: \[ D = \frac{E}{m} \]

Amount of energy \( E \) deposited by radiation into body of mass \( m \).

1 Gray (Gy) = 1 Joule/kg (Energy/mass)
1 rad = 1 centigray = 10 milligrays (1 rad = 1cGy = 10 mGy)
Nominal background radiation absorbed dose 100 mrad/year = 1 mGy/yr.

TL/unit dose is material specific. It describes the probability for a material to develop thermoluminescence (TL) under radiation exposure. This has to be determined by independent analysis typically by exposure to well defined radioactive sources. For metals: TL/unit dose = 0
experimental set-up

heater with temperature control; blue filter for red light glow absorption and photomultiplier with scintillator for TL photon measurement.
Example 1

Measurement of TL with an calibrated source gives 52000 TL-cts/s after an exposure to 0.1Gy radiation.

TL/dose = 520000 TL-cts/(s·Gy)

The TL curve shows 21000 TL-counts/s at an average annual dose of 1 mGy/y

Measurement of TL with an calibrated source gives 52000 TL-cts/s after an exposure to 0.1Gy radiation.

TL/dose = 520000 TL-cts/(s·Gy)

\[
\text{Age} = \frac{21000 \text{[s}^{-1}]}{1 \cdot 10^{-3} \text{[Gy/y]} \cdot 520000 \text{[s}^{-1} \cdot \text{Gy}^{-1}]} = 4038 \text{y}
\]
The Plateau Test

two portions of the sample are TL tested, one after additional exposure to radioactive source (β radiation) and one without additional exposure - paleodose.

Ratio of the two TL curves should provide a plateau in the TL range.

short-lived TL components
The plateau method

The plateau method – initially developed as an independent test – provides a more reliable method since with this relative approach the systematic uncertainties in the absolute dose rates cancel out.

\[
\text{Age} = \frac{\text{paleodose}}{\text{annual dose}}
\]

The paleodose is the natural dose received by the sample since its last heating (production); it can be determined from the plateau ratio \(R\) between the paleodose and the paleodose plus the source related dose from the sample irradiation. The annual dose is material dependent and must be measured.
Paleodose Determination

\[ R = \frac{N}{N + N_\beta} \]
\[ R \cdot (N + N_\beta) = N \]
\[ R \cdot N_\beta = N(1 - R) \]
\[ N = \frac{N_\beta}{(R^{-1} - 1)} \]

If \( R = 0.5 \) \((R^{-1} = 2)\) the sample received during the source irradiation the same dose as naturally over its life time. If \( R = 0.33 \) \((R^{-1} = 3)\) the sample received during the source irradiation twice the natural life time dose.
Example 2

\[ R = 0.47; \quad N = \frac{N_\beta}{(1/0.47 - 1)} = 0.886 \cdot N_\beta \]

with \( N_\beta = 10 \text{ Gy} \);  Paleodose: \( N = 8.86 \text{ Gy} \)
Annual Dose Determination

For most pottery samples the TL is produced in roughly equal proportions by the nuclear radiation from potassium $^{40}$K ($\beta$, $\gamma$ emitter), thorium ($\alpha$-emitter), and uranium ($\alpha$-emitter) plus its additional $\beta$ and $\gamma$ radiation which is emitted along the decay chains. Minor contributions yield from rubidium contamination ($\beta$-emission) and cosmic radiation bombardment.

\[
\text{Annual dose}: D = D'_\alpha + D_\beta + D_\gamma + D_{cr}
\]

$\alpha$ radiation saturates the TL traps due to its high ionization probability, therefore only 10-15% of the $\alpha$ leads to TL dose.

\[
D'_\alpha = k_\alpha \cdot D_\alpha \quad k_\alpha \approx 0.1 - 0.15
\]
fine and coarse grain method

• the fine grain method seeks to maximize the $\alpha$-dose in sample powder of 3-10 µm grain size!

• the coarse grain method is based only on $\beta$ and $\gamma$ induced luminescence using a coarse powder with more than 500 µm grain size!
Annual doses for typical pottery

<table>
<thead>
<tr>
<th></th>
<th>Alpha</th>
<th>Effective alpha&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Beta</th>
<th>Gamma</th>
<th>Effective totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>—</td>
<td>—</td>
<td>0.83</td>
<td>0.24</td>
<td>1.07</td>
</tr>
<tr>
<td>Rubidium</td>
<td>—</td>
<td>—</td>
<td>0.02</td>
<td>—</td>
<td>0.02</td>
</tr>
<tr>
<td>Thorium</td>
<td>7.39</td>
<td>1.11</td>
<td>0.29</td>
<td>0.51</td>
<td>1.91</td>
</tr>
<tr>
<td>Uranium</td>
<td>8.34</td>
<td>1.25</td>
<td>0.44</td>
<td>0.34</td>
<td>2.03</td>
</tr>
<tr>
<td>Cosmic</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>15.73</td>
<td>2.36</td>
<td>1.58</td>
<td>1.24</td>
<td><strong>5.18</strong></td>
</tr>
</tbody>
</table>

<sup>a</sup> The values are quoted in gray per 1000 years (Gy/ka). The values given correspond to pottery and soil having 1% potassium, 0.005% rubidium, 10 ppm natural thorium and 3 ppm natural uranium.

<sup>b</sup> The effective alpha contribution assumes a value of 0.15 for $k$, the alpha effectiveness in inducing TL relative to the effectiveness of the beta and gamma radiation. This contribution is appropriate when the 'fine-grain' technique is being used.
Example 3 (fine grain method)

Annual dose for ‘typical’ pottery and soil conditions can be estimated (neglecting Cosmic Ray Dose):

\[ D = (k \cdot D_\alpha + D_\beta + D_\gamma) \]
\[ D = (2.36 \cdot 10^{-3} + 1.58 \cdot 10^{-3} + 1.24 \cdot 10^{-3}) \text{[Gy/y]} \]
\[ D = 5.18 \cdot 10^{-3} \text{[Gy/y]} \]

Comparison with the paleodose yields an age of:

\[
\text{Age} = \frac{\text{paleodose}}{\text{annual dose}} = \frac{8.86 \text{[Gy]}}{5.18 \cdot 10^{-3} \text{[Gy/y]}} = 1710 \text{[y]}
\]
Uncertainties & Problems

If sample has been exposed to light for considerable time, bleaching may occur, de-excitation of TL traps by photon interaction. TL drops, suggesting a lower paleodose & age.

\[ TL \approx 0.72 \cdot TL \approx 0.15 \cdot TL \]

since age is proportional to paleodose, significant errors can occur!

a) natural TL curve
b) after 1h light exposure
c) after 24 h light exposure
bleaching time dependence

Since the light exposure causes photon induced de-excitation of intra-band states the TL drops exponentially with exposure time $t$.

$$TL(t) = TL_0 \cdot e^{-\kappa \cdot t}$$

$\kappa = \text{material constant}$

Quartz is more slowly bleached than Feldspar, if $\kappa$ and light exposure time $t$ is known, corrections can be applied.
bleached piece of pottery

unbleached case:

\[
\text{Age} = \frac{\text{paleodose}}{\text{annual dose}} = \frac{8.86 \text{ [Gy]}}{5.18 \cdot 10^{-3} \text{ [Gy/y]}} = 1710 \text{ [y]}
\]

\[\kappa = 0.33: \text{ 1 h bleached case: paleodose is reduced to 72%:}\]

\[
\text{Age} = \frac{\text{paleodose}}{\text{annual dose}} = \frac{6.38 \text{ [Gy]}}{5.18 \cdot 10^{-3} \text{ [Gy/y]}} = 1231 \text{ [y]}
\]

sample appears considerably younger!
water uptake and water damage

Pottery within a meter or so from ground level are typically wet! Water uptake has direct impact on annual dose since it acts as absorber material for the radiation. Wet pottery has lower annual dose suggesting a higher age of pottery sample.

Reduction in dose rates for $\alpha$, $\beta$, and $\gamma$ exposure is:

\[
\begin{align*}
  k_{\alpha}^{\text{wet}} &= \frac{k_{\alpha}^{\text{dry}}}{1 + 1.5 \cdot f \cdot w} \\
  k_{\beta}^{\text{wet}} &= \frac{k_{\beta}^{\text{dry}}}{1 + 1.25 \cdot f \cdot w} \\
  k_{\gamma}^{\text{wet}} &= \frac{k_{\gamma}^{\text{dry}}}{1 + 1.14 \cdot f \cdot w}
\end{align*}
\]

water absorbs $\alpha$-radiation 50% more efficiently than dry clay, water is 25% more efficient in absorbing $\beta$-radiation but only 14% more efficient for $\gamma$-radiation.

$f$: fraction of water retained in soil material (0.95 in UK, 0.6 in Italy)

$w$: saturation of water uptake; obtained by weighting wet and dry sample ($w=0.05-0.3$)
wet piece of pottery

in soaked soil, \( f = 0.95 \), soaked piece of pottery, \( w = 0.3 \).
If sample has a paleodose of 8.86 Gy like a dry sample:

\[
D = \left( k_{\alpha}^{\text{wet}} \cdot D_{\alpha} + k_{\beta}^{\text{wet}} \cdot D_{\beta} + k_{\gamma}^{\text{wet}} \cdot D_{\gamma} \right)
\]

\[
D = \left( 0.7 \cdot 2.36 \cdot 10^{-3} + 0.74 \cdot 1.58 \cdot 10^{-3} + 0.76 \cdot 1.24 \cdot 10^{-3} \right) \text{[Gy/y]}
\]

\[
D = 3.76 \cdot 10^{-3} \text{ [Gy/y]} \quad \text{about 73\% reduction in annual dose}
\]

\[
\text{Age} = \frac{\text{paleodose}}{\text{annual dose}} = \frac{8.86 \text{ [Gy]}}{3.76 \cdot 10^{-3} \text{ [Gy/y]}} = 2356 \text{ [y]}
\]