Thermochronology, cosmogenic isotopes and dating of young sedimentary rocks
Part 8: Usage of U-Pb and U-Th geochronology in sedimentary environment

István Dunkl
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Intro: Where are the geotherms?
Geothermometry in basins by: vitrinite reflectance, bitumen refl.,
graptolite refl., Raman spectroscopy, conodont alteration,
spore colour, fluorescence, Rock-Eval, clay mineralogy
Let's start the dating work: research concept, mineral separation
Fission track dating: - nuclear physics
- age equation, statistics
- track lengths

Volcanic events (= formation ages)
Basement exhumation (= cooling ages)
Complex T histories of basins & thermal modelling
Detrital chronology (provenance by single-grain ages)

(U-Th)/He thermochronology
K/Ar, Ar/Ar, Luminescence, ESR and Cosmogenic dating of sediments

U/Pb and U/Th dating of sediments
Two U isotopes: \( \frac{{^{238}U}}{{^{235}U}} = 137.88 \)

\( ^{238}\text{U} \rightarrow \text{intermediates} \rightarrow ^{206}\text{Pb} \)

\[ T_{\frac{1}{2}} = 4.47 \times 10^9 \text{ years} \]

\( ^{235}\text{U} \rightarrow \text{intermediates} \rightarrow ^{207}\text{Pb} \)

\[ T_{\frac{1}{2}} = 0.71 \times 10^9 \text{ years} \]

\( ^{232}\text{Th} \rightarrow \text{intermediates} \rightarrow ^{208}\text{Pb} \)

\[ T_{\frac{1}{2}} = 14.1 \times 10^9 \text{ years} \]
Major methods used for U-Pb geochronology

- Isotope Dilution – Thermal Ionization Mass Spectrometry (ID-TIMS)
- Single crystal evaporation
- Secondary Ion Mass Spectrometry (SIMS, Ion Probe, or “SHRIMP”)
- Proton Induced X-ray Emission (PIXE)
- Solution ICP-MS
- Laser-Abblation ICP-MS
- Electron microprobe analysis (EMP)

Applications in sedimentary environment

- Dating of volcanic ash layers
- Provenance (age distribution, fingerprint method)
- Mineralization in diagenetic conditions
Secondary ion mass spectrometry

Chemical analyses

[Williams, 2008]
Polished surface and "rim piercing" method of laser ablation

![Diagram showing zircon mounts for conventional and rim piercing methods.](Image)

Fig. 3. A sketch of the mounts used in the conventional and rim piercing methods for dating detrital zircons. When zircons are dated in a conventional mount (A) the zircon is sectioned in half and polished so that the rim is exposed only as a narrow zone at the margin of the grain, which is normally too narrow to date by conventional means. The rim piercing method (B) involves mounting the unsectioned grain on adhesive tape and drilling directly into the rim at the top of the grain.

[Campbell et al., 2005]
Time-resolved signal of laser ablation

[Frei and Gerdes, 2008]
Comparison of techniques applied at zircon U-Pb dating

SIMS
10 - 20 micron spot size
< 2 microns depth
cia 30 minutes per analysis
0.5 - 5 % 2 sigma precision

LA ICPMS
30 - 60 micron spot size
10 - 20 microns depth
cia 4 minutes per analysis
1 - 10 % 2 sigma precision

[Košler and Tubrett, 2004]
## U-Pb data presentation

### LA-SF-ICP-MS U-Pb data for the 91500 zircon

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>91500-1</td>
<td>6119</td>
<td>66</td>
<td>13</td>
<td>0.51</td>
<td>1.83099</td>
<td>3.1</td>
<td>0.17740</td>
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<td>0.75</td>
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<td>2.0</td>
<td>1057</td>
<td>33</td>
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<tr>
<td>91500-2</td>
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<td>66</td>
<td>13</td>
<td>0.56</td>
<td>1.85158</td>
<td>3.3</td>
<td>0.17878</td>
<td>2.4</td>
<td>0.74</td>
<td>0.07511</td>
<td>2.2</td>
<td>1064</td>
<td>35</td>
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</tbody>
</table>

- a. Within-run background-corrected mean 207Pb signal in counts per second [cps].
- b. U and Pb concentrations and Th/U ratios are calculated relative to GJ-1 reference zircon.
- c. Corrected for background and within-run Pb/U fractionation and normalised to reference zircon GJ-1 (ID-TIMS values/measured value); 207Pb/235U calculated using (207Pb/206Pb)/238U/206Pb + 1/137.88.
- d. Rho is the error correlation defined as the quotient of the propagated errors of the 206Pb/238U and the 207/235U ratio.
- e. Quadratic addition of within-run errors (2 s.d.) and daily reproducibility of GJ-1 (2 s.d.).
- f. Corrected for mass-bias by normalising to GJ-1 reference zircon (~0.6 per atomic mass unit) and common Pb using the model Pb composition of Stacey and Kramers (1975).

[Frei and Gerdes, 2008]
Comparison of methods

ID-TIMS:  
- 1 analysis per hour  
- $100 per analysis ($300 at MIT!)  
- ± 0.3% accuracy from whole crystal

SIMS:  
- 4 Analyses per hour  
- $25 per analysis  
- 10-35 micron beam diameter  
- ~1 micron pit depth (great spatial resolution!!)  
- ± 1% accuracy

LA-MC-ICPMS:  
- 40 analyses per hour  
- $8 per analysis  
- 10-50 micron beam diameter  
- ~12 micron pit depth  
- ± 1% accuracy

[G. Gehrels]
### Most frequently dated minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>U content (ppm)</th>
<th>Common Pb (% of total Pb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircon</td>
<td>1 to &gt;10 000</td>
<td>&lt;2%</td>
</tr>
<tr>
<td>Monazite</td>
<td>282 to &gt;50 000</td>
<td>&lt;2%</td>
</tr>
<tr>
<td>Baddeleyite</td>
<td>58 to 3410</td>
<td>&lt;2%</td>
</tr>
<tr>
<td>Rutile</td>
<td>&lt;1 to 390</td>
<td>&lt;2 to 95%</td>
</tr>
<tr>
<td>Xenotime</td>
<td>5000 to 29 000</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Titanite</td>
<td>4 to 500</td>
<td>5 to 40%</td>
</tr>
<tr>
<td>Allanite</td>
<td>130 to 600</td>
<td>5 to 30%</td>
</tr>
</tbody>
</table>


[Košler and Tubrett, 2004]
Closure temperatures (?)

**Closure Temp:** the temperature at which a cooling mineral can no longer exchange isotopes with its surroundings.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Method</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircon</td>
<td>U-Pb</td>
<td>&gt;800</td>
</tr>
<tr>
<td>Monazite</td>
<td>U-Pb</td>
<td>&gt;800</td>
</tr>
<tr>
<td>Titanite (Sphene)</td>
<td>U-Pb</td>
<td>600</td>
</tr>
<tr>
<td>Garnet</td>
<td>Sm-Nd</td>
<td>&gt;550</td>
</tr>
<tr>
<td>Hornblende</td>
<td>K-Ar</td>
<td>500</td>
</tr>
<tr>
<td>Muscovite</td>
<td>Rb-Sr</td>
<td>500</td>
</tr>
<tr>
<td>Muscovite</td>
<td>K-Ar</td>
<td>350</td>
</tr>
<tr>
<td>Apatite</td>
<td>U-Pb</td>
<td>350</td>
</tr>
<tr>
<td>Biotite</td>
<td>Rb-Sr</td>
<td>300</td>
</tr>
<tr>
<td>Biotite</td>
<td>K-Ar</td>
<td>280</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>K-Ar</td>
<td>200</td>
</tr>
<tr>
<td>Apatite</td>
<td>Fission Track</td>
<td>120</td>
</tr>
</tbody>
</table>

Closure temperatures for common minerals for different isotopic systems. Note that closure temperatures for different systems in the same minerals can vary.

[W. Siebel]
U-bearing phases and minerals used for U-Pb dating

**U-minerals**
- Uraninite, Pechblende, Brannerite
- Carnotite, Autunite, Tobernite

**Common accessory minerals that usually do not need common lead correction**
- Zircon
- Monazite
- Xenotime
- Baddeleyite

**Common lead correction needed**
- Apatite
- Titanite (Sphene)
- Allanite (Ortite)
- Rutile
- Cassiterite
- Perovskite

- Opal
- Calcite
Why zircon?
From which rocks?

do not hesitate to sample ugly-looking, even strongly weathered rocks -e.g. bentonites-, but the ideal case if you see quartz (and biotite)
Zoning and heterogeneous metamictization in old zircons

Fig. 2. Backscattered images of selected analysed zircons. The scale bar is 100 μm long; white dotted circles represent individual spots.

[Paquette et al., 2003]
Provenance

[Veevers et al., 2005]
Paleowinds inferred from detrital-zircon geochronology of upper Paleozoic loessite, western equatorial Pangea

Figure 2. Cumulative probability plots of detrital-zircon ages for studied samples. Area under each curve represents summed Gaussian distribution of individual ages and associated errors for each grain. Discordant ages (by more than 5%) or grains with elevated common Pb were disregarded in these plots (Table DR-1; see text footnote 1). Small letters over peaks reflect inferred source direction of winds (in paleocoordinates) relative to interpreted source area: se—southeasterly winds; ne—northeasterly winds; w—westerly winds; e—easterly winds.

[Soreghan et al., 2002]
Provenance of sandstone boulders in a salt dome

[Dunkl, unpublished]
Electron microprobe dating of monazite

[Nagy et al., 2003]
Monazite petrochronology: age domain maps
(Williams et al. 1999; Goncalves et al. 2005)

extract element concentrations from chemical maps (Th, U, Pb, Y)
solve age (Montel) equation pixel-by-pixel for selected domains or entire grain
link to spot analyses and other textural information

Goncalves et al., Am. Min., 2005
Diagenetic monazite

Fig. 3. Summary of diagenetic history in relation to Nd isotope evolution.

[Evans and Zalasiewitz, 1996]
Diagenetic monazite

Regression results for U-Pb analysis of diagenetic phases from Silurian mudrocks.

Age = 417 ± 11 Ma (2σ)
MSWD = 107

- • authigenic monazite (in situ)
- □ authigenic monazite (placer)
- ▲ apatite and illite

Fig. 6. U–Pb regression age for the diagenetic phases of this study.

[Evans and Zalasiewitz, 1996]
Fig. 3. Scanning electron microscope BSE images of titanite. Ovals (about 25 μm in diameter) indicate locations of SHRIMP analyses,

[Aleinikoff et al., 2007]
Sphene

Fig. 5. Discrimination diagrams showing correlation of color variations and chemical compositions. (A) Th/U vs. \(^{206}\text{Pb}^{238}\text{U}\).

[Aleinikoff et al., 2007]
Fig. 6. $T-t$ path of UHPM rocks in the South Dabie Mountains. Gar = garnet, Omph = omphacite, Rut = rutile, Phen = phengite, Mon = monazite, Bi = biotite, Epid = epidote. Data sources: Li et al.
U–Pb dating of MVT ore-stage calcite
(cc ~ 0.x ppm U)

Fig. 1. U–Pb calcite–galena isochron for the Avecilla Mine (Penyagolosa Subbasin). Calculated by the model 1 algorithm of Ludwig (1999).

[Grandia et al., 2000]
U–Pb dating of calcite concretions from Cambrian black shales and the Phanerozoic time scale

Carsten Israelson a,* , Alex N. Halliday a , Bjørn Buchardt b

Fig. 2. (a) Concordia diagram for Sample 6, indicating Pb loss or U gain (discordia MSDW = 1.4). The errors on 207 Pb*/235 U ratios are between 0.4% and 0.8%, and on 206 Pb*/238 U ratio between 0.3% and 0.6%. (b) Data from Sample 8, where most
Figure 4.12 (a) Geological setting of the Yeelirrie carnitite deposit hosted in channelized calcrete, Western Australia (after Mann and Deutscher, 1978; Carlisle, 1983). (b) Model depicting the setting and processes involved in the formation of carnitite deposits in calcretized channels (after Carlisle, 1983).
Opal

[Amelin and Back, 2006]
Fig. 4. Concentrations of U, Th, and $^{204}\text{Pb}$ in the studied opals. Diagonal lines show constant U–$^{204}\text{Pb}$ and U–Th ratios; the lines are labelled with the values of respective ratios.

[Amelin and Back, 2006]
Figures a) and b) illustrate the lead isotope ratios for different samples. Figure a) shows the relationship between $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{235}\text{U}$ for translucent matrix (squares) and clear veins (circles). The graph indicates a linear trend with points scattered along the line, suggesting a consistent ratio over the range of samples tested.

Figure b) presents a similar relationship between $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{238}\text{U}/^{204}\text{Pb}$ for translucent matrix and clear veins. Again, the points form a linear trend, indicating a consistent isotope ratio.

The data supports the hypothesis that the translucent matrix has an age of 10.1 ± 4.2 Ma with an initial $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of $4 ± 260$, and MSWD = 90. Similarly, the clear veins show an age of 3.45 ± 0.28 Ma with an initial $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of $282 ± 08$, and MSWD = 1.2.

[Amelin and Back, 2006]
Fig. 7. (A) Transmitted light image of opal sample HD2074 from Yucca Mountain, Nevada, USA, showing SHRIMP spots. (B) $^{206}\text{Pb} - ^{234}\text{U} - ^{238}\text{U}$ ages vs. distance diagram. Ages have been calculated from the common-Pb corrected Pb–U ratios normalised using sample M21277 as a standard. Distance was measured from the outer termination of the sample in direction perpendicular to the layering.

[Nemchin et al., 2006]
U-Pb dating of a speleothem of Quaternary age

David A. Richards,1,*† Simon H. Bottrell,1 Robert A. Cliff,1 Klaus Ströhle,1 and Peter J. Rowe2

Abstract—We demonstrate that U-Pb dating is a promising method for secondary carbonate materials of Quaternary age and older by obtaining a $^{206}\text{Pb}^*/^{238}\text{U}$ age for a speleothem with high U (>10 $\mu$g g$^{-1}$) and very low Pb (<10 ng g$^{-1}$) that is supported by an independent $^{230}$Th age. Thermal ionisation mass-spectrometry

Facit:
needs lucky composition & a very very clean lab.
Geochronology using the decay of uranium

István Dunkl

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Part 2: U-series dating

($^{230}$Th/U dating, U/Th disequilibrium method)

Focus:

principles, methodology, statistics

applicability, limitations

case studies
Decay chains - secular equilibrium
238U decay chain half-lives

[Graph showing half-lives for various isotopes in the decay chain of 238U, including 4.47 Ga, 248 ka, 75.2 ka, 1.7 ka, 22 y, 138 d, 24 d, 6.7 h, 3.8 d, 27 m, 3 m, 20 m, 1.3 m, 7.5 m, 5 d, 4.2 m.]

[from D. Patterson]
Decay series equation

Reflects balance between decay and in-growth:

\[ N_2 = N_2^0 e^{-\lambda_2 t} + \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \]

"Amt daughter present "
"Daughter remaining from that present initially"
"Balance between daughter produced and that which has subsequently"

Useful approximation:

\[ (N_2) = (N_2)^0 e^{-\lambda_2 t} + (N_1)^0 (1 - e^{-\lambda_2 t}) \]

At \( t >> t_{1/2} \) of \( N_2 \):

\[ (N_2) = (N_1)^0 \]

\[ \frac{(^{230}\text{Th})}{(^{232}\text{Th})} = \frac{(^{230}\text{Th})_0}{(^{232}\text{Th})} e^{-\lambda_{230} t} + \frac{(^{238}\text{U})_0}{(^{232}\text{Th})} (1 - e^{-\lambda_{230} t}) \]

"Activity of \(^{230}\text{Th} \) present"
"Activity of \(^{230}\text{Th} \) remaining of that present initially"
"Balance between \(^{230}\text{Th} \) produced and that which has subsequently decayed"

Nuclides:
1: parent
2: daughter
0: initial amount

[Cooper and Reid]
U-series fractionation and accessible age range

\[ \frac{N_{2\lambda_2}}{N_{1\lambda_1}} \]

- $^{226}\text{Ra}/^{230}\text{Th}$
- $^{231}\text{Pa}/^{235}\text{U}$
- $^{230}\text{Th}/^{234}\text{U}$
- $^{234}\text{U}/^{238}\text{U}$

2 = daughter  
1 = parent

[Schmitt, 2009]
Initial isotope ratios are never ideal - correction needed

[Uncertainty of 230Th/234U with time from Calsteren and Thomas, 2006]
Recoil effect and leaching process results in **non-mass dependent isotope fractionation** where the solid phase is depleted in $(\text{234U}/\text{238U})$ and the liquid phase is enriched.
Scope

environmental science
oceanography
hydrology
science-based archaeology

magma chamber evolution and volcanic hazard prediction
global climatic change through dating of authigenic carbonate deposits
human evolution through dating of bone
groundwater evolution
Materials

Zircon
Plag, Amph, Cpx, Mt, (magmatic Ca-garnet)
corals
molluscan shells
carbonate cement
marine apatite
lacustrine carbonates (marl)
speleotheme, travertine
pedogenic silica and carbonate "caliche", "calcrete"
bones, tooth enamel
(peat)
ferruginous concretions and rinds
opal
ice, water
Secular equilibrium

For a crystal with 100 ppm U, this means:

<table>
<thead>
<tr>
<th>nuclide</th>
<th>$\lambda$ a$^{-1}$</th>
<th>$t_{1/2}$ a</th>
<th>ppb</th>
<th>parent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U</td>
<td>$2.794 \times 10^{-6}$</td>
<td>246,000</td>
<td>6</td>
<td>$^{238}$U</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>$9.217 \times 10^{-6}$</td>
<td>75,200</td>
<td>2</td>
<td>$^{238}$U</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>$4.272 \times 10^{-4}$</td>
<td>1,622</td>
<td>0.04</td>
<td>$^{238}$U</td>
</tr>
<tr>
<td>$^{231}$Pa</td>
<td>$2.134 \times 10^{-5}$</td>
<td>32,480</td>
<td>0.03</td>
<td>$^{235}$U</td>
</tr>
</tbody>
</table>

Ultra-trace element analysis needed

[Schmitt, 2009]
Methods

(1) Bulk separates: partial and total dissolution
   Chemical separation (column chemistry)
(2) In situ dating (single grains or rock chips in polished mounts)

Gamma spectrometry
Apha spectrometry
Solution ICP-MS
Laser-ablation ICP-MS
Thermal ionization mass-spectrometry (TIMS)
Synchrotron radiation X-ray microanalysis
SHRIMP
Data presentation

<table>
<thead>
<tr>
<th>Depth (mbsf)</th>
<th>$^{238}$U (ppm)</th>
<th>$^{230}$Th (ppt)</th>
<th>$(^{232}$Th/$^{230}$Th)</th>
<th>$\delta^{234}$U(0) (%e)</th>
<th>$(^{230}$Th/$^{238}$U)</th>
<th>Age$_{raw}$ (ka)</th>
<th>Detrital (%)</th>
<th>Age$_{corr}$ (ka)</th>
<th>$\delta^{234}$U(T)$_{corr}$ (%e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1008</td>
<td>7.60 ± 0.02</td>
<td>109.74 ± 0.68</td>
<td>164.30 ± 1.23</td>
<td>105.17 ± 2.52</td>
<td>0.883 ± 0.006</td>
<td>167.0 ± 2.73</td>
<td>0.64</td>
<td>163.30 ± 3.30</td>
<td>166.88 ± 3.70</td>
</tr>
</tbody>
</table>

[Robinson et al., 2002]

Table 2. Isotopic and Age Data for Samples

<table>
<thead>
<tr>
<th>Sample HD#</th>
<th>Unit</th>
<th>Type</th>
<th>wt mg</th>
<th>ppm U</th>
<th>$^{232}$Th ppm</th>
<th>$^{230}$Th/232Th</th>
<th>$^{230}$Th/238U</th>
<th>$^{230}$Th/238U</th>
<th>$^{234}$U/238U</th>
<th>$^{234}$U/238U</th>
<th>$^{234}$U/238U</th>
<th>$^{230}$Th/U Age (ka)</th>
<th>Initial $^{234}$U/238U</th>
<th>T-γ</th>
<th>$^{234}$U/238U Age (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1608-a</td>
<td>1</td>
<td>1</td>
<td>113</td>
<td>5.5</td>
<td>3.5</td>
<td>4.8</td>
<td>1.002 ± 0.11</td>
<td>1.003 ± 0.25</td>
<td>0.959 ± 0.22</td>
<td>0.00</td>
<td>***</td>
<td>***</td>
<td><strong>t</strong></td>
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<td></td>
</tr>
<tr>
<td>1608-b</td>
<td>1</td>
<td>1</td>
<td>65</td>
<td>9.3</td>
<td>2.4</td>
<td>11.2</td>
<td>0.967 ± 0.008</td>
<td>0.965 ± 0.11</td>
<td>0.981 ± 0.008</td>
<td>+0.01</td>
<td>&gt;401</td>
<td>&lt;.96</td>
<td>-0.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1608-c</td>
<td>1</td>
<td>5</td>
<td>114</td>
<td>3.9</td>
<td>1.9</td>
<td>6.3</td>
<td>0.971 ± 0.014</td>
<td>0.967 ± 0.022</td>
<td>0.999 ± 0.015</td>
<td>0.00</td>
<td>&gt;307</td>
<td>1.00 ± 0.03</td>
<td>-0.68</td>
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<tr>
<td>1729-a</td>
<td>4</td>
<td>5</td>
<td>109</td>
<td>18.2</td>
<td>2.7</td>
<td>18.2</td>
<td>0.893 ± 0.007</td>
<td>0.889 ± 0.008</td>
<td>1.408 ± 0.010</td>
<td>-0.26</td>
<td>102 ± 2</td>
<td>1.54 ± 0.01</td>
<td>-0.53</td>
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<tr>
<td>1729-b</td>
<td>4</td>
<td>4</td>
<td>73</td>
<td>17.4</td>
<td>0.7</td>
<td>70.8</td>
<td>1.005 ± 0.004</td>
<td>1.005 ± 0.004</td>
<td>1.324 ± 0.003</td>
<td>0.00</td>
<td>141 ± 2</td>
<td>1.48 ± 0.00</td>
<td>+0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1729-d</td>
<td>4</td>
<td>2</td>
<td>107</td>
<td>16.7</td>
<td>1.5</td>
<td>30.4</td>
<td>0.931 ± 0.004</td>
<td>0.929 ± 0.005</td>
<td>1.367 ± 0.006</td>
<td>-0.15</td>
<td>115 ± 2</td>
<td>1.51 ± 0.01</td>
<td>-0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1729-h</td>
<td>4</td>
<td>1</td>
<td>145</td>
<td>13.8</td>
<td>0.2</td>
<td>206</td>
<td>0.827 ± 0.007</td>
<td>0.827 ± 0.007</td>
<td>1.433 ± 0.003</td>
<td>-0.01</td>
<td>89 ± 1</td>
<td>1.56 ± 0.00</td>
<td>+0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1610-c1a</td>
<td>5</td>
<td>1</td>
<td>51</td>
<td>19.3</td>
<td>2.7</td>
<td>26.7</td>
<td>1.205 ± 0.005</td>
<td>1.213 ± 0.008</td>
<td>1.164 ± 0.005</td>
<td>+0.34</td>
<td>474 ± 46</td>
<td>1.63 ± 0.07</td>
<td>+0.97</td>
<td>510</td>
<td>± 50</td>
</tr>
<tr>
<td>1610-c5</td>
<td>5</td>
<td>1</td>
<td>41</td>
<td>16.0</td>
<td>3.2</td>
<td>18.8</td>
<td>1.230 ± 0.009</td>
<td>1.244 ± 0.013</td>
<td>1.159 ± 0.008</td>
<td>+0.34</td>
<td>&gt;1040</td>
<td>&lt;1.96</td>
<td>520 ± 50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Mathematically-recombining following letters and numbers
2 From Coe et al. (1995)
3 Inner ring (adjacent to core)
4 Measured, given as actual
5 Corrected for detrital U
6 Error correlation for $^{230}$Th/$^{238}$U
7 From equations in Ludwig and Titter
8 Case a 10,000-trial Monte Carlo simulation
9 Assumed half lives which lives recently determined by Cheng et al. no effect on the interpretations.
10 Back-calculated from the present-δ

[Ludwig and Paces, 2002]
Data presentation

lines show evolution for specific initial \( \frac{^{234}U}{^{238}U} \) (labeled) straight, thin lines are isochrons, labeled in ka.

[Ludwig and Paces, 2002]
1 Methods providing age estimates
   A RADIOMETRIC METHODS
       Uranium-Thorium
       Protactinium
       Lead$^{210}$
       Potassium-Argon
       Fission track
       Luminescence
       Radiocarbon
       Caesium$^{137}$
       Tritium
       Electron spin resonance
   B INCREMENTAL METHODS
       Dendrochronology
       Varve chronology
       Lichenometry
       annual ice layers

2 Age equivalent horizons (Isochrons)
   Palaeomagnetism
   Tephrochronology
   Orbitally-tuned oxygen isotope stratigraphy

3 Chemical indications of relative chronology
   Amino-acid diagenesis
   Fluorine/Uranium/Nitrogen content
   Obsidian Hydration
   Weathering/Pedogenesis

Figure 5.1 Ranges of the various dating methods discussed in the text. Broken lines show possible extensions with further improvements in techniques; wavy lines indicate that dating is limited to specific time intervals within the Quaternary.
Eruption dating
major pitfall: recycled zircon crystals

[Bacon and Lowenstern, 2005]
Residence time of magma - correlation with the size of eruption

[Reid, 2008]
Marine reservoir for initial isotope ratio

- U (VI) is relatively soluble

- seawater
  
  3.3 ppb U (appears to be conservative in the ocean)
  0.5*10^{-4} ppb 232Th

- 230Th and 231Pa are particle-reactive; i.e. it tends to attach to surfaces rapidly, and so it is removed from seawater on a time scale of ~30 years.

- occurs at low concentrations in seawater
  
  0.7*10^{-8} ppb 230Th
  
  (<0.1 dpm/100kg at the surface; ~1 dpm/100kg in deep waters)

- corals incorporate uranium (~2ppm) but very little 230Th
Corals

(one line = one data)

Fig. 1. Ablation traces of corals analysed in this study (each trace represents a single analysis). For thick walled coral species such as *Diploria* sp. (A), [Potter et al., 2005]
Usage on lakes (authigenic carbonate)

Fig. 4. Sampling depth in a sediment core of Hawes Water marls plotted against inferred ages for pollen marker horizons and U-series ages (with uncertainty), for authigenic sediment. Hawes Water, NW Lancashire, UK, is a small shallow lake and is much more responsive to climatic and hydrological change than large deep-water lakes, Marshall et al. (personal communication). The research focused on the stable isotope and trace element record from ostracods and authigenic carbonate to reconstruct changes in temperature, hydrology and aquatic productivity. U-series ages match with a proxy chronology based on pollen horizons and stable isotopic data.

[Calsteren and Thomas, 2006]
U-series dating of speleothemes
climate, earthquakes

Figure 6. Natural breakage and regrowth of travertine at the Y-junction in the Big Room. The Great Sonoran Earthquake of 1887 may have caused the damage.

[Ford and Hill, 1999]

The Speleothem formation was associated with warm interglacial or interstadial conditions when groundwater circulation was not impeded by temperatures below freezing. No samples were dated between ~140-165 ka B.P. or from 15-30 ka B.P., thus indicating cold, glacial conditions (GASCOYNE, 1992)
In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology

Fig. 4. Uranium concentration, $[^{234}\text{U}/^{238}\text{U}]$ (□) and $[^{230}\text{Th}/^{234}\text{U}]$ (◊) profiles (top and bottom) measured in situ by two separate laser ablation-MC-ICPMS scans along a sectioned fossil coral from the MIS Stage 5e reef tract at Karma, Huon Peninular. The SEM image (middle) shows the position of the two laser ablation scans, and the position of an aragonite to calcite diagenesis front in relation to distance along the two scans. Trend lines for the mean $[^{234}\text{U}/^{238}\text{U}]$ and $[^{230}\text{Th}/^{234}\text{U}]$ values obtained in the aragonitic part of the coral are continued using a smooth fit curve through the diagenetically altered (calcitic) part of the coral. The variability of measured $[^{234}\text{U}/^{238}\text{U}]$ and $[^{230}\text{Th}/^{234}\text{U}]$ values, averaged over 10 successive mass spectrometer cycles, reflects the very low count rates obtained on the $^{230}\text{Th}$ and $^{234}\text{U}$ isotopes due to the low, ppm level abundance of $^{238}\text{U}$ in the sample. The scale of the SEM image is the same as the compositional profiles. Both scans were undertaken at 0.6 mm/min using a 100 μm diameter laser spot and 20 Hz laser pulse rate.

[ Eggins et al., 2005 ]
Recrystallized aragonite–calcite speleothems

[Ortega et al., 2005]
Recrystallized aragonite–calcite speleothems

(nuclear microprobe analysis)

[Ortega et al., 2005]
Archaeology: Dating of calcite laminations covering paintings
(6300 years & also 29000 y. ago?)

Small red anthropomorph with weapons and linear geometric motif
in red, black and green in style thought to post date Austronesian settlement.

[Aubert et al., 2007]
Dunes
(pedogenic carbonate)

Question

[Herczeg and Chapman, 1991]
Pedogenic silica and carbonate

Fig. 7. Polished slab of HD1726b rind showing sampled areas of inner- and midrinds (outlined), with resulting $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ages, respectively. $^{230}\text{Th}/^{238}\text{U}$ age of inner rind is $>390$ ka.

Fig. 8. Scanning electron micrograph of portion of HD1610 rind. Light gray areas are calcite, dark gray are silica (based on dominant Ca and Si peaks, respectively, in the energy-dispersive X-ray fluorescence spectrum).

[Ludwig and Paces, 2002]
Pedogenic silica and carbonate

[Ludwig and Paces, 2002]
Peat

- organic material adsorbs U
- siliciclastic contribution (mainly clay) carries Th
- top and base of the sequence are open systems (forget geochronology there!)
- pro: can agree well with TL dating
- contra: not always applicable

[Heijnis and van der Plicht, 1992]
Chemical sedimentation

Fig. 3. Oolites. Top, a and b; the line is 0.2 mm long. Bottom, c and d, thin sections; the line is 0.5 mm long

[Lemoalle and Dupont]
Ferruginous concretions and rinds

("Bohnenerz", swamp iron pisoids)

**Fig. 3.** Th-index mixing line plot for coeval Gilbert River Fe/Mn oxide/oxyhydroxide overgrowths on calcretes used to estimate pure oxidic $^{230}\text{Th}/^{234}\text{U}$ activity ratio (slope = $0.223 \pm 0.024$; y-intercept = $0.53 \pm 0.11$; $r^2 = 0.9577$).

[Short et al., 1989]
U-series dating of ice

hardest task

- with or without grain contamination (where are the nuclides?)
- pro: no matrix
- contra: extremely high risk of contamination

[Fireman; Goldstein et al., 2004]
Groundwater

Table 1  Decay series isotopes considered for groundwater dating

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay series</th>
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<tbody>
<tr>
<td>(^{4}\text{He})</td>
<td>stable</td>
<td>(2^{38}\text{U}, 2^{35}\text{U}, 2^{32}\text{Th})</td>
</tr>
<tr>
<td>(^{222}\text{Rn})</td>
<td>3.82 days</td>
<td>(2^{38}\text{U})</td>
</tr>
<tr>
<td>(^{224}\text{Ra})</td>
<td>3.64 days</td>
<td>(2^{32}\text{Th})</td>
</tr>
<tr>
<td>(^{226}\text{Ra})</td>
<td>1600 years</td>
<td>(2^{38}\text{U})</td>
</tr>
<tr>
<td>(^{228}\text{Ra})</td>
<td>5.75 years</td>
<td>(2^{32}\text{Th})</td>
</tr>
<tr>
<td>(^{234}\text{U})</td>
<td>244000 years</td>
<td>(2^{38}\text{U})</td>
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<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>Time constant</th>
<th>Expected dating range</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{4}\text{He}/^{222}\text{Rn})</td>
<td>(P_{\text{He}})</td>
<td>(10^3) \ldots (10^6) years</td>
</tr>
<tr>
<td>(^{224}\text{Ra}/^{226}\text{Ra})</td>
<td>(\lambda_{228})</td>
<td>(100) \ldots (5000) years</td>
</tr>
<tr>
<td>(^{226}\text{Ra}/^{224}\text{Ra})</td>
<td>(\lambda_{226})</td>
<td>(1) \ldots (30) years</td>
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<td>(^{228}\text{Ra}/^{224}\text{Ra})</td>
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<td>(^{228}\text{Ra}/^{226}\text{Ra})</td>
<td>(\lambda_{228})</td>
<td>(1) \ldots (5000) years</td>
</tr>
<tr>
<td>(^{234}\text{U}/^{238}\text{U})</td>
<td>(\lambda_{234})</td>
<td>(5 \times 10^4) \ldots (10^6) years</td>
</tr>
</tbody>
</table>

[Gellermann et al., 1990]

Water

[Plummer et al., 2001]
Groundwater

*Fig. 1* Schematic box model of a unit volume of an aquifer. 1 = rock (minerals), 2 = sorbing particles (e.g. clay), 3 = fluid.

transport of radionuclides in the water by advection (v)

leaching of radionuclides from the rock (e)

removal of radionuclides from the water by precipitation (r)

reversible exchange between water and rock surface (R)

radioactive decay and production

[Gellermann et al., 1990]