Precise two chronometer dating of Pleistocene travertine: The $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ approach

Jost Eikenberga,*, Guido Vezzu¹, Irene Zumsteg¹, Sixto Bajo¹, Max Ruethia, Georg Wysslingb

¹ Paul Scherrer Institute, CH-5232 Villigen (PSI), Switzerland
b Büro Wyssling AG, CH-8118 Pfaffhausen (ZH), Switzerland

Received 23 March 2000; received in revised form 22 November 2000; accepted 8 January 2001

Abstract

In order to determine the geochemical evolution of a freshwater limestone cave system located in central Switzerland (Hell Grottoes at Baar/Zug,) young postglacial tufaceous limestone and travertine precipitates were investigated using the $^{230}\text{Th}/^{234}\text{U}$ ingrowth system. Additional analyses of further radionuclides within the $^{238}\text{U}$ decay chain, i.e. $^{226}\text{Ra}$ and $^{210}\text{Pb}$, showed that the Th/U chronometer started with insignificant inherited $^{230}\text{Th}$ over the entire formation period of the travertine setting (i.e. $^{230}\text{Th}(0) = 0$). A contribution from detrital impurities with $^{230}\text{Th}/^{234}\text{U}$ in secular equilibrium could be precisely subtracted by applying isochron dating of cogenetic phases and recently formed travertine. The resulting precise $^{230}\text{Th}/^{234}\text{U}$ formation ages were found to be consistent with the geological stratigraphy and were furthermore used to demonstrate the applicability of the next geologically important chronometer in the $^{238}\text{U}$-decay series, based on decay of excess $^{226}\text{Ra}$ normalized to the initial, i.e. $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$. This system is suitable for dating phases younger than 7000 yr when the correction of a detritus component increasingly limits the precision of the $^{230}\text{Th}/^{234}\text{U}$ chronometer. Analytical solutions of the coupled $^{234}\text{U}/^{230}\text{Th}/^{226}\text{Ra}$ radionuclide system predicted that the $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ chronometer is independent of the actual $^{230}\text{Th}$ activity build up from decay of $^{234}\text{U}$, if the systems starts with zero inherited $^{230}\text{Th}(0)$. The data set confirmed this hypothesis and showed furthermore that the initially incorporated $^{226}\text{Ra}$ excess must have remained almost uniform in all limestone over a period of at least 7000 yr, i.e. 4–5 half-lives of $^{226}\text{Ra}$. This is concluded because (i) the $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ ages agreed well with those derived from $^{230}\text{Th}/^{234}\text{U}$, (ii) all data plot within uncertainty on the $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ decay curve and (iii) the atomic Ba/Ca ratio was found to be constant in the travertine material independent of the sample ages. Provided that such boundary conditions hold, $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ should be applicable to materials which are suitable for $^{230}\text{Th}/^{234}\text{U}$ dating in sedimentology and oceanography, i.e. travertine, corals, phosphorites, etc., and should strongly support $^{230}\text{Th}/^{234}\text{U}$ for samples that have been formed a few thousand years ago. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The travertine limestone caves (“Höllgrotten”, Engl. Hell Grottoes) investigated in this study are located near Lucerne at Zug/Baar, Switzerland (Fig. 1). Up to now it has not been possible to develop a convincing model of the geological setting and evolution of the massive speleothem. The underlying sedimentary strata suggests that the freshwater calcite precipitations were formed during global warming in the Holocene, i.e. less than 10,000 yr ago and fresh precipitates show that the formation of travertine is still active. Previous attempts using the most suitable dating methods available ($^{14}$C radiocarbon method, pollen analyses) for such a young setting have failed, because the carbon isotope composition in the extremely small fractions of fossil organic residues is strongly disturbed by carbon of inorganic origin from precipitating calcite. Pollen analysis is also not applicable due to strong dissolution of organic matter. However, for geological systems which have been developed less than 300 kyr ago, radionuclides from the U and Th decay series may be used as chronometers, provided that fractionation processes, such as different solubility, cause activity disequilibrium between the different members ($^{238},^{234}\text{U},^{230}\text{Th},^{226}\text{Ra}$, etc.) in the waters where the precipitates are forming (Edwards et al., 1987; Burnett et al., 1988; Sturchio and Binz, 1988; Osmond and Ivanovich, 1992; Kaufman,
We therefore applied $^{230}$Th/$^{234}$U ingrowth-dating on the travertine precipitates from this locality. Since the isotope data indicated deposition of travertine in the Holocene, we also investigated the potential applicability of the next geologically important chronometer in the $^{238}$U-decay series, based on decay of excess $^{226}$Ra; $^{226}$Ra$_{ex}$/^{226}$Ra(0). Although $^{226}$Ra$_{ex}$ dating of speleothem has been rarely applied in the past, there are some interesting investigations suggesting that decay of excess inherited $^{226}$Ra can be useful in obtaining formation ages and growth rates of Holocene sediments (i.e. Koide et al., 1976; Kim and Burnett, 1985; Latham et al., 1986; Sturchio, 1990; Latham and Schwarcz, 1992). While $^{230}$Th/$^{234}$U ingrowth-dating covers a time span from about 4–300 kyr (where the system reaches secular equilibrium), $^{226}$Ra excess-dating ($T_{1/2} = 1600$ yr) is ideal to investigate younger samples ranging from a few hundred years to about 7–8 kyr (or up to 5 half-lives). $^{226}$Ra$_{ex}$ chronometry is thus potentially a good complementary tool to support $^{230}$Th/$^{234}$U. However, three major requirements have to be fulfilled in order that $^{226}$Ra$_{ex}$ dating yields reliable results: (i) correct subtraction of a detrital, non-authigenic component, (ii) insignificant inherited, unsupported $^{230}$Th(0) in the precipitating authigenic material and (iii) a constant initial concentration of $^{226}$Ra(0) in all samples independent on the time of system closure. This study therefore investigates these three boundary conditions, presents an analytical-numerical approach to calculate precise $^{226}$Ra$_{ex}/^{234}$U ages and focuses on the geological interpretation of the growth history of the cave system investigated here.

2. Geology and hydrochemistry

2.1. Geological setting

The *Hell Grottoes* belong to the lower part of the Lorze Valley, which was covered by the Muota-Reuss glacier during the last glaciation. After melting of the ice, strong erosion exposed more than 300 m thickness of quaternary sediments such as tills and highly permeable gravel sequences and, in the region of the *Hell Grottoes* (at the bottom of the valley) additionally the underlying less permeable strata (*Upper Freshwater Molasse*). Springs here continuously discharge infil-
trated rain and groundwater at the contact between these sequences (Fig. 1). Throughout the Holocene a tufaceous limestone-complex with a volume of about 200,000 m³ (Heim, 1919) was built up. The deposit was mined for the production of brick stone during the 19th century (cf. Fig. 1 old and present day surface) until large caves were discovered and the mining was stopped in order to preserve the cave system. The freshwater precipitates consist mainly of porous tufaceous limestone that formed at the surface, assisted by assimilating plants (moss, algae). In the overhanging cliffs finely structured tuffcurtains were built up around tree roots and moss garlands, leading to the formation of the caves. As soon as the caves were closed by further growth of tuffcurtains, massive crystalline travertine precipitations coated the caves inside. Some of the caves were completely sealed by these precipitations which led to formation of lakes inside (Wyssling and Eikenberg, 2000).

2.2. Calcite precipitation

The limestone complex was formed via decomposition of organic matter in the soil by oxygen consuming bacteria causing increase in CO₂ as can be summarized by the simplified reaction

\[ \text{H}_2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}. \]  

1

If the groundwater table is covered with less transmissive sediment or soil layers that derived from till, only fractions of carbon dioxide can escape to the atmosphere leading to a partial conversion via hydrolysis into hydrogen bicarbonate and dissolution of calcite (Krauskopf, 1979). When the groundwater, supersaturated with respect to pCO₂, discharges again on surface, CO₂ equilibrates with the atmosphere and is partially released as indicated by the following equation:

\[ 2\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}. \]  

2

With release of CO₂ the bulk reaction is shifted to the right side, which causes precipitation of calcite. While plants such as moss, shrub and tree roots are acting as crystallisation seeds for large amounts of carbonate precipitation on the surface, the rate of crystallization of pure travertine inside the caves is much slower because of the higher partial pressure of CO₂ in a semi-open system (Eq. 2).

3. Analytical methods

3.1. Sampling strategy

A compilation of the samples analyzed is presented in Table 1. The sampling strategy included the following considerations: (a) sampling of recently formed precipitations to obtain the initial value for ²²⁶Ra(0), the maximum amount of inherited, not-supported ²³⁰Th(0), and the variability of the U/Th ratio in the present day detritic, i.e. non-authigenic impurities; (b) sampling along profiles to check on the consistency of the isotope ages with the strata and to obtain growth rates; (c) sampling of co-genetically formed limestone to check on the reproducibility of the isotope ages and U/Th

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample strategy</th>
<th>Geological and mineralogical description</th>
<th>²³⁰Th/²³⁴U age (kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(b)</td>
<td>Fine grained calcite tuff from the bottom of the deposit (profile I)</td>
<td>8.8 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>(b)</td>
<td>Fine laminated, light brownish travertine on top of profile II</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>(a)</td>
<td>Recent precipitations strongly intergrown with detrital clay minerals</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>(b,c)</td>
<td>Brownish travertine crust from the surface of a small palaeolake</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>(b,c)</td>
<td>Cogenetic aliquot of #4 from the other side of the palaeolake</td>
<td>3.9 ± 0.3</td>
</tr>
<tr>
<td>6</td>
<td>(d)</td>
<td>Fine grained, tufaceous limestone with inclusions of sandy tuff grains</td>
<td>7.1 ± 0.4</td>
</tr>
<tr>
<td>7</td>
<td>(b)</td>
<td>Porous calcite tuff on top of the lower cave system (profile I)</td>
<td>5.3 ± 0.3</td>
</tr>
<tr>
<td>8</td>
<td>(d)</td>
<td>Massive travertine from a level close to type 4, 5 samples</td>
<td>4.1 ± 0.3</td>
</tr>
<tr>
<td>9</td>
<td>(b)</td>
<td>Sample from the upper layer of the fine laminated limestone (profile I)</td>
<td>6.2 ± 0.4</td>
</tr>
<tr>
<td>10/1+2</td>
<td>(a,c)</td>
<td>Recent precipitations from a spring outside the caves (two aliquots)</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>11</td>
<td>(b)</td>
<td>Travertine from a massive flowstone layer (profile II)</td>
<td>5.1 ± 0.3</td>
</tr>
<tr>
<td>12</td>
<td>(b)</td>
<td>Travertine from the bottom of a massive flowstone layer (profile II)</td>
<td>5.9 ± 0.3</td>
</tr>
<tr>
<td>13</td>
<td>(b)</td>
<td>Fine grained tufaceous limestone on the basement of profile I</td>
<td>7.9 ± 0.4</td>
</tr>
<tr>
<td>14/1+2</td>
<td>(c)</td>
<td>Two co-genetic porous tufts from a wall of a cave outside the deposit</td>
<td>6.5 ± 0.5</td>
</tr>
<tr>
<td>14/3</td>
<td>(c)</td>
<td>Snail embedded in formation containing #14 (cogenetic aliquot)</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>15</td>
<td>(d)</td>
<td>Purple travertine crystals on the surface of samples of type 4 + 5</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>16</td>
<td>(d)</td>
<td>Massive stalagmites (re-crystallised travertine of the first generation)</td>
<td>7.1 ± 0.4</td>
</tr>
<tr>
<td>17</td>
<td>(d)</td>
<td>Fine laminated massive light brownish travertine</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>18</td>
<td>(a)</td>
<td>Very young carbonate crusts (white, thin plates) outside the cave</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td>19</td>
<td>(a)</td>
<td>Very young calcite crust on the surface of a 10y old electric wire</td>
<td>&lt;0.4</td>
</tr>
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</table>
composition of older detrital impurities via isochron straight lines, and (d) sampling of further selected material to specifically investigate the geological evolution of the cavern system at the particular study area. The assignment of the corresponding samples to items (a–d) is given in Table 1.

3.2. Sample preparation

Because of the very low radionuclide concentrations (typically between 0.3 and 10 mBq/g) samples of about 40 g were homogenized to fine powdered powders with grain size < 200 µm. While one aliquot of 10 g was set aside for analysis of (volatile) 210Po, another aliquot of 15 g was first heated to 500°C for 2 h (to destroy traces of organic components which reduce the chemical recoveries) and then split into two aliquots: 5 g for U/Th isotope analysis and 10 g for determination of 226Ra via 222Rn emanation (see below). To avoid isotope disturbances caused by infiltration of recent (acid) rainwater into the upper layers of the travertine caves (dissolution–re-deposition), all sample surfaces were cleaned by abrasion of a layer of a few mm thickness. However, some of the very fine grained tufaceous limestone samples which could not be abraded mechanically exhibited a significant excess of 210Po compared to limestone samples which could not be abraded mechanically. Rainwater into the upper layers of the travertine caves (dissolution–re-deposition), all sample surfaces were cleaned by abrasion of a layer of a few mm thickness. However, some of the very fine grained tufaceous limestone samples which could not be abraded mechanically exhibited a significant excess of 210Po compared to limestone samples which could not be abraded mechanically. Rainwater into the upper layers of the travertine caves (dissolution–re-deposition), all sample surfaces were cleaned by abrasion of a layer of a few mm thickness. However, some of the very fine grained tufaceous limestone samples which could not be abraded mechanically exhibited a significant excess of 210Po compared to limestone samples which could not be abraded mechanically.

3.3. Analytical techniques

Rock samples: After complete sample dissolution in HNO3 and addition of the chemical yield calibration spikes (232U, 228Th, 209Po) the following nuclides were analyzed mainly using z-spectrometry: 238U, 234U, 232Th, 230Th and 226Ra (the latter via its short-lived progenies 222Rn and 210Po). U and Th were separated chromatographically and consecutively on one column using UTEVA resin (Horwitz et al., 1993) produced by EiChrom Inc., Darien, USA, and the sample discs were prepared via electrolytic deposition using HNa2SO4–Na2SO4 buffer solution (Bajo and Eikenberg, 1999). 226Ra was determined indirectly via its short-lived daughter 210Po because the radioassay of Po is simple and yields highly precise results. The separation of Po was as follows: precipitation of Fe-hydroxide with NH4OH, dissolution of the precipitate in 1 M HCl, in the presence of ascorbic acid to prevent deposition of Fe. Po was then separated via spontaneous deposition on silver discs. Radioassay of all these planar sources was performed using ultra-low-level high-resolution (16 keV) semiconductive surface barrier detectors (system Octete, Ortec Inc., USA). While 210Po could be taken as a measure for 226Ra for samples > 100 yr, i.e. 5 half-lives of 210Pb, all other samples, which could have been formed more recently, were also analyzed utilizing emanation of 222Rn into an organic cocktail. Counting of organically bound 222Rn and its very short-lived progenies 218Po and 214Po was then carried out under optimized settings for z/β discrimination, background scatter and counting efficiency (Eikenberg et al., 1999) using low level z/β-LSC (LS-counter, TriCarb 2550 TR/LL, Packard SA, Meriden, CT, USA).

Water samples: In freshwater, 226Ra and its progenies 210Pb and 210Po are likely to be in a state of disequilibrium, due to several sources and sinks for 210Po and its geochemical relevant progenitors 210Pb, 222Rn and 226Ra (Harada et al., 1989, Plater et al., 1995, Eikenberg et al., 2001a). Therefore it was essential to analyze 226Ra directly, which was done similarly to the procedure given by Moore et al. (1995) via sorption of Ra on MnO2. After sampling, the 11 water samples were set aside for about 2 weeks to allow unsupported 226Ra to decay and were then spiked using 226Ra/224Ra tracer solution to obtain the chemical yield precisely. Following the spiking each sample was exposed to MnO2-coated polyvinyl discs for about 2 days and, thereafter, analyzed directly using z-spectrometry (detailed procedure in Eikenberg et al., 2001b).

In addition to the radioanalytical investigations, bulk chemical analyses were carried out applying ICP-MS and AAS (cations) and ion chromatography (anions). These investigations yielded the concentrations of all major and some minor stable elements in the carbonates as well as the waters (Ba, Sr, Ca, etc.).

4. Theory of 226Ra/230Th/234U dating

Reducing the complex 238U decay series into geologically relevant subsystems (i.e. nuclides with half-lives greater than a few years) the following precursor–progeny relations hold

\[
238\text{U} \rightarrow 234\text{U} \rightarrow 230\text{Th} \rightarrow 226\text{Ra} (222\text{Rn})
\]

\[
\rightarrow 210\text{Pb}(210\text{Po}),
\]

where the nuclides in brackets tend rapidly towards secular equilibrium with their progenitors \((222\text{Rn} \approx 3\) weeks, \(210\text{Po} \approx 1\) yr) and hence can be used as a measure of the activity of their parent nuclides. So far, two methods using mother/daughter relationships within the 238U decay chain are mainly applied in the fields of...
sedimentology and oceanography (i) $^{230}\text{Th}/^{234}\text{U}$ ingrowth-dating for systems which evolved between 10 and 300 kyr (Edwards et al., 1987; Bischoff et al., 1988; Burnett et al., 1988; Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991; Kaufman, 1993, etc.) and (ii) $^{210}\text{Pb}$ excess-decay dating (supplied from decay of soil-emanated $^{222}\text{Rn}$ into the atmosphere). The latter method is used mainly to determine sedimentation rates in lakes for sample ages of up to about 100 yr (Oldfield et al., 1978; Robbins, 1978). The third geologically meaningful chronometer which uses the decay of excess $^{226}\text{Ra}$ has been applied much more rarely because this method has to consider various boundary conditions (e.g. Koide et al. 1976; Kim and Burnett, 1985; Latham et al., 1986; Sturchio, 1990). However, this chronometer fills the time gap between the two more established chronometers and is suitable for dating between $\approx$ 100 yr and about 7–8 kyr or 5 half-lives of $^{226}\text{Ra}$. This situation is illustrated in Fig. 2 which shows the evolution of the activity ratios in the $^{238}\text{U}$ series for hypothetical cases with initial daughter/parent ratios of 2 (twice daughter excess) and 0 (i.e. zero inherited daughter activity at the time of formation). The bold lines in Fig. 2 indicate all three chronometers of relevance in natural terrestrial systems (formation). The bold lines in Fig. 2 indicate all three chronometers of relevance in natural terrestrial systems.

In the following we present a detailed analytical approach for the coupled parent daughter system $^{226}\text{Ra}^{230}\text{Th}^{234}\text{U}^{238}\text{U}$. A complex analytical solution for $^{230}\text{Th}^{234}\text{U}^{238}\text{U}$ was first presented by Kaufman and Broecker (1965) who showed that, due to an unknown $^{234}\text{U}/^{238}\text{U}$ initial, $^{230}\text{Th}^{234}\text{U}$ ages have to be obtained iteratively. However, for systems in which the $^{234}\text{U}/^{238}\text{U}$ activity ratios are close to unity (i.e. secular equilibrium), decay of $^{234}\text{U}$ depends on decay of the long lived parent $^{238}\text{U}$ or

$$^{234}\text{U}(t) = ^{234}\text{U}(0)e^{-\lambda_{234}t},$$

where $\lambda_{238}$ is the decay constant of the parent $^{238}\text{U}$. Since decay of $^{238}\text{U}$ proceeds extremely slowly ($T_{1/2} = 4.5 \times 10^9$ yr) the activity of $^{234}\text{U}$ (supported from $^{238}\text{U}$) remains almost constant in samples which formed less than a few 10 million years ago. Furthermore, if the sample material is as young as a few thousand years, decay of slight excess of $^{234}\text{U}$ ($T_{1/2} = 2.5 \times 10^5$ yr) can also be disregarded. Given this situation, the activity of the next geologically relevant daughter, $^{230}\text{Th}$, is not dependent on a change in $^{234}\text{U}$, i.e.

$$^{230}\text{Th}(t) = ^{230}\text{Th}(0)e^{-\lambda_{230}t} + ^{234}\text{U}(1 - e^{-\lambda_{234}t}).$$

While the first term on the righthand side of Eq. (5) refers to the decay of an initially inherited component of $^{230}\text{Th}$, the second term describes the ingrowth of $^{230}\text{Th}$ in a mineral incorporating uranium. For samples starting without significant inherited $^{230}\text{Th}$, the first term in Eq. (5) can be neglected, i.e. yielding the boundary condition $^{230}\text{Th}(t=0) = 0$. As noted above for young minerals $< 10$ kyr with $^{234}\text{U}^{238}\text{U}$ a second boundary conditions holds, i.e. $^{234}\text{U}(t) = ^{234}\text{U}(0)$. This is of advantage for calculating the evolution of the next daughter, $^{226}\text{Ra}$, with time. The complex decay system involving $^{234}\text{U}$, $^{230}\text{Th}$ and $^{226}\text{Ra}$ was solved using the computer program MAPLE 5 (Radfern, 1996) and, the following analytical relation was obtained (neglecting 2nd order of the terms $1/\lambda_{230}$ and $1/\lambda_{238}$):

$$^{226}\text{Ra}(t) = ^{226}\text{Ra}(0)e^{-\lambda_{226}t} + ^{234}\text{U}^{226}\text{Ra}(1 - e^{-\lambda_{234}t}) - ^{230}\text{Th}(1 - e^{-\lambda_{230}t}),$$

where, as above, the first term refers to decay of initially incorporated $^{226}\text{Ra}$, while the second describes the delayed ingrowth of $^{226}\text{Ra}$ via ingrowth of $^{230}\text{Th}$. Provided that the boundary conditions given above are fulfilled, these relations show clearly that the $^{230}\text{Th}$ ingrowth is dependent only on $^{234}\text{U}$ and, therefore, the $^{238}\text{U}$ supported $^{226}\text{Ra}$ ingrowth is also dependent on the activity of $^{234}\text{U}$ alone. Hence under such ideal conditions we can conclude that for this coupled system there is no need to determine $^{230}\text{Th}$ analytically, this couple can be referred as $^{226}\text{Ra}_{ex}^{234}\text{U}$ chronometer or (as shown below) normalized to initial radium as $^{226}\text{Ra}_{ex}^{226}\text{Ra}(0)$. The $^{230}\text{Th}^{234}\text{U}$ and $^{226}\text{Ra}_{ex}^{234}\text{U}$ ingrowth relationships are shown theoretically in Fig. 3 for an ideal system which started under the boundary conditions defined above, and for three different initial ($^{226}\text{Ra}_{ex}^{234}\text{U})_0$ activity ratios of 0.2, 0.5 and 1.
5. Results and discussion

The results of the U and Th isotope analysis are presented, in terms of their activities, in Table 2. The typical relative uncertainties (in 2σ) are 234U, 238U: 1–3%, 234U/238U: 2–5%, 230Th: 4–10%, 232Th for samples with 234U/232Th activity ratios of ~100, about 10–30%.

While the activities of the U-isotopes are fairly constant in the travertine samples, 230Th is more variable because of different sample ages and/or contribution of a detrital component also containing 232Th and 238U with all progenies in secular equilibrium (see discussion below). In an average sample (for instance #4, 5, 8) the activities of 230Th are very low (~0.2 mBq/g or ~3 x 10^-15 mol/g. For this reason all samples were counted for about one week. The activities of 210Po and 222Rn are given in Table 3 along with a compilation of the 230Th/234U and 226Raex/234U(0) ages and the results of the bulk chemical investigations are summarized in Table 4 including the results for 226Ra in the water sample.

5.1. Dating with the 230Th/234U chronometer

5.1.1. Correction for non-authigenic (detrital) material

One of the major requirements for correct use of the 230Th/234U chronometer on a single sample is knowledge of the initial activity values at the time when the system’s clock started. In the case of limestone precipitations there is a further complication because the freshly precipitating, authigenic phases are generally intergrown to a certain degree with detrital material (mainly clays) containing U and Th of different age. However, as discussed in a compilation given by Kaufman (1993) it is reasonable to assume that such material is older than a few 100 kyr, i.e. all members within the U and Th decay series are in or close to secular equilibrium (234U = 230Th = 226Ra). This means that independent of the degree of the detrital impurities, internal isochrons

![Diagram](image)

Fig. 3. Theoretical parent/daughter ingrowth/decay relationships for the chronometers 230Th/234U and 226Raex/234U as a function of time for systems starting without initial 230Th and for three sets of initial 226Raex/234U activity ratios of 0.2, 0.5 and 1.0.

Table 2

<table>
<thead>
<tr>
<th>#</th>
<th>238U (mBq/g)</th>
<th>234U (mBq/g)</th>
<th>230Th (mBq/g)</th>
<th>232Th (mBq/g)</th>
<th>234U/230Th</th>
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<td>1</td>
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<td>0.21</td>
<td>0.02</td>
<td>250.1</td>
<td>10.5</td>
<td>1.31</td>
<td>0.037</td>
</tr>
<tr>
<td>9</td>
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<td>5.92</td>
<td>0.45</td>
<td>0.10</td>
<td>59.2</td>
<td>4.5</td>
<td>1.31</td>
<td>0.055</td>
</tr>
<tr>
<td>10/1</td>
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<td>4.04</td>
<td>0.38</td>
<td>0.28</td>
<td>14.4</td>
<td>1.4</td>
<td>1.33</td>
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</tr>
<tr>
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<td>3.94</td>
<td>0.40</td>
<td>0.30</td>
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<td>1.3</td>
<td>1.28</td>
<td>0.005</td>
</tr>
<tr>
<td>11</td>
<td>5.53</td>
<td>7.09</td>
<td>0.34</td>
<td>0.01</td>
<td>709.4</td>
<td>34.0</td>
<td>1.28</td>
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<tr>
<td>12</td>
<td>9.45</td>
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<td>0.66</td>
<td>0.02</td>
<td>816.4</td>
<td>43.9</td>
<td>1.30</td>
<td>0.052</td>
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<tr>
<td>13</td>
<td>6.67</td>
<td>8.41</td>
<td>0.64</td>
<td>0.04</td>
<td>205.1</td>
<td>15.6</td>
<td>1.26</td>
<td>0.070</td>
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<td>3.83</td>
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<td>18.2</td>
<td>2.3</td>
<td>1.30</td>
<td>0.058</td>
</tr>
<tr>
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<td>8.62</td>
<td>0.56</td>
<td>0.02</td>
<td>431.1</td>
<td>28.0</td>
<td>1.28</td>
<td>0.062</td>
</tr>
<tr>
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<td>24.8</td>
<td>1.54</td>
<td>0.06</td>
<td>413.3</td>
<td>25.7</td>
<td>1.29</td>
<td>0.059</td>
</tr>
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<td>4.16</td>
<td>5.14</td>
<td>0.18</td>
<td>0.01</td>
<td>509.0</td>
<td>17.8</td>
<td>1.24</td>
<td>0.033</td>
</tr>
<tr>
<td>16</td>
<td>13.5</td>
<td>17.1</td>
<td>1.09</td>
<td>0.01</td>
<td>1750.3</td>
<td>109.0</td>
<td>1.26</td>
<td>0.064</td>
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<tr>
<td>17</td>
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<td>0.14</td>
<td>0.03</td>
<td>172.1</td>
<td>4.7</td>
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<td>0.020</td>
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<td>0.03</td>
<td>228.1</td>
<td>1.3</td>
<td>1.31</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

*a gw = present day groundwater.*
Table 3
Measured $^{210}$Po and $^{222}$Rn activities as well as calculated activities of the components $^{226}$Ra_{aut} and $^{226}$Ra_{ex}. A comparison of $^{230}$Th/$^{234}$U and $^{226}$Ra(0) formation ages is also presented$^a$

<table>
<thead>
<tr>
<th>Sample #(in sequence with increasing U/Th-age)</th>
<th>$^{210}$Po (mBq/g)</th>
<th>$^{222}$Rn (mBq/g)</th>
<th>$^{226}$Ra_{aut} (mBq/g)</th>
<th>$^{226}$Ra_{ex} (mBq/g)</th>
<th>$^{230}$Th/$^{234}$U age (kyr)</th>
<th>$^{226}$Ra(0) age (kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.38 ± 0.02</td>
<td>0.33 ± 0.02</td>
<td>0.02 ± 0.03</td>
<td>8.8 ± 0.4</td>
<td>&gt;7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.39 ± 0.02</td>
<td>0.38 ± 0.07</td>
<td>0.34 ± 0.03</td>
<td>2.6 ± 0.3</td>
<td>3.0 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.41 ± 0.02</td>
<td>0.33 ± 0.07</td>
<td>0.28 ± 0.02</td>
<td>3.7 ± 0.3</td>
<td>3.9 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.34 ± 0.02</td>
<td>0.29 ± 0.07</td>
<td>0.31 ± 0.02</td>
<td>3.9 ± 0.3</td>
<td>3.9 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.47 ± 0.03</td>
<td>n.a.</td>
<td>0.35 ± 0.03</td>
<td>7.1 ± 0.4</td>
<td>&gt;7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.82 ± 0.15</td>
<td>0.63 ± 0.11</td>
<td>6.65 ± 0.15</td>
<td>5.3 ± 0.3</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.35 ± 0.02</td>
<td>n.a.</td>
<td>0.32 ± 0.02</td>
<td>4.1 ± 0.3</td>
<td>3.6 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.43 ± 0.02</td>
<td>n.a.</td>
<td>0.30 ± 0.03</td>
<td>6.2 ± 0.4</td>
<td>5.8 ± 2.7</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.13 ± 0.04</td>
<td>1.19 ± 0.15</td>
<td>0.77 ± 0.04</td>
<td>0.5 ± 0.4</td>
<td>0.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.33 ± 0.02</td>
<td>n.a.</td>
<td>0.32 ± 0.02</td>
<td>5.1 ± 0.3</td>
<td>5.0 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.52 ± 0.03</td>
<td>n.a.</td>
<td>0.50 ± 0.03</td>
<td>5.9 ± 0.3</td>
<td>5.8 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.54 ± 0.03</td>
<td>n.a.</td>
<td>0.49 ± 0.03</td>
<td>7.9 ± 0.4</td>
<td>6.5 ± 4.2</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.53 ± 0.03</td>
<td>0.60 ± 0.11</td>
<td>0.26 ± 0.04</td>
<td>6.5 ± 0.5</td>
<td>5.3 ± 1.9</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.40 ± 0.02</td>
<td>n.a.</td>
<td>0.39 ± 0.02</td>
<td>3.5 ± 0.3</td>
<td>2.8 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.77 ± 0.03</td>
<td>n.a.</td>
<td>0.76 ± 0.03</td>
<td>7.1 ± 0.4</td>
<td>&gt;7</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.40 ± 0.02</td>
<td>n.a.</td>
<td>0.36 ± 0.02</td>
<td>2.2 ± 0.2</td>
<td>2.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>0.48 ± 0.03</td>
<td>n.a.</td>
<td>0.47 ± 0.03</td>
<td>1.7 ± 0.3</td>
<td>2.0 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>2.41 ± 0.08</td>
<td>1.11 ± 0.14</td>
<td>1.05 ± 0.12</td>
<td>&lt;0.4</td>
<td>&lt;0.1</td>
<td></td>
</tr>
</tbody>
</table>

$^a$n.a. = not analyzed, (a) not determined due to surface contamination with excess $^{210}$Po.

Table 4
Bulk chemical compositions of six travertine samples and present day groundwater

<table>
<thead>
<tr>
<th>Sample #(in sequence with increasing U/Th-age)</th>
<th>$^{230}$Po (mBq/g)</th>
<th>$^{222}$Rn (mBq/g)</th>
<th>$^{226}$Ra_{aut} (mBq/g)</th>
<th>$^{226}$Ra_{ex} (mBq/g)</th>
<th>$^{230}$Th/$^{234}$U age (kyr)</th>
<th>$^{226}$Ra(0) age (kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>0.39</td>
<td>0.41</td>
<td>0.41</td>
<td>0.38</td>
<td>0.40</td>
<td>0.40</td>
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<tr>
<td>#10</td>
<td>0.05</td>
<td>0.11</td>
<td>0.05</td>
<td>0.07</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>#2</td>
<td>3.29</td>
<td>2.79</td>
<td>3.60</td>
<td>3.55</td>
<td>3.72</td>
<td>3.61</td>
</tr>
<tr>
<td>#4</td>
<td>399</td>
<td>380</td>
<td>396</td>
<td>392</td>
<td>397</td>
<td>385</td>
</tr>
<tr>
<td>#12</td>
<td>0.25</td>
<td>0.23</td>
<td>0.17</td>
<td>0.26</td>
<td>0.30</td>
<td>0.21</td>
</tr>
<tr>
<td>#13</td>
<td>0.19</td>
<td>0.19</td>
<td>0.19</td>
<td>0.19</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td>g.w. = present day groundwater.</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>calculated from radiochemical determination.</td>
<td>4.05</td>
<td>3.75</td>
<td>4.35</td>
<td>3.82</td>
<td>3.90</td>
<td>3.97</td>
</tr>
<tr>
<td>Mg/Ca</td>
<td>8.2 × 10^-3</td>
<td>7.3 × 10^-3</td>
<td>9.1 × 10^-3</td>
<td>9.1 × 10^-3</td>
<td>9.4 × 10^-3</td>
<td>9.4 × 10^-3</td>
</tr>
<tr>
<td>Sr/Ca</td>
<td>6.3 × 10^-4</td>
<td>6.1 × 10^-4</td>
<td>4.3 × 10^-4</td>
<td>6.6 × 10^-4</td>
<td>7.6 × 10^-4</td>
<td>5.5 × 10^-4</td>
</tr>
<tr>
<td>Ba/Ca</td>
<td>4.8 × 10^-4</td>
<td>5.0 × 10^-4</td>
<td>4.6 × 10^-4</td>
<td>4.8 × 10^-4</td>
<td>4.8 × 10^-4</td>
<td>4.7 × 10^-4</td>
</tr>
<tr>
<td>Ra/Ca</td>
<td>7.5 × 10^-14</td>
<td>7.9 × 10^-14</td>
<td>2.8 × 10^-14</td>
<td>2.1 × 10^-14</td>
<td>3.5 × 10^-14</td>
<td>3.9 × 10^-14</td>
</tr>
<tr>
<td>Ra/Ba</td>
<td>1.6 × 10^-10</td>
<td>1.6 × 10^-10</td>
<td>6.1 × 10^-11</td>
<td>4.4 × 10^-11</td>
<td>7.4 × 10^-11</td>
<td>8.3 × 10^-11</td>
</tr>
</tbody>
</table>

connecting all cogenetic phases can be written by normalizing the $^{230}$Th/$^{234}$U decay/ingrowth relationship to $^{232}$Th, or

$$\frac{^{230}\text{Th}(t)}{^{232}\text{Th}} = \frac{^{230}\text{Th}(0)}{^{232}\text{Th}} e^{-\lambda_{230}t} + \frac{^{234}\text{U}}{^{232}\text{Th}} (1 - e^{-\lambda_{230}t}),$$

(7)

where $\lambda_{230}$ is the decay constant of $^{230}$Th and the slope $m$ (or the isochron = $1 - e^{-\lambda_{230}t}$) yields the age of all (cogenetic) samples which have been formed simultaneously. Basically, relation 7 is useful to distinguish between two mixed phases (e.g. travertine, detrital silicates) and therefore to eliminate the uncertainties on predominantly $^{230}$Th(0). A thorough explanation of $^{230}$Th/$^{232}$Th/$^{234}$U/$^{232}$Th isochron relationships, introduced first by Allègre and Condomines (1976), can be obtained from the reviews by Gill et al. (1992) or MacDougall (1995) and several successful demonstrations have been presented for dating authigenic sediments (Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991; Kaufman, 1993; Israelson et al., 1997; Kaufman et al., 1998). A typical isochron relationship of the samples investigated here is shown in Fig. 4 for two simultaneously formed fine grained travertine from the bottom of the deposit (#14/1 and #14/2) including a fossil.
Fig. 4. $^{230}\text{Th}/^{232}\text{Th}$ vs. $^{234}\text{U}/^{238}\text{U}$ isotope diagram showing isochrons connecting cogenetic travertine of different age (6.5 kyr, and present day). Both regression lines intersect the equilibrium at $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ = 1.3, indicating uniform U/Th ratios of the detrital component in all samples from the deposit. The analytical uncertainties are given as 2σ.

snail (#14/3) which could be purified from the surrounding material of type #14. The isochron straight line intercepts with the equilibrium or the detrital component (i.e. the line on which all samples are in secular equilibrium or $^{230}\text{Th}/^{234}\text{U} = 1$) at $^{230}\text{Th}/^{232}\text{Th}$ (or $^{234}\text{U}/^{232}\text{Th}$) = 1.3 + 0.1. A second regression line in Fig. 4 connects the U/Th isotope data of two recently formed young precipitates taken from a spring outside the limestone caves, more (#3) or less (#10, two aliquots) strongly intergrown with detrital material, as well as very young travertine coatings (#19) overgrowing a 10 yr old electric wire. These zero age samples define the present day mixing line, which intersects the equilibrium at $^{230}\text{Th}/^{232}\text{Th}$ = 1.3 + 0.1. This horizontal line therefore documents (at least for recently formed limestone) a uniform $^{230}\text{Th}/^{232}\text{Th}$ ratio for the detrital component. In addition to this, another sequence of co-genetic phases was collected, that are two travertine samples taken from the same sea level of a paleolake, (#4 and 5). Clearly two samples are not sufficient for calculation of an isochron slope, but a construction line connecting these samples with the detrital $^{230}\text{Th}/^{232}\text{Th}$ ratio defined by the other co-genetic samples is, within error, consistent with the U/Th isotope ratios of #4 and 5.

It is, therefore, very likely that all travertine analyzed here contain detrital inclusions with identical $^{238}\text{U}/^{232}\text{Th}$ ratios because the three slopes cover a period in which most of the travertine was deposited (i.e. between present day and $\approx$ 9000 yr). Given this situation all other samples should be datable applying the $^{230}\text{Th}/^{234}\text{U}$ isotope pair without the need of constructing individual isochrons, i.e. via analysis of several cogenetic phases or sample leachates to obtain one single formation age. With a constant U/Th ratio in the detrital phase, correction for such impurities can be simply obtained via subtraction of $^{230}\text{Th}$ times the detrital U/Th ratio from measured $^{234}\text{U}_m$ and $^{230}\text{Th}_m$ or, for instance, for $^{234}\text{U}$

$$^{234}\text{U}_{aut} = ^{234}\text{U}_m - k^{232}\text{Th}_m,$$

where $k$ refers to the $^{234}\text{U}/^{232}\text{Th}$ ratio of the impure detritus and the subscript ‘aut’ refers to the $^{234}\text{U}$ activity in the pure, authigenic material. Following the detritus correction, the $^{230}\text{Th}/^{234}\text{U}$ age can be obtained simply by rearranging Eq. (5), i.e.

$$t_{age} = \frac{1}{\lambda} \ln \left(1 - \frac{^{230}\text{Th}_{aut}}{^{234}\text{U}_{aut}}\right).$$

Since in addition for young systems < 10 kyr the $^{234}\text{U}$ activity remains almost constant (decay of maximum 3% if not supported by $^{238}\text{U}$), the equipoint can be directly used to extract the U/Th ratio of the detrital phases. Since $^{234}\text{U}/^{238}\text{U}$ = 1.3 for typical travertine (Table 1) like $^{230}\text{Th}/^{232}\text{Th}$ on the equipoint, a $^{238}\text{U}/^{232}\text{Th}$ activity ratio of 1.0 results for the detrital phase. Converted to more convenient mass units, this corresponds to a $^{232}\text{Th}/^{238}\text{U}$ mass ratio of 3 which is typical for crustal silicate rocks.

5.1.2. Maximum inherited initial $^{230}\text{Th}/^{234}\text{U}$ ratios in recently forming calcite

Eq. (9) does not contain any term relating to a component of inherited or excess (i.e. unsupported) $^{230}\text{Th}$, or a change of the activity of $^{234}\text{U}_{aut}$ with time, as does Eq. (5). In the case of uranium, the samples are characterized by similar $^{234}\text{U}/^{238}\text{U}$ ratios of 1.28 + 0.04 (mean value of all data in Table 2) indicating rather low excesses of $^{234}\text{U}$ in comparison with $^{238}\text{U}$. This means that for system closure times < 10 kyr, the change in $^{234}\text{U}/^{238}\text{U}$ from decay of excess $^{234}\text{U}$ is extremely small (< 1% for samples which crystallized 10 kyr ago). Since the change of the U-isotope activity ratio is still less for younger samples, it can be reasonably considered that the $^{234}\text{U}$ activity remained constant in all samples analyzed here.

The second assumption ($^{230}\text{Th}(0) = 0$) is somewhat more difficult to prove, because, although the solubility of Th$^{4+}$ in aqueous solutions is orders of magnitude below that of UO$_2^{2+}$ (Fuger and Oetting, 1976; Langmuir, 1978; Langmuir and Herman, 1980; OECD, 1992), there remains the possibility that $^{230}\text{Th}$ (from decay of dissolved $^{234}\text{U}$) forms colloids or adsorbs on suspended matter as has been shown to be the most likely case for its presence in river and ground waters (Langmuir and Herman, 1980, Tricca, 1997). We therefore analyzed fresh groundwater from which travertine is continuously precipitating. Radioassay of this water including complete digestion of all particles in
HF-HNO₃ yielded no detectable activity of ²³⁰Th as well as ²³²Th (<1 × 10⁻⁵ Bq/l).Expressed in mass units these detection limits convert to: ²³⁰Th < 3 × 10⁻¹⁴ g/l and ²³²Th < 3 × 10⁻⁹ g/l, i.e. detection limits which do not exceed the values obtained from non-turbulent river waters and estuaries as reported, for instance, by Anderson et al. (1995) using high sensitivity thermal ion mass spectrometry (TIMS). In contrast to Th, a significant activity of U-isotopes (²³⁴U = 16.5 mBq/l) was measured, yielding an ²³⁰Th/²³⁴U activity ratio < 6 × 10⁻⁴. Assuming conservatively that the co-precipitation yield for unsupported ²³⁰Th exceeds that of ²³⁴U by a factor of 10, the initial (²³⁰Th/²³⁴U)aut activity ratios in the recently formed limestone still remain < 6 × 10⁻³, i.e. a value which is consistent to the (²³⁰Th/²³⁴U)aut activity ratios obtained for the recently formed travertine samples #10 and #19.

5.1.3. Maximum inherited initial ²³⁰Th/²³⁴U ratios in older samples

Thus, in summary, it can be concluded that the present day precipitates do not incorporate significant quantities of ²³⁰Th(0), but how can one further prove that the present day water is chemically similar to its composition a few thousand years ago? To answer this question the ²³⁴U/²³⁸U ratios in the rock and water samples can be used, because independent of the precipitation yield of uranium in the individual samples, the ²³⁴U/²³⁸U ratio should remain constant in solid and aqueous phases if the limestone precipitated from one water source with uniform ²³⁴U/²³⁸U. Fig. 5 shows that, within error, the U-isotope ratios of the rock samples remained constant at 1.28 ± 0.06 independent of the time of formation and that this value also agrees with the present day ²³⁴U/²³⁸U ratio in the corresponding groundwater (at 1.27 ± 0.04). The data therefore suggest that the precipitates are likely to have formed from a chemically similar water source, the more so, since the concentrations of stable elements such as Na⁺ and, in particular, the bivalent ions, Mg²⁺, Ba²⁺, SO₄²⁻ in six samples analyzed here (Table 4, and Ba/Ca ratios in Fig. 5) are almost identical.

There are, in addition, two further points which support the assumption that the travertine investigated here did not incorporate significant amounts of inherited ²³⁰Th. For samples > 8 kyr more than 97% of initial ²²⁶Ra excess has decayed, therefore ²²⁶Ra and ²³⁰Th should be in a fixed transient activity equilibrium. As will be shown below (discussion on Ra) this is indeed confirmed by comparison of the ²²⁶Ra/²³⁰Th data of such old samples to the theoretical value obtained when calculating with ²³⁰Th(0) = 0.

The other point is that the ²³⁰Th/²³⁴U ages are consistent with the relative succession of the geological strata. The continuously increasing ²³⁰Th/²³⁴U formation ages with depth is indicated for two profiles through the tufaceous limestone outside and travertine flow stones inside the lower cave system (Table 5, Fig. 1). Table 5 shows that samples with variable initial (²³⁰Th/²³⁴U)aut in the order of 6 × 10⁻³ (which introduces an error of up to 1 kyr) are likely to violate the relative age sequence in the profile.

5.2. Dating with the ²²⁶Raex/²²⁶Ra chronometer

5.2.1. Previous studies

In a similar manner to the ²³⁰Th/²³⁴U pair normalized to long-lived ²³²Th, isochron dating using ²²⁶Ra/²³⁰Th was introduced by Williams et al. (1986) to investigate magma genesis and several applications in volcanology have been presented since (Williams, 1987; Condomines et al., 1988; Volpe and Hammond, 1991; Volpe, 1992; Volpe and Goldstein, 1993; Chabaux and Allègre et al., 1994). Since, beside ²²⁶Ra, no long-lived Ra isotope can be found in nature, it was suggested to use stable Ba as normalization isotope because this element behaves chemically in an analogous manner to Ra. However if short-lived systems are considered, precise ages can be obtained by normalizing ²²⁶Ra (T₁/₂ = 5.7 yr) to ²²⁶Ra. A good example of the applicability of ²²⁶Raex/²²⁶Ra chronometry was presented by Sturchio (1990) who investigated the diagenetic transformation from aragonite to calcite at Mammoth Hot Spring, Wyoming. Due to the short half-life of ²²⁸Ra this chronometer is suitable only for samples that formed less than 20–30 yr ago. For precipitations that formed a few thousand years ago further interesting examples can be found in the literature, demonstrating that non-normalized ²²⁶Ra-excess dating may also yield meaningful ages. Applications were presented for marine sediments (Koide et al., 1976) or phosphorites (Kim and Burnett, 1985) as well as travertine and speleothem (Latham...
et al., 1986; Romano et al., 1987; Sturchio, 1990). The study of Latham et al. (1986) showed, for instance, good concordance between $^{14}$C- and $^{226}$Ra$_{ex}$-ages in a Mexican stalagmite. Kim and Burnett (1985), however, measured in phosphate nodules from the Peru/Chile seafloor with U/Th ages > 10 kyr repeatedly $^{226}$Ra/$^{230}$Th ratios below unity, speaking for removal of $^{226}$Ra in rather old samples where both nuclides should be in transient equilibrium. While most of the investigations assume that ingrowth of $^{226}$Ra from decay of $^{230}$Th is not significant (and hence do not consider any corrections), Koide et al. (1976) discussed an approach to correct for $^{226}$Ra supported from decay of $^{230}$Th (however not considering dynamic ingrowth of $^{230}$Th from $^{234}$U). A detailed analytical solution of the complex system $^{238}$U/$^{234}$U/$^{230}$Th/$^{226}$Ra was presented by Kim and Burnett (1985) who extended the analytical solution given by Kaufman and Broecker (1965) for the U/Th system to $^{226}$Ra. In order to obtain $^{226}$Ra$_{ex}$-ages such complex solutions have to be solved iteratively. However, provided that the boundary conditions $^{230}$Th(0) = 0 and $^{234}$U(0) = $^{234}$U(0) are correct, there is simple way to calculate precise $^{226}$Ra$_{ex}/^{234}$U or $^{226}$Ra$_{ex}/^{226}$Ra(0) ages considering changing activity concentrations of $^{226}$Ra supported by ingrowth of $^{230}$Th.

5.2.2. Correction for non-authigenic (detrital) material

After having shown that at least for the samples investigated here (i) detrital impurities can be subtracted using a constant U/Th ratio in that phase and that (ii) all samples started without significant amounts of inherited $^{230}$Th, it is possible to apply the analytical solution for ingrowth and decay of $^{226}$Ra, the third geochronologically important radionuclide in the $^{238}$U decay series. Since the second term in Eq. (6) describes the $^{230}$Th supported ingrowth of $^{226}$Ra ($^{226}$Ra$_{sup}$), the amount of the residual excesses of $^{226}$Ra surviving the decay of initially incorporated Radium can be calculated as follows:

$$^{226}\text{Ra}_{ex}(t) = ^{226}\text{Ra}_{aut} - ^{226}\text{Ra}_{sup}(t),$$

(10)

where $^{226}\text{Ra}_{aut}$ is the total activity of $^{226}$Ra in the pure authigenic phase. Assuming secular equilibrium between $^{230}$Th and $^{226}$Ra in the detrital phase yields, similar to

$$^{226}\text{Ra}_{aut} = ^{226}\text{Ra}_{m} - k^{226}\text{Th}_{m}.$$  

(11)

5.2.3. Comparison of the $^{226}$Ra$_{aut}$/$^{234}$U data with the $^{226}$Ra$_{ex}$-decay/$^{226}$Ra$_{sup}$-ingrowth relationship

Eq. (10) shows clearly that calculation of $^{226}$Ra$_{ex}(t)$ still requires knowledge of two components, $^{226}$Ra$_{aut}$ (which can be simply calculated by use of Eq. (11)) and $^{226}$Ra$_{sup}(t)$ from ingrowth of the precursor $^{230}$Th. The evolution of $^{226}$Ra$_{sup}(t)$ normalized to $^{234}$U is shown in Fig. 6 taking $^{226}$Ra(0)/$^{234}$U from the most recently formed sample (#19, discussion next paragraph), as a fixed parameter. In contrast to Fig. 3 two more curves are presented in this figure, i.e. the decay of $^{226}$Ra$_{ex}$ and the $^{230}$Th supported ingrowth of $^{226}$Ra, i.e. $^{226}$Ra$_{sup}$. It is indicated that $^{226}$Ra$_{sup}$ is strongly delayed because at short times both terms, $\lambda_{230}(1-e^{-226})$ and $\lambda_{226}(1-e^{-226})$, in Eq. (6) yield very similar values, while with increasing life time of the system the term $\lambda_{226}(1-e^{-226})$ tends more rapidly towards 1 than the ingrowth term of $^{230}$Th. This leads to a transient, fixed equilibrium between $^{230}$Th$^{+}$ and $^{226}$Ra$^{+}$tending to $\lambda_{230}/(\lambda_{226} - \lambda_{230}) = 1.02$ for $T_{1/2}^{226}$Ra. It is now interesting to compare the measured $^{226}$Ra$_{aut}$/$^{234}$U data with the $^{226}$Ra$_{ex}(t)$/$^{234}$U decay/ingrowth curve. To be able to do this, two parameters have to be known (i) the age of the samples obtained from an independent method, and (ii) the value for $^{226}$Ra(0)/$^{234}$U. While the sample ages were taken from the $^{230}$Th/$^{234}$U chronometer, the initial $^{226}$Ra(0)/$^{234}$U was obtained from the most recently formed sample (#19), in which there is a disequilibrium between $^{210}$Po and $^{222}$Rn (Table 2) and which must, therefore, be younger than 100 yr (c.f. Fig. 2, $^{210}$Pb/$^{226}$Ra relationship). Provided that the initial ratio $^{226}$Ra(0)/$^{234}$U at system closure remained invariant, all samples should plot, within error, on the $^{226}$Ra(0)/$^{234}$U decay + ingrowth curve. This is, however, not the case, indicating that the initial $^{226}$Ra(0)/$^{234}$U ratio varies from sample to sample (at least due to varying U-concentrations, Table 2) and cannot be used directly as a dating tool.

---

**Table 5**

$^{230}$Th/$^{234}$U ages of samples from profiles through the tufaceous limestone outside and travertine flow stones inside the lower cave system. The locations of 6 of the 8 samples from both profiles are also shown in the magnification of the lower cave system in Fig. 1.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$^{230}$Th/$^{234}$U age (kyr)</th>
<th>Distance from bottom (cm)</th>
<th>Growth rate (cm/kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5.3 ± 0.3</td>
<td>550</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>6.2 ± 0.4</td>
<td>350</td>
<td>120</td>
</tr>
<tr>
<td>13</td>
<td>7.9 ± 0.4</td>
<td>150</td>
<td>170</td>
</tr>
<tr>
<td>1</td>
<td>8.8 ± 0.4</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$^{230}$Th/$^{234}$U age (kyr)</th>
<th>Distance from bottom (cm)</th>
<th>Growth rate (cm/kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.6 ± 0.3</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>4.5</td>
<td>3.7 ± 0.3</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>5.1 ± 0.3</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>12</td>
<td>5.9 ± 0.3</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

---

more than one order of magnitude with respect to 226Raex(t)/226Ra(0).

5.2.4. Comparison of the 226Raex/226Ra(0) ages with the 230Th/234U ages

Since decay of the excess 226Ra component follows first order exponential decay, i.e. 226Raex(t) = 226Ra(0)e^{-λ226t}, the relationship presented in Eq. (10) can be rearranged in a similar manner to other dating systems based on decay of an excess component (such as 14C/12C dating), i.e. as 226Raex/226Ra(0) or as follows:

\[
\frac{226\text{Ra}_{\text{ex}}(t)}{226\text{Ra}(0)} = \frac{226\text{Ra}_{\text{aut}}}{226\text{Ra}(0)} - \frac{226\text{Ra}_{\text{sup}}(t)}{226\text{Ra}(0)} = e^{-\lambda_{226}t} \tag{12}
\]

or resolved to the time of formation, respectively,

\[
t_{\text{age}} = -\frac{1}{\lambda_{226}} \ln \left( \frac{226\text{Ra}_{\text{aut}} - 226\text{Ra}_{\text{sup}}(t)}{226\text{Ra}(0)} \right). \tag{13}
\]

As shown in Eq. (6) the component 226Ra_{sup}(t) is dependent on time as well as on the specific 234U activity of each sample. For the samples investigated here 226Ra_{sup}(t) was simply obtained using the sample ages determined individually via 230Th/234U. The resulting data are illustrated in Fig. 7 as 226Ra_{ex}(t)/226Ra(0) versus time, taking 226Ra(0) = 226Ra_{aut} from the most recently formed travertine (#19) as the initial. All those samples which started with identical initials to #19 should plot on the theoretical 226Ra_{ex}/226Ra(0) decay curve. Indeed, most of the data plot on or close to the curve, and even samples which exhibit ages 4 times the half-life of 226Ra still fit well to the decay curve. Note, that after correction for 226Ra_{sup} the residing component 226Ra_{ex} of the oldest samples (i.e. #1, 6, 13, 16) is extremely small (<0.1 mBq/g or <3 x 10^{-15} g/g), but still calculable within 30–50% uncertainty. From the youngest to the oldest samples the data cover a range of uncertainties: 2 kyr (or 50%), 5 kyr (or 20%), 10 kyr (or 2%). The regression analysis through the data results in a slope which is very similar to the theoretical 226Ra decay curve and yields a half-life of 1560 ± 150 yr, i.e. a value which is close to generally accepted value of 1600 yr (Firestone and Shirley, 1996).

5.2.5. Comparison of 226Ra(0) with bulk chemical analyses

Although the isotope data argue for a uniform initial input of 226Ra into the precipitating material, there is...
further proof provided from the bulk chemical analysis to justify this conclusion. Table 4 summarizes the major ionic components in 6 travertine samples and in the groundwater. The minor constituents are not shown, because their contributions were found to be very low and almost below the analytical detection limits (traces of Fe, Si, Mn, Al, P, Cu, Cr, etc. < 0.005 mg/g). Only sample 10 contains significant traces of Si and Al of ca. 0.01 mg/g, indicating impurities of the calcite with silicate material (probably of clay mineralogical composition). These additions are consistent with the higher concentration of $^{232}$Th in #10 (Table 2) compared to the other five pure calcite samples presented in Table 4 (#2, 4, 12, 13, 19). Assuming similar densities of detritus and pure travertine, as well as comparable concentrations of uranium in both phases, the detrital contribution in sample #10 amounts to about 5–10%, while in all other samples this contribution is less than 1%. The concentrations of Ca$^{2+}$ confirm this conclusion because the Ca/CaCO$_3$ weight ratio of pure calcite is 0.40 and this value was obtained for the five pure travertine samples. The authigenic phase is hence pure calcite in which about 1% of the cations (i.e., Ca$^{2+}$) is substituted by Mg$^{2+}$. There is, in addition, a slight contribution of SO$_4^{2-}$ to the anions (CO$_3^{2-}$). The latter forms probably individual phases, such as celestite (SrSO$_4$), which is a typical low temperature mineral associated in limestone formations (Hurlbut and Klein, 1977). Presence of such phases could explain the higher variability of Sr$^{2+}$ in comparison to other earth alkaline elements (Mg$^{2+}$, Ba$^{2+}$).

In particular, as Ra is an earth alkaline element behaving chemically similar to Ba, it is interesting to study the variation of Ba in the rock samples. Since the concentration of Ca in the authigenic carbonate phase is uniform it is most suitable to use the Ba/Ca ratios as a measure of the variability of Ba in the authigenic material. As Fig. 5 indicates, this ratio is highly constant ($0.49 \pm 0.02 \times 10^{-3}$) for all six samples and no trend with sample age can be observed, which corroborates the conclusion made above of uniform initial $^{226}$Ra(0) with time. It is also interesting to note that the Ra/Ba ratio in the water is very similar to that in the most recently formed samples, #19, i.e. $(\text{Ra/Ba})_{\text{water}}/(\text{Ra/Ba})_{19} = 1.4$. This indicates that the co-precipitation yield is similar for these homologue elements.

### 5.2.6. Calculation of $^{226}$Ra$_{ex}$ ages for samples with unknown $^{226}$Ra$_{sup}$

As shown in the right term of Eq. (13) calculation of $^{226}$Ra$_{ex}/^{226}$Ra(0) ages depend on the component $^{226}$Ra$_{sup}(t)$, which changes with time. To obtain an estimate on the fraction of the component $^{226}$Ra$_{sup}$ (supported from $^{234}$U and $^{230}$Th) on total $^{226}$Ra in the authigenic phase, we plotted the ratio ($^{226}$Ra$_{ex}/^{226}$Ra$_{sup}$) as a function of the time since system closure and for different initial $^{226}$Ra(0)/$^{234}$U activity ratios of 0.2, 0.5 and 1.0 (Fig. 9). It is obvious that for sample ages ranging from present to 2000 yr before present, the fraction of $^{226}$Ra$_{sup}$ on total $^{226}$Ra is fairly low (< 10%) but, for formation ages preceding that time, a correction for $^{226}$Ra$_{sup}$ becomes essential, especially if the samples started with low initial $^{226}$Ra(0)/$^{234}$U ratios. To circumvent rather extensive iteration procedures, we present a more practical way to calculate $^{226}$Ra$_{ex}$-ages via expression of Eq. (12) as difference of two terms, i.e.,

$$F(t) = \frac{^{226}\text{Ra}_{\text{aut}} - ^{226}\text{Ra}_{\text{sup}}(t)}{^{226}\text{Ra}(0)} - e^{-^{226}\text{Ra}_t}.$$

Our consideration is as follows: If $F(t) = 0$, it is required that both terms in Eq. (12) have to give identical values. Such a situation exists at one fixed moment, which is exactly the time of the mineral formation. The function $F(t)$ can be calculated with time as the free parameter, if $^{226}$Ra$_{aut}$, $^{226}$Ra(0) as well as U and Th isotopes have been determined analytically. The age is obtained from the intersection of $F(t)$ with the horizontal line where $F(t) = 0$. To demonstrate this we present, in Fig. 10, an illustration on the evolution of $F(t)$. Two examples are shown, (i) a $^{226}$Ra$_{aut}$/$^{226}$Ra (0) activity ratio of 0.5 (termed type A curve series) and (ii) $^{226}$Ra$_{aut}$/$^{226}$Ra (0) = 0.25 (type B curve series). Series A and B split into four separate curves marked with the indices 0 to 3 which refer to different initial $^{226}$Ra(0)/$^{234}$U ratios of 0.2, 0.5, 1.0 and $\infty$, respectively. For both curve type series it is shown that with increasing concentration of uranium, the component $^{226}$Ra$_{sup}$ contributes more to $^{226}$Ra$_{aut}$ which increases the $^{226}$Ra$_{ex}$/$^{226}$Ra(0) age.
5.2.7. Excesses of $^{210}\text{Po}$ on sample surfaces and check on closed system behavior

As noted in the analytical section, recent infiltration of rainwater may lead to a significant disequilibrium between $^{226}\text{Ra}$ and $^{210}\text{Pb}$-$^{210}\text{Po}$ on the rock surfaces. One fine grained sample with a highly porous surface (#7), which could not be purified mechanically confirms this observation. Analysis of $^{226}\text{Ra}$ via emanation of short-lived $^{222}\text{Rn}$ ($T_{\frac{1}{2}} = 3.8 \text{ d}$) into a liquid scintillation cocktail yielded a value which is much closer to the expected $^{226}\text{Ra}$ activities of material with comparable formation ages (#4, 5, 8, 11, 12) while $^{210}\text{Po}$ - $^{210}\text{Pb}$ is in large excess. Since it cannot be ruled out that the surface of #7 exhibits additional slight excesses of sorbed $^{226}\text{Ra}$, this sample was not included in the comparison of the isotope data with U/Th-ingrowth and $^{226}\text{Ra}_{\text{ex}}$-decay ages. On the other hand, for samples with abraded surfaces (i.e. for which surface effects causing isotope disequilibrium could be ruled out) combined analysis of $^{226}\text{Ra}$ and $^{222}\text{Rn}$ is helpful for the selection of very young samples ($< 100 \text{ yr}$) and for $^{210}\text{Po}$ ($< 100 \text{ Pb}$) and $^{222}\text{Rn}$ ($< 100 \text{ Ra}$) are not in secular equilibrium. Such samples are useful to obtain a value for $^{226}\text{Ra}(0)$ and a good example for short-term disequilibrium between $^{210}\text{Pb}$ and $^{226}\text{Ra}$ is indicated for sample #19 (fresh precipitated limestone covering a 10 yr old electric wire).

The use of taking $^{210}\text{Po}$ (advantage: “fast chemistry”) besides $^{222}\text{Rn}$ as a measure of $^{226}\text{Ra}$ in samples with formation ages exceeding 5 times the half-life of $^{210}\text{Pb}$ or $t > 100 \text{ yr}$ is a tool to demonstrate closed system behavior, if both isotopes yield identical activity concentrations. We therefore additionally selected 5 abraded samples (#2, 4, 5, 10, 14/1) for analysis via the $^{222}\text{Rn}$ emanation method. The data in Table 3 clearly show that the activity ratio of $^{210}\text{Po}/^{222}\text{Rn}$ (or $^{210}\text{Pb}/^{226}\text{Ra}$) is almost unity or that these nuclides are in secular equilibrium. Closed system behavior can also be investigated if much older sample material is considered, because in samples as old as 7 kyr 97% of authigenic $^{226}\text{Ra}$ is supplied from $^{230}\text{Th}$, i.e $^{226}\text{Ra}_{\text{out}} \approx 3^{226}\text{Ra}_{\text{sup}}$. If there would be leakage of the rare gas $^{222}\text{Rn}$ through the crystal lattice one would measure a much lower apparent $^{226}\text{Ra}$ content (or calculate negative ages). However, as the data show, there is no visible trend indicating preferential loss of $^{222}\text{Rn}$.

6. Geological evolution of the travertine deposit

The results of $^{230}\text{Th}/^{234}\text{U}$ as well as $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ dating of tufaceous freshwater limestone and travertine coatings inside caves contribute in understanding the origin of the Hell Grottoes cave system. The isotope data confirm the assumption that the Hell Grottoes travertine formed in the last 9000 yr in common with other freshwater limestone complexes in Europe (e.g. Krka Falls, Yugoslavia). The highest limestone deposition rate was probably during the Holocene climate optimum (Hypsithermal) between 8000 and 5500 yr when about 80–90% of the limestone complex was built up. Subsequently, the tufaceous limestone precipitation decreased dramatically, and in the last few thousand years there has been only little limestone precipitation on the surface, while in the closed cavities travertine flow-layers were formed and stalagmite nodules started to grow. Our interpretation of the growth history of the
travertine deposit is based on the geographic location from where the samples were taken as well as their ages. In addition, considering the stratigraphic sequence of the limestone complex, we added isolines of identical age to the geological profile shown in Fig. 1. Clearly, such isolines remain somewhat speculative because the structure of the limestone complex is similar and because large parts were removed previously (and no samples were preserved during the mining activity).

Our interpretation of a strong decrease of the tufaceous limestone precipitation in the last few thousand years is most presumably caused by a change of the vegetation in the water recharge area in the Lorze Valley which is a large moor. During the Holocene this moor gradually grew from a fen to a bog which still exists today. The appearance of the limestone precipitation is directly connected with the development of the moor. In the fen, the percolating rainwater is acidified by uptake of CO₂ from decomposition of organic matter and by formation of humic acids. As soon as such acidified waters come into contact with the underlying clastic limestone sediments, some lime will dissolve and dissociate. Consequently, when the groundwater discharges again, carbon dioxide escapes into the atmosphere and, due to a rise in pH, limestone starts to precipitate. However, with the change of a fen to a much thicker bog, less water can percolate through the underlying sediments, because with thickness the moor becomes less transmissive which causes storage of the water and surface run-off. This situation is shown schematically in Fig. 11 where the relative precipitation rate of limestone according to our view is given along with literature based relative precipitation rate of rainwater and change in temperature over the last 10,000 yr (Patzelt, 1995; Burga and Perret, 1998). The tremendous decrease of the limestone formation in more recent times is most likely due to a rapid change of the shallow moor to a massive bog in the cause of pronounced rainfall in the early Atlantikum. If this explanation is valid throughout, the isotope ages also fix the change in the moor from a fen to a bog at the end of the Holocene climate optimum.

Fig. 11. Schematic reconstruction of the growth evolution of the limestone complex of the Hell Grottoes and the development of the catchment area from a fen to a bog in the cause of temperature increase and high rainfall intensities during the early Atlantikum. The temperature curves and relative water precipitation data are redrawn after Patzelt (1995).
7. Conclusions

$^{238}\text{U}$ series disequilibrium dating of young tufaceous freshwater travertine from the limestone caves Hell Grotto at Lucerne, Switzerland yielded $^{230}\text{Th}/^{234}\text{U}$ formation ages ranging from recent time to about 9 kyr ago and therefore indicate that the authigenic deposit was formed during global warming in the Holocene. The major part of the limestone complex formed during a warm and humid period 8000–6000 yr before present and the travertine filling of the caves extended to about 3000 yr b.p. Correction of slight impurities of detrital silicates in the authigenic travertine via U/Th isochron relationships yielded almost identical $^{232}\text{Th}/^{234}\text{U}$ ratios for the silicate material, thus allowing the same correction procedure to be applied for all samples (i.e. internal isochrons to obtain one age for several co-genetic samples were unnecessary). The resulting individual ages of about 20 calcite samples hence sufficed to reconstruct the geological history of this deposit.

The ages obtained by $^{230}\text{Th}/^{234}\text{U}$ ingrowth-dating were then used to test the applicability of the $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ chronometer that is based on decay of excess $^{226}\text{Ra}$ in the authigenic precipitates. This chronometer is most suitable to investigate samples that formed between a few hundred years and up to about 7000 yr ago, corresponding to 4–5 half-lives of $^{226}\text{Ra}$ and therefore fits ideally into the time gap between the two established U-series chronometers, i.e. $^{210}\text{Po}$ (suitable from 0–100 yr) and $^{230}\text{Th}/^{234}\text{U}$ (from 4–200 kyr, see Appendix A). For further investigations it is recommended to use the same sample material which is suitable for $^{230}\text{Th}/^{234}\text{U}$ chronology studies (e.g. speleothem such as calcite tuffs, marine phosphorites or biochemically formed materials as corals, etc.). If the U and Th isotope analyses show that the sample material does not contain significant quantities of inherited $^{230}\text{Th}(0)$, $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ dating can strongly support $^{230}\text{Th}/^{234}\text{U}$, in particular if young samples are strongly intergrown with detrital impurities. However, to obtain geologically meaningful $^{226}\text{Ra}_{\text{ex}}/^{226}\text{Ra}(0)$ ages, the initial value of incorporated excess $^{226}\text{Ra}$, i.e. $^{226}\text{Ra}(0)$, has to be uniform independent of the time of system closure. To study the stability of uniform $^{226}\text{Ra}(0)$ over time it is further useful to determine the concentration of the chemically analogous behaving element Ba as well (normalization isotope) and, if $^{210}\text{Po}$ is taken as a measure for $^{226}\text{Ra}$, sample surfaces should be abraded to exclude excesses of sorbing $^{210}\text{Po}$ or $^{210}\text{Pb}$, introduced by surrounding present day groundwater, on surface sites.

Acknowledgements

We wish to thank H. Schmid for the permission to take samples from the historical limestone cave. We also acknowledge with thanks the discussions with Ch. Schuler, G. Butterweck and N.E.A. Crompton during preparation of this work, the support by R. Kündig for figure painting and the critical review performed by J. Kramers, P. Rowe and C. Schluechter. This research was partially supported by the Swiss Inspectorate for the Safety of Nuclear Installations, HSK.

Appendix A. Evaluation of the analytical uncertainties in $^{234}\text{U}–^{230}\text{Th}–^{226}\text{Ra}$ dating

A.1. The system $^{230}\text{Th}/^{234}\text{U}$

The evaluation of the overall analytical uncertainties in radiochemistry include statistical or random errors from counting radioactive decay as well as systematic errors resulting from laboratory operations and from uncertainties of the activity concentrations of radio-nuclide calibration tracers (spikes) which are used for isotope dilution analysis (Taylor, 1982; Faure, 1986; Ivanovich and Murray, 1992; Attendorn and Bowen, 1997). The random uncertainties (or type A, see Seymour et al., 1992; ISO, 1995) can be calculated by considering the total counted net impulses $I_i$ of any nuclide with mass number $i$ (here $i = 230\text{Th}$, $232\text{Th}$, $234\text{U}$, $238\text{U}$, $210\text{Po}$) and $J_i$ of the isotope dilution spikes ($^{226}\text{Th}$, $232\text{U}$, $209\text{Po}$). For ultra low level counting systems the absolute uncertainty $\sigma$ of a measured $x$-peak is given by the Poisson distribution, i.e. $\sigma = \sqrt{I_i}$ which is justified since background pulses ($I_0$) using high-purity $x$-detectors are insignificant compared to the measured count rates of the sample nuclides (typically in this work for the peak region of $^{234}\text{U}$: $I_0 < 5$, $I_{234} \approx 5000$ counts under the counting conditions as given below). Following the law of error propagation for the division of two measured quantities (for instance for a spiked uranium analysis) the uncertainty on the sample/spike ratio, $I_{234}/J_{232}$ is given as follows:

$$\sigma \left( \frac{I_{234}}{J_{232}} \right) = I_{234} \frac{\sqrt{(\Delta I_{234})^2 + (\Delta J_{232})^2}}{J_{232}}$$

(A.1)

or, with $\sigma = \sqrt{I_i}$, a more simplified expression is obtained (cf. Wilson, 1965)

$$\sigma \left( \frac{I_{234}}{J_{232}} \right) = I_{234} \frac{1}{J_{232}} \sqrt{\frac{1}{I_{234}} + \frac{1}{J_{232}}}$$

(A.2)

For calculation of a sample nuclide activity such as $^{234}\text{U}$ using reference $^{232}\text{U}$-spike additions, the following relation holds (A.3):

$$a_{234} = \frac{I_{234}}{J_{232}} a_{232}.$$  

(A.3)

The same relation holds for calculation of the Th isotopic composition ($^{232}\text{Th}$, $^{230}\text{Th}$) in the sample adding...
Rearranging this expression and considering the propagation yields

\[ \frac{a_{230}}{a_{234}} = \frac{I_{230} J_{232}}{I_{234} J_{232}} \]  

(A.4)

Partial derivation according to the law of error propagation yields

\[ \sigma \left( \frac{a_{230}}{a_{234}} \right) = \frac{I_{230} J_{232}}{I_{234} J_{232}} \sqrt{ \frac{1}{I_{230} + I_{234} + J_{228} + J_{232}} } \]  

(A.5)

For calculation of the uncertainty of \( ^{230}\text{Th}/^{234}\text{U} \) formation ages, the mother/daughter growth relation

\[ ^{230}\text{Th}(t) = ^{234}\text{U}(1 - e^{-230\text{Th}(t)}) \]  

has to be solved for \( t \). Rearranging this expression and considering the measured counts \( I_i \) and \( J_i \) instead of activities it follows:

\[ t = -\frac{1}{J_{230}} \ln \left( 1 - \frac{I_{230} J_{232}}{I_{234} J_{228}} \right) \]  

(A.6)

Considering all internal and external derivations the following expression is finally obtained:

\[ \sigma(t) = \frac{1}{J_{230}} \frac{1}{J_{234} J_{228}} \sqrt{ \frac{1}{I_{230} + I_{234} + J_{228} + J_{232}} } \]  

(A.7)

Relation (A.7) is valid only for ideal systems containing pure, authigenic minerals. However, such ideal conditions do not relate to the travertine analyzed here because the authigenic young carbonate phase were always found to be mixed with some (old) detrital material containing \( ^{232}\text{Th} \) and \( ^{238}\text{U} \) in secular equilibrium with all their progeny nuclides. Since in this case the activity of \( ^{234}\text{U} \) is equal to that of the daughter \( ^{230}\text{Th} \) (i.e. \( a_{234} = a_{230} \)), correction of detrital impurities from measured \( ^{230}\text{Th} \) is simply obtained as follows:

\[ I_{230,\text{cor}} = I_{230,\text{m}} - k I_{232} \]  

(A.8)

where the subscripts cor and m refer to the detritus corrected and measured impulses of \( ^{230}\text{Th} \) and \( ^{234}\text{U} \) and \( k \) to the \( ^{230}\text{Th} / ^{232}\text{Th} \) ratio in the detritus component. Incorporating the correction term for detritus contribution into Eq. (A.6), the partial differentiation yields

\[ \sigma(t) = \frac{1}{J_{230}} \frac{1}{I_{234} J_{228}} \frac{I_{230}}{I_{230,\text{cor}} J_{232}} - 1 \times \sqrt{ \frac{I_{230,\text{m}} + k^2 I_{232}}{I_{230,\text{cor}} J_{232}} + \frac{1}{I_{234} J_{228}} + \frac{1}{J_{228}} + \frac{1}{J_{232}} } \]  

(A.9)

To calculate the uncertainty of \( ^{230}\text{Th} /^{234}\text{U} \) dating for typical sample material analyzed here (Fig. 12, we inserted the following typical values for the parameters in Eq. (A.9): \( ^{234}\text{U} = 6 \text{ mBq/g}, \) sample weight = 4 g, counting efficiency = 35%, chemical recovery = 95%, total counting time = one week. This yields \( I_{234} \approx 5000 \) counts. \( I_{230} \) was calculated using \( I_{230}(t) = I_{230}(1 - e^{-230\text{Th}(t)}) \). Furthermore, since the chemical recoveries were comparable for \( U \) and \( Th \) we inserted \( J_{228}/J_{232} = 1 \); and to demonstrate the effect of detrital contribution to authigenic material, we plotted a sequence of sample mixtures with different \( ^{234}\text{U}/^{232}\text{Th} \) ratios ranging from 500 to 10, or (with \( k = 1.3 + 0.1 \)) relative contributions of authigenic uranium of as high as 99 to 87% on the total sample mixture (Fig. 12). From this plot it is obvious that samples with \( ^{234}\text{U}/^{232}\text{Th} \) ratios of 10 and below are not suitable for \( U/Th \) dating if the sample age is below 5 kyr. For travertine that precipitated about 30 kyr ago, the relative uncertainty is passing through a minimum and for formation ages above that value, the \( ^{230}\text{Th} /^{234}\text{U} \) ratio rapidly progresses towards secular equilibrium (leading to \( I_{234}/I_{230} \rightarrow 1 \), i.e. \( \sigma(t) \rightarrow \infty \)), while in the right term in Eq. (A.9) the component \( I_{230,\text{cor}} \) becomes similar to \( I_{230,\text{m}} \) with progressing \( t \), because then significant quantities of \( ^{230}\text{Th} \) have been built in that exceed by far detrital \( ^{230}\text{Th} \).
A.2. The system $^{226}Ra_{\text{ex}}/^{226}Ra(0)$

In contrast to $^{230}Th/^{234}U$ this chronometer requires at least two samples for determining (i) $^{226}Ra_{\text{ex}}$ in the material to be dated and (ii) $^{226}Ra(0)$ in very young samples in which decay of $^{226}Ra(0)$ is of importance. As described above, radioassay of both samples is performed using yield spike isotopes (i.e. $^{209}Po$ besides $^{210}Po$). Providing secular equilibrium between $^{210}Po$ and $^{210}Pb$, for two samples, the following equations (A.1)–(A.4) can be applied yielding

$$
\sigma(t) = \frac{1}{I_{^{226}Ra}} \sqrt{\frac{I_{210}(s,m)}{I_{210}(s,\text{cor})} + k^2 \frac{I_{232}(s)}{I_{232}(s,\text{cor})}} + \frac{\Delta I_{210}(s,\text{sup})}{I_{210}(s,\text{cor})} + \frac{I_{232}(s)}{I_{232}(s,\text{cor})} \Delta k^2 + \frac{\Delta R_{239}^2}{R_{239}^2}.
$$

Considering additional correction for detrital contamination (c.f. Eq. (A.8)) it follows for the uncertainty of an $^{226}Ra_{\text{ex}}/^{226}Ra(0)$ age

$$
\sigma(t) = \frac{1}{I_{^{226}Ra}} \sqrt{\frac{I_{210}(s)}{I_{232}(s,\text{cor})} + \frac{I_{210}(s,\text{cor})}{I_{210}(s,\text{cor})} \Delta k^2 + \frac{\Delta R_{239}^2}{R_{239}^2}}.
$$

In contrast to $^{230}Th/^{234}U$ it is obvious that the detritus correction increases the uncertainty in $^{226}Ra_{\text{ex}}$-dating less significantly, however, the initial $^{226}Ra(0)/^{234}U$ ratio has a strong influence on the accuracy of the sample ages using this chronometer (Fig. 13).

**References**


