

$^{230}\text{Th}/\text{U}$ -dating of fossil corals and speleothems

DENIS SCHOLZ & DIRK HOFFMANN^{*)}

Abstract: Both marine and terrestrial carbonates can be precisely dated by U-series disequilibrium methods in the age range <600 ka (thousands of years). Here we focus on $^{230}\text{Th}/\text{U}$ -dating of reef corals and speleothems. The requirements, potential but also the problems of $^{230}\text{Th}/\text{U}$ -dating of both archives are presented and discussed. Fossil reef corals are used as indicators for past sea level fluctuations and as high-resolution palaeoclimate archives. These applications require precise and accurate dating, which can be achieved using $^{230}\text{Th}/\text{U}$ -dating. However, many fossil corals show evidence for post-depositional open-system behaviour. This limits the accuracy of $^{230}\text{Th}/\text{U}$ -ages of fossil corals rather than the analytical precision. We present and discuss the currently available methods to identify altered corals and also review three recently developed open-system dating approaches. Speleothems are very important climate archives because they are found in most continental areas and can be used to investigate and directly compare spatially variable climate conditions. They usually show no evidence for open-system behaviour but may contain significant amounts of initial detrital ^{230}Th . We discuss the currently available correction techniques and methods to derive the most reliable ages. Furthermore, we give an overview of the state of the art techniques for U-series isotopes measurements.

[$^{230}\text{Th}/\text{U}$ -Datierung fossiler Korallen und Speläotheme]

Kurzfassung: Marine und terrestrische Karbonate können im Altersbereich von bis zu 600.000 Jahren mit Uranreihen-Ungleichgewichtsmethoden sehr präzise datiert werden. In diesem Artikel wird die $^{230}\text{Th}/\text{U}$ -Datierung von Riffkorallen und Speläothemen dargestellt. Anforderungen, Potenzial aber auch Probleme der Datierung beider Archive werden eingehend diskutiert. Fossile Riffkorallen werden sowohl als Anzeiger der Meeresspiegelschwankungen der Vergangenheit als auch als Paläoklimaarchiv mit sehr hoher Auflösung genutzt. Für beide Anwendungen werden äußerst präzise und zuverlässige Alter benötigt, die mit der $^{230}\text{Th}/\text{U}$ -Methode bestimmt werden können. Viele fossile Riffkorallen zeigen jedoch Anzeichen von nachträglicher diagenetischer Veränderung, welche die Genauigkeit der $^{230}\text{Th}/\text{U}$ -Alter mehr limitiert als die Messgenauigkeit. Die Methoden zur Identifikation diagenetisch veränderter Korallen werden dargestellt, und drei in den letzten Jahren entwickelte Methoden zur Datierung von Korallen, die sich als offene Systeme verhalten haben, werden diskutiert. Speläotheme sind bedeutende Klimaarchive, da sie in fast allen Gegenden vorkommen, was es ermöglicht, Klimaveränderungen in verschiedenen Gebieten zu untersuchen und direkt miteinander zu vergleichen. Sie zeigen in der Regel keine Anzeichen für nachträgliche Störungen des U-Th-Systems können aber in Einzelfällen signifikante Mengen von initialem ^{230}Th enthalten. Die gängigen Korrekturverfahren und Methoden, um zuverlässige Datierungen zu erhalten, werden dargestellt. Weiterhin geben wir einen Überblick über die derzeitigen Methoden zur Messung von Uranreihenisotopen.

Keywords: $^{230}\text{Th}/\text{U}$ -dating, fossil corals, speleothems, palaeoclimate reconstruction, mass spectrometry

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1 Introduction

Palaeoclimate archives such as ice cores, deep sea sediments or speleothems provide important insights about natural climate variability, which are urgently needed to understand the mechanisms driving our climate system and hence to quantify and potentially predict (anthropogenic) future climate change. A key aspect of palaeoclimate reconstruction is the accurate determination of the *timing* of past climate changes, which provides fundamental information about the phasing of change and, therefore, about potential links between climate in different regions or between climate and the forcing mechanisms driving it (HENDERSON 2006).

Carbonates such as corals or speleothems can be accurately and precisely dated using U-series disequilibrium methods. This method is based on the radioactive decay of radionuclides within the naturally occurring decay chains. There are three decay chains, each starts with an actinide nuclide (i.e., ^{238}U , ^{235}U , and ^{232}Th) having a long half live (all have $T_{1/2} > 7 \times 10^8$ a) and ultimately ends with different stable isotopes of lead (Fig. 1). In an undisturbed system all daughter nuclides reach a state of radioactive equilibrium with the parent nuclide after a few million years. Natural processes that fractionate the nuclides within a decay chain result in a disequilibrium between the activity of the parent and the daughter isotopes. The return to equilibrium then allows quantification of time and, thus, dating of the timing of chemical or physical fractionation (BOURDON et al. 2003).

U-series disequilibrium dating methods can, in principle, be applied to all materials that form accompanied by a constrained parent-daughter disequilibrium, such as marine carbonates (reef and deep sea corals, carbonate bank sediments, molluscs and foraminifera), lacustrine carbonates (tufa and inorganically precipitated sediments), terrestrial carbonates (speleothems and travertine) and peat deposits (GEYH 2008). However, U-series dating of each of these materials is associated with particular problems. For example, mollusc shells and foraminifera

were shown to take up and exchange U after deposition violating the basic closed-system assumption of U-series dating (next section). Hence, U-series dating cannot be reliably applied to these materials. Reef building corals and speleothems (i.e., secondary carbonates precipitated in caves), however, can be accurately and precisely dated using U-series methods. For these materials U-series dating methods are widely used because they provide by far the most reliable and precise ages for samples younger than 600 ka (thousands of years). Here, we focus on mass spectrometric U-series dating of corals and speleothems. A review of $^{230}\text{Th}/\text{U}$ -dating of other marine and terrestrial carbonates is given by EDWARDS et al. (2003).

Fossil reef corals were successfully dated for the first time with U-series methods by BARNES et al. (1956) using alpha-counting techniques, followed by numerous studies in the 1960's and 1970's (e.g., BROECKER et al. 1968; MESOLELLA et al. 1969). With the advent of modern thermal ionisation mass spectrometry (TIMS, section 2.3.2) the precision of U-series dating significantly improved. This led to increasing research on fossil reef corals and the application for sea level reconstruction in the late 1980's and early 1990's (e.g., BARD et al. 1990; CHAPPELL & POLACH 1991; CHEN et al. 1986; EDWARDS et al. 1986; GALLUP et al. 1994).

The potential of using U-series dated proxy records in speleothems, such as oxygen and carbon isotopes for palaeoclimate reconstruction was already indicated by the pioneering work in the 1960's and 1970's (e.g., HENDY & WILSON 1968). Within the past two decades improvements in analytical techniques allowed (i) more precise $^{230}\text{Th}/\text{U}$ -ages to be obtained from much smaller sample sizes and (ii) a variety of proxies to be measured at very high spatial resolution (i.e., in the range of μm). Because speleothems are found in most continental areas, spatially variable climate changes can be investigated and directly compared. Thus, it has recently been hypothesized that for palaeoclimate research, the next two decades might be „the age of the speleothem“ (HENDERSON 2006).

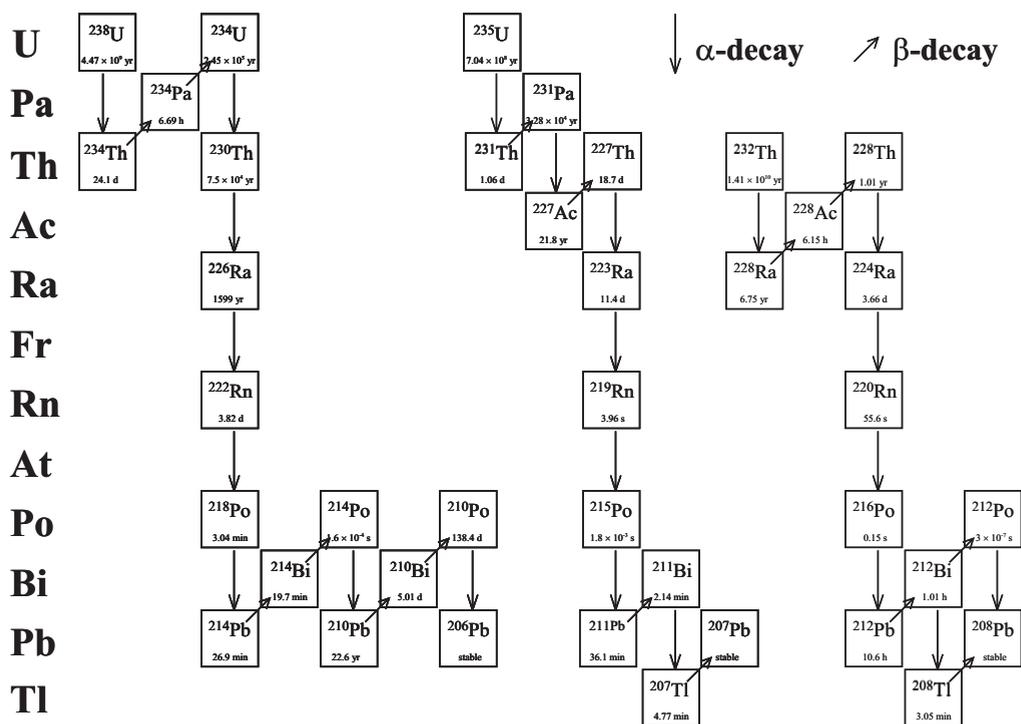


Fig. 1: Schematic drawing of the ^{238}U , ^{235}U and ^{232}Th decay chains (from SCHOLZ 2005). The half-lives of the nuclides are indicated in the boxes.

Abb. 1: Schematische Darstellung der Zerfallsreihen von ^{238}U , ^{235}U und ^{232}Th . Die Halbwertszeiten sind in den jeweiligen Boxen angegeben.

2 Basics

2.1 Geochemistry of U and Th

Typical U concentrations of the continental crust range from 0.1 to 6 $\mu\text{g/g}$. ^{238}U is the most abundant U isotope (99.2745 %), and ^{232}Th is the most abundant Th isotope (~100 %). The average Th/U weight ratio in crustal rocks is ~3.5 (WEDEPOHL 1995). The half-lives of ^{238}U ($T_{1/2} = 4.4683 \times 10^9$ a, JAFFEY et al. 1971), ^{235}U ($T_{1/2} = 0.70381 \times 10^9$ a, JAFFEY et al. 1971), and ^{232}Th ($T_{1/2} = 14.01 \times 10^9$ a, HOLDEN 1990) are much longer than those of their daughters in the decay chain (Fig. 1). Thus, the activities of parent and daughter isotopes reach a state of secular equilibrium in naturally occurring undisturbed materials within several million

years. However, natural processes can disrupt the state of equilibrium, which is the key of the U-series disequilibrium dating methods. A state of disequilibrium in the ^{238}U decay chain can either result from elemental fractionation of Th from U or from isotope fractionation between ^{234}U and ^{238}U .

The elemental fractionation is a result of the different geochemical behaviour of U and Th. U mainly exists in two oxidation states in nature (U^{4+} and U^{6+}), and at the Earth's surface it is dominant in its soluble U^{6+} form. It is soluble as uranyl ion $(\text{UO}_2)^{2+}$ and in various uranyl carbonate forms (IVANOVICH & HARMON 1992). In a reducing environment, however, it occurs mainly in the U^{4+} state where it is insoluble and, thus, far less mobile than U^{6+} . In contrast, Th,

which occurs in terrestrial material mainly in the 4+ oxidation state, is insoluble in natural waters (IVANOVICH & HARMON 1992), and, thus, under natural conditions usually transported in minerals or adsorbed onto particles. As a consequence, groundwater, fluvial water and seawater contain dissolved U but essentially no Th. Hence, in contrast to U, Th is not incorporated in secondary carbonates during their formation resulting in an initial Th/U disequilibrium.

Fractionation of ²³⁴U and ²³⁸U is produced by the α -recoil effect. An α -decay (e.g., decay of ²³⁸U, Fig. 1) results in the emission of a He nucleus with finite kinetic energy. This has a twofold effect: (i) The daughter nuclide is slightly displaced from its parent's original site and, thus, either directly ejected into an adjacent phase or more easily removed subsequently. (ii) The crystal lattice is damaged by the α -particle along the trajectory (BOURDON et al. 2003). Therefore, the daughter nuclide is subsequently more easily mobilized than its parent e.g., during weathering processes. As a consequence, ²³⁴U/²³⁸U isotope ratios of ground and river water are usually higher than the equilibrium value (CHABAUX et al. 2003; PORCELLI & SWARZENSKI 2003).

2.2 Calculation of ²³⁰Th/U-ages

The activity, *A*, of a number of atoms of a radioactive nuclide, *N*, is defined as the number of decay events per unit of time:

$$A = \frac{dN}{dt} = -\lambda N, \quad (1)$$

where λ is the decay constant defined as $\ln(2)/T_{1/2}$.

In the following, activities and activity ratios are indicated by parenthesis, e.g., (²³⁸U). The temporal development of the activities of the individual isotopes within a decay chain is described by a system of differential equations, which can be solved by standard methods (IVANOVICH & HARMON 1992).

In contrast to U, Th is not incorporated in secondary carbonates. Thus, the initial activity of ²³⁰Th, (²³⁰Th)_{init.}, is zero. If we further assume that the decay system remains closed after deposition (i.e., both U and Th isotopes are neither lost nor gained) and take into account that the half-life of ²³⁸U is much longer than that of ²³⁴U and ²³⁰Th (Fig. 1), the development of (²³⁴U/²³⁸U) and (²³⁰Th/²³⁸U) is described by equations (2) and (3) (see IVANOVICH & HARMON 1992, for derivation):

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)(t) = \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{\text{init.}} - 1\right) e^{-\lambda_{234} t} + 1 \quad (2)$$

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)(t) = (1 - e^{-\lambda_{230} t}) + \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)(t) - 1\right) \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} (1 - e^{-(\lambda_{230} - \lambda_{234}) t}), \quad (3)$$

where (²³⁴U/²³⁸U)_{init.} is the initial (²³⁴U/²³⁸U) activity ratio, and the λ_i are the decay constants for ²³⁰Th and ²³⁴U, respectively. The most recent values for the decay constants of ²³⁰Th and ²³⁴U are $\lambda_{230} = 9.1577 \times 10^{-6} \text{ a}^{-1}$ and $\lambda_{234} = 2.8263 \times 10^{-6} \text{ a}^{-1}$ (CHENG et al. 2000). Note that Eqs. (2) and (3) are only valid if two basic assumptions are fulfilled: (i) no presence of initial ²³⁰Th and (ii) the system remains closed after deposition. If one of these assumptions is violated, the resulting ²³⁰Th/U-age might be biased substantially and, thus, without significance. However, if both assumptions are fulfilled, the measurement of (²³⁴U/²³⁸U) and (²³⁰Th/²³⁸U) allows the calculation of the time since the formation of the sample. Fig. 2 shows the temporal development of (²³⁰Th/²³⁸U) and (²³⁴U/²³⁸U) for two different values of (²³⁴U/²³⁸U)_{init.}. (²³⁴U/²³⁸U) is often given in the δ -notation in per mil:

$$\delta^{234}\text{U} = \frac{\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) - \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{eq}}{\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{eq}} \cdot 1000$$

$$= \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right) - 1 \right) \cdot 1000, \quad (4)$$

where $(^{234}\text{U}/^{238}\text{U})_{eq}$ indicates $(^{234}\text{U}/^{238}\text{U})$ in secular equilibrium.

Eq. (2) alone cannot be used for age calculations because $(^{234}\text{U}/^{238}\text{U})_{init.}$ is generally not known. Fortunately, Eq. (3) only requires the present $(^{230}\text{Th}/^{238}\text{U})$ and $(^{234}\text{U}/^{238}\text{U})$ of the sample to solve for age, which can both be measured. Since Eq. (3) cannot be analytically solved for t , the age calculation must be done either graphically or numerically. The corresponding error of the age can be calculated using numerical methods, such as Monte-Carlo simulation (LUDWIG 2003). A common way to visualize the temporal development of the activity ratios is to plot $(^{234}\text{U}/^{238}\text{U})$ vs. $(^{230}\text{Th}/^{238}\text{U})$ (Fig. 3).

2.3 Analytical techniques

$^{230}\text{Th}/\text{U}$ -dating requires precise and accurate measurement of the relevant U and Th isotope abundances to obtain the isotope activity ratios needed to calculate an age according to Eqs. (2) and (3). The isotopes ^{238}U , ^{234}U , ^{230}Th have a different atomic mass and all decay by alpha emission (Fig. 1). Two methods are commonly used for U and Th isotope measurements: alpha spectrometry and mass spectrometry. Both techniques require prior chemical separation and purification of U and Th from the CaCO_3 matrix (IVANOVICH & HARMON 1992). A detailed description of the sample preparation chemistry is given by HOFFMANN (in press). Since U and Th behave differently during separation and purification, a tracer (or „spike“) is required, such as a solution of ^{236}U and ^{229}Th with known accurately calibrated U-Th ratio. A defined

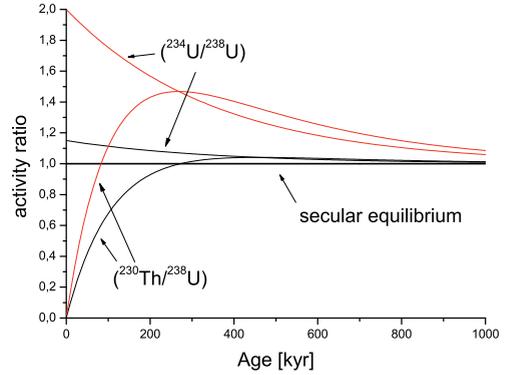


Fig. 2: Temporal development of $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ under closed system conditions with no initial Th. Two cases of initial $(^{234}\text{U}/^{238}\text{U})$ are shown: $(^{234}\text{U}/^{238}\text{U})_{init.} = 1.15$ (black line) and $(^{234}\text{U}/^{238}\text{U})_{init.} = 2.0$ (red line). The development of $(^{230}\text{Th}/^{238}\text{U})$ depends on that of $(^{234}\text{U}/^{238}\text{U})$ (Eq. (3)), which in turn depends on $(^{234}\text{U}/^{238}\text{U})_{init.}$ (Eq. 2). The limit of the dating range is reached when secular equilibrium is established. It is obvious that the dating range depends on $(^{234}\text{U}/^{238}\text{U})_{init.}$. For marine samples, which usually have $(^{234}\text{U}/^{238}\text{U})_{init.} = 1.15$ (black line, see next section), the dating range is $\sim 600,000$ a (EDWARDS et al. 2003). For other samples, such as speleothems, higher values of $(^{234}\text{U}/^{238}\text{U})_{init.}$ can be found, and older samples may still be datable.

Abb. 2: Zeitliche Entwicklung der Aktivitätsverhältnisse $(^{234}\text{U}/^{238}\text{U})$ und $(^{230}\text{Th}/^{238}\text{U})$ unter Annahme eines geschlossenen Systems. Es werden zwei Fälle unterschieden: $(^{234}\text{U}/^{238}\text{U})_{init.} = 1.15$ (schwarze Kurve) und $(^{234}\text{U}/^{238}\text{U})_{init.} = 2.0$ (rote Kurve). Die Entwicklung von $(^{230}\text{Th}/^{238}\text{U})$ hängt von der von $(^{234}\text{U}/^{238}\text{U})$ ab, welche wiederum von $(^{234}\text{U}/^{238}\text{U})_{init.}$ abhängt. Die Grenze der Datierbarkeit ist erreicht, wenn sich das säkulare Gleichgewicht eingestellt hat. Es ist offensichtlich, dass diese Grenze von $(^{234}\text{U}/^{238}\text{U})_{init.}$ abhängt. Für marine Proben, die in der Regel ein initiales $(^{234}\text{U}/^{238}\text{U})$ Aktivitätsverhältnis von 1.15 haben (schwarze Kurve, s. nächster Abschnitt), ist das Limit der Datierungsmethode ca. 600 000 Jahre (EDWARDS et al. 2003). Für andere Proben, wie z.B. Speläotheme, sind höhere Werte für $(^{234}\text{U}/^{238}\text{U})_{init.}$ nicht ungewöhnlich. In diesen Fällen können auch ältere Proben noch datiert werden.

quantity of the tracer needs to be added to the sample prior to the separation procedure (isotope-dilution technique). Hence, additionally to the above mentioned isotopes, the abundances of ^{236}U (and/or ^{233}U) and ^{229}Th also have to be determined. Furthermore, ^{232}Th is measured as a proxy for detrital components.

2.3.1 Alpha spectrometry

Radioactive decay of the isotopes mentioned above is accompanied by the emission of an alpha particle with isotope specific energy. Thus, one possibility of measuring the relative isotope abundances is alpha spectrometry. However, alpha spectrometry is meanwhile of

minor importance for $^{230}\text{Th}/\text{U}$ -dating of corals and speleothems due to the limits in precision and requirements in sample sizes. In brief, after separation, U and Th fractions are deposited as a thin layer on a flat surface such as metal planchet, e.g., by electrodeposition. The planchet is then placed in a sample chamber at high vacuum beneath a detector, which detects the occurrence and energy of alpha particles. A U or Th isotope measurement takes a few days, and the precision is in the range of a few percent, which limits the dating range to 300 ka. Another disadvantage of alpha spectrometry compared to mass spectrometry is the rather big sample size required for one measurement (usually more than 1 μg total U).

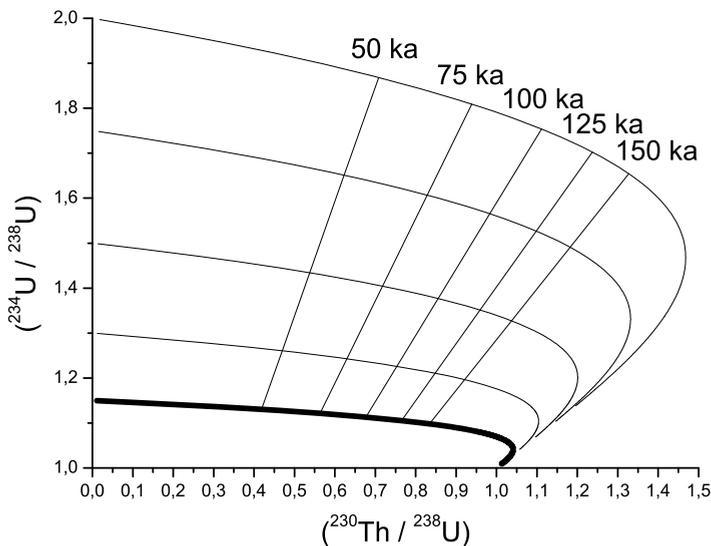


Fig. 3: $(^{234}\text{U}/^{238}\text{U})$ vs. $(^{230}\text{Th}/^{238}\text{U})$ plot for different values of $(^{234}\text{U}/^{238}\text{U})_{\text{init.}}$. Each curve starts with $(^{230}\text{Th}/^{238}\text{U}) = 0$ but with another value of $(^{234}\text{U}/^{238}\text{U})_{\text{init.}}$. The bold curve corresponds to $(^{234}\text{U}/^{238}\text{U})_{\text{init.}} = 1.15$, the value measured on modern sea water, and represents the seawater evolution curve. All curves finally converge to secular equilibrium. The vertically tilted straight lines represent isochrons for a specific age as indicated by the corresponding labels. All combinations of activity ratios of an isochron correspond to the same age. This plot is very useful to detect post-depositional open-system behaviour (next section).

Abb. 3: $(^{234}\text{U}/^{238}\text{U})$ vs. $(^{230}\text{Th}/^{238}\text{U})$ Diagramm für verschiedene Werte von $(^{234}\text{U}/^{238}\text{U})_{\text{init.}}$. Jede Kurve startet bei $(^{230}\text{Th}/^{238}\text{U}) = 0$ jedoch mit einem anderen Wert für $(^{234}\text{U}/^{238}\text{U})_{\text{init.}}$. Die fettgedruckte Kurve gilt für $(^{234}\text{U}/^{238}\text{U})_{\text{init.}} = 1.15$, welches der heutige Wert von Meerwasser ist, und heißt daher *seawater evolution curve*. Alle Kurven konvergieren gegen das säkulare Gleichgewicht. Die vertikalen Gerade sind Isochronen für die angegebenen Alter. Alle Kombinationen von Aktivitätsverhältnissen auf einer Isochrone entsprechen dem gleichen Alter. Dieses Diagramm ist sehr nützlich, um nachträgliche Störungen des Systems zu erkennen (s. nächster Abschnitt).

2.3.2 Mass spectrometry

$^{230}\text{Th}/\text{U}$ -dating is now largely done using mass spectrometry. Thus, this technique is presented in more detail here. Basically, a mass spectrometer directly measures the relative isotope abundances via the mass to charge ratio of ionised isotopes in a sample. The concept was first introduced almost a century ago in 1913 by Thompson. It is based on the deflection of charged particle beams in a magnetic field depending on the mass to charge ratio. A review of early developments of mass spectrometry can be found in DE LAETER (1998). Technical advances in thermal ionisation mass spectrometry (TIMS) in the 1980's led to a significant improvement in precision and detection limits (EDWARDS et al. 1987). In the last 10–15 years further improvements in plasma source mass spectrometry, especially the advent of multi collector inductively coupled plasma mass spectrometry (MC-ICPMS) led to a further shift to this technique (e.g., GOLDSTEIN & STIRLING 2003; HALLIDAY et al. 1998). Here we focus on TIMS and MC-ICPMS because those are currently the most important techniques for high precision U and Th isotope measurements. The basic concept of mass spectrometry is: (i) ionisation of isotopes, (ii) acceleration of the charged particles using a high potential difference, and (iii) the separation of charged particle beams with different mass to charge ratio in a magnetic field. The intensities of the separated ion beams then have to be detected to obtain the relative abundance. Thus, there are three main parts of a mass spectrometer: ion source, mass analyser and detector system.

A TIMS is a solid source mass spectrometer. The purified U and Th solutions are placed on a filament, e.g., made of Rhenium, which is placed in the ion source of the mass spectrometer. The sample chamber is evacuated to high vacuum, and the filament then heated by an electric current. Atoms are thermally released from the filament and a certain proportion (<1 %) also ionised. The ions are accelerated by a high potential in the ion source, and the ion beam is focused into the mass analyser section. The mass analyser of a TIMS is a magnetic

field. Typically, a U or Th isotope measurement takes a few hours. The total U needed for one analysis is in the range of a few tens to hundreds of nanograms, and precisions of a few per mil can be achieved.

A MC-ICPMS is a plasma source mass spectrometer. The ion source consists of a torch, in which an Ar plasma is generated by a radio frequency (RF) coil. The purified U and Th sample is dissolved in a weak acid, and these solutions are nebulised in a spray chamber and mixed with Ar sample gas. The mixture is then injected into the plasma, which has a temperature of about 8000 K, and almost completely ionised (>90 %). The ions are transferred from the plasma at atmospheric pressure into the mass spectrometer at high vacuum via the interface region, where more than 90 % of the ions are lost. Inside the mass spectrometer an extraction voltage accelerates the ions via electrical lenses into the mass-analyser section. A modern MC-ICPMS is usually equipped with a combination of an electrostatic analyser (ESA) and magnetic analyser (Nier-Johnson geometry). In contrast to TIMS, the ESA, which is essentially an energy filter, is needed because of the larger energy spread of the ions. The ionisation and transfer efficiency of a modern MC-ICPMS is in the range of 1 %. The measurement time of one U or Th sample is 10–20 minutes with precisions comparable to TIMS. For MC-ICPMS $^{230}\text{Th}/\text{U}$ -dating typically a total U load of about 5 – 10 ng is needed (HOFFMANN et al. 2007). Further details can be found in GOLDSTEIN & STIRLING (2003).

The detector system is largely the same for TIMS and MC-ICPMS. It is usually a combination of Faraday cup detectors and ion counter devices. Ion beam intensities larger than 1 mV can be measured on Faraday cups. Small ion beams are detected using ion counters, such as secondary electron multipliers or Daly detectors. U isotopes, for example, are usually measured with a combination of an ion counting system for the minor ^{234}U and ^{236}U isotopes and Faraday cups for the more abundant ^{235}U and ^{238}U isotopes. The isotope beams are ideally measured simultaneously (static) to avoid

biases by unstable beam intensities. If the detector system has only one ion counter, two static measurements are done, one with ^{234}U on the ion counter and ^{238}U on a Faraday cup and another with ^{236}U on the ion counter and ^{238}U on a Faraday cup. The measured raw isotope ratios need to be corrected for several instrumental biases, such as ion-counter-Faraday-cup gain, ion counter darknoise, Faraday cup baseline, peak tailing („abundance sensitivity“) and mass fractionation (e.g., HOFFMANN et al. 2007).

In summary, precise and accurate U-Th isotope ratio measurements can be done with TIMS and MC-ICPMS, with MC-ICPMS allowing the use of smaller sample sizes. An accurate correction of instrumental biases and accurately calibrated spikes are essential for reliable dating results. Currently, the limit for $^{230}\text{Th}/\text{U}$ -dating is in the range of approximately 600 ka.

3 $^{230}\text{Th}/\text{U}$ -dating of reef corals

3.1 ^{238}U , ^{234}U and ^{230}Th in seawater

River runoff from the continents is the dominant supply of U to the oceans with an estimated flux of $\sim 11 \times 10^9$ g/a ($\pm 35\%$) (IVANOVICH & HARMON 1992). Additional sources of U in the ocean are, e.g., wind-blown dust and groundwater discharge. While the former is unlikely to be significant ($< 3\%$ of the riverine U flux), the latter is very difficult to estimate because both the total flux and the average U concentration of groundwater are poorly known. U is mainly removed from the oceans into reducing marine sediments where U becomes insoluble in the U^{4+} state. The oceanic U budget is in balance within the level of uncertainty, and seawater has a near constant U concentration of 3.3 ppb (CHEN et al. 1986) indicating a residence time of ~ 400 ka.

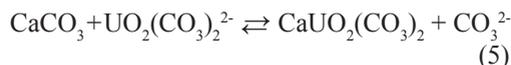
Seawater ($^{234}\text{U}/^{238}\text{U}$) is elevated compared to secular equilibrium, which is related to the α -recoil effect in minerals on the continents and in marine sediments. Most measured seawater ($^{234}\text{U}/^{238}\text{U}$) values are around 1.146 (CHEN et al. 1986; ROBINSON et al. 2004a), one study yielded a slightly higher value (1.149 ± 0.002 , DELANGHE et al. 2002). All these values are calculated using the half-lives reported by CHENG et al. (2000).

Potential changes in palaeo seawater ($^{234}\text{U}/^{238}\text{U}$) with *time* are most likely to be induced by changes in the riverine input, and several studies used models to place limits on how much marine ($^{234}\text{U}/^{238}\text{U}$) could have changed over Late Quaternary time scales (e.g., CHEN et al. 1986; HAMELIN et al. 1991; RICHTER & TUREKIAN 1993). These studies revealed that seawater $\delta^{234}\text{U}$ should not have changed more than 10–20 ‰ compared to its modern value during the last several hundred ka. This is further confirmed by U-series analysis of U-rich slope sediments suggesting that seawater $\delta^{234}\text{U}$ remained within 15 ‰ of its modern value within the last 360 ka (HENDERSON 2002). Recent studies indicate shifts in seawater ($^{234}\text{U}/^{238}\text{U}$) at times of major glacial-interglacial transitions involving large variations in sea levels (ESAT & YOKOYAMA 2006; ROBINSON et al. 2004b), but during periods of high sea level (i.e., interglacials) seawater $\delta^{234}\text{U}$ should have been in the range of $146 \pm 10\%$.

Th generally exists as a neutral hydroxide species in the oceans and is highly insoluble. Because of its high particle reactivity, it has a distinct tendency to become incorporated in colloids or adsorbed onto particle surfaces (IVANOVICH & HARMON 1992). Thus, ^{230}Th produced by decay of ^{234}U in the water column is rapidly removed by sorption to particles, which settle from the water column. The average residence time of Th in seawater is estimated as ~ 20 a (HENDERSON & ANDERSON 2003) resulting in ($^{230}\text{Th}/^{238}\text{U}$) values that are 105 times lower than secular equilibrium (MOORE 1981).

3.2 Incorporation of U-series isotopes into reef corals

The dominant form of U in seawater is the large uranyl carbonate anion $\text{UO}_2(\text{CO}_3)_3^{4-}$, and with descending pH, the species $\text{UO}_2(\text{CO}_3)_3^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^0$ prevail. A comparison of several U substitution mechanisms showed that U incorporation into reef corals occurs most likely according to the following reaction (SHEN & DUNBAR 1995; SWART & HUBBARD 1982):



A variety of studies showed that the U/Ca ratio of scleractinian corals is controlled by the absolute U concentration of seawater (SHEN & DUNBAR 1995; SWART & HUBBARD 1982), water temperature (MIN et al. 1995; SHEN & DUNBAR 1995), coral growth rate, and coral species (CROSS & CROSS 1983). However, despite of these effects molar U/Ca ratios of surface corals are within about 30% of the seawater value of 1.3×10^{-6} (EDWARDS et al. 2003). Isotope fractionation between ^{234}U and ^{238}U seems not to occur during coral growth, which is demonstrated by the good agreement of the average $\delta^{234}\text{U}$ value measured on modern corals (i.e., 146.6 ± 1.4 ‰, DELANGHE et al. 2002) with the seawater value.

Molar $^{232}\text{Th}/^{238}\text{U}$ values of young surface corals are typically slightly lower than seawater values (CHEN et al. 1986). This shows that U and Th are not largely fractionated during aragonite formation and are incorporated into coral skeletons in their proportions in seawater. Consequently, the low ($^{230}\text{Th}/^{238}\text{U}$) activity ratio in seawater leads to close to zero initial ($^{230}\text{Th}/^{238}\text{U}$) activity ratio in corals, which is one of the basic premises for U-series dating.

3.3 Reliability of $^{230}\text{Th}/\text{U}$ -coral ages

The reliability of U-series ages of fossil reef corals depends on the validity of the two basic premises of $^{230}\text{Th}/\text{U}$ -dating. As discussed in the previous section, most reef building surface corals do not contain substantial initial ^{230}Th . Comparison of $^{230}\text{Th}/\text{U}$ -ages of corals with ages known a priori from counting of annual density bands showed that initial ^{230}Th levels are negligible in corals containing less than 100 pg/g of ^{232}Th (EDWARDS et al. 2003). ^{232}Th concentrations between several hundred and 1000 pg/g (COBB et al. 2003) or even higher (SCHOLZ et al. 2004; STIRLING et al. 1998) have been reported. However, values of this magnitude still do not result in significant shifts in $^{230}\text{Th}/\text{U}$ -ages for corals older than several ka, because the initial

^{230}Th will be negligible compared to that produced by decay of ^{234}U . Only for very young corals (i.e., younger than a few thousand years) high ^{232}Th content indicates the presence of significant levels of initial ^{230}Th and makes an appropriate correction necessary. This requires knowledge of the initial ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio. Investigation of samples with known age showed isotopic $^{230}\text{Th}/^{232}\text{Th}$ ratios between 0 and 2×10^{-5} for marine and $\sim 4 \times 10^{-6}$ for terrestrial sources (COBB et al. 2003). With these values upper and lower limits for the correction can be estimated.

The validity of the closed-system assumption is more difficult to assess. During periods of low sea level (e.g., glacial periods) most fossil reef corals were exposed to meteoric water for a substantial period of time. This bears the risk of the aragonitic coral skeletons being recrystallised to calcite by dissolution or reprecipitation processes. Because calcite was shown to incorporate much less U than aragonite (REEDER et al. 2000), such processes are supposed to be accompanied with significant loss of U. Therefore, the calcite content of fossil corals is used as an indication for post-depositional recrystallisation and should not exceed 1%. The calcite content of a coral matrix can be precisely determined by X-ray diffraction (XRD).

Another test for open-system behaviour is the comparison of the total U content of fossil corals and their modern counterparts. Numerous studies on various coral species showed that the primary U concentration ranges from 1.5 to 4 $\mu\text{g/g}$ (e.g., AMIEL et al. 1973; CROSS & CROSS 1983; GVIRTZMAN et al. 1973; SWART & HUBBARD 1982), and within one coral specimen variations of several percent are possible (MIN et al. 1995; SHEN & DUNBAR 1995). Due to the rather large variability of U concentration in modern corals the total U content can only serve as a broad indicator for open system behaviour. Nevertheless, post-depositional uptake and/or loss of U might result in substantial age bias. For example, SCHOLZ et al. (2007) presented evidence for post-depositional U redistribution in coral reefs on Barbados, which leads to a maximum age bias of 30 ka for corals

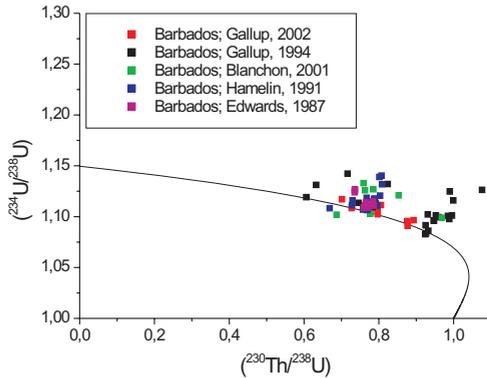


Fig. 4: A compilation of the activity ratios measured on fossil reef corals from Barbados, West Indies. The error bars are smaller than the plot-symbols. All corals are of the genus *Acropora palmata*. It is evident that most corals plot above the seawater evolution curve and, thus, have elevated initial $(^{234}\text{U}/^{238}\text{U})$. Data are taken from BLANCHON & EISENHAEUER (2001), EDWARDS et al. (1987), GALLUP et al. (2002; 1994) and HAMELIN et al. (1991).

Abb. 4 : Zusammenstellung von gemessenen Aktivitätsverhältnissen an fossilen Riffkorallen von Barbados. Die Fehlerbalken sind kleiner als die Symbole. Alle Korallen gehören zu der Gattung *Acropora palmata*. Es ist offensichtlich, dass die meisten Datenpunkte oberhalb der *seawater evolution curve* liegen und somit erhöhte $(^{234}\text{U}/^{238}\text{U})_{\text{init}}$ haben. Die Daten stammen aus BLANCHON & EISENHAEUER (2001), EDWARDS et al. (1987), GALLUP et al. (2002; 1994) und HAMELIN et al. (1991).

from Marine Isotope Stage (MIS) 6.5 (~175 ka before present). Elevated ^{232}Th can also be related to post-depositional contamination from detrital sources and, therefore, be an indication for open-system behaviour.

However, post-depositional open-system behaviour needs to be reliably identified in corals. Because corals incorporate ^{234}U and ^{238}U in the same ratio as they occur in modern seawater, the initial coral $(^{234}\text{U}/^{238}\text{U})$, which can be calculated using the $^{230}\text{Th}/\text{U}$ -age in Eq. (2), should agree with modern seawater $(^{234}\text{U}/^{238}\text{U})$. Equivalently, the $(^{230}\text{Th}/^{238}\text{U})$ and $(^{234}\text{U}/^{238}\text{U})$ activity ratios of a fossil coral should plot on the seawater evolution curve, which describes the temporal development of activity ratios

under closed-system conditions with the initial $(^{234}\text{U}/^{238}\text{U})$ of modern seawater (bold line in Fig. 3). A significant deviation of the initial $(^{234}\text{U}/^{238}\text{U})$ from the seawater value indicates open-system behaviour and the $^{230}\text{Th}/\text{U}$ -age has to be considered non-reliable.

However, the analytical precision of mass spectrometric analyses indicates that initial $(^{234}\text{U}/^{238}\text{U})$ varies significantly between different corals and that in fact most fossil reef corals display initial $(^{234}\text{U}/^{238}\text{U})$ in excess of modern seawater and recent corals (e.g., BARD et al. 1992; BARD et al. 1991; EDWARDS et al. 1987; HAMELIN et al. 1991; HENDERSON et al. 1993; KU et al. 1990) (Fig. 4).

All coral data shown in Fig. 4 correspond to past sea level highstands, i.e., MIS 5 and 7. As discussed in Section 3.1, seawater $(^{234}\text{U}/^{238}\text{U})$ should have been within 1 % of the modern value during such periods. Thus, the large variation in initial $(^{234}\text{U}/^{238}\text{U})$ of corals cannot reflect changes in the marine U isotopic composition and is a clear evidence for open-system behaviour. The fact that even samples, which are apparently pristine according to mineralogical criteria, show elevated initial $(^{234}\text{U}/^{238}\text{U})$ suggests that the isotopic system is more sensitive to post-depositional changes than any petrographic or general geochemical parameter (CHEN et al. 1991; ZHU et al. 1993). Therefore, the premise of closed-system behaviour is not generally warranted for fossil reef corals, and the accuracy of $^{230}\text{Th}/\text{U}$ -ages is more limited due to the isotopic anomalies than analytical precision (BARD et al. 1992; STIRLING et al. 1995).

To detect diagenetically altered corals, various reliability criteria were developed (e.g., compare STIRLING et al. 1998), and only $^{230}\text{Th}/\text{U}$ -ages that fulfil these criteria are believed to be *strictly* reliable:

- Initial $(^{234}\text{U}/^{238}\text{U})$ within a specific range of modern seawater $(^{234}\text{U}/^{238}\text{U})$
- U content within the range of modern analogues from the same region
- ^{232}Th concentrations lower than 1 ppb
- Calcite content lower than 1 %
- Primary aragonitic textures

An additional rigorous test for open-system behaviour is combined $^{231}\text{Pa}/\text{U}$ and $^{230}\text{Th}/\text{U}$ -dating (EDWARDS et al. 2003). The application of both dating methods to the same coral sample allows identification of isotopically altered corals, which otherwise would have passed all criteria. Recent measurements on 14 corals with initial $\delta^{234}\text{U}$ values within 8% of modern seawater from Barbados showed that six had discordant $^{231}\text{Pa}/\text{U}$ and $^{230}\text{Th}/\text{U}$ -ages (CUTLER et al. 2003; GALLUP et al. 2002). This demonstrates processes that have affected Pa, Th, and/or U, but not $\delta^{234}\text{U}$ (EDWARDS et al. 2003).

3.4 Open-system dating of fossil reef corals

Since obviously most fossil corals show evidence for post-depositional diagenesis, an approach to reliably date these corals would represent a major improvement. Therefore it is a current research focus to understand the mechanisms of coral diagenesis on U-Th isotopes and develop correction techniques for open-system dating.

Several authors have proposed diagenetic scenarios, such as post-depositional U and Th gain/loss to explain the observed isotopic anomalies in fossil reef corals (e.g., BAR-MATTHEWS et al. 1993; CHEN et al. 1991; FRUIJTIER et al. 2000; HAMELIN et al. 1991; HENDERSON et al. 1993). Most diagenetically altered fossil reef corals show elevated initial $\delta^{234}\text{U}$. Several studies detected a correlation between $\delta^{234}\text{U}$ and the $^{230}\text{Th}/\text{U}$ -age (FRUIJTIER et al. 2000; STEIN et al. 1993; ZHU et al. 1993) and also between $\delta^{234}\text{U}$ and $(^{230}\text{Th}/^{238}\text{U})$ (GALLUP et al. 1994; SCHOLZ et al. 2004; STIRLING et al. 1998; THOMPSON et al. 2003; VILLEMANT & FEUILLET 2003). Other studies, however, found no general correlations (CHEN et al. 1991).

BENDER et al. (1979) were the first who presented a diagenetic open-system model for fossil reef corals. They assumed that all corals suffered continuous addition of ^{234}U and ^{230}Th . Subsequently, KU et al. (1990) proposed a model, based on gain or loss of both ^{234}U and ^{238}U through continuous exchange with U in groundwater or soil water. GALLUP et al.

(1994) detected a rough correlation between initial $\delta^{234}\text{U}$ and $^{230}\text{Th}/\text{U}$ -age in Barbados corals. On the basis of the observed relation between $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ (Fig. 3), they modelled the diagenetic processes assuming continuous addition of ^{234}U and ^{230}Th . However, this model has two serious problems: (i) it is difficult to show that the diagenetic trends are such as described by the model when there are only a limited number of coeval corals. Furthermore, in many cases corals do not show the same diagenetic trends or no trend at all (EDWARDS et al. 2003; POTTER et al. 2004; SCHOLZ et al. 2004; SCHOLZ et al. 2007). (ii) It is not reasonable that ^{234}U and ^{230}Th should be added at similar rates because of their very different chemical behaviour (Section 2.1). In theory, the redistribution of these isotopes should rely on transport by groundwater or porewater, but the model results suggest that the different solubilities of U and Th do not play a significant role in how they are transported and deposited. GALLUP et al. (1994) proposed that the nuclides are transported on particles in the water, such as organic colloids. Many authors have proposed mechanisms to explain this problem. CHEN et al. (1991) proposed that some ^{238}U , ^{234}U , and ^{230}Th may be leached out of one part of the coral by chemical reactions and deposited onto another part. As a mechanism for ^{234}U addition they proposed that ^{234}Th as the recoil daughter nuclide of ^{238}U (Fig. 1) is likely to be hydrolysed and adsorbed onto a solid surface before decaying to ^{234}U .

More recently, three models dealing with open-system behaviour of fossil reef corals were published (SCHOLZ et al. 2004; THOMPSON et al. 2003; VILLEMANT & FEUILLET 2003). The model of VILLEMANT & FEUILLET (2003) takes into account possible initial ^{230}Th excess and continuous selective redistribution (i.e., gain and/or loss) of ^{234}U , ^{234}Th , and ^{230}Th controlled by α -recoil processes. The THOMPSON et al. (2003) model explains the positive correlation between $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ by coupled addition of particle-reactive ^{234}Th and ^{230}Th , which is produced by decay of dissolved U and α -recoil mobilisation of U daughters. In

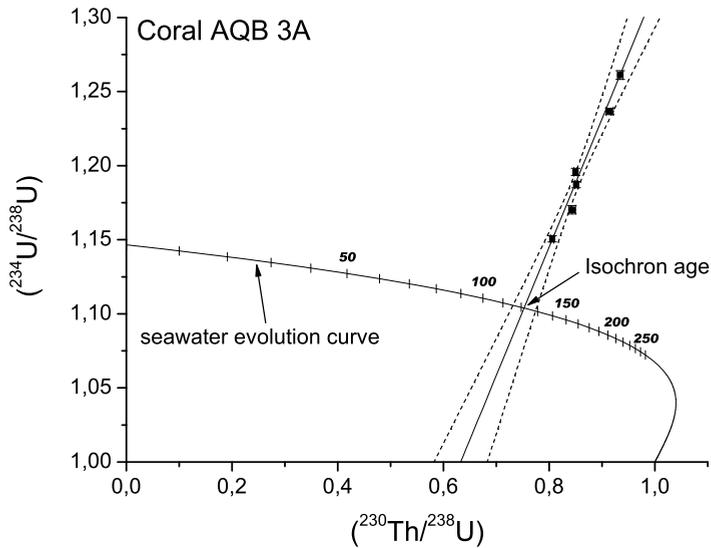


Fig. 5: (taken from SCHOLZ & MANGINI 2006): Isochron plot for coral AQB 3A from Aqaba, Jordan (SCHOLZ et al. 2004). The activity ratios measured in six different sub-samples show a high linear correlation between $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ ($R = 0.99$). The labels on the seawater evolution curve represent the corresponding $^{230}\text{Th}/\text{U}$ -ages in ka. The isochron age is calculated from the intersect of the isochron with the seawater evolution curve. The dashed curves represent confidence bands at 95% confidence level. Isochron age errors can be calculated from the intersects of the confidence bands with the seawater evolution curve.

Abb. 5: (übernommen aus SCHOLZ & MANGINI 2006): Isochronen Diagramm für Koralle AQB 3A aus Aqaba, Jordanien (SCHOLZ et al. 2004). Die Aktivitätsverhältnisse, die an sechs verschiedenen Teilproben der Koralle gemessen wurden, zeigen eine starke lineare Korrelation zwischen $(^{234}\text{U}/^{238}\text{U})$ und $(^{230}\text{Th}/^{238}\text{U})$ ($R = 0.99$). Die Beschriftungen an der *seawater evolution curve* zeigen die entsprechenden $^{230}\text{Th}/\text{U}$ -Alter in ka. Das Isochronen Alter wird aus dem Schnittpunkt der Isochrone mit der *seawater evolution curve* berechnet. Die gestrichelten Kurven sind die entsprechenden 95%-Konfidenzbänder. Der Fehler des Isochronenalters wird aus den Schnittpunkten des Konfidenzbänder mit der seawater evolution curve bestimmt.

contrast to GALLUP et al. (1994), the authors of both models suggest that their models can be used to correct $^{230}\text{Th}/\text{U}$ -ages of samples with initial $\delta^{234}\text{U}$ deviating from the modern seawater value. They term these ages *open-system ages*. Because both models assume very similar redistribution mechanisms, the calculated $^{230}\text{Th}/\text{U}$ -ages are similar. Corals that were affected by other diagenetic processes (e.g., gain/loss of U) cannot be dated because the models take only into account the described redistribution process. Thus, such corals must be rejected, e.g., by application of standard screening criteria (Section 3.3). However, there are problems with the α -recoil based models: (i)

The trends between $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ observed at different localities worldwide are not the same. In general, the data points from a given terrace are not all co-linear within analytical error, as required for an exact $^{230}\text{Th}/\text{U}$ -age correction with these models (EDWARDS et al. 2003). (ii) Impossibly large volumes of carbonate are necessary to maintain the concentration of dissolved U required to produce the isotopic anomalies observed in most fossil reef corals (THOMPSON et al. 2003).

SCHOLZ et al. (2004) proposed a different model to date diagenetically altered reef corals. They assumed that different sub-samples of an individual coral gained different amounts of

U with high ($^{234}\text{U}/^{238}\text{U}$), possibly followed by U loss proportional to U gain. This results in a linear correlation between ($^{230}\text{Th}/^{238}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$), similar to the models of THOMPSON et al. (2003) and VILLEMANT & FEUILLET (2003). In contrast to these models, however, the slope of the addition line (referred to as isochron) is not defined by the model but depends on the timing of U gain and loss, respectively, and hence, on the specific diagenetic history of the analysed coral. The isochron is obtained from a linear fit of the data on a ($^{234}\text{U}/^{238}\text{U}$) vs. ($^{230}\text{Th}/^{238}\text{U}$) diagram, and the coral isochron age is calculated from the intersect of the isochron with the seawater evolution curve (Fig. 5).

The isochron model (SCHOLZ et al. 2004) can also explain the activity ratios of fossil corals plotting below the seawater evolution curve if one assumes that the gained U has a lower ($^{234}\text{U}/^{238}\text{U}$) activity ratio than the coral. Because coral isochron dating does not account for elevated ^{232}Th and aragonite recrystallisation, prior screening with standard screening criteria is still required. The isochron age error is calculated by propagation of the uncertainties of the isochron (SCHOLZ & MANGINI 2006).

Meanwhile, the three open-system models have been applied in several studies to derive palaeoclimatic information (ANDERSEN et al. 2008; FELIS et al. 2004; FRANK et al. 2006; POTTER et al. 2004; THOMPSON & GOLDSTEIN 2005; THOMPSON & GOLDSTEIN 2006; WAELBROECK et al. 2008). However, both conventional $^{230}\text{Th}/\text{U}$ -dating and the three open-system models are associated with specific problems. For example, investigation of several sub-samples from the same coral specimen has shown that the real age uncertainty of both conventional $^{230}\text{Th}/\text{U}$ -ages and the open-system ages calculated by the THOMPSON et al. (2003) model is substantially larger than suggested by the quoted uncertainties (SCHOLZ & MANGINI 2007). In addition, the widely used „strict“ reliability criteria are not sufficient to identify all corals that were altered by other diagenetic processes than assumed by the models (SCHOLZ & MANGINI 2007). In general, all models should

only be applied to coral data, which have been demonstrated to be altered by the underlying processes. Application to published coral data may result in both wrong $^{230}\text{Th}/\text{U}$ -ages and substantial underestimation of the age uncertainty (SCHOLZ & MANGINI 2007).

After all, despite of almost 40 years of intensive examination of the U-series systematics of fossil reef corals, a number of aspects that produce the diagenetic alterations have not been satisfactorily explained so far. Thus, it has been extremely difficult to develop a general correction technique for diagenetically altered fossil reef corals, although several promising models have been proposed.

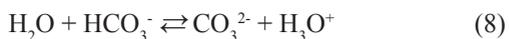
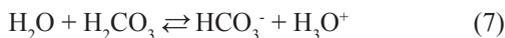
4 $^{230}\text{Th}/\text{U}$ -dating of speleothems

4.1 Growth and occurrence of speleothems

Speleothems such as stalagmites, stalactites or flowstones are secondary cave deposits and grow in karst areas in almost all parts of the world. A detailed overview of the different forms of speleothems is given e.g. by HILL & FORTI (1997). In brief, speleothem growth can be explained as follows: Meteoric water seeps through the soil above a cave and becomes enriched in CO_2 due to the high pCO_2 of the soil zone, which results from the respiration of plant roots and decay of organic material. In the soil zone pCO_2 levels can reach values of up to 100,000 ppm (McDERMOTT 2004). This results in the production of carbonic acid according to Eq. (6):



which dissociates according to Eqs. (7) and (8):



Calcium carbonate is dissolved as described by Eq. (9), when the highly corrosive percolating water comes into contact with the carbonate bedrock:



The resulting equilibrium concentration of Ca^{++} and HCO_3^- in the drip water depends on several parameters such as temperature, pCO_2 and whether dissolution occurs in a closed or an open system (KAUFMANN 2003; McDERMOTT 2004). The pCO_2 of cave air is usually higher than atmospheric pCO_2 but, depending of the degree of cave ventilation, much lower than in the soil zone. Thus, the CO_2 dissolved in the water entering the cave degases to the cave atmosphere. The drip water becomes supersaturated with respect to calcite, and CaCO_3 precipitates forming speleothems.

Stalagmite growth was first quantitatively described by DREYBRODT (1988; 1999). More recently, several models were developed describing the growth rate and shape of stalagmites depending on cave temperature, drip rate, pCO_2 of both the soil zone and the cave and also the mixing parameter, which accounts for mixing of the impinging drop with the existing solution film on top of the stalagmite (KAUFMANN 2003; MÜHLINGHAUS et al. 2007; ROMANOV et al. 2008b).

4.2 U incorporation into speleothems

Dissolution of the carbonate bedrock above the cave also results in accumulation of traces of several elements in the drip water, such as Mg, Sr, Ba and also U. Their concentration in the drip water mainly depends on their concentration in the host rock and the corresponding partitioning coefficient. The trace elements are then co-precipitated with speleothem calcite. Thus, the U-concentration in speleothems ranges from near zero to more than $100 \mu\text{g/g}$ (FORD & WILLIAMS 2007).

The U and Th isotopes, which are relevant for $^{230}\text{Th}/\text{U}$ -dating (Fig. 1, Section 2.2), are in secular equilibrium in the host rock (Fig. 2) because the karst bedrock usually has an age of several million years. However, due to the different geochemical behaviour of U and Th (Section 2.1) the activity ratios established in the percolating cave drip water are substantially different from secular equilibrium. Th is insoluble in natural water and, thus, the

($^{230}\text{Th}/^{238}\text{U}$) of drip water is zero - one of the basic premises for $^{230}\text{Th}/\text{U}$ -dating. In contrast, the ($^{234}\text{U}/^{238}\text{U}$) of drip water is usually larger than secular equilibrium due to the preferential leaching of ^{234}U resulting from α -recoil (Section 2.1), unless the host rock is already depleted in ^{234}U . The ($^{234}\text{U}/^{238}\text{U}$) of drip water depends on (i) the age of the bedrock and (ii) the time available for the dissolution of the bedrock. In theory, slowly percolating water and, thus, a long residence time should result in high drip water ($^{234}\text{U}/^{238}\text{U}$). In contrast, high rainfall events and, as a consequence, fast percolating waters and, thus, a short residence time should result in ($^{234}\text{U}/^{238}\text{U}$) close to secular equilibrium. However, unambiguous interpretation of ($^{234}\text{U}/^{238}\text{U}$) and quantification of the responsible processes remain difficult (PORCELLI & SWARZENSKI 2003). In any case, drip water ($^{234}\text{U}/^{238}\text{U}$) can vary substantially for different cave systems and is also usually not constant in time for an individual cave. Thus, there is no uniform initial ($^{234}\text{U}/^{238}\text{U}$) for speleothems like e.g. for marine carbonates, such as reef corals (Section 3). This does not affect the application of $^{230}\text{Th}/\text{U}$ -dating to speleothems because the initial ($^{234}\text{U}/^{238}\text{U}$) is not needed for the age calculation (Eq. 3).

4.3 Reliability of speleothem $^{230}\text{Th}/\text{U}$ -ages

Again, the speleothem sample has to meet the two basic premises of $^{230}\text{Th}/\text{U}$ -dating. The validity of the first assumption (i.e., no initial ^{230}Th) is usually assessed by measuring the concentration of detrital ^{232}Th . The second assumption is more difficult to verify. As mentioned in the previous section, there is no general initial ($^{234}\text{U}/^{238}\text{U}$) as for marine carbonates, which could be used as a reliability criterion. However, due to their natural occurrence in caves speleothems are not as exposed to meteoric waters as e.g. reef corals. Thus, even very old stalagmites are usually very well preserved and show no evidence for post-depositional diagenesis (WOODHEAD et al. 2006).

However, violation of one of the basic premises cannot be a priori excluded and the reliability of $^{230}\text{Th}/\text{U}$ ages needs to be assessed. Initial ^{230}Th

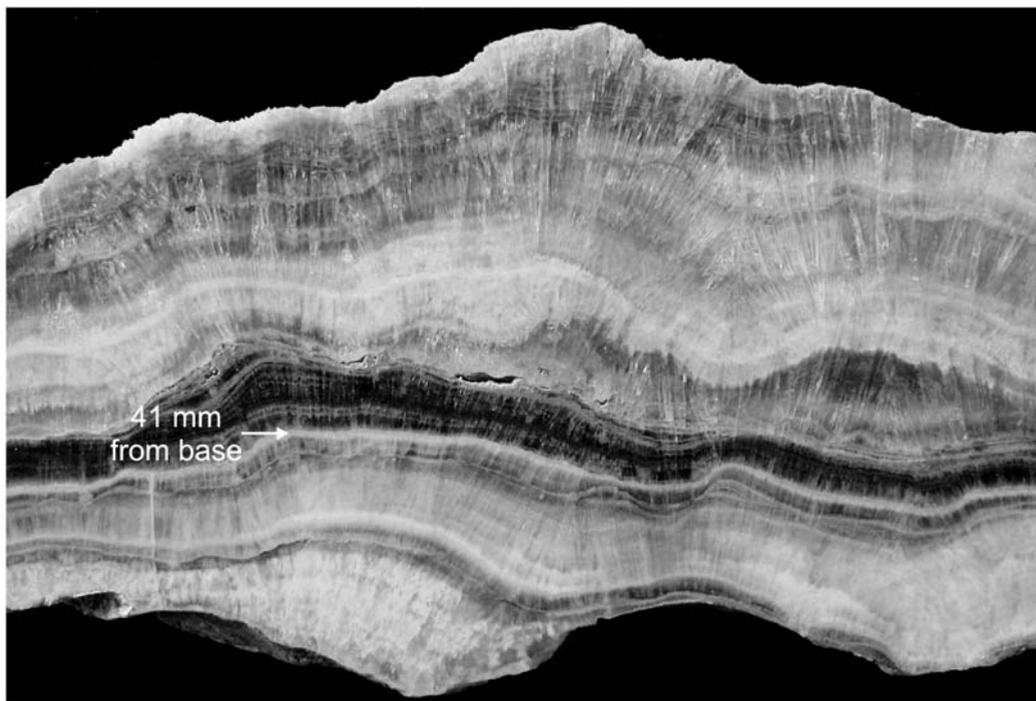


Fig. 6: Flowstone SPA 59 from Spannagel cave, Austrian Alps. There are clearly visible distinct growth layers. The chronology of SPA 59 is shown in Fig. 7. The picture was provided by C. Spötl.

Abb. 6: Flowstone SPA 59 aus der Spannagel Höhle in den österreichischen Alpen. Unterschiedliche Wachstumslagen sind sehr gut zu erkennen. Das Altersmodell für SPA 59 ist in Abb. 7 dargestellt. Das Foto wurde von C. Spötl zur Verfügung gestellt.

(i.e., not produced by in situ decay of ^{234}U and ^{238}U in the sample) is generally accompanied by a larger amount of ^{232}Th because the $^{230}\text{Th}/^{232}\text{Th}$ isotope ratio in most crustal materials is around 5×10^{-6} (WEDEPOHL 1995). For $^{230}\text{Th}/\text{U}$ -dating the ^{232}Th concentration of a sample is routinely also measured in addition to the isotopes required for the age calculation (Section 2.3). Samples containing more than an acceptable value of initial ^{230}Th can be identified based on the assumption that detrital ^{232}Th is accompanied by ^{230}Th in a defined ratio. However, it is not possible to correct the measured ($^{230}\text{Th}/^{238}\text{U}$) using a universally applicable ($^{230}\text{Th}/^{232}\text{Th}$) ratio because this ratio varies substantially in possible detrital source materials. Two correction procedures were suggested: (i) correction for detrital contamination using an a priori estimate of the isotopic composition of the detrital phase and the corresponding

uncertainty (HELLSTROM 2006; LUDWIG 2003), and (ii) direct determination of the isotopic composition of the detrital phase using isochron techniques (BECK et al. 2001; LUDWIG 2003; LUDWIG & TITTERINGTON 1994). The $^{230}\text{Th}/\text{U}$ -ages of speleothems with ($^{230}\text{Th}/^{232}\text{Th}$) within a range that indicates significant Th contamination (i.e., ($^{230}\text{Th}/^{232}\text{Th}$) $< 100 - 300$, RICHARDS & DORALE 2003) should either be corrected for the effect of contamination or rejected (HELLSTROM 2006). A criterion to test the reliability of the $^{230}\text{Th}/\text{U}$ -ages of speleothems is that the ages must be in stratigraphic order. Basically, the $^{230}\text{Th}/\text{U}$ -age of the upper layers must be younger than that of those below because stalagmites grow from the bottom up depositing growth layers (KAUFMANN 2003; MÜHLINGHAUS et al. 2007; ROMANOV et al. 2008b) (Fig. 6). Thus, the ages down the growth axis of a stalagmite must

become progressively older. Age inversions of dated layers, i.e., a $^{230}\text{Th}/\text{U}$ -age of a sub-sample that is significantly older or younger than suggested by the stratigraphy, indicate that at least one of the determined ages is wrong. This may have several reasons: (i) Post-depositional open-system behaviour, i.e., violation of the closed-system assumption, (ii) inadequate correction for detrital contamination, (iii) underestimation of the age uncertainty resulting either from the analysis itself or the applied correction for contamination, or (iv) a mistake during the analysis or the sample preparation. In any case, age inversions have to be cross-checked by analysis of additional samples from the same horizon. Otherwise, they must be accounted for by assigning the corresponding ages with an appropriately enlarged age uncertainty.

4.4 Speleothem age-distance model

To determine the age of a stalagmite at the depths of the proxy measurements, an age model is constructed, which mathematically describes the relationship between the distance from the top/bottom of the stalagmite and the age of the stalagmite. However, although an increasing number of papers presenting high precision $^{230}\text{Th}/\text{U}$ ages of speleothems were published in the last decade, a standard approach to derive an age model on the basis of the measured ages (compare Fig. 6) has not been established yet. Some authors use linear interpolation of the $^{230}\text{Th}/\text{U}$ -ages between the depth of the dated samples (WANG et al. 2005), others apply least squares polynomial fits (SPÖTL & MANGINI 2002). Other studies, in turn, apply various kinds of smoothing splines (SPÖTL et al. 2006; VÖLLWEILER et al. 2006) or even more sophisticated methods (DRYSDALE et al. 2005; DRYSDALE et al. 2004; GENTY et al. 2006) based on the general growth systematics of speleothems (KAUFMANN 2003). The age model is crucial because the timing or duration determined for a specific event, e.g., indicated by a peak in a stable isotope curve, depends on the method used to calculate the age model. This is especially problematic because $^{230}\text{Th}/\text{U}$ -dating

is usually not performed at the depth of the corresponding peak. Thus, a generalised method to construct speleothem age models is desirable, which would not only guarantee the comparability of stalagmite records from different laboratories but also make the most efficient use of the U-series ages. A general approach to estimate the uncertainty of stalagmite age models is also needed (DRYSDALE et al. 2004; GENTY et al. 2006; HEEGAARD et al. 2005; SPÖTL et al. 2006).

4.5 $^{230}\text{Th}/\text{U}$ -dating of speleothems and palaeoclimate reconstruction

The chronology of speleothem growth provides important palaeoclimatic information. For example, the timing of speleothem growth itself is related to the climatic conditions above the cave. In cold and/or dry environments even a slight cooling/drying may result in a cessation of speleothem growth (HOLZKÄMPER et al. 2004; HOLZKÄMPER et al. 2005; SPÖTL et al. 2006). Timing of speleothem formation can also be related to global climate and sea level changes (BARD et al. 2002; RICHARDS et al. 1994). Speleothems found in submerged caves indicate that the caves were not flooded at some time in the past because speleothems only form when the cave is air filled. Therefore, in tectonically stable regions the timing of the growth of speleothems collected from submerged caves unambiguously indicates that the cave was above sea level and constrains times of lower sea levels.

Furthermore, the speleothem growth rate is related to precipitation intensity, temperature and vegetation cover above the cave, which in turn is related to climate (DRYSDALE et al. 2005; DRYSDALE et al. 2004; McDERMOTT 2004; MÜHLINGHAUS et al. 2007).

An accurate and precise chronology is essential for using speleothems as palaeoclimate archives. Speleothems provide numerous proxies of palaeoclimate, which can be measured with very high spatial resolution (HENDERSON 2006). Most palaeoclimate studies using speleothems apply precisely dated high-resolution stable isotope profiles (i.e., $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$), which have contributed much information to the un-

derstanding of the climate system within the last decade (BAKER et al. 2007; CRUZ JR et al. 2005; DRYSDALE et al. 2005; FLEITMANN et al. 2003; GENTY et al. 2003; HOLZKÄMPER et al. 2004; MANGINI et al. 2005; NEFF et al. 2001; NIGGEMANN et al. 2003b; NIGGEMANN et al. 2003a; PARTIN et al. 2007; SPÖTL & MANGINI 2002; SPÖTL et al. 2002; WANG et al. 2004; WANG et al. 2005; ZANCHETTA et al. 2007). The $\delta^{13}\text{C}$ signal recorded in speleothems depends on several parameters both in the soil zone and in the cave (McDERMOTT 2004) and is, therefore, complicated to interpret. However, the understanding of the effects influencing stalagmite $\delta^{13}\text{C}$ has improved in recent years (MICKLER et al. 2004; MICKLER et al. 2006; MÜHLINGHAUS et al. 2007; ROMANOV et al. 2008a). In combination with a thorough monitoring of the studied

cave system the application of $\delta^{13}\text{C}$ for palaeoclimate reconstruction is possible (BAR-MATTHEWS et al. 2000; DRYSDALE et al. 2004; FRISIA et al. 2006; GENTY et al. 2006; GENTY et al. 2003; MÜHLINGHAUS et al. 2007). High resolution trace element profiles may reveal variation in precipitation intensity (HUANG & FAIRCHILD 2001; JOHNSON et al. 2006; ROBERTS et al. 1998; TREBLE et al. 2003; VERHEYDEN et al. 2000).

4.6 $^{230}\text{Th}/\text{U}$ -dating of speleothem SPA 59

We present a case study of $^{230}\text{Th}/\text{U}$ -dating of a flow stone (SPA 59) collected in the Spannagel cave, Austrian Alps. The present mean annual temperature in the cave is around 2°C and, thus, just above the freezing point. Since speleothems do not form below this point, periods of speleo-

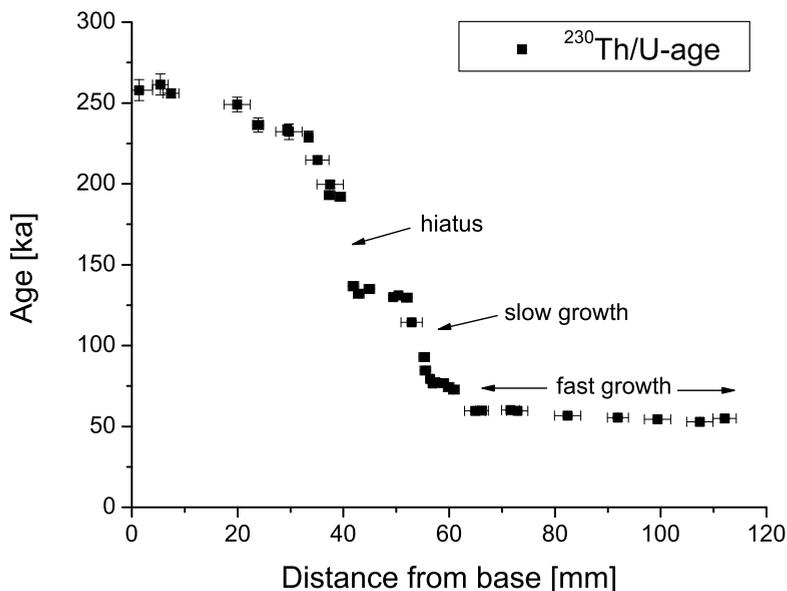


Fig. 7: TIMS $^{230}\text{Th}/\text{U}$ -dating results for flowstone SPA 59 from Spannagel cave (modified after HOLZKÄMPER et al. 2005). The speleothem grew in several phases between 50 and 270 ka, which correspond to interglacials as defined in the SPECMAP chronology (IMBRIE et al. 1984). Periods of fast and slow growth, respectively, as well as a longer hiatus between ~ 140 and ~ 190 ka are indicated.

Abb. 7: TIMS $^{230}\text{Th}/\text{U}$ -Datierungsergebnisse für Flowstone SPA 59 aus der Spannagel Höhle (geändert nach HOLZKÄMPER et al. 2005). Dieser Speläothem wuchs in mehreren Phasen zwischen 50 und 270 ka, die entsprechenden Interglazialen in der SPECMAP Chronologie zugeordnet werden können (IMBRIE et al. 1984). Phasen schnellen bzw. langsamen Wachstums sowie ein längerer Hiatus zwischen 140 und 190 ka sind eingezeichnet.

them formation correspond to past warm phases (HOLZKÄMPER et al. 2005; SPÖTL et al. 2007). Thus, the timing of the beginning and end of speleothem growth, respectively, is of particular interest. A chronology based on TIMS $^{230}\text{Th}/\text{U}$ -dating of SPA 59 was previously published by HOLZKÄMPER et al. (2005). More recently a high spatial resolution MC-ICPMS $^{230}\text{Th}/\text{U}$ -dating study of the hiatus between MIS 7 and 5 was performed by HOFFMANN et al. (submitted).

The spatial resolution of $^{230}\text{Th}/\text{U}$ dating that can be achieved depends on the sampling as well as the mass spectrometry technique that is used. There is a variety of different techniques to obtain sub-samples from speleothems. Usually a stalagmite is cut in two halves along the growth axis and the surface is then polished to identify growth layers. Samples for $^{230}\text{Th}/\text{U}$ -dating can be taken from a growth layer by a handheld drill. A disadvantage of this sampling technique is that the obtained powders are prone to contamination and cannot be cleaned prior to chemical treatment. Another possibility is to cut slices from the speleothem and then cut subsamples, e.g., using a band saw. The obtained solid pieces of carbonate can be chemically cleaned prior to further analytical work. This technique, however, is more destructive than using a handheld drill.

Fig. 6 shows the section of flowstone SPA 59 from Spannagel cave, Austrian Alps, analysed by HOLZKÄMPER et al. (2005). The corresponding TIMS $^{230}\text{Th}/\text{U}$ -dating results, based on 37 analyses along the 11 cm of growth are presented in Fig. 7. TIMS results were obtained on sample sizes between 50 and 200 mg, which were sampled using a band saw. The flowstone formed between 260 and 55 ka, mostly during the warm phases of Marine Isotope Stages (MIS) 7, 5 and 3. There are substantial differences in growth rates, with fast growth around 250, 135 and 55 ka. In contrast growth was very slow between 125 and 75 ka. Furthermore, there is a distinct 55 ka long hiatus between 190 and 135 ka.

SPA 59 has an exceptionally high U concentration (between 10 and 168 $\mu\text{g}/\text{g}$, HOLZKÄMPER et al. 2005) allowing the use of samples smaller

than 1 mg for MC-ICPMS analysis. Hence, $^{230}\text{Th}/\text{U}$ -dating can be performed at very high spatial resolution. HOFFMANN et al. (submitted) cut a 1 mm thick sample slice off the flowstone section previously analysed by HOLZKÄMPER et al. (2005) for high spatial resolution MC-ICPMS $^{230}\text{Th}/\text{U}$ dating. Six carbonate pieces of 0.5 – 1 mg were then cut from SPA 59 between 39 and 44 mm from the base at a spatial resolution of 0.8 mm using a diamond coated wire saw (Fig. 8). The sample pieces were cleaned by ultrasonication in ultra-pure water to remove potential surface contamination or residuals from the cutting process. The dried small pieces were stripped off the section with a razorblade and weighed before processing through U and Th separation and purification chemistry and MC-ICPMS analysis (HOFFMANN 2008). Fig. 9 shows the high resolution dating results in comparison with the previous TIMS chronology. The dating results agree well both below and above a white layer at the position of the hiatus indicated in Fig. 7, though the data were obtained in two different laboratories using different spikes and mass spectrometric techniques. However, the higher spatial resolution obtained using MC-ICPMS shows a dating problem associated with the white layer according to the stratigraphy criterion. Samples taken from the white layer are not in stratigraphic order. The $^{230}\text{Th}/\text{U}$ -age at 40 mm from base is apparently too old and another sample, taken at 41 mm, is out of range for $^{230}\text{Th}/\text{U}$ dating (Fig. 9). This indicates U loss, which is supported by lower U concentration in the white area (39 and 13 $\mu\text{g}/\text{g}$, respectively) compared to the clear and dense crystal below and above the white layer (64 and 134 $\mu\text{g}/\text{g}$, respectively). Thus, this section cannot be reliably dated by the $^{230}\text{Th}/\text{U}$ -method. The problem was not recognised in the study of HOLZKÄMPER et al. (2005) because they used larger sample sizes and TIMS.

Current research is concerned with MC-ICPMS $^{230}\text{Th}/\text{U}$ dating of microsamples, e.g., using a micromill or the laser ablation technique to further increase spatial resolution. Microsamples of SPA 59 with masses of about 0.09 - 0.1 mg can be prepared using a micromill. Micromill sam-

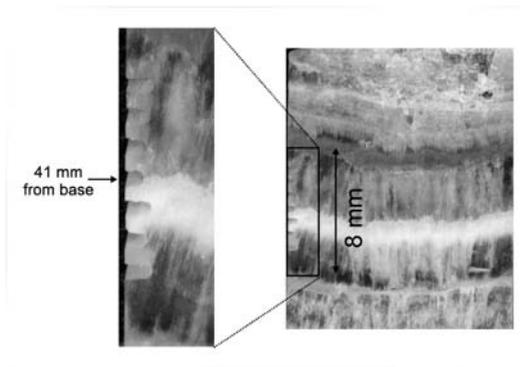


Fig. 8: A 1 mm thick slice of flowstone SPA 59. The white layer in the middle is at 41 mm from base at the position of the hiatus between MIS 7 and MIS 5. Six samples of a weight of about 1 mg were cut using a wire saw. The wire saw cuts are shown in the enlarged section. The small pieces between the cuts were stripped off and analysed for U-Th using MC-ICPMS.

Abb. 8: 1 mm dicke Scheibe von Flowstone SPA 59. Die weiße Lage in der Mitte befindet sich in 41 mm Abstand von der Basis in der Position der Wachstumsunterbrechung zwischen MIS 7 und MIS 5. Mit einer Drahtsäge wurden sechs Proben von ca. 1 mg herausgesägt. Die Schnitte der Säge sind in der vergrößerten Darstellung zu sehen. Die kleinen Karbonatstücke zwischen den Schnitten wurden entnommen und mittels MC-ICPMS auf ihren U- und Th-Gehalt untersucht.

pling procedures for $^{230}\text{Th}/\text{U}$ -dating are similar to those outlined in CHARLIER et al. (2006) for Sr isotope measurements (HOFFMANN et al. submitted). The laser ablation (LA) technique allows fast and direct $^{230}\text{Th}/\text{U}$ dating of speleothems without prior chemical separation at a spatial resolution of a few hundred μm . The precision of LA-MC-ICPMS can be similar to alpha spectrometry with samples sizes orders of magnitudes smaller (HOFFMANN et al. submitted).

5 Conclusions

Both fossil reef corals and speleothems are important archives of the climate of the past and can be reliably dated using U-series disequilibrium methods. The dating range of the $^{230}\text{Th}/\text{U}$ -method is between 500 and 600 ka depending

on both analytical precision and initial ($^{234}\text{U}/^{238}\text{U}$). Using state of the art mass spectrometric techniques such as TIMS and MC-ICPMS, accurate and very precise ages can be obtained. However, several criteria must be fulfilled to obtain reliable ages.

Most fossil corals show evidence for post-depositional diagenetic alteration, which is an indication for open-system behaviour. There have been several reliability criteria established to identify unaltered corals, but these are not able to detect all altered corals (SCHOLZ & MANGINI 2007). Several open-system dating models have been developed to calculate reliable ages from altered corals (SCHOLZ et al. 2004; THOMPSON et al. 2003; VILLEMANT & FEUILLET 2003), but each model is associated with specific problems and should only be applied if the underlying assumptions are valid (SCHOLZ & MANGINI 2007). The understanding of the mechanisms of coral diagenesis and the development of appropriate correction approaches is a major goal of current research.

Most speleothems show no evidence for post-depositional open-system behaviour but some may contain significant amounts of initial ^{230}Th , indicated by elevated ^{232}Th content. There are two correction approaches available to account for detrital contamination: (i) Direct determination of the isotopic composition of the detrital phase using isochron techniques or (ii) correction using an a priori estimate of the $^{230}\text{Th}/^{232}\text{Th}$ composition of the detrital phase with the corresponding uncertainty. The application of both approaches results in increased age uncertainty. Although an increasing number of speleothem studies with high precision $^{230}\text{Th}/\text{U}$ dating have been published in the last decade, a standard approach for the derivation of an age model on the basis of the determined ages has not been established yet. This is one of the goals of current research concerning $^{230}\text{Th}/\text{U}$ -dating of speleothems. Very high spatial resolution dating using laser ablation and micromill techniques with precisions comparable to alpha spectrometry are currently being developed (HOFFMANN 2008; HOFFMANN et al. submitted).

If the above mentioned criteria are met, it is

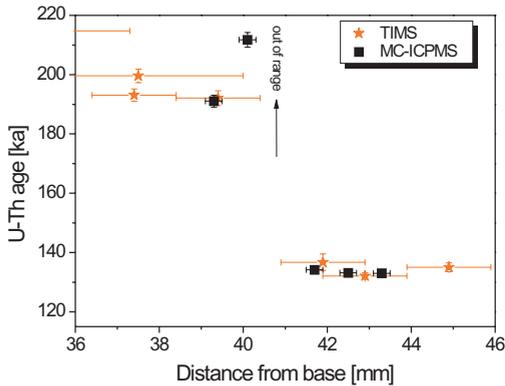


Fig. 9: TIMS and MC-ICPMS $^{230}\text{Th}/\text{U}$ -dating results for SPA 59. Below and above the white layer the results are in good agreement. However, sub-samples taken from the white layer are not in stratigraphic order indicating U loss.

Abb. 9: Ergebnisse der TIMS bzw. MC-ICPMS $^{230}\text{Th}/\text{U}$ -Datierung von SPA 59. Oberhalb und unterhalb der weißen Lage stimmen die Ergebnisse beider Methoden gut überein. Proben, die aus der weißen Lage entnommen wurden, stimmen nicht mit der Stratigraphie überein, was ein Anzeichen für nachträglichen U Verlust ist.

possible to derive very accurate and precise $^{230}\text{Th}/\text{U}$ -ages of both reef corals and speleothems. Their accuracy depends on several factors, such as the accuracy of the spike calibration and the correction of instrumental biases.

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