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Uranium-series and radiocarbon dating of speleothems – methods and limitations

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ABSTRACT:

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^{14}C ages of speleothems are usually younger than the Uranium-Series ages. The difference is often explained by changes of atmospheric radiocarbon concentration in the past, and in fact, speleothems have been used as a material for radiocarbon time scale calibration. However in other works large spread of data points has been obtained. Comparison with the ^{14}C calibration data suggests that many ^{14}C of speleothems ages are too young or the Uranium-Series ages too old. ^{14}C dates of speleothems are commonly treated with caution, because of the reservoir effect, producing an apparent age, which is usually not accurately known. However, the reservoir effect may be of minor importance when compared to contamination with younger carbon.

Key words: Uranium-Series dating, Radiocarbon Dating, Speleothems, Geochronology.

INTRODUCTION

For time measurement we need a special instrument – a clock. If we want to use any particular process for geological time determination we must know initial state – "zero point" and a function describing dependence of the investigated process on time – time scale. The uncertainties of these estimations determine the error of time estimation.

For dating of speleothems one uses a U-Series clock and sometimes radiocarbon clock. For both of these clocks we should know possible sources of errors of the zero point and time scale estimations.

METHODS OF SPELEOTHEMS DATING

In the literature, one can find results of speleothem dating obtained by means of several different methods. The most commonly used is the uranium-thorium method. For speleothems, radiocarbon (^{14}C), thermoluminescence (TL) and electron spin resonance (ESR) methods are applicable, too.

Uranium-thorium method

Uranium series disequilibrium dating of speleothems is based on the fact that various nuclides of the ^{238}U series behave differently in meteoric weathering systems (Text-fig. 1). Isotopes of Uranium are easily mobilised as $(UO_2)^{2+}$ (often as a carbonate complex), while Thorium becomes adsorbed onto clay minerals. In consequence, a speleothem contains ^{238}U and ^{234}U and is essentially free from their daughter nuclide, ^{230}Th. After deposition, ^{230}Th is formed by disintegration of ^{234}U, and the U-Series approaches radiogenic equilibrium.

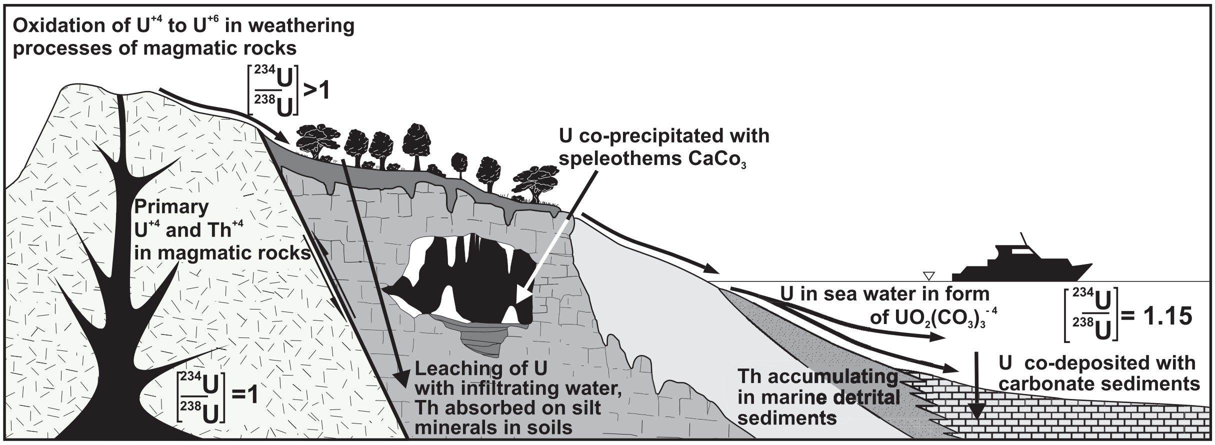

Fig. 1. Simplified scheme of Uranium and Thorium circulation in hypergenic processes (after HERCMAN 2000)

In this way, the ^{230}Th-^{234}U disequilibrium method determines the time since the calcite formation. However, the reliability of this method is based on three assumptions: (1) initial conditions are well defined (*i.e.* the sample must have been free from ^{230}Th at the moment of deposition); (2) the sample must have behaved as a geochemically closed system since deposition; (3) the sample contains sufficient Uranium for analysis of nuclide concentrations.

The first assumption is fulfilled only when the sample is free from detrital admixtures. Detrital particles contain both ^{230}Th and ^{232}Th, so that contamination can be detected by the appearance of the ^{232}Th peak in the Thorium spectra. Within the analytical precision that is available with α-spectrometry technique, contamination <5 % (*i.e.* ^{230}Th/^{232}Th>=20) has no significant effect on the determined age, and therefore can be neglected. However, for the ^{230}Th/^{232}Th ratios distinctly lower than 20, the amount of ^{230}Th that was brought into the sample at t=0 must be taken into account, and the age corrected appropriately. This can be done in several ways (see IVANOVICH & HARMON 1982, SCHWARCZ & LATHAM 1989, PRZYBYŁOWICZ & *al.* 1991). As no physical means is available to separate completely the detritus from the carbonate matrix, it is necessary to find a good chemical procedure to correct for this detrital component.

The widely used correction procedure is to assume a constant of ^{230}Th/^{232}Th ratio in the detritus, and to subtract ^{230}Th equivalent to the product of this ratio and the sample ^{232}Th activity. Authors usually take this constant between 1.5 and 2.

A much better method is the isochron method (OSMOND & *al*. 1970, KU & LIANG 1984, SCHWARCZ & LATHAM 1989). In this method one uses isotope data obtained from the leachates of several samples, which are believed to contain different proportions of a single type of authigenic carbonate and a single type of detritus. The results of independent analysis of all of the sub-samples are used for construction of isochrones. Basing on the isochrones, corrected ^{230}Th/^{234}U and ^{234}U/^{238}U activity ratios are determined.

The assumption (2) is usually satisfied for non-porous, macro-crystalline speleothems, which are the most suitable materials for dating.

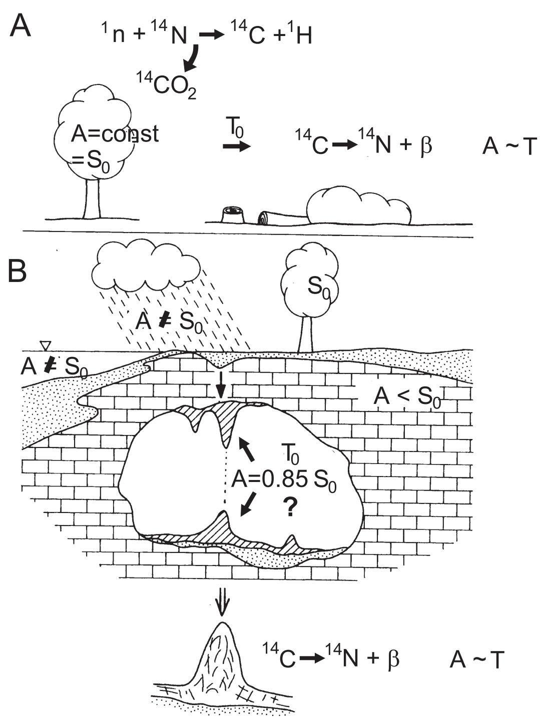

Fig. 2. Simplified illustration of fundamentals of radiocarbon dating of terrestrial organisms (A) and speleothems (B) (after HERCMAN 2000)

Radiocarbon method

Dating of speleothems by means of the ^{14}C technique was introduced in the early years of the application of the radiocarbon method. An obvious question in the dating of speleothems and other carbonates precipitated from bicarbonates dissolved in groundwater, concerns knowledge of the initial ^{14}C concentration (Text-fig. 2). It has been shown by several authors that this value might be assumed to be equal to *ca.* 85 % of the ^{14}C concentration in contemporary land vegetation (of the so-called 'modern carbon'; BASTIN & GEWELT 1986, GEWELT 1985, TALMA & VOGEL 1992). Actually, initial ^{14}C concentration in speleothems ranges from 50 % to more than 100 % of modern carbon (GEWELT 1986, GEYH & HENNING 1986, HERCMAN 1991). The ^{14}C activity in the sample must then be corrected for the initial ^{14}C activity of the speleothem, which differs significantly from that of the standard of modern carbon. This effect is known as the 'reservoir effect', and it results in the so-called 'apparent age' of the speleothems and other freshwater calcite samples.

COMPARISON OF DATING RESULTS

Results of speleothem dating, obtained with the U-series and ^{14}C methods, differ significantly from each other.

Usually ^{14}C ages of speleothems are younger than the U-Series ages. Several authors (e.g. VOGEL 1983, VOGEL & KRONFELD 1997) explained the difference by changes of atmospheric radiocarbon concentration in the past, and in fact, used speleothems as a material for radiocarbon time scale calibration. However, in other studies (e.g. HOLMGREN & *al*. 1994, GOSLAR & *al*. 2000) a large spread of data points has been obtained. Comparison with the ^{14}C calibration data suggests that

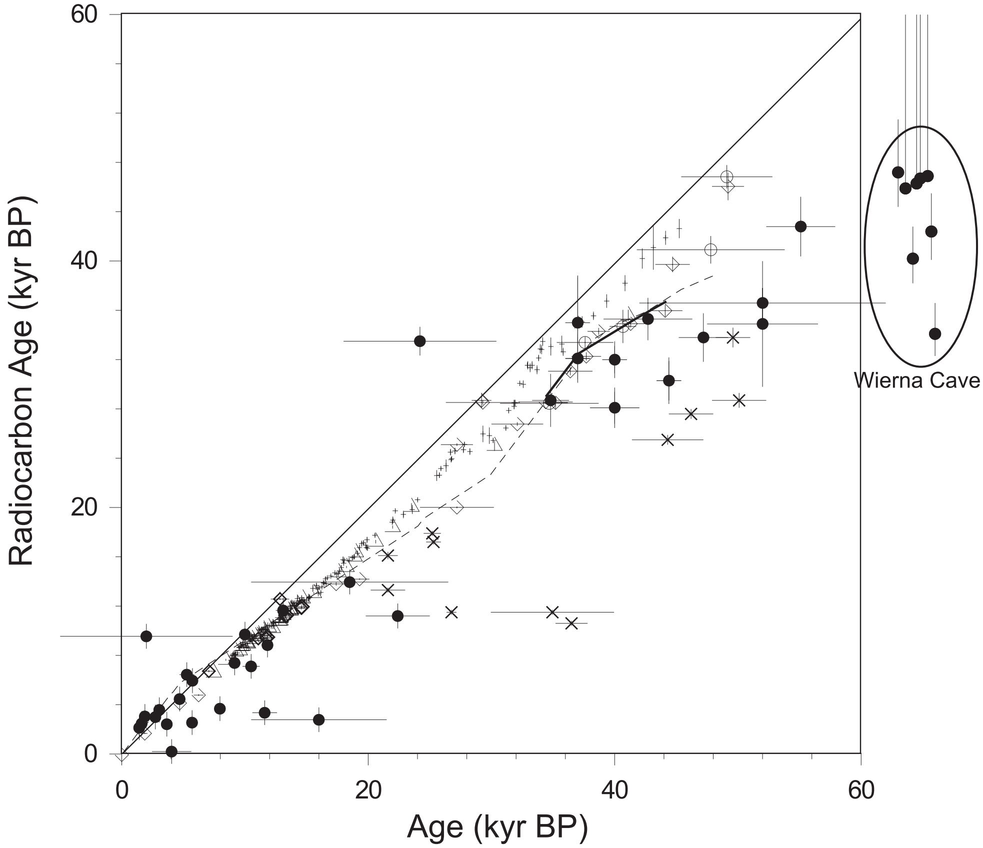

Fig. 3. Comparison of pairs of ^{14}C and U-series dates of speleothems: open circles (GOSLAR & *al.* 2000), black triangles (VOGEL 1983, VOGEL & KRONFELD 1997), crosses (HOLMGREN & *al.* 1994) and corals (open squares: BARD & *al*. 1990, 1993). Black circles at the right side of graph represent the results of dating of stalagmite from Wierna Cave (see text). Thick line: transfer function of radiocarbon time scale obtained from comparison of frequency distribution of ^{14}C and U-series ages (after GOSLAR & *al*. 2000)

many ^{14}C ages are too young or U-Series ages too old. It is necessary to look for the possible source of this effect (Text-fig. 3).

Zero point estimation error

Radiocarbon dates of speleothems are obviously affected by the 'reservoir effect', because the ^{14}C in precipitating speleothems is diluted with the ^{14}C-free carbon from leached carbonate rocks. Therefore, the radiocarbon age of the speleothem is greater than that of organisms deriving carbon from the atmosphere, by the so-called 'apparent age'. In the range of the ^{14}C calibration curve, the dilution factor can be assessed when the absolute age of speleothem is known. Recent compilation of bibliographic data (GENTY & MASSAULT 1997) suggests that the dilution factors range between 0.71 and 0.91 (corresponding to apparent ages between 700 and 2700 years), with a mean value of about 0.81 (apparent age of 1700 years). In our collection, a reasonable value of apparent age is shown by the speleothem from the Slobody Cave, which is fairly constant throughont the Holocene (between 2300 and 2700 years). However, for most of samples the reservoir age is not known exactly, and for the correction of ^{14}C age one usually assumes a value between 1000 and 2000 years.

Another problem is that the ^{14}C concentration in the atmosphere itself was not constant. The relationship between calendar and ^{14}C ages of "atmospheric" samples, (^{14}C calibration curve) was recognised long ago for the Holocene (STUIVER 1993). In recent years great improvement in radiocarbon calibration beyond the Holocene has been obtained (STUIVER & VAN DER PLICHT 1998).

For the U-Series method the zero point error is connected with the content of detrital Thorium, which is not produced from the decay of ^{234}U in the speleothem. Age correction for initial Thorium content is routinely performed by its subtraction from the measured total ^{230}Th (if the $^{230}Th/^{232}Th$ activity ratio is <20). The content of initial ^{230}Th is determined through the measurement of ^{232}Th activity, with the assumption of a known $^{230}Th/^{232}Th$ activity ratio in the detrital contamination. That ratio is, however, not known exactly, and based on a compilation of bibliographic data, it is usually assumed between 1 and 2. A better approach is to use a isochrone method, but it needs much more material than standard analysis (a minimum of 5-6 points should be used for isochrone construction). Recent work (WHITEHEAD & *al.* 1999) suggests that the initial Thorium content gives tinitial apparent age of 2000-2500 years.

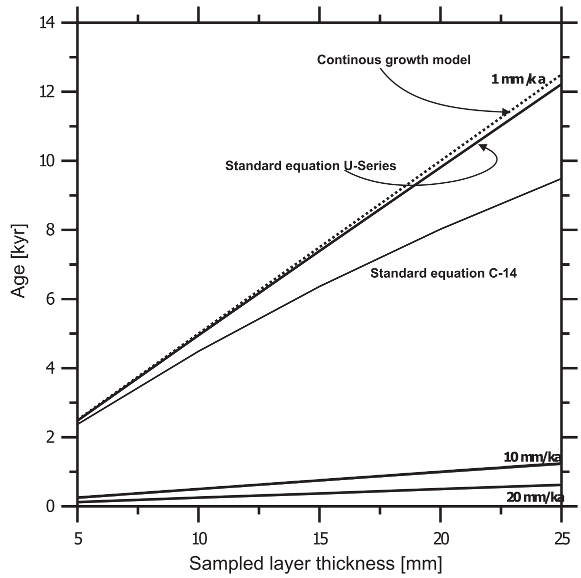

Fig. 4. Influence of growth rate on Uranium-Series and Radiocarbon dating results (calculations for youngest layer of speleothem) for growth rate 1, 10 and 20 mm per thousand years. Thick lines: standard U-Series and ^{14}C equations. Dotted line: continuous growth model (for growth rate 10 and 20 mm/kyrs the lines for different models overlay one another)

Time scale estimation errors

Two types of uncertainties occur in the estimation of function describing the time dependence of any process. The first one is not exact knowledge of function parameters. Decay constants are known with limited accuracy and the processes of radioactive decay are stochastic.

Even more important are the uncertainties of second type, because sometimes it is difficult to estimate their magnitude. These are all of the mechanisms, that influence or disturb the process used for time determination.

One of these problems is the time of speleothem growth. For measurement of isotopic ratios we take a speleothem layer that is several millimetres thick. The time of its growth may be long, depending on the growth rate. Usually the date is treated as the mean age of the layer (= the age of the middle point). However the functions, that describe radioactive disintegration (and activity changes) are non-linear, and the mean age is not equal to the age of the middle point. If we use a linear model of speleothem growth we can estimate the influence of this process on the age. It seems to be much stronger for the radiocarbon method than for the U-Series method (Text-fig. 4). Luckily the speleothem

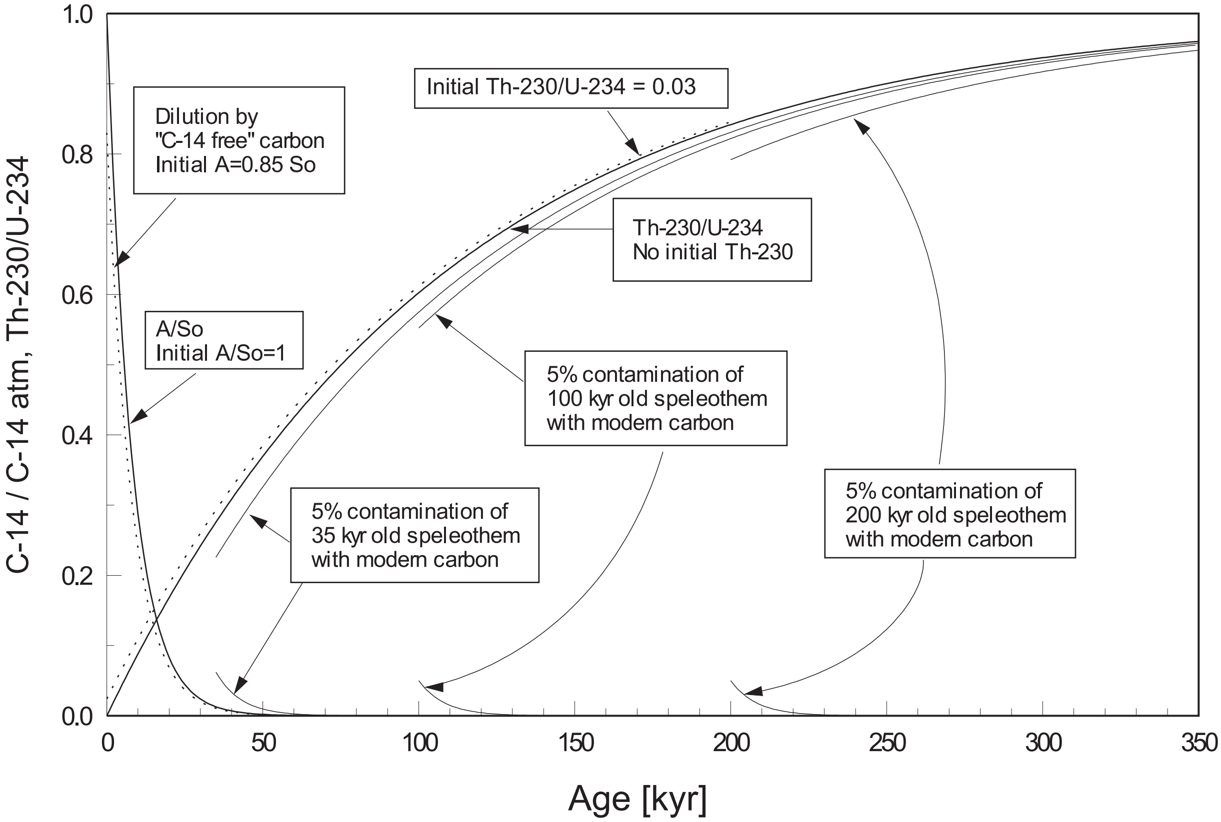

Fig. 5. Influence of contamination with the young material on Time projection of ^{14}C activity and $^{230}Th/^{234}U$ activities ratio in the speleothems (after HERCMAN 2000)

growth rate is usually high enough to make the effect of a finite layer thickness not so large.

The next problem is connected with changes of isotope content – so-called open system. One of the simplest situations is contamination with young carbonate. This is an effect of crystallisation of younger (or modern) carbonate in the original structure of a porous speleothem. Such contamination distinctly affects the ^{14}C ages of old samples, while its influence on the U-Th ages is much smaller. For example, contamination of a 40 ka old speleothem with 5% of modern carbonate would change the U-Th age by less than 2 thousand years, while the ^{14}C age would change by almost 15 thousand years (Text-fig. 5). Contamination with younger carbon is evident in the stalagmite from the Wierna Cave (GOSLAR & *al*. 2000). This speleothem, dated with the U-Th to 314 ka (at the top) and >300 ka (older part), gave 4 finite ^{14}C ages, one of them even less than 40,000 ^{14}C BP.

Other open system problems are caused by the migration of (atoms ions) within structure of fossil material. This is characteristic of some kind of materials, especially for bones and mollusc shells. Bones provide

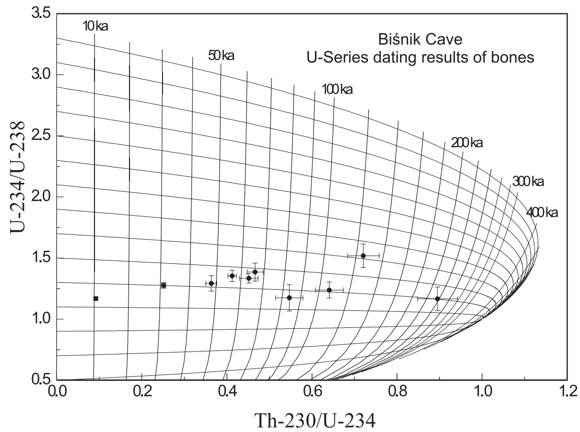

Fig. 6. Uranium-Series isotopic ratios of bones from Biśnik Cave. The near horizontal lines show the time evolution of $^{234}U/^{238}U$, in a closed system with no initial ^{230}Th. The near vertical lines represent isochrones (lines of constant age)

systems are definited open for the migration of Uranium (and/or Thorium). Bones of living animals are characterised by very low concentrations of Uranium. In fossil bones, the concentration of Uranium is usually several times higher than in fresh bones. A similar problem is connected with the dating of mollusc shells. The standard test (see IVANOVICH & HARMON 1982) – using $^{230}Th/^{232}Th$ *vs.* $^{234}U/^{232}Th$ plot seems to be insufficient. As an example we can present the dating results of bones from Biśnik Cave (Kraków-Wieluń Upland, Poland). The results of measurements lay along one evolution line of $^{234}U/^{238}U$ (in the error range) as is characteristic for closed system samples – but we know that it was an open system and that Uranium accumulation at this site was very strong (Text-fig. 6).

CONCLUSIONS

Radiocarbon dates of speleothems are commonly treated with caution, because of the reservoir effect, producing an apparent age, which is usually not accurately known. However, in the light of our data, and some previous research (HOLMGREN & *al*. 1994), the reservoir effect may be of minor importance when compared to contamination with younger carbon. In fact one should be very cautious, when forwarding speleothem samples for dating with any method.

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