^{230}Th/U-dating of a late Holocene low uranium speleothem from Cuba

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Abstract. We present 22 U-series ages for a stalagmite from north-western Cuba based on multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) and thermal ionisation mass spectrometry (TIMS). Our results reveal that the stalagmite continuously grew within the last ~1400 a. Low uranium content of the sample and thus, extremely low ^{230}Th concentrations limit the precision and accuracy of ^{230}Th/U-dating by TIMS. Samples measured by MC-ICPMS show a high variability of ^{232}Th content along the growth axis with some sections significantly affected by initial ^{230}Th from a detrital phase. An a-priori bulk earth ratio for (^{238}U/^{232}Th) cannot be used to accurately account for this initial ^{230}Th. Using an age model based on the ^{230}Th/U ages determined on samples with low or negligible ^{232}Th concentration, we find that the (^{238}U/^{232}Th) activity ratio of the detrital phase is an order of magnitude larger than the bulk earth value, indicating the importance of an accurately determined correction factor.

1. Introduction

The Caribbean represents an important area to obtain information about past natural climate variability in the tropical region and its relationship to climate forcing mechanisms, such as changes in insolation. Speleothems are important archives for high resolution climate reconstructions and can be accurately dated by U-series disequilibrium dating methods [1]. The two most precise analytical techniques for the determination of U and Th isotope ratios are multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) and thermal ionisation mass spectrometry (TIMS) with precisions between per mill and percent, depending on the U content and the age of the sample [2]. Applicability of ^{230}Th/U-dating on speleothems is based on the prerequisite that no initial ^{230}Th (i.e., not produced by in situ decay of ^{234}U and ^{238}U) is incorporated when the $CaCO_3$ forms and that the crystal remains a closed system after deposition [3]. However, in practice small quantities of initial ^{230}Th are often incorporated during precipitation of speleothem $CaCO_3$. Usually, the ^{232}Th concentration is used as a proxy

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for initial ^{230}Th [4], and the ^{230}Th/^{232}Th activity ratio (henceforth activity ratios are indicated by parentheses, e.g., (^{230}Th/^{232}Th)) indicates whether a correction needs to be applied. As a threshold for mass spectrometric analyses an activity ratio between 100 and 300 has been suggested [5, 6]. There are different methods to estimate the extent of contamination with initial ^{230}Th: (1) direct measurement of the isotopic composition of the contaminating phase using an isochron technique on multiple sub samples [4]. (2) Assuming an a-priori estimate for the isotopic composition of the contaminating phase [3, 7, 8], e.g., the bulk earth ^{232}Th/^{238}U concentration ratio of the upper crust of 3.8 [9] and secular equilibrium for ^{230}Th, ^{234}U and ^{238}U. Depending on the (^{230}Th/^{232}Th) of the sample the correction may have a significant effect on the ^{230}Th-^{234}U-^{238}U activity ratios, and it is obvious that the accuracy of the corrected ratios depends on the accuracy of the correction factor. Using the a-priori estimate, the effect of propagating the assumed uncertainty of the isotopic composition of the contaminating phase through the age calculation may also be quite severe [8]. Thus, in case that a correction for detrital contamination is applied, precise direct measurement of the isotopic composition of the contaminating phase is required. The compostition of detrital phases can be very different from the a-priori assumed bulk earth value, e.g., due to partial leaching effects, Th adsorbtion, alpha recoil or non silicate origin of the detrital phase prior to deposition [8].

Here we present U-series data of a stalagmite from western Cuba that has an extremely low ^{230}Th concentration. Thus, the effect of potential contamination with initial ^{230}Th is very large. Since no distinct growth layers are visible, isochrons are not applicable and an alternative method is used to constrain the (^{238}U/^{232}Th) of the contaminating phase. First, a robust age model using uncorrected (^{230}Th/^{238}U) and (^{234}U/^{238}U) ratios is derived from sub samples with low ^{232}Th concentration measured with high precision MC-ICPMS. Then the dating results of samples with elevated ^{232}Th concentration are compared with this age model to estimate the (^{238}U/^{232}Th) of the contaminating phase. This enables the derivation of a sample specific (^{230}Th/^{232}Th) for the correction.

2. Location, sample and methods

Dos Anas cave (Pinar del Rio, north-western Cuba, 22° 23' N, 83° 58' W) has a total length of ca. 14 km and is part of the Majaguas Cantera cave system [10]. Stalagmite Cuba Grande (CG) grew in Dos Anas cave at an elevation of ∼100 m above sea level and ∼150 m under the surface. The sampling location, which is located in the Salon de la Cimitarra, lies in a distance of ca. 1.5 km from the cave entrance. The 720 mm long stalagmite sample consists of pure white calcite, as confirmed by X-ray diffraction analysis. No distinct growth layers are visible (Fig. 1).

22 MC-ICPMS and TIMS U-series ages were determined along the growth axis of CG. Ten MC-ICPMS measurements were performed using a ThermoFinnigan Neptune MC-ICPMS at the Bristol Isotope Group, and twelve analyses were performed on a Finnigan MAT 262 RPQ TIMS at the Heidelberg Academy of Sciences. The key difference between both methods is the transfer efficiency of isotopes, which is $\ll$1% with TIMS, but ∼1% with MC-ICP-MS [2]. For young samples with low uranium content, the MC-ICPMS technique thus enables both a higher precision of ^{230}Th/U-dating and to use smaller sample sizes. For both methods sample masses between 0.5 and 1 g were used for one analysis. The average span of time included in one sample should, thus, be the same for MC-ICPMS and TIMS. Due to the smaller sample size required for analysis, however, the precision of the MC-ICPMS ages is much higher. Chemical preparation of the samples follows the methods described in Hoffmann et al. (2007) [11] and Hoffmann (2008) [12] for MC-ICPMS and in Scholz et al. (2004) [13] for TIMS. Different U and Th spikes were used in both laboratories. The calibration of both spikes and an inter-laboratory comparison is described in Hoffmann et al. (2007) [11]. The comparison did not show any significant differences for the two spike solutions. Ages were initially calculated based on uncorrected (^{230}Th/^{238}U) and

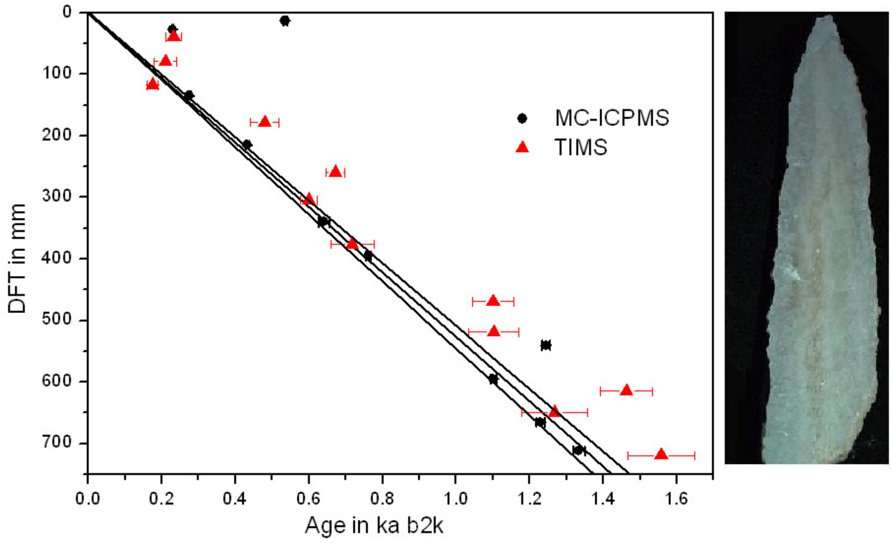

Figure 1. (left) Ages determined by the MC-ICPMS (black circles) and the TIMS method (red triangles), without any detrital correction. Ages are given in ka b2k as a function of distance from top (DFT) in mm. The linear age model for the MC-ICPMS data yields a mean growth rate of 526 μm/a (black line). The corresponding 95 % confidence limits are also shown. The two uppermost and the sample at 540 mm DFT have not been considered for the linear fit. (right) Picture of stalagmite CG.

($^{234}U/^{238}U$) and corrected ratios, using a bulk earth ($^{238}U/^{232}Th$) of 0.8 where decay products of detrital ^{238}U are assumed to be in secular equilibrium. The quoted age uncertainties include uncertainties from the detrital correction. Details about uncertainties of MC-ICPMS can be found in Hoffmann et al. (2007) [11]. All uncertainties are quoted at 95 % confidence level.

3. Results

All $^{230}Th/U$ dating results are shown in Fig. 1, and a table with all data can be found in the supplementary information. Ages are given in ka before the year 2000 (ka b2k). The U content of the samples ranges from 90 to 200 ng/g. ^{230}Th concentrations vary between 0.01 and 0.06 pg/g of sample. Analysis of such small concentrations of ^{230}Th is more precise using the MC-ICPMS technique, hence the focus of further examinations is on the MC-ICPMS data. Seven ages determined by MC-ICPMS suggest nearly linear growth during the last ∼1370 years. The calculated age model using a linear fit has a slope of $0.00190(\pm 2 \cdot 10^{-5})$ ka/mm, which corresponds to a growth rate of $526(\pm 11)$ μm/a. The fit was forced through the origin since the dripsite was active when the stalagmite was removed from the cave. Three ages at 13, 27 and 540 mm distance from top (DFT) are not in stratigraphic order and have, thus, not been considered for this fit. The ages determined by the TIMS method generally exhibit older ages than the MC-ICPMS data and a larger scatter (Fig. 1).

Fig. 2 shows the ages determined by MC-ICPMS in comparison to the ($^{230}Th/^{232}Th$) of the samples. The three samples at 13, 27 and 540 mm DFT show a substantially lower ($^{230}Th/^{232}Th$) than the other samples suggesting a higher degree of detrital contamination. Since these three ages do not plot on the straight line determined by the less contaminated ages, this suggests that the applied correction using a ($^{238}U/^{232}Th$) of 0.8 is inadequate to account for the effect of detrital contamination. The samples at 13, 27 and 540 mm DFT show a ($^{230}Th/^{232}Th$) ratio

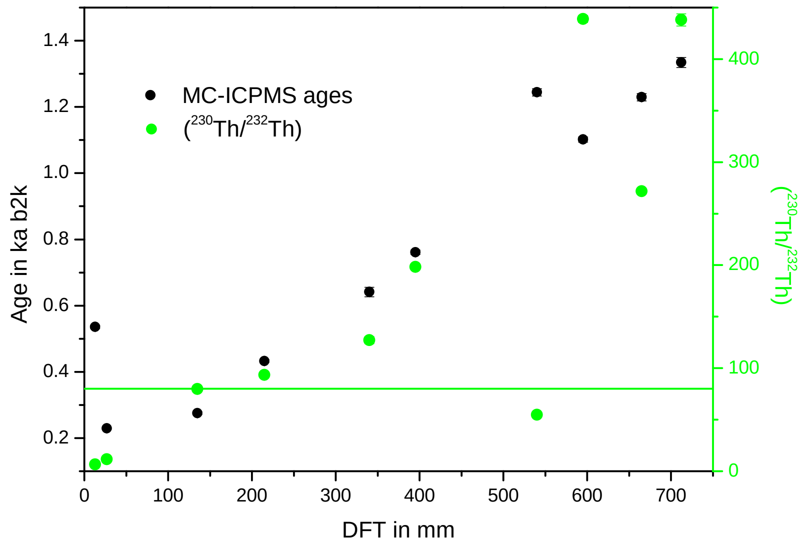

Figure 2. MC-ICPMS dating results (black circles) and (^{230}Th/^{232}Th) (green circles). The three ages at 13, 27 and 540 mm DFT are not in stratigraphic order, and the corresponding samples have a significantly lower (^{230}Th/^{232}Th) than 80 (green line).

below 80, which we use as a threshold to identify results that require a detritus correction.

4. Discussion

A strict constraint for the age of sub-samples taken along the growth axis of a stalagmite is, that ages must become progressively older from top to bottom [2, 8, 14, 15]. Three ages at 13, 27 and 540 mm DFT are not in stratigraphic order and therefore do not fulfill this criterion (Figs. 1 and 2). Assuming that the true age-depth relationship for stalagmite CG is described by the linear age model determined using the samples with low ^{232}Th content (Fig. 1), the (^{238}U/^{232}Th) for the correction of the samples with elevated ^{232}Th can be estimated. We find that the activity ratios of the samples at 13, 27 and 540 mm DFT need to be corrected with (^{238}U/^{232}Th) ratios of 6.1, 8.7 and 9.6, respectively, to obtain corrected ages in agreement with the linear age-depth model. The mean of the three (^{238}U/^{232}Th) ratios is 8($\pm$4) (2σ standard deviation of the average value), almost an order of magnitude bigger than the bulk earth factor, which is normally used to account for detrital contamination. This (^{238}U/^{232}Th) is now used to recalculate all ages determined by MC-ICPMS and TIMS. The results are shown in Fig. 3.

The corrected age of the uppermost sample dated by the MC-ICPMS method is out of range using the mean correction factor of 8. This is due to the fact that in this case the assumed ^{230}Th concentration of the detrital phase is larger than the total ^{230}Th concentration. Thus, the corrected concentration of ^{230}Th becomes negative, and the ^{230}Th/U age equation cannot be solved. Instead we use the maximum value to maintain positive results and the minimum value of the confidence range of the correction factor (6 and 4 respectively) to estimate the age range for this sample.

The corrected TIMS ages are still not in stratigraphic order and in general exhibit older ages than the results from MC-ICPMS. This suggests that the scatter in the TIMS data is not solely

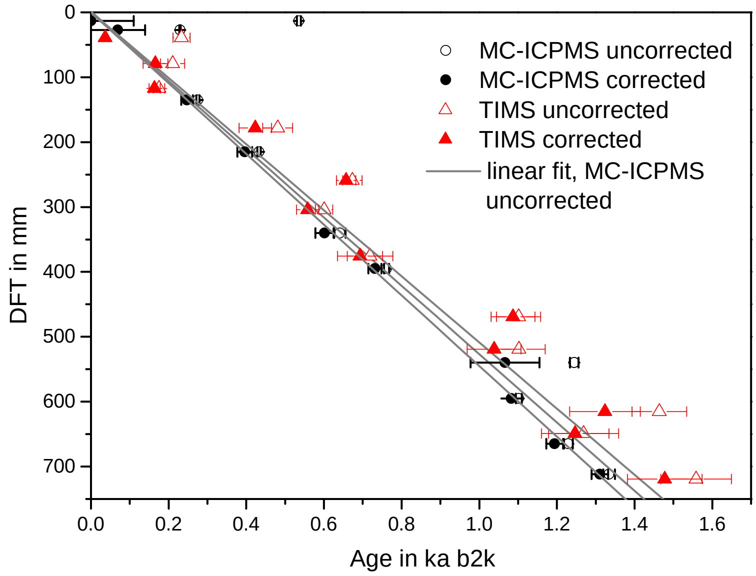

Figure 3. MC-ICPMS dating results, corrected with a (^{238}U/^{232}Th) of 8 (filled black circles) and without correction (open black circles). TIMS ages are shown as filled red triangles for the corrected resulst, black open triangles for uncorrected. The age model determined by the uncorrected MC-ICPMS data is shown as a gray line.

due to contamination with initial ^{230}Th. Differences in spike calibration can be excluded as the reason for the apparently too old TIMS ages since the inter-laboratory comparison did not show significant differences [11]. In contrast, we speculate that a relatively large contribution of the background intensity to the ^{230}Th signal is the reason for this scatter, which also limits the precision that can be achieved by TIMS. Taking into account the relatively large uncertainties of the TIMS ages, the TIMS age model would be in agreement with the age model based on MC-ICPMS results.

5. Conclusions

Results from 22 MC-ICPMS and TIMS ^{230}Th/U age determinations on a Holocene low U stalagmite from north-western Cuba show that MC-ICPMS measurements generally yield smaller errors, which is due to the higher sensitivity especially for ^{230}Th and hence better counting statistics. Furthermore, a background contribution for TIMS measurements becomes significant for samples with low U content due to extremely small count rates.

Initial ^{230}Th has a significant effect on such samples and requires an accurately determined detrital correction factor. Since isochrons are not applicable, an alternative approach was used: subsamples with negligible detritral contribution allow derivation of an age model, which constrains the detrital (^{230}Th/^{232}Th) of the other samples. We find a (^{230}Th/^{232}Th) that is an order of magnitude larger than the bulk earth value commonly applied for detrital correction. A similarly elevated initial (^{230}Th/^{232}Th) has also been reported by Beck et al. (2001) [14] for a stalagmite from the Bahamas and may result from incorporation of carbonate dust during formation.

The sample specific (^{238}U/^{232}Th) can be used to correct results of samples with significantly higher ^{232}Th concentration. For the Cuban stalagmite CG we find a value of 8($\pm$4) to correct for detrital components.

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