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**Improved U-Th dating of carbonates with high initial ^{230}Th using
stratigraphical and coevality constraints**

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1

2 **Abstract**

3 With high precision measurements now achievable by MC-ICPMS, the uncertainty on
4 the initial ^{230}Th content can be the major source of uncertainty for U-Th ages of carbonates.
5 The initial ^{230}Th content is usually derived from the ^{232}Th content of the sample and the initial
6 $^{230}\text{Th}/^{232}\text{Th}$ ratio calculated using isochron techniques or using stratigraphical constraints
7 along the speleothem growth axis. These two methods are based on different hypotheses and
8 have not been couple previously. Here, we present a new algorithm called STRUTages that
9 combines stratigraphical and coevality constraints in order to obtain the best estimate on the
10 initial $^{230}\text{Th}/^{232}\text{Th}$ ratio of each sample. STRUTages and isochron results are compared on a
11 suite of speleothems and a coral core. Comparison of the U-Th and growth-band counted ages
12 of the coral core demonstrates the validity of the STRUTages approach. An Octave (Matlab-
13 compatible) script allowing the use of stratigraphical and coevality constraints is provided.

14

15 **Keywords:** STRUTages; U-Th dating; speleothem; coral; isochron; stratigraphical; coeval
16 constraints

17

18 **Highlights:**

- 19 * We present a new method to constrain the initial ^{230}Th content of coeval samples.
- 20 * It is compatible with the stratigraphical constraint method of Hellstrom (2006).
- 21 * Combination of both methods allows an improved dating of carbonates.
- 22 * The method is validated on independently dated (growth band counting) samples.
- 23 * A script performing both stratigraphical and coeval sample constraints is provided.

24

1. Introduction

The ^{230}Th - ^{234}U - ^{238}U dating method is widely applied to carbonate samples (speleothems, corals). It generally allows an accurate determination of the age of these paleoclimatic and paleoenvironmental archives over the last 500 ka. This method assumes that the carbonate has remained a closed system since its formation and that all the ^{230}Th in the sample comes from the radioactive decay of ^{234}U . However, for speleothems and to a lesser extent for corals, this last assumption is often false and this can have a significant effect on the apparent age, particularly for young (< 50 ka) speleothems and/or speleothems with a low U content and/or a high detrital Th content. It is therefore necessary to correct for the ^{230}Th present in the carbonate at the time of its formation. It becomes all the more critical with the high analytical precision provided by MC-ICPMS, the U-Th content of most carbonate sample can be determined at a permil or sub-permil level, so that the uncertainty on the initial ^{230}Th content of the speleothem becomes a significant, if not prominent, source of uncertainty on the age (Dorale et al., 2004).

The degree of ^{230}Th initial is generally indicated by the presence of ^{232}Th . In early studies, it was assumed that samples with ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio > 20 did not require corrections (Bischoff and Fitzpatrick, 1991). However, with the improvement of dating techniques, more recent studies propose with that the influence of this detrital fraction on age determination is significant for measured ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio as high as 300 (Hellstrom, 2006).

It is possible to deduce and subtract the initial ^{230}Th content of a speleothem or a coral from its ^{232}Th content, if the initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio is known. This initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio can be estimated or determined by measurements. The average crustal U/Th ratio combined with the assumption that ^{230}Th is in secular equilibrium with ^{238}U has been

1 widely used to estimate the initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio. However, several studies have
2 demonstrated that this value does not reflect the whole range of initial Th activity ratio,
3 because clay is not the only Th source (e.g. Beck et al., 2001; Hellstrom 2006) and because
4 the U/Th ratio in detrital particles and colloids can vary strongly (Marchandise et al., 2014).
5 Drip water in caves, sea water or modern calcium carbonate are also used to determine the
6 initial Th activity ratio $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ at the formation of the speleothem (Hu et al., 2008,
7 Wortham et al., 2013). This initial ratio can also be deduced directly from an isochron
8 constructed with several subsamples from the same laminae (or group of laminae) of the
9 speleothem having different U/Th ratios (Dorale et al., 2004). However, $(^{230}\text{Th}/^{232}\text{Th})_{A0}$
10 obtained on one stratigraphical level with an isochron or by the measurement of modern
11 calcite or aragonite may not be valid throughout the speleothem or coral. More recently, the
12 “stratigraphical constraint” method was developed to determine the range of $(^{230}\text{Th}/^{232}\text{Th})_{A0}$
13 that keeps speleothem samples in stratigraphical order after correction for the initial ^{230}Th
14 content (Hellstrom, 2006). These two methods require different sample set: the isochron
15 method uses several samples of the same age, whereas the stratigraphical method uses several
16 samples of different ages. The isochron method is widely used and many researchers draw
17 upon the freely-available software `Isoplot` (Ludwig, 2003) to calculate $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ in an
18 isochron diagram. On the other hand, no software performing the “stratigraphical constraint”
19 method has been published so far.

20 Recently, we developed our own routine to obtain stratigraphical constraints on very
21 young (<400 a) and detritus-rich speleothems (Pons-Branchu et al., 2014). Initially, our goal
22 was to reproduce the method described in Hellstrom (2006). However, it rapidly appeared that
23 a program would be much more practical if it could combine samples of increasing ages
24 through the speleothem (the stratigraphical method) with samples from the same
25 stratigraphical level (hereafter called subsamples), whether they are “replicates” of a given

layer or they are purposefully analyzed to obtain an isochron (generally, $n > 2$). This corresponds to the effective sampling of many speleothems, indeed (Ersek et al., 2009). Beyond the practical aspect of treating coeval and non-coeval samples, we primarily aim at better constraining the initial ^{230}Th content of the speleothem by combining the information brought by all available samples in a self-consistent manner. Indeed, it is not straightforward to combine the uncertainties obtained on the same speleothem by isochron(s) and stratigraphical constraints because these two methods are based on different assumptions and they use common information so that they are not independent and related in a complex manner.

We have developed a new method to evaluate the age of coeval subsamples. This method is compatible in terms of assumptions and calculation process with the stratigraphical method developed by Hellstrom (2006). Here, we describe this method, present a few applications illustrating the possibility and limits of the method and provide an open source program called `STRUTages` (STRatigraphical and coeval constraints on U-Th ages) that allows applying the stratigraphical constraint method (with or without coeval sub-samples) to a broad range of datasets.

2. Method

2.1. Principle of the stratigraphical constraints from non-coeval samples

U-Th ages, $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ and corresponding uncertainties were calculated following the stratigraphical method developed by Hellstrom (2006), which is based on a Monte Carlo simulation (see description in Albarède, 1995, for example). Monte Carlo estimates of errors of a function are obtained by repeatedly perturbing (N trials) the input data according to their assigned errors and error distribution. At each trial, random values are generated to simulate:

1- measured $^{234}\text{U}/^{238}\text{U}$, $^{232}\text{Th}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios expressed as $(^{234}\text{U}/^{238}\text{U})_A$, $(^{232}\text{Th}/^{238}\text{U})_A$ and $(^{230}\text{Th}/^{238}\text{U})_A$ (with Gaussian distributions centered on the mean measured ratios and with two standard deviations (2σ) of the distribution given by the two standard deviation on the measured ratios). There is no covariance between these ratios, so α -counting data cannot be treated with STRUTages.

2- Mean $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ of the speleothem: R_{i_mean} . This is chosen from a large range of plausible values (exponential distribution of the activity ratio ranging from 0.1 to 30)

3- Maximum percentage of variability of $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ within the speleothem (uniform distribution ranging from 0% to 100%): ΔR_i .

4- For each sample analyzed in the speleothem, a specific R_i within the range defined by R_{i_mean} and by the maximum percentage of variability ΔR_i : uniform distribution ranging from $R_{i_mean} - \Delta R_i$ to $R_{i_mean} + \Delta R_i$.

Step 4 defines the individual $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ ratios (R_i) of each simulated sample of the speleothem within the range determined by steps 2 and 3.

Step 5: trials with no physical meaning (if they are just due to the statistical uncertainties on the analyses) or corresponding to an open system behavior were discarded. This was the case when:

- $(^{230}\text{Th}/^{238}\text{U})_A < (^{232}\text{Th}/^{238}\text{U})_A \times R_i$ (i.e. less ^{230}Th in the sample today than at the time of formation)

- $(^{230}\text{Th}/^{238}\text{U})_A - 1 > ((^{234}\text{U}/^{238}\text{U})_A - 1) \times \lambda_{230} / (\lambda_{230} - \lambda_{234})$ (i.e. sample plotting on the right of the infinite age line in a $(^{230}\text{Th}/^{238}\text{U})_A$ versus $(^{234}\text{U}/^{238}\text{U})_A - 1$ diagram and corresponding to the “forbidden zone” for which no finite age exists).

Sample ages were calculated for each trial with the randomized values obtained at steps 1 and 5, by solving numerically the equation:

$$\begin{aligned} \left({}^{230}\text{Th}/{}^{238}\text{U} \right)_A = & 1 - e^{-\lambda_{230}t} \left(1 - \left({}^{232}\text{Th}/{}^{238}\text{U} \right)_A \times \left({}^{230}\text{Th}/{}^{232}\text{Th} \right)_{A0} \right) \\ & + \left(\left({}^{234}\text{U}/{}^{238}\text{U} \right)_A - 1 \right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left(1 - e^{-(\lambda_{230} - \lambda_{234})t} \right) \end{aligned} \quad (1)$$

Any trial in which the calculated ages were not in the stratigraphical order or in which negative ages were obtained were discarded (Fig. 1a,b). From 10^4 to 10^{10} iterations were performed to obtain at least a few hundred valid solutions with positive ages in the stratigraphical order. Only these valid iterations were averaged to determine the most probable ages and $({}^{230}\text{Th}/{}^{232}\text{Th})_{A0}$ in the speleothem or coral (hereafter called “archive”).

For a given $R_{i_mean} - \Delta R_i$ pair, a single successful trial is a sufficient condition to guarantee that the samples can be in stratigraphical order within the analytical uncertainties (Fig. 1.a). However, it is not a necessary condition because a single trial does not cover the whole range of uncertainty on each sample age (Fig 1.b). Nevertheless, with the large number of trials performed, it is likely that the successful trials should allow a reasonable mapping of the valid $R_{i_mean} - \Delta R_i$ pairs.

When two or more coeval subsamples from the same stratigraphic level are present in the speleothem or the coral, two different constraints can be used to account for these subsamples: the loose coevality constraints and the strict coevality constraints. We describe these in the following sections.

2.2. Weak constraints for “loosely” coeval samples: the loose coevality constraints

When two or more subsamples of the same stratigraphical level of the archive are analyzed, they are not compared to each other. They are just compared with the sample of the previous and of the next stratigraphic level. The ages of these subsamples are simply replaced by a doublet made of the lowest and the highest ages among the subsamples. This doublet then replaces the whole subsamples suite in the sample series for the stratigraphical age test.

This treatment corresponds to a weak constraint imposed by the subsamples on R_{i_mean} and ΔR_i . The subsamples just have to be younger than the sample from the previous (older) level and older than the next sample (younger) level. However, these subsamples do not have to have the same age. It corresponds to a situation where the replicates were sampled in an area where the laminae are poorly visible and/or of very slow growth rate, so that the synchronicity of the “replicates” is not certain. From the modeling point of view, it provides a screening of $R_{i_mean}-\Delta R_i$ pairs allowing the stratigraphical order of the samples. These pairs will be used in the next step to add up age constraints on coeval subsamples.

2.3. Strong constraints for strictly coeval samples: the strict coevality constrain.

When subsamples of one or several stratigraphical levels are present, we add new constraints: the ages of all the subsamples from the same level must be equal within analytical uncertainties (Fig. 1ef). We note that it is not sufficient to take the intersection of the age ranges of the subsamples calculated in Section 2.3., because the initial ^{230}Th correction introduces a strong covariance between the ages of the subsamples (see Section 3.2). This effect can be easily understood by considering two subsamples with partly overlapping error bars after the “loose coevality constraints” test: discarding trials with the oldest ages of the

oldest subsamples (these ages stand above the age intersection of the subsamples) will also discard the oldest ages of the youngest subsample (although they belonged to the common age range) because all these ages are likely to have been obtained with same the lowest R_{i_mean} values. Hence, two replicates having a common age range with the “loose coevality constraints” may end up with significantly smaller age ranges after the “strict coevality constraints”. In some case, the overlapping may disappear and the trial is then discarded.

In the previous sections, at each trial, the stratigraphical test was based on only one randomly-chosen age of each sample because it was sufficient to set ages in order, but it is not sufficient to determine if the subsample ages are equal. The age range of each sample was obtained by compiling the age of the successful trials.

We must now determine for each successful $R_{i_mean}-\Delta R_i$ pairs obtained at the Section 2.2. if the subsample ages are equal within uncertainties. For each successful pair, the $(^{234}\text{U}/^{238}\text{U})_A$, $(^{232}\text{Th}/^{238}\text{U})_A$ and $(^{230}\text{Th}/^{238}\text{U})_A$ are randomized about 1000 times and used to calculate the age range of each sample (subsamples or not). The age ranges of all replicates from the same layer are then compared to determine their intersection. Only trials with all ages in the stratigraphical order and replicate ages within the replicate age intersection are selected as valid. All other trials are discarded. Hence, we obtain for each sample and subsample an age range that fulfill within the analytical uncertainties both the stratigraphical order for sample from different layers and the synchronicity of subsamples of a given stratigraphical level.

2.4. Computing considerations

The program was computed using the Octave freeware (<http://www.gnu.org/software/octave/>). Octave is compatible with Matlab and it can be enabled on Linux, OS X, BSD and Windows operating systems. Here we use Octave 4.0.0 on a PC computer with the Windows operating system. Due to the large number of trials (up to 10^{10}) required to obtain enough valid solutions, constraints exist for both the running time of the program and the number of trials that can be stored in the memory.

The calculation time was optimized by using matrix operations whenever it was possible. Equation 1 was solved numerically to obtain the sample ages. We initially used the built-in functions of Octave (`fsolve` and `fzero`) to solve Equation 1. However, they turned out to be slow when solving a large number of equations. Therefore, we used the Newton-Raphson algorithm that generally converges rapidly and that can be written under a matrix form to solve thousands of equations simultaneously (Albarède, 1995, Quarteroni and Saleri, 2006). The effectiveness of the algorithm convergence was tested by:

- calculating the evolution of the $(^{234}\text{U}/^{238}\text{U})_{\text{A}}$ and $(^{230}\text{Th}/^{238}\text{U})_{\text{A}}$ activity ratios in a closed system with prescribed values of the $(^{234}\text{U}/^{238}\text{U})_{\text{A0}}$ activity ratio ranging from 0.8 to 10, of the prescribed $(^{230}\text{Th}/^{238}\text{U})_{\text{A0}}$ activity ratio equal to zero and for prescribed ages ranging from 1 a to 800 ka which are, effectively, the lower and upper limits to use U-Th dating. The $(^{232}\text{Th}/^{238}\text{U})_{\text{A}}$ ratio was set to zero because the purpose was only to check the algorithm convergence.

- recalculating the sample age with $(^{234}\text{U}/^{238}\text{U})_{\text{A}}$ and $(^{232}\text{Th}/^{238}\text{U})_{\text{A}}$ as input values

- comparing prescribed and calculated ages.

The calculated age deviates from the true age by less than 0.001 % for a sample of 1 a and no more than 0.1 % for a sample of 800 ka. This is negligible compared to the propagation of statistical uncertainties on the measurement. There is very good agreement

between the ages calculated on individual samples by STRUTages and Isoplot (Tab. 1), as illustrated by 2 numerical examples derived from Ludwig (2003).

The STRUTages.m (Santa Elina data) and STRUTages_acc.m (Newton algorithm accuracy test) scripts and the user manual are given in electronic supplements.

2.5. Carbonate samples for program testing

In the following, the impact of the age correction model on carbonate dating is illustrated by two speleothems in contrasting environments and one coral core:

- A detritus-rich and young speleothem sampled in the Santa Elina prehistoric shelter (15°28'S, 56°48'W, Mato Grosso, Brasil). In this 9 cm-long stalagmite, laminated and porous zones alternate. U-Th data suggests ages younger than 10 ka (Pons-Banchu and Fontugne, unpublished data), whereas stratigraphically-ordered ¹⁴C ages suggest that the speleothem age is less than 560 a (Fontugne, unpublished data). This is an upper limit because no dead carbon correction is applied for these young ages. In this speleothem, three stratigraphical levels were analyzed. For one of these level, 3 subsamples were analyzed (Table ES1 in the electronic supplement).

- A detrital-rich and young (< 5500 a) speleothem sampled in the Rupt du Puits cave in the East of France (Pons-Banchu, 2001; Jaillet et al., 2006). This speleothem developed in an active karstic system covered by Cretaceous deposits (clay and sands). Eight stratigraphical levels of this speleothem were analyzed (Table ES2 in the electronic supplement). For one of these levels, three subsamples were analyzed.

- A subtidal coral core (92MC) from the Espiritu Santo island (Vanuatu) in the Eastern Pacific ocean (Shen et al., 2008). The coral material expected to be less than 100 years old. It lived in an open-ocean environment with no direct riverine inputs. However, the ²³⁰Th/²³²Th ratio of

the local seawater varies due to deep water upwelling during La Nina events. It has been dated by both U-Th and band-counting in order to test the accuracy of young U-Th ages. Therefore, it gives a unique opportunity to test the STRUTages method. Six stratigraphical levels were analyzed in this core (Table ES3 in the electronic supplement). Four sub-samples were analyzed for each of the two youngest levels:

- Subsamples (1#a to 1#d) of the youngest level with an age of 13 ± 0.5 a determined by growth band counting do not plot on a single isochron (Shen et al., 2008). Three subsamples (1#a to 1#c) yield an acceptable isochron age of 12 ± 1.3 a and an initial activity ratio $R_i = 1.0$. The age of the other subsample (1#d) when corrected with a R_i value of 1.0 and yielded an age of 19.0 ± 1.2 a. This overestimated age comes from an underestimation of the R_i value of this subsample which may have grown during a short upwelling event (see below).
- Four subsamples (2#a to 2#d) with an age of the 30.5 ± 0.5 a determined by growth band counting yield an isochron age of 29.2 ± 1.3 a and $R_i = 4.5$. This high R_i value may be related to the upwelling of deep water Shen et al. (2008).

3. Results

For each archive, we first present the ages calculated with strict coevality constraints only and we compare them with isochron ages obtained with Isoplot. Then, we present the results obtained with the STRUTages with the loose and strict coevality constraints on the whole sample set. Uncertainties on age and R_i are given as 95% probability errors (5th and 95th percentiles because some age and R_i distributions are not Gaussian). Combining the mean (normally associated with the standard deviation) and percentiles (normally associated with

the median) may appear mathematically heterodox, but it is consistent with `Isoplot` format for non-Gaussian age distributions (Ludwig, 2003).

3.1. Santa Elina

U-Th ages (2.39 ± 0.28 , 2.36 ± 0.29 and 2.37 ± 0.22 ka) of the three coeval subsamples obtained with the strict coevality constraints are compatible within the uncertainty of the isochron age of 2.3 ± 2.5 ka calculated with using `Isoplot`.

The five samples can be placed in stratigraphical order for very low values of the ΔR_i ($<1\%$) with or without coeval subsample constraints (Table 2, Figure 2a). There is a clear decrease in the uncertainties of ages when coeval subsample constraints are included (Figure 2b). This goes together with a reduction of the range R_i values when coeval subsample constraints are included. We note that the ages of the three coeval subsamples are identical and have identical uncertainties whether they are calculated with or without the stratigraphical constraints of the other samples. It means that in the case of Santa Elina, the age constraints come only from the three coeval samples at the top of the speleothem and that putting these samples in stratigraphical order with the 2 older samples brings no more constraints on age and R_i .

3.2. Rupt du Puits

The age of the three coeval subsamples of the Rupt du Puits speleothems are not very precisely constrained ($\approx 5.3 \pm 0.4$ ka) by the coeval constraints alone because there is an insufficient range of ^{232}Th - ^{238}U for the samples (Table 3). This age is consistent within uncertainties with the isochron age obtained with `Isoplot` (5.6 ± 0.7 ka). The ages obtained with the stratigraphical constraints alone ($4.92 +0.15/-0.16$ ka, $4.8 +0.13/-0.12$ ka, $4.94 +0.14/-0.15$ ka) fall on the low end of the estimates made with the coeval constraints alone.

The stratigraphical constraints give smaller uncertainties (Fig. 3, Tab. 3) due to the occurrence of much larger range of $^{232}\text{Th}/^{238}\text{U}$ fractionation along the speleothem (up to a factor 50).

Adding the strict constraints of coeval samples to the stratigraphical constraints provides a small but significant improvement of the uncertainty of about 10% for each sample.

3.3. Santo coral core

It is not possible to obtain successful simulations for the four subsamples of the youngest stratigraphical level or for the whole speleothem with ΔR_i values lower than $\approx 50\%$. (Fig. 4). Therefore, we calculate ages and R_i values for $\Delta R_i < 70\%$. This value was chosen a priori and somewhat arbitrarily.

The ages determined by STRUTages on the two sets of subsamples of the first and second levels are consistent within uncertainties with the ages determined with Isoplot. As for the Santa Elina and for the Rupt du Puits speleothems, uncertainties determined by STRUTages are generally (4 point data sets of level 1 and 2) smaller than uncertainties determined with Isoplot of the coral core. However, very consistent results are obtained for the 3 point data set of the youngest level by STRUTages ($14.2 \pm 1.5/-1.1$ y, $14.1 \pm 0.9/-0.8$ a and $14.5 \pm 0.8/-0.9$ a) and Isoplot (14.2 ± 1.0 a) (Tab. 4).

All the ages calculated by STRUTages with the coeval subsample constraints agree within uncertainties with the ages determined by band counting (Figure 5).

4. Discussion

4.1 Comparing STRUTages with isochron ages for coeval subsamples

1 Isochrones are the most appropriate method to determine the age of coeval samples
2 (e.g. Allègre, 2008). Therefore, it is important to compare STRUTages ages with isochron
3 ages. Since ^{230}Th and ^{234}U are both radioactive and radiogenic, isochron age determination is
4 often done by drawing isochrons in the $(^{230}\text{Th}/^{238}\text{U})_{\text{A}}$ versus $(^{232}\text{Th}/^{238}\text{U})_{\text{A}}$ and $(^{234}\text{U}/^{238}\text{U})_{\text{A}}$
5 versus $(^{232}\text{Th}/^{238}\text{U})_{\text{A}}$ diagrams or other diagram pairs that completely define the ^{234}U - ^{238}U -
6 ^{230}Th - ^{232}Th system (Geyh, 2008). However, full uncertainty propagation is difficult with
7 paired diagrams because they share common information. This difficulty is circumvented by
8 considering a single isochron line in three-dimensional space, i.e. $(^{230}\text{Th}/^{238}\text{U})_{\text{A}}$ - $(^{234}\text{U}/^{238}\text{U})_{\text{A}}$ -
9 $(^{232}\text{Th}/^{238}\text{U})_{\text{A}}$, which can be done using the Isoplot program (Ludwig and Titterton, 1994, Ludwig, 2003).

11 The three fundamental assumptions of an isochron are that (1) the samples must have
12 been formed at the same time, (2) their parent and daughter isotope ratios were initially
13 homogeneous which corresponds to a single source of initial R_i and (3) they have behaved as
14 a closed-system. When sample scattering around the isochron exceeds analytical errors, at
15 least one of the following failures affects the samples: 1) multiple detrital components (Dorale
16 et al. 2004), 2) multiple ages, or 3) an open-system history (Borsato et al., 2003).

17 In contrast to the single R_i value (corresponding to a single detrital source) assumption
18 of the isochron method, the basis of the age calculation with the strict coevality constraints is
19 to adjust the R_i ratio of each subsample in order to obtain a common age for all these
20 subsamples. With different assumptions, STRUTages and isochron methods may produce
21 different ages. In Section 3, we noted that there is a good agreement (within uncertainties)
22 between the mean U-Th ages calculated with the different methods, but that isochron
23 uncertainties are often larger than the STRUTages uncertainties. It can be related to the data
24 scattering around the calculated isochron, which is quantified by the Mean Square of
25 Weighted Deviates, or MSWD (Ludwig, 2006). MSWD values $\gg 1$ indicate more scatter

than predicted by the analytical errors. Values ≤ 1 correspond to a good fit of the data by the isochron. Looking at the examples given in Section 3, it appears that:

-when $MSWD < 1$ (e.g. subsamples 1#1-3 of the Santo coral core and Rupt du Puits speleothem), both methods give similar uncertainties. In this case, the different subsamples plot on the isochrons with a well-defined R_i value. The age uncertainty corresponds to the analytical scattering and there is no additional uncertainty such as R_i variability due to multiple detrital components. In this favorable case, STRUTages and Isoplot should give similar results, as it is the case for the subsamples 1#a,b,c of the Santo coral. In the Rupt du Puits case, the ages given by STRUTages ($\approx 5.3 \pm 0.4$ ka) and Isoplot largely overlap (5.6 ± 0.7 ka) but the mean age of STRUTages is about 0.3 ka older than the mean Isoplot age. This is because R_i ($= 0.2 \pm 0.6$) is poorly defined by Isoplot (there is small range in $^{232}\text{Th}/^{238}\text{U}$ between the three coeval sub-samples, see Table ES2) and it includes negative values with no physical reality (but that may correspond to an open-system behavior). Conversely, STRUTages simulates only positive R_i values ($R_i = 0.36 + 0.37/-0.24$). As a consequence, STRUTages calculates larger initial ^{230}Th corrections and lower mean ages than Isoplot.

- when $MSWD \gg 1$ (Santa Elina, subsamples 1#1-4 of the Santo coral core), the samples are scattered around the isochron: the fit is poor. Isoplot propagates this scattering into to the age uncertainty, whereas STRUTages minimizes this scattering by adjusting the R_i of each sample to obtain a common age for the whole subsample set. Hence, for large $MSWD$ values, the different hypothesis of Isoplot and STRUTages lead to different uncertainties. Therefore checking the validity of these hypotheses will be crucial for STRUTages (see Section 4.2.).

4.2 Combining stratigraphical and strict coevality constraints

The stratigraphical constraints method is presented as possibly more appropriate to correct of speleothem samples for detrital contamination than isochron because it explicitly assumes that the detrital Th is of variable isotopic composition, whereas isochron techniques assumes a homogeneous detrital end-member that may not be representative of the whole speleothem (Hellstrom, 2006). Why then do we introduce strict coevality constraints with STRUTages? While STRUTages calculates R_i ranges that bring coeval sub-samples within the same age range, it does not directly use these R_i values to correct for the initial thorium of the samples collected on other stratigraphical level like one would do with an isochron. Instead, STRUTages selects for each sample the range of R_i that is most likely to fulfill both coevality and stratigraphic constraints. It influences the non-coeval sample ages because:

- The restricted age range of coeval samples puts an upper limit on the possible ages of younger samples and a lower limit on the possible ages of older samples)
- the R_i range imposed by strict coevality constraints may restrict the range of possible R_i of the whole sample set or require high ΔR_i to fulfill all the constraints simultaneously.

When the R_i ranges of all the samples have a common intersection (this is the case for Santa Elina and Rupt du Puits), any R_i value in this intersection can be used to correct the initial Th content of all the samples and will leave them in the stratigraphical order. Conversely, when the intersection of all the R_i ranges is null, a certain range of variability (ΔR_i) is required leave all the samples in the stratigraphical order (Santo coral core with strong constraints). These two types of behavior were extensively discussed for the stratigraphical method without coevality constraints (Hellstrom, 2006, Pons-Branchu et al., 2014).

The Santa Elina and the Rupt du Puits speleothems are two extreme cases of the relative weight of stratigraphical and strict coeval samples:

- For Santa Elina, most of the constraint on R_i come from the strict coevality constraints on the 3 coeval subsamples. This is reflected by the significant decrease of the uncertainties on ages and R_i when the strict coevality constraints are included (Figure 2) and to the similar age and R_i ranges obtained for the three SE-top samples alone or with SE 43-46 and SE 78-83 (Table 2, with strict coevality constraints).
- By contrast, in the Rupt du Puits speleothem, most constraints come from the stratigraphical constraints on the non-coeval samples due to the large range in $^{232}\text{Th}/^{238}\text{U}$ (up to a factor 50) ratio along the speleothem (see electronic supplement, Table ES2). This is reflected in the similar uncertainties on ages and R_i with or without strict coevality constraints (Fig. 3b). As a consequence, the ages of the 3 subsamples (R69-6abc) are much better defined by the weak constraints applied to the whole speleothem than by the strict constraints on coeval samples alone (Tab. 3). The impact of the strong constraints on coeval samples is restricted to a 10% decrease of the uncertainties, when the strong constraints on coeval samples are applied to the whole speleothem.

The two previous examples illustrate the interplay between the different constraints used in the model. However, they do not guarantee the validity of the modeled ages.

For the Santa Elina speleothem, there is a significant disagreement between the ages obtained with the loose and strict coevality constraints and the ^{14}C ages that are all less than 550 a. This may be due to:

1- U-Th ages can be overestimated compared to ^{14}C ages in case of U loss (Plagnes et al. 2003). This is possible considering that the Santa Elina speleothem grows in a rock shelter. Alternatively, ^{14}C -rich young organic matter can contaminate carbonates but it usually concerns old carbonates (Holmgren et al., 1994; Goslar et al., 2000).

2- The $(^{230}\text{Th}/^{232}\text{Th})_A$ ratios of the Santa Elina samples range from 0.6 to 1.9, within the range of possible values for the $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ ratio. So, it is possible that the Santa Elina speleothem is very young (550 a or less) so that $(^{230}\text{Th}/^{232}\text{Th})_{A0} \approx (^{230}\text{Th}/^{232}\text{Th})_A$ and that $(^{230}\text{Th}/^{232}\text{Th})_A$ variations just reflect $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ variations. In this case, there is no discrepancy between the U-Th and the ^{14}C ages (remember that the ^{14}C ages are not corrected for the dead carbon).

It is beyond the scope of this article to choose between these two hypotheses. However it highlights two important methodological implications:

- 1) If the U-Th behaves as an open system, STRUTages ages are meaningless.
- 2) Whatever the real ages are, a trivial solution is that all Santa Elina U-Th ages are equal to zero if $(^{230}\text{Th}/^{232}\text{Th})_{A0} \approx (^{230}\text{Th}/^{232}\text{Th})_A$. However STRUTages does not find this solution. One reason is that the exponential distribution used to randomized R_{i_mean} favor low R_{i_mean} values (and thus large ages). Thus trials with $R_i \approx 0.35$ are more likely to appear than trials with $R_i \approx 1.6$ -1.9 necessary to set the ages of samples SE 43-46 mm/top and SE 78-83 mm/top close to zero.

Even if the zero age solution is statistically less probable than the one proposed by STRUTages, it does not mean that it is the correct one. In such a case with $(^{230}\text{Th}/^{232}\text{Th})_A$ ratios in the range permitted for $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ and with high

($^{232}\text{Th}/^{238}\text{U}$)_A, ratios geochemical arguments or absolute dating are required to determine the correct age.

The Santo coral core provides the opportunity to compare modeled age with true ages obtained by growth band counting on a coral in which variations of the initial ($^{230}\text{Th}/^{232}\text{Th}$)_A activity ratio are clearly documented. The good agreement (within uncertainties) between the modelled and the counted ages gives confidence (at least in this example) to the reliability of the STRUTages method. The uncertainties on the ages modeled with STRUTages are generally larger than those obtained with isochrons by Shen et al. (2008). However, two points must be noted:

- the good agreement between the U-Th ages of Shen et al. (2008) and counted ages for samples 3,4,5 and 6 is due to the choice of a R_i of 1 (isochron 1) rather than 4.5 (isochron 2) for these samples. This choice was obviously influenced by the known counted ages. However, generally carbonates are dated by the U-Th method because no counted age is available.
- To be self-consistent in their approach, Shen and coworkers apply a R_i ratio of 1.0 to sample 1#d and hence significantly overestimate its age.

Hence, STRUTages combines efficiently the stratigraphical constraints of Hellstrom (2006) and the constraints on coeval samples that are traditionally treated by isochrons.

One of the sources of uncertainty with the stratigraphical constraint model is the maximum value of ΔR_i (the variability of the R_i ratio within the speleothem) that should be used to evaluate the ages and their uncertainties. In some cases, the variability of R_i is well established in corals (Shen et al, 2008) or in speleothems (Dorale et al., 2004). However, there

1 is a risk that a need of using large values of ΔR_i to set samples in stratigraphical order
2 corresponds to an open system problem (Hellstrom, 2006). While the stratigraphic model does
3 not favor a particular ΔR_i value, the few studies using the stratigraphical constraint methods
4 have used ΔR_i values on the low side of the possible range (Hellstrom, 2006, Pons-Branchu et
5 al., 2014). It has the advantage of reducing the uncertainties on the modelled ages but may
6 lead to an underestimation of these uncertainties. The problem is that at present only too few
7 studies focus on the variability of the $(^{230}\text{Th}/^{232}\text{Th})_A$ activity ratio of detrital material in
8 speleothems (Beck et al., 2001, Carolin et al. 2013, Labonne et al., 2002, Meyer et al., 2012,
9 Richards and Dorale, 2003, Yuan et al., 2004, Moseley et al., 2014) or corals (Shen et al.,
10 2008). Seawater is used to determine the $(^{230}\text{Th}/^{232}\text{Th})_{A0}$ activity ratio of corals (Shen et al.,
11 2008). However, the residence time of Th is very short (1 year at most) in the surface ocean
12 so that the $(^{230}\text{Th}/^{232}\text{Th})_A$ activity ratio of seawater may significantly evolve through time.
13 More studies are needed to have a better view of the variability of R_i in speleothems and
14 corals.

15 STRUTages adjusts the R_i of each coeval subsample of a given stratigraphical level
16 to obtain the same age for each subsample. Unlike the isochron method, it does not consider
17 the possibility for open system behavior. In general, speleothems develop in protected
18 environments, so that open system behaviors are rare. When it occurs, it can be detected by
19 mineralogical studies (Borsato et al., 2003, Scholz et al., 2014). In corals, the detection of
20 calcite in aragonitic coral species is a strong indication of open system behavior. The
21 $^{234}\text{U}/^{238}\text{U}$ initial ratio in corals is also used as a clue for open or closed system behavior, as
22 this ratio is expected to display small variations over the past climatic cycles (Robinson et al.,
23 2006). However, some diagenetic alterations could be not detected by these means and further
24 geochemical analyses could be necessary (Bar-Matthews et al., 1993; Pons-Branchu et al.,
25 2005). If, for a given speleothem, the range of the $(^{230}\text{Th}/^{232}\text{Th})$ activity ratio of the potential

1 detrital thorium sources is known, STRUTages is well suited to propagate the corresponding
2 uncertainties.

4 **Conclusion**

5 The combination of the stratigraphical constraints proposed by Hellstrom (2006)
6 together with the strict coevality constraints proposed here provides a robust way to
7 constraints the initial ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio of stratified carbonates. Compared to the
8 isochron method it has the advantage of not requiring the assumption of a single
9 ($^{230}\text{Th}/^{232}\text{Th}$)_{A0} initial activity ratio value and to allow the change of this ratio along the
10 speleothem/coral or within a stratigraphical horizon. From that respect, the strict coevality
11 constraints provide an alternative to isochrons to calculate the age of samples with less
12 restrictive assumption. The field of application of this method is not restricted to carbonate
13 dating. It could be useful for U-Th dating of Quaternary-aged lava flow sequences and may be
14 also applicable to other isotopic systems with initial isotope heterogeneities.

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1

2 Table 1: STRUTages-Isoplot comparison for selected synthetic samples.

	$(^{230}\text{Th}/^{238}\text{U})_{\text{A}}^*$ $2\sigma^{**}$	$(^{234}\text{U}/^{238}\text{U})_{\text{A}}$ $2\sigma^{**}$	Isoplot age (ka) +/- ^{***}	STRUTages age (ka) +/- ^{***}
<i>≈330 ka old sample</i>	1.130 ±0.6%	1.140 ±0.5%	331 +17/-15	332 +14/-13
<i>sample on the infinite age line</i>	1.65 ± 5%	1.43 ± 4%	552 +370/-200	569 +321/-191

3 *: initial ^{230}Th assumed to be 0. **:relative uncertainty. ***:95% confidence error (absolute
4 value).
5

Table 2: Simulation results for the Santa Elina speleothem.

	Weak constraints		Strong constraints (all samples)		strong constraints (3 subsamples only)		Isoplot isochron (3 subsamples only)	
	mean age +/- (ka)	R _i +/- (AR)	mean age +/- (ka)	R _i +/- (AR)	mean age +/- (ka)	R _i +/- (AR)	mean age ± 2σ (ka)	R _i +/- (AR)
SE Top B	2.3 +1.6/-1.6	0.35 +0.24/-0.23	2.39 +0.17/-0.18	0.34 +0.3/-0.3	2.39 +0.17/-0.18	0.34 +0.3/-0.3	2.3 ± 2.5 MSDW = 25	0.35±0.41
SE Top C	2.2 +1.8/-1.9	0.35 +0.24/-0.23	2.36 +0.18/-0.17	0.34 +0.3/-0.3	2.36 +0.18/-0.17	0.34 +0.3/-0.3		
SE-Top D	2.2 +1.1/-1.2	0.35 +0.24/-0.23	2.37 +0.15/-0.15	0.34 +0.3/-0.3	2.37 +0.15/-0.15	0.34 +0.3/-0.3		
SE 43-46 mm/top	5.4 +0.9/-0.9	0.35 +0.24/-0.23	5.61 +0.47/-0.47	0.34 +0.3/-0.3				
SE 78-83 mm/top	7.7 +1.5/-1.6	0.35 +0.24/-0.23	8.17 +0.60/-0.60	0.34 +0.3/-0.3				

Table 3: Simulation results for the Rupt du Puits speleothem.

	Weak constraints		Strong constraints (all samples)		strong constraints (3 subsamples only)		Isoplot isochron (3 subsamples only)	
	mean age +/- (ka)	R _i +/- (AR)	mean age +/- (ka)	R _i +/- (AR)	mean age +/- (ka)	R _i +/- (AR)	mean age ± 2σ (ka)	R _i +/- (AR)
R69-1	4.12 +0.31/-0.55	0.77 +0.12/-0.11	4.16 +0.27/-0.46	0.76 +0.09/-0.08				
R69-3	4.45 +0.05/-0.04	0.77 +0.12/-0.11	4.45 +0.04/-0.04	0.76 +0.09/-0.08				
R69-4	4.74 +0.10/-0.10	0.77 +0.12/-0.11	4.75 +0.09/-0.09	0.76 +0.09/-0.08				
R69-6a	4.92 +0.15/-0.16	0.77 +0.12/-0.11	4.92 +0.12/-0.13	0.76 +0.09/-0.08	5.3 +0.3/-0.4	0.36 +0.37/-0.24	5.6 ± 0.7	0.2 ± 0.6
R69-6b	4.81 +0.13/-0.12	0.77 +0.12/-0.11	4.82 +0.12/-0.11	0.76 +0.09/-0.08	5.2 +0.3/-0.4	0.36 +0.37/-0.24		
R69-6c	4.94 +0.14/-0.15	0.77 +0.12/-0.11	4.93 +0.12/-0.13	0.76 +0.09/-0.08	5.3 +0.3/-0.4	0.36 +0.37/-0.24		
R69-7	5.09 +0.10/-0.10	0.77 +0.12/-0.11	5.09 +0.10/-0.10	0.76 +0.09/-0.08				
R69-9	5.37 +0.07/-0.08	0.77 +0.12/-0.11	5.38 +0.07/-0.07	0.76 +0.09/-0.08				

Table 4: Simulation results for the Santo coral core.

	Weak constraints (all samples)		Strong constraints (all samples)		strong constraints (4 subsamples only)		Isoplot isochron (4 subsamples only)		strong constraints (3subsamples only)		Isoplot isochron (3 subsamples only)	
	mean age +/- (a)	R _i +/- (AR)	mean age +/- (a)	R _i +/- (AR)	mean age +/- (a)	R _i +/- (AR)	mean age ± 2σ (a)	R _i +/- (AR)	mean age +/- (a)	R _i +/- (AR)	mean age ± 2σ (a)	R _i +/- (AR)
1 #1	7.6 +5.6/-6.4	2.5 +1.4/-1.2	12.0 +2.6/-3.2	1.5 +0.7/-0.6	10.4 +3.1/-3.9	1.8 +1.2/-0.9	15.9±5.6	0.8±2.1	14.2 +1.5/- 1.1	1.0 +0.3/-0.7	14.2±1.0	1.0±0.4
1 #2	12.2 +1.8/-2.2	2.6 +1.7/-1.3	12.0 +2.1/-2.8	2.8 +2.4/-1.6	10.5 +3.0/- 3.9	3.8 +4.5/-3.1			14.1 + 0.9/- 0.8	1.0 +0.2/-0.3		
1 #3	12.0 +2.3/-2.9	2.6 +1.7/-1.3	12.2 +2.4/-3.2	2.5 +2.0/-1.4	10.4 +3.1/-4.0	3.4 +3.5/-2.5			14.5 +0.8/-0.9	1.0 +0.3/-0.3		
1 #4	15.9 +2.7/-3.5	2.6 +1.7/-1.3	13.1 +2.2/-3.2	4.0 +1.6/-1.2	10.6 +3.1/-4.1	5.1 +3.0/-2.0			MSWD = 18			
2 #1	31.7 +1.6/-1.9	2.6 +1.7/-1.3	31.3 +2.0/-2.3	3.1 +2.1/-1.8	29.4 +0.9/-1.0	4.6 +0.5/-0.4	28.7±2.8	4.7±1.6				
2 #2	31.3 +2.1/-2.7	2.6 +1.7/-1.3	30.9 +2.6/-2.9	2.9 +2.0/-1.7	28.9 +1.0/-1.0	4.6 +0.5/-0.4						
2 #3	31.0 +1.9/-2.3	2.6 +1.7/-1.3	30.6 +2.3/-2.7	2.9 +2.1/-1.7	28.9 +1.0/-1.0	4. +0.5/-0.4						
2 #4	34.1 +3.5/-4.6	2.8 +1.7/-1.3	31.4 +2.6/-3.4	3.8 +1.2/-1.0	29.2 +1.1/-1.2	4.6 +0.5/-0.4			MSWD = 2.7			
3	36.0 +3.1/-3.8	2.3 +1.5/-1.2	35.8 +3.2/-3.4	2.4 +1.4/-1.2								
4	45.8 +0.9/-1.0	2.6 +1.7/-1.3	45.7 +1.0/-1.1	3.0 +2.1/-1.8								
5	56.0 +1.7/-2.2	2.6 +1.7/-1.3	55.5 +2.3/-2.6	3.1 +2.2/-1.8								
6	65.4 +5.8/-7.3	2.6 +1.6/-1.3	64. 2+7.3/- 7.7	2.8 +1.7/-1.6								

1 **Figure Caption**

2

3 **Figure 1:** Principle of the stratigraphical and coevality constraints as calculated in
4 STRUTages. **a:** example of valid simulation for a stalagmite without coeval samples. **b:**
5 example of discarded simulation for a stalagmite without coeval samples. Cases a and b
6 correspond to the Hellstrom (2006) approach with no coeval samples. **c:** example of valid
7 simulation with the loose coevality constraints applied to coeval samples. **d:** example of
8 discarded simulation with the loose coevality constraints applied to coeval samples. **e:**
9 example of valid simulation with the strict coevality constraints applied to coeval samples. **f:**
10 example of discarded simulation with the strict coevality constraints applied to coeval
11 samples. Circles and ellipses represent the ages simulated during one trial with the loose
12 coevality constraints. On sub-figures e and f, the small black squares represent the results of
13 the calculated ages used to reconstruct the full error-bar of the sample ages.

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15 **Figure 2:** Monte Carlo simulation results for the Santa Elina speleothem. **a:** ΔR_i versus R_{i_mean}
16 for the successful trials with the loose coevality constraints. **b:** Age distribution with the loose
17 coevality constraints applied to trials with $\Delta R_i < 1\%$. **c:** ΔR_i versus R_{i_mean} for the successful
18 trials with the strict coevality constraints. **d:** Age distribution with the strict coevality
19 constraints applied to trials with $\Delta R_i < 1\%$ (about 1000 successful trials were obtained by
20 specifically running STRUTages with ΔR_i values $< 1\%$). Coeval samples are underlined.

21 **Figure 3:** Monte Carlo simulation results for the Rupt du Puits speleothem. **a:** ΔR_i versus
22 R_{i_mean} for the successful trials with the loose coevality constraints. **b:** Age distribution with
23 the loose coevality constraints applied to trials with $\Delta R_i < 1\%$. **c:** ΔR_i versus R_{i_mean} for the

1 successful trails with the strict coevality constraints. d: Age distribution with the strict
2 coevality constraints applied to trials with $\Delta R_i < 1\%$ (about 1000 successful trails were
3 obtained by specifically running STRUTages with ΔR_i values $< 1\%$). Coeval samples are
4 underlined.

5 **Figure 4:** Monte Carlo simulation results for the Santo coral core. a: ΔR_i versus R_{i_mean} for
6 the successful trails with the loose coevality constraints. b: Age distribution with the loose
7 coevality constraints applied to trials with $\Delta R_i < 1\%$. c: ΔR_i versus R_{i_mean} for the successful
8 trails with the strict coevality constraints. There is no successful trial for $\Delta R_i < 50\%$. d: Age
9 distribution with the strict coevality constraints applied to trials with $\Delta R_i < 70\%$. Coeval
10 samples are underlined.

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12 **Figure 5:** Comparison of the calculated ages with the counted ages of the Santo coral. a:
13 STRUTages versus counted ages. b: isochron and isochron-derived ages from Shen et al.
14 (2008) versus counted ages. The continuous line is the 1:1 line.

15

Stratigraphical order test

Coeval subsamples : loose coevality constraints

Coeval subsamples : strict coevality constraints

Figure 1

Figure 2 (Santa Elina)

Figure 3 (Rupt du Puits)

Figure4 (Santo coral core)

Figure 5