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Research paper

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

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ABSTRACT

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

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 ($^{230}Th/^{232}Th$) activity ratio >20 did not require corrections (Bischoff and Fitzpatrick, 1991). However, with the improvement of dating technics, more recent studies propose with that the influence of this detrital fraction on age determination is significant for measured ($^{230}Th/^{232}Th$) 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 $^{230}Th/^{232}Th$ activity ratio is known. This initial $^{230}Th/^{232}Th$ 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 widely used to estimate the initial $^{230}Th/^{232}Th$ activity ratio. However, several studies have demonstrated that this value does not reflect the whole range of initial Th activity ratio, because clay is not the only Th source (e.g. Beck et al., 2001; Hellstrom, 2006) and because the U/Th ratio in detrital particles and colloids can vary strongly (Marchandise et al., 2014). Drip water in caves, sea water or modern calcium carbonate are also used to determine the initial Th activity ratio, $(^{230}Th/^{232}Th)_{A0}$, at the formation of the speleothem (Hu et al., 2008; Wortham et al., 2013). This initial ratio can also be deduced directly from an isochron constructed with several subsamples from the same laminae (or group of laminae) of the speleothem

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having different U/Th ratios (Dorale et al., 2004). However, $(^{230}Th/^{232}Th)_{A0}$ obtained on one stratigraphical level with an isochron or by the measurement of modern calcite or aragonite may not be valid throughout the speleothem or coral. More recently, the "stratigraphical constraint" method was developed to determine the range of $(^{230}Th/^{232}Th)_{A0}$ that keeps speleothem samples in stratigraphical order after correction for the initial ^{230}Th content (Hellstrom, 2006). These two methods require different sample set: the isochron method uses several samples of the same age, whereas the stratigraphical method uses several samples of different ages. The isochron method is widely used and many researchers draw upon the freely-available software `Isoplot` (Ludwig, 2003) to calculate $(^{230}Th/^{232}Th)_{A0}$ in an isochron diagram. On the other hand, no software performing the "stratigraphical constraint" method has been published so far.

Recently, we developed our own routine to obtain stratigraphical constraints on very young (<400 a) and detritus-rich speleothems (Pons-Branchu et al., 2014). Initially, our goal was to reproduce the method described in Hellstrom (2006). However, it rapidly appeared that a program would be much more practical if it could combine samples of increasing ages through the speleothem (the stratigraphical method) with samples from the same 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` (STRatgraphical 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, $(^{230}Th/^{232}Th)_{A0}$ 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 $^{234}U/^{238}U$, $^{232}Th/^{238}U$ and $^{230}Th/^{238}U$ activity ratios expressed as $(^{234}U/^{238}U)_A$, $(^{232}Th/^{238}U)_A$ and $(^{230}Th/^{238}U)_A$ (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 $(^{230}Th/^{232}Th)_{A0}$ 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 $(^{230}Th/^{232}Th)_{A0}$ 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 $(^{230}Th/^{232}Th)_{A0}$ 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:

- $(^{230}Th/^{238}U)_A < (^{232}Th/^{238}U)_A \times R_i$ (i.e. less ^{230}Th in the sample today than at the time of formation)
- $(^{230}Th/^{238}U)_A - 1 > ((^{234}U/^{238}U)_A - 1) \times \lambda_{230}/(\lambda_{230} - \lambda_{234})$ (i.e. sample plotting on the right of the infinite age line in a $(^{230}Th/^{238}U)_A$ versus $((^{234}U/^{238}U)_A - 1)$ 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:

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

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 $(^{230}Th/^{232}Th)_{A0}$ 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. 1a). However, it is not a necessary condition because a single trial does not cover the whole range of uncertainty on each sample age (Fig. 1b). Nevertheless, with the large number of trails performed, it is likely that the successful trails 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