

# U-series dating applied to speleothems from Los Covachos Cave, South of Spain

J. M. Alcaraz-Pelegrina, A. Martínez-Aguirre, J. Rodríguez-Vidal

**Abstract** U-series dating method is applied to speleothems from Los Covachos Cave in the south of Spain. A combination of solvent extraction method with ion-exchange resins is used for uranium and thorium isotopes. Uranium concentrations are low and for younger samples correction by detrital contamination is necessary. Ages obtained range from 30 to 135 ky with a hiatus between 50 and 80 ky BP. Changes in uranium isotopes activity ratios indicate a change in climatic conditions.

**Keywords** U–Th dating · Speleothem · Los Covachos Cave

## Introduction

Uranium series disequilibrium in natural systems could help to study numerous geological, climatic and archaeological problems [1]. In particular, the disequilibrium between uranium and thorium isotopes could be applied to date several types of materials in sediments: either authigenic minerals or detrital materials [2, 3]. In this way, U/Th

dating of carbonates allows us to obtain dates from carbonates as old as 350–500 Ky [4] and in the last decades has been applied to numerous geological, climatic and archeological problems [5–8]. It is generally accepted that continental carbonates (speleothems and travertines) are formed in warm Quaternary episodes [9]. Hence, they are good warm-climate markers in regions such as the Mediterranean, although there are records of substantial accumulations of carbonates in cold episodes [10].

The Iberian peninsula is very rich in carbonates systems from Quaternary and the last few decades have seen much work on them. However, there are few reports on U-series dating in these systems [11–16].

Among the different applications of carbonates dating is the study of karst evolution. In the south of Spain there are many karsts which its time evolution can be studied from U-series dating of speleothems and carbonates deposits. Speleothems are carbonates formed in a cave environment from seepage waters which deposits  $\text{CaCO}_3$ . Flowstones are speleothems that are thinly laminated deposits formed from groundwaters flowing down cave walls and floors.

The purpose of this study was to determine U–Th ages on speleothem deposits from Los Covachos Cave. Its principle aim is methodological but the implications for karst evolution are considered to establish some time references for the evolution of the site.

Los Covachos Cave is located in the South of Spain (Fig. 1) and forms part of a larger mountainous group known as Sierra Norte in Seville, near to Almaden de la Plata town (North of Seville) [17]. The cave is 540 m length and have 28 m of height difference. It have a high diversity of speleothems located in walls, soils and roofs. Some of these deposits are damaged due to human visits.

Weathering have found some speleothems formed some meters under the surface in cave roofs or walls a few

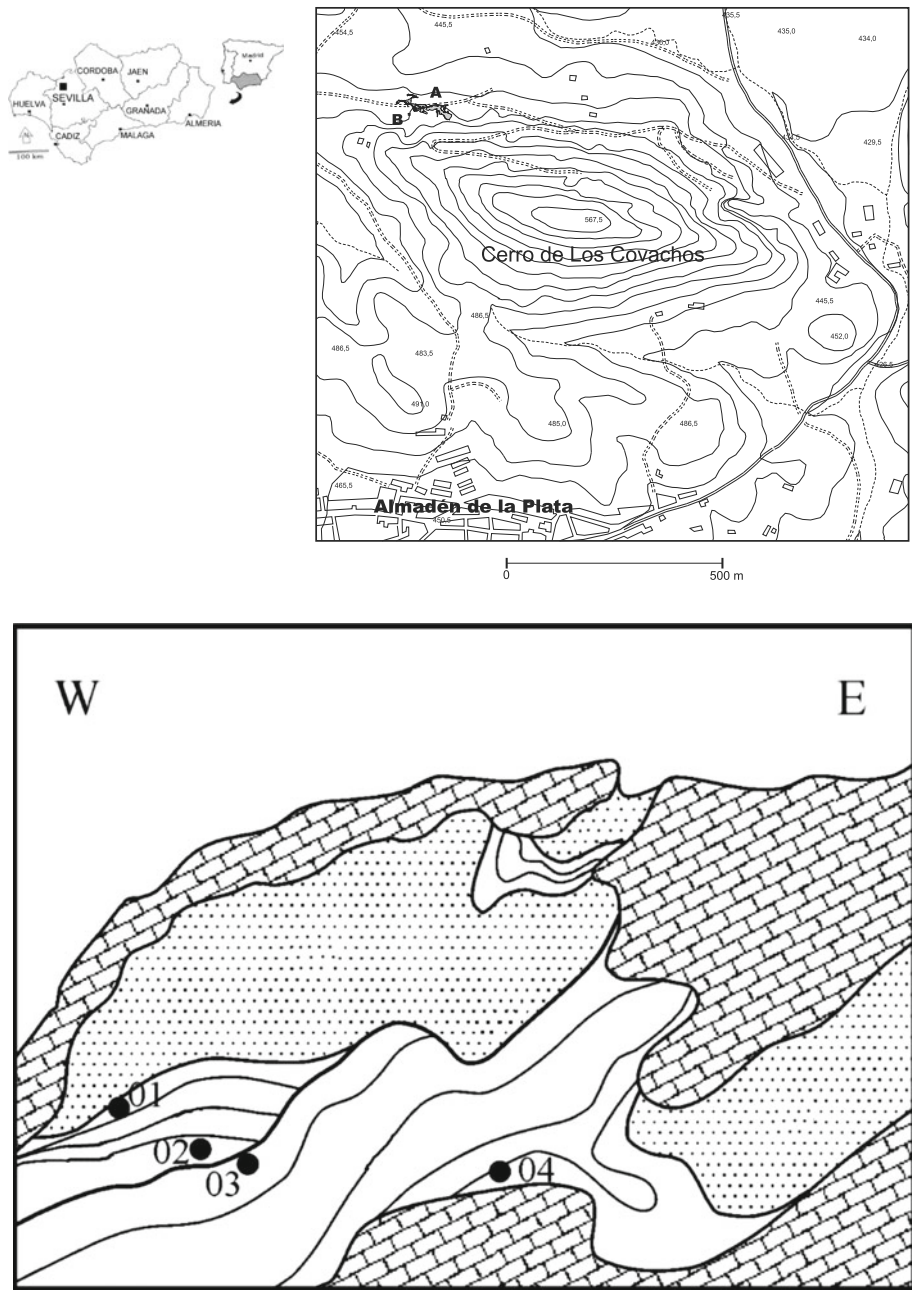
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**Fig. 1** Geographical situation of Los Covachos mountain and stratigraphic section of the quarry's cave with location of the speleothem samples.  
*Upperbox:* **A** location of the cave and **B** location of the quarry's cave



thousand years ago. Dating of these exhumed speleothems and its relation with different stages of landscape evolution allows us to establish a chronology of the karst in this place. In particular, one of these exhumed speleothems formed a quarry located 100 m western the cave entry that could help to establish a chronology of the site.

The U–Th series is used for dating carbonate deposits because uranium's water-solubility allows its precipitation with calcite. However, thorium is quickly absorbed or precipitated as insoluble hydrolysates when brought into solution [18, 19]. As a result, when calcite is formed, it contains uranium but is thorium-free. The growth of  $^{230}\text{Th}$  from its parents enables us to obtain the age of the system

[1]. Unfortunately, most calcite deposits of interest to geology, archaeology,... are dirty calcite: the carbonates are mixed with detrital materials that have been deposited with the carbonates. These detrital materials contain uranium and thorium isotopes, and for this reason it is necessary to correct the result obtained from the analysis of carbonates.

Because detrital  $^{230}\text{Th}$  is always accompanied by  $^{232}\text{Th}$ , the presence of detrital materials can be recognized by the presence of  $^{232}\text{Th}$  in the thorium spectrum of the samples, and correction for the detrital contribution can be achieved using various correction methods [20]. All correction methods consider the carbonate sample as a mixture of

pure carbonate and detrital material mixed with pure carbonate. Detrital material includes all materials containing uranium and thorium isotopes.

Leachate–residue methods (L/R method) [21, 22] calculate activity ratios in carbonates from those in leachate and insoluble residue of a sample. There are two L/R methods: correction scheme I [4] and correction scheme II [22]. To obtain activities in pure carbonate, the first assumes secular equilibrium in the detrital material and no fractionation between thorium isotopes during dissolution, while correction scheme II assumes no fractionation between uranium and thorium isotopes. In numerous situations, such assumptions are not met, and thus the two methods have limited application.

The leachate–leachate method (L/L method) [23] uses various leachates of coeval subsamples of a carbonate to obtain activity ratios in pure carbonates from the slopes of the two isochrons described by

$$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)_L = \left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_C \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)_L + \frac{r_0}{r_2} \left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)_D - \frac{r_8}{r_2} \left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_C \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)_D \quad (1)$$

$$\left(\frac{^{234}\text{U}}{^{232}\text{Th}}\right)_L = \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_C \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)_L + \frac{r_4}{r_2} \left(\frac{^{234}\text{U}}{^{232}\text{Th}}\right)_D - \frac{r_8}{r_2} \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_C \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)_D \quad (2)$$

where the isotope symbol indicates activity of that isotope, and subscripts C, D, and L mean carbonate, detrital material and leachate fraction respectively. The only assumption of the L/L method is that if fractionation occurs, it must be the same for all samples. Moreover, fractions  $r_i/r_j$  must be the same for all samples, where  $r_i$  represents the fraction of isotope  $i^1$  in detrital material leachate during dissolution.

The total sample dissolution method (TSD methods) [24, 25] totally dissolves the sample, obtaining similar isochrons to those described for the L/L method, with  $r_i$  values equal to one. It is more time-consuming as the samples must be dissolved completely, and it can be applied only to inhomogeneous samples in order to obtain different values for the activity ratios to define the isochrons.

Some works [26, 27] include the U and Th contribution from admixed detritus in carbonate and initial Th in the hydrogenous component, but this approach basically makes two corrections using L/R methods.

Of the methods mentioned above, the so-called L/L method seems to give good results, and can be applied to practically all types of impure carbonates [28, 29].

<sup>1</sup>  $i = 8$  for  $^{238}\text{U}$ ,  $i = 4$  for  $^{234}\text{U}$ ,  $i = 0$  for  $^{230}\text{Th}$  and  $i = 2$  for  $^{232}\text{Th}$ .

## Materials and methods

A total of five samples were taken from the Cerro and Cave of Los Covachos. Four of them were taken outside the cave in a quarry located 100 m westside the cave entrance. This quarry is a deposit of exhumed speleothems as shows in Fig. 1. Samples AP1 and AP2 were taken above a clay layer where a change in speleothem grown orientation occurs, and were treated as impure carbonates because they present a brown coloration. Otherwise, samples AP3 and AP4 were taken below the clay layer and were treated as pure carbonates because they not seem to have impurities with carbonate as they present a white colour. The other sample, AP-5, was taken inside the cave and it is a flow-stone closing the entrance to the Galeria del Equipo that have numerous archaeological remains.

### Uranium series dating

For pure carbonates, 40–50 g of sample were dissolved using 2 M nitric acid. For impure carbonates, it is necessary to obtain the 4–6 coeval, carbonate-detrital mixture, required for each isochron age determination of a sample according to L/L method [28]. We used here the procedure summarized below. First, the sample is crushed and homogenized. Subsamples of 40–50 g are taken and dissolved with different nitric acid concentrations. Here, differences in activity concentrations are due to the distinct nitric acid concentrations. Some of the subsamples were also fired at 900 °C for 3 h prior to dissolution in order to have a wider range of values [24]. This procedure give better results that take various subsamples containing varied carbonate-detrital material proportions and dissolve them with the same acid [30].

During dissolution a known amount of  $^{232}\text{U}$  and  $^{229}\text{Th}$  is added for yield calculations.  $^{229}\text{Th}$  is used as thorium spike because impure carbonates have a certain  $^{228}\text{Th}$  content.

For both pure and impure carbonates, the solution is separated by filtration as soon as possible after dissolution to avoid thorium reabsorption onto the detrital residue. An iron carrier ( $\text{FeCl}_3$ ) is added to solution and iron hydroxides are precipitated at pH 9 with concentrated ammonia. Uranium and Thorium isotopes co-precipitated with iron hydroxides.

Procedures for the isolation and purification of uranium and thorium isotopes are based on the use of ion-exchange resins or solvent extraction methods [1]. In some cases, for carbonates samples, specially with impure ones, we have observed that ion-exchange resins could be not used because an insoluble material co-precipitated with iron hydroxides and block the columns of ion-exchange resin resulting in low recovery yields. For this reason, we use a combination of solvent extraction with ion-exchange

resins. Thus, a solvent extraction method with tributylphosphate (TBP) is used to backextract uranium and thorium from dissolution and to separate uranium from thorium [31]. As some uranium traces are also backextracted with thorium, an anion-exchange resin is used for thorium purification.

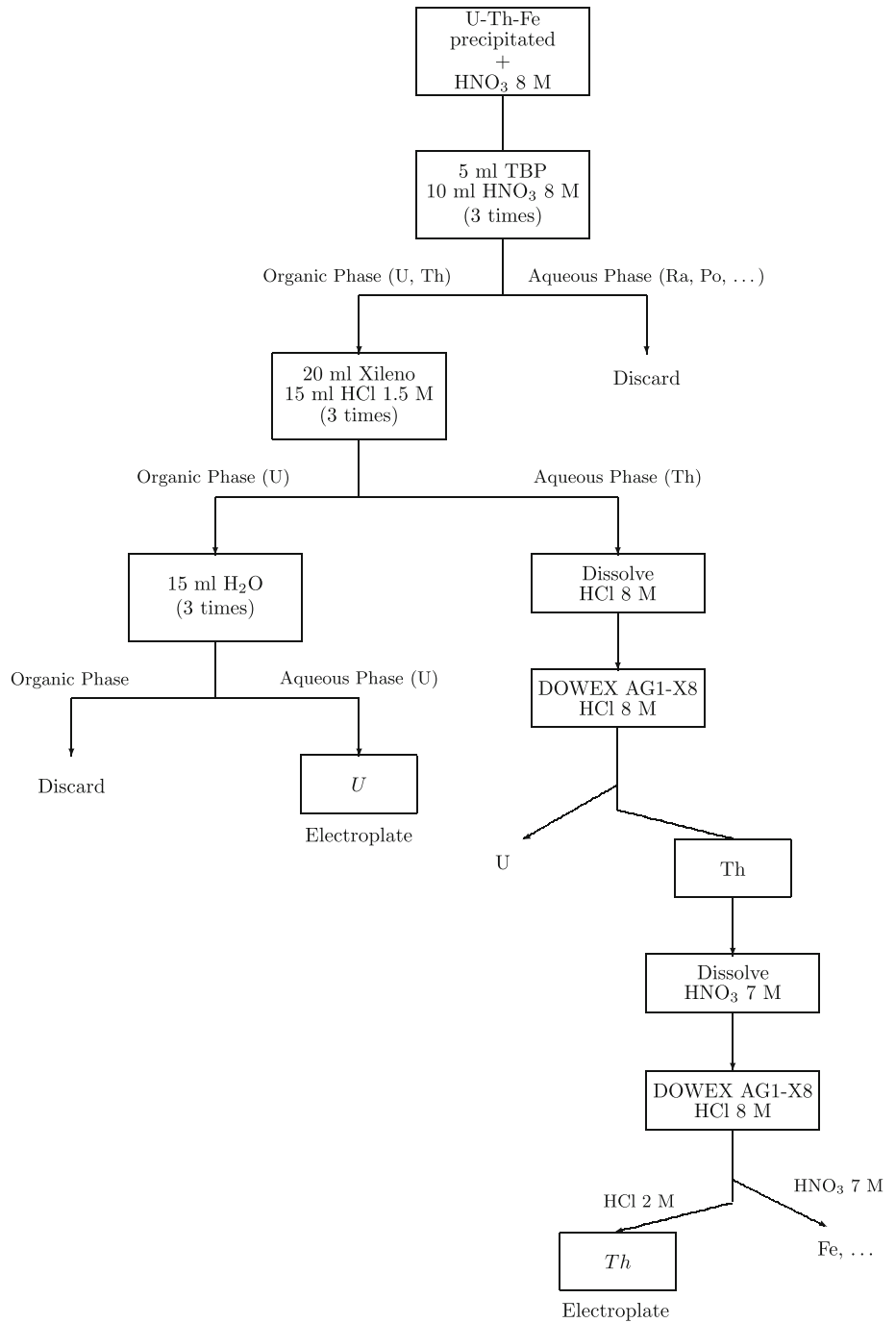
Figure 2 shows a scheme of the radiochemical method used for the isolation of uranium and thorium isotopes described in the next paragraphs.

*U-Th solvent extraction*

Step 1: The precipitate is dissolved in 10 ml of 8M HNO<sub>3</sub> and 5 ml of TBP is used to backextract uranium and thorium from dissolution into the organic phase. The aqueous phase is rejected. Repeat this step three times.

Step 2: 20 ml of Xylene and 15 ml of 1.5 M HCl are added to organic phase containing uranium and thorium

**Fig. 2** Simplified scheme of the procedures for the isolation and purification of uranium and thorium isotopes (see text for detail)



isotopes. After shaking for about 5 min, uranium isotopes remain in organic phase and thorium isotopes pass into aqueous phase. Once both phases are separated, this step is repeated twice.

Step 3: Uranium isotopes are back-extracted from the organic phase with distilled water: 15 ml of distilled water are added to organic phase and after 5 min shaking, uranium isotopes move to aqueous phase. This step is repeated three times. The aqueous phase with uranium isotopes is ready for electroplating.

### Th purification

As commented before, the thorium fraction needs further purification using an anion-exchange resin. A few ml of iron carrier is added to thorium dissolution, and iron hydroxides are precipitated.

Step 1: Pyrex glass column (12 mm diameter) is filled till 4 cm height with anion exchange resin Dowex AG1-X8 in chloride form and washed with 40 ml of 8M HCl. The flow rate is controlled by the diameter of the output orifice (4 mm).

Step 2: Iron hydroxides precipitate is dissolved in 1:1 volume of 8 M HCl and concentrated HCl (5 ml each). This solution is passed through the column. Thorium isotopes comes out in the effluent while uranium isotopes are adsorbed on the column resin.

Step 3: Some iron carrier is added to thorium solution from previous step and thorium isotopes are co-precipitated with iron hydroxides at pH 9 using concentrated ammonia.

Step 4: Pyrex glass column (6 mm diameter) is filled till 4 cm height with anion exchange resin Dowex AG1-X8 and washed with 20 ml of 7M HNO<sub>3</sub>. The flow rate is controlled by the diameter of the output orifice (2 mm).

Step 5: The precipitate containing thorium isotopes is dissolved with 5 ml of 7M HNO<sub>3</sub> and added to the column. Thorium is adsorbed in the column while iron and other impurities pass through the resin. 20 ml of 7M HNO<sub>3</sub> is used to elute iron and impurities from the column.

Step 6: The adsorbed thorium is finally collected by adding 20 ml of 2M HCl to the column. This solution is ready for electroplating.

Some 0.3 M NaSO<sub>4</sub> is added to the final solutions, which are evaporated to dryness. The electrodeposition of uranium and thorium is performed for 1 h at 1.2 A following the method described in [32].

The sample discs obtained in electrodeposition are measured by alpha spectrometry [33, 34]. The alpha spectrometer system used was equipped with PIPS detectors and showed good stability over the 3–7 days of counting time generally required for each planchet. Moderate-to-high recovery yields and well-resolved spectra provided analytically reliable results.

### Results

Table 1 shows analytical results for pure carbonates and uranium concentration, activities ratios and nominal ages for impure carbonates. For impure carbonates we include

**Table 1** U–Th analytical results for samples of Los Covachos Cave

Sample	<sup>238</sup> U ppm	<sup>234</sup> U <sup>238</sup> U	<sup>230</sup> Th <sup>234</sup> U	<sup>230</sup> Th <sup>232</sup> Th	ρ <sub>0242</sub>	ρ <sub>0282</sub>	ρ <sub>8242</sub>	Age ka
AP1-A (2)	0.0120 ± 0.0014	1.134 ± 0.069	0.586 ± 0.032	3.00 ± 0.26	0.711	0.454	0.500	94 ± 8
AP1-B (7)	0.0109 ± 0.0011	1.127 ± 0.062	0.706 ± 0.043	2.88 ± 0.21	0.664	0.445	0.496	128 ± 15
AP1-C (2)(F)	0.0138 ± 0.0010	1.107 ± 0.054	0.942 ± 0.072	2.30 ± 0.14	0.645	0.472	0.532	>350
AP1-D (7)(F)	0.0142 ± 0.0006	1.014 ± 0.048	1.022 ± 0.100	2.28 ± 0.15	0.524	0.664	0.597	>350
AP2-A (2)	0.0064 ± 0.0009	1.283 ± 0.084	0.745 ± 0.123	2.57 ± 0.18	0.634	0.344	0.362	137 <sup>+53</sup> <sub>-37</sub>
AP2-B (4)	0.0069 ± 0.0003	1.158 ± 0.058	0.410 ± 0.034	4.36 ± 0.46	0.621	0.619	0.539	57 ± 6
AP2-C (7)	0.0076 ± 0.0003	0.993 ± 0.050	0.564 ± 0.040	3.41 ± 0.32	0.708	0.710	0.760	90 ± 10
AP2-D (2)(F)	0.0086 ± 0.0004	0.928 ± 0.069	1.061 ± 0.128	1.92 ± 0.13	0.350	0.560	0.398	>350
AP2-E (7)(F)	0.0076 ± 0.0004	1.060 ± 0.068	0.900 ± 0.101	1.71 ± 0.12	0.557	0.552	0.631	237 <sup>+191</sup> <sub>-67</sub>
AP3	0.0146 ± 0.0014	1.006 ± 0.115	0.514 ± 0.052	25 ± 4	–	–	–	78.2 ± 11.5
AP4	0.0081 ± 0.0008	1.139 ± 0.066	0.713 ± 0.076	ND	–	–	–	130 <sup>+30</sup> <sub>-23</sub>
AP5	0.0327 ± 0.0010	0.988 ± 0.030	0.891 ± 0.046	45 ± 8	–	–	–	243 <sup>+63</sup> <sub>-39</sub>

Number in parentheses indicates nitric acid concentration used during sample dissolution. (F) indicates fired samples prior to dissolution. Errors are 1 – σ

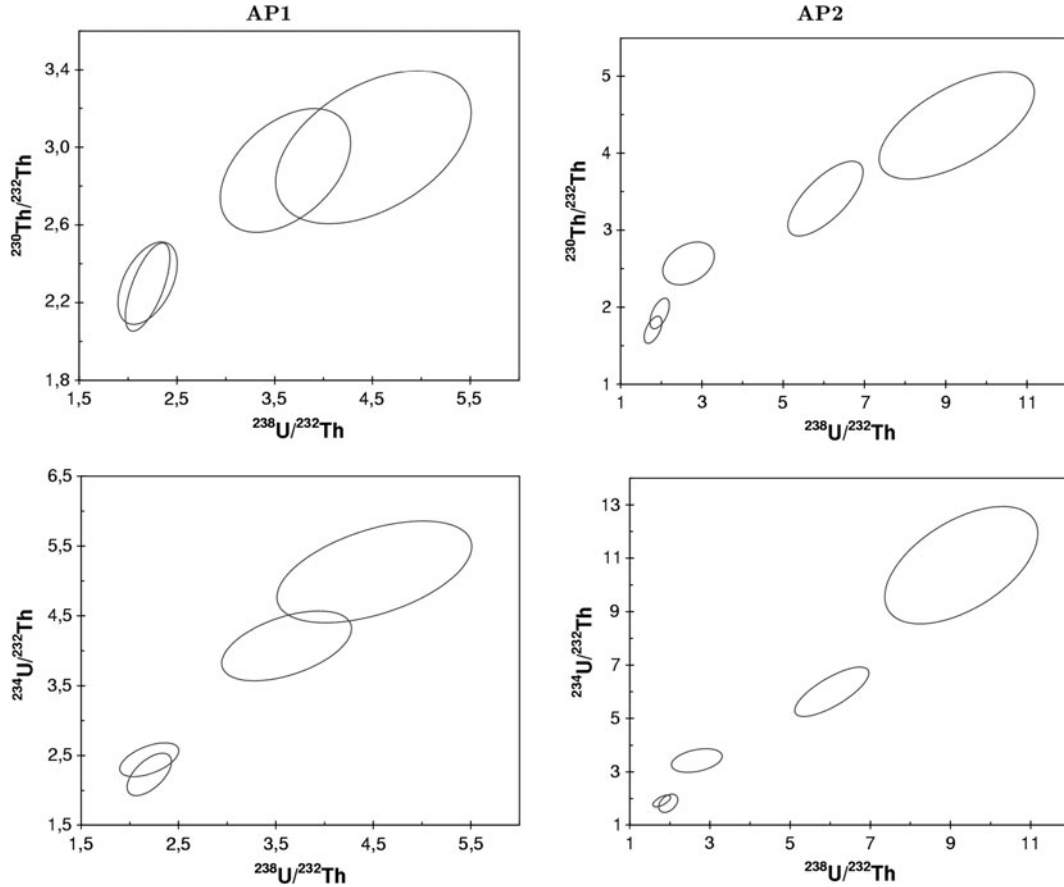
ND Not detected

**Table 2** Ages and initial  $\frac{^{234}\text{U}}{^{238}\text{U}}$  for Los Covachos Cave samples

Sample	$\frac{^{230}\text{Th}}{^{234}\text{U}}$	$\frac{^{234}\text{U}}{^{238}\text{U}}$	Edad	$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_o$	MSWD	P.o.f.
AP-1	$0.281 \pm 0.097$	$1.256 \pm 0.249$	$35.5 \pm 9.9$	$1.283 \pm 0.275$	0.28	0.891
AP-2	$0.345 \pm 0.049$	$1.050 \pm 0.095$	$45.7 \pm 6.5$	$1.057 \pm 0.108$	1.67	0.123
AP-3	$0.514 \pm 0.052$	$1.006 \pm 0.115$	$78.2 \pm 11.5$	$1.007 \pm 0.143$		
AP-4	$0.713 \pm 0.076$	$1.139 \pm 0.066$	$130^{+30}_{-23}$	$1.200 \pm 0.096$		

AP-1 and AP-2 ages were obtained using UISO program. Errors are 1 –  $\sigma$

MSWD mean square of weighted deviates of the data from the regression lines, P.o.f. is the probability of fit as reported by UISO program



**Fig. 3** Rosholt diagrams (2D version) of impure samples for illustration purposes only because the activity ratios in carbonate fraction and ages are based on a 3D isochron fit

error correlations used in Rosholt diagrams. These error correlations are calculated according [35] as also ages of impure carbonates that are obtained using UISO [36] and ISOPLOT [37] programs. These ages are included in table 2 together with initial  $\frac{^{234}\text{U}}{^{238}\text{U}}$ . Figure 3 shows Rosholt diagrams for impure carbonates as 2D versions for illustration purposes only because the activities ratios  $\frac{^{230}\text{Th}}{^{234}\text{U}}$  and  $\frac{^{234}\text{U}}{^{238}\text{U}}$  in carbonate fraction are derived by a 3D fit to the data.

U activities range from 0.006 to 0.03 ppm, sufficient to be measured easily by  $\alpha$ -spectrometry as 40–50 g were taken for each sample. Moderate to high recovery yields

and well resolved spectra provided analytically reliable results.

As can be seen in Table 1, samples AP3 and AP4 were free from detrital  $^{230}\text{Th}$  contamination or it can be ignored as  $^{232}\text{Th}$  activities are very low and are lower than  $^{230}\text{Th}$  activities errors. Uranium concentration in these samples range from 0.008 (AP4) to 0.015 (AP3) ppm. Thus, AP4, situated in the bottom of the quarry, results in an age of  $130^{+30}_{-23}$  ky BP. Sample AP3 is younger, resulting in an age of  $78.2 \pm 11.5$  ky BP. Initial  $\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_o$  are  $1.01 \pm 0.14$  for AP3 and  $1.20 \pm 0.09$  for AP4. This change in uranium

activities ratios reflects a change in climatic conditions indicated by the clay layer situated over sample AP3 location which represents a gap in speleothem growth.

In Table 1 we can see that samples AP1 and AP2 had detrital  $^{230}\text{Th}$  contamination indicated by  $^{232}\text{Th}$  activities that give activities ratios for thorium isotopes between 1.7 and 4. Thus, for some subsamples we obtained ages higher than 350 ky because of this detrital contribution.  $^{232}\text{Th}$  activities are low, from 0.01 to 0.08, but  $^{230}\text{Th}$  activities are so. For this reason, it is not possible to reject detrital contribution and the samples were treated as impure carbonates. For sample AP1 we prepared four coeval samples in order to use the L/L method to obtain activities ratios in carbonate fraction. Two of these subsamples were fired previously to dissolution with nitric acid as indicated in Table 1. This table shows that activities in fired samples are higher than those of unfired samples. This difference is higher in thorium isotopes. In this case, fired samples have activities that are twice those of unfired samples. No difference exists between activities obtained in samples dissolved with 2 M nitric acid and those dissolved with 7 M nitric acid, neither in fired or unfired samples. In Fig. 3, Rosholt diagrams are represented as 2D versions for illustration purposes only as commented above. For sample AP1,  $\frac{^{230}\text{Th}}{^{232}\text{Th}}$  ranges from 2.3 to 3 whereas  $\frac{^{238}\text{U}}{^{232}\text{Th}}$  and  $\frac{^{234}\text{U}}{^{232}\text{Th}}$  have similar range, from 2.2 to 4.5 the first and from 2.2 to 5.1 the second. These ranges are not wide, but allow us to define isochrons. Error correlations are closed to 0.5 and have similar values in all samples. Age obtained using UISO program for AP1 is  $35.5 \pm 9.9$  ky BP and initial uranium activities ratio was  $1.28 \pm 0.28$ . For sample AP2 we prepared five coeval samples, two of them were fired previously to dissolution with nitric acid. Uranium activities do not differ from fired and unfired samples and neither from different nitric acid concentrations, indicating that detrital has little contribution to uranium activities. For thorium isotopes, as in sample AP1, fired samples have higher activities than unfired samples for the same nitric acid concentration. Figure 3 shows a wider range of activities ratios than those of sample AP1, with thorium isotopes activities ratios ranging from 1.7 to 4.4 and activities ratios from uranium isotopes with  $^{232}\text{Th}$  ranging from 1.8 to 11. As expected, AP2 is older than AP1,  $45.7 \pm 6.5$  ky BP obtained with UISO, but errors result in similar ages from the two locations, indicating a 10 ky period to develop this part of the quarry. Initial uranium activities ratio for sample AP2 is  $1.06 \pm 0.11$ .

Thus, quarry beneath clay layer range from  $130^{+30}_{-23}$  to  $78.2 \pm 11.5$  ky BP, a near 60 ky period of carbonate growth. From 78.2 to 50 ky BP, a change in climatic conditions occurs as indicated by clay layer and no speleothem growth and a change in uranium isotopes activities ratios that

decrease from 1.25 at 135 ky BP to secular equilibrium at 78.2 ky BP. After this stop in speleothem growth, another change in climatic conditions occur 50 ky ago and the quarry shows another speleothem formation period of 10 ky.

Sample AP5 was taken inside the cave and has the highest uranium concentration of all samples analyzed,  $0.033 \pm 0.001$  ppm.  $^{232}\text{Th}$  activity is  $0.007 \pm 0.001$  mBq/g, lower than  $^{230}\text{Th}$  activity error. Thus, no detrital correction is necessary. This sample is also the oldest sample with an age of  $243^{+63}_{-39}$  ky BP and initial uranium activities ratios equal to  $0.976 \pm 0.059$ . As commented above, this sample was a flowstone closing the entrance to the Galeria del Equipo that has numerous archaeological remains.

## Conclusion

The U-series method has been applied to speleothems from Los Covachos cave. A combination of solvent extraction method with ion-exchange resins has been used for uranium and thorium isotopes. Uranium concentration in the samples analyzed are low and they range from 0.07 to 0.18 mBq/g. Although  $^{232}\text{Th}$  activities are low,  $^{230}\text{Th}$  activities are so. For this reason, some of the samples has been treated as impure carbonates and it was necessary to correct by detrital contamination. For the quarry near to the cave entrance, ages obtained are in stratigraphic order with older samples lower in quarry stratigraphy. Clay layer in the quarry represents a hiatus of 30 ky in speleothem growth located between 45 and 75 ky ago.

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