

Isotopic fractionation during leaching of impure carbonates and their effect on uranium series dating

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Abstract

Experiments were designed to evaluate the behaviour of detritus during the leaching of impure carbonates by applying the U-Th isochron technique. We used one natural detritus and a pure, well-dated CaCO₃, alone and in artificial mixtures. One set of experiments was designed to study the effects of sample pre-treatment on the detritus and a second set to examine the effect of acid attacks on both the carbonate and the detritus fractions in a mixture of constant proportions. For both sets of data, the extracted fraction from the detritus was calculated for ²³⁸U, ²³⁴U, ²³⁰Th and ²³²Th and their constancy established. These conditions are necessary to apply the L/L method [Schwarcz, H.P., Latham, A.G., 1989. Dirty calcites. 1.—Uranium-series dating of contaminated calcite using leachates alone. *Chemical Geology (Isotopes Geoscience Section)* 80, 35–43] for U/Th dating. Finally, the L/L method was applied to the artificial impure carbonate and the resulting age is found in agreement with the age of the pure carbonate sample. We concluded that conditions of the L/L method to be applied for ageing impure carbonates hold.

1. Introduction

Isotopes from the ²³⁸U decay chain have been widely used to evaluate the time when certain geological systems were initially formed along with the study of their evolution through time. Particularly, the evaluation of the isotopic disequilibrium between ²³⁰Th and ²³⁴U has been used for dating of carbonate precipitates from natural waters. The solubility of U combined with the insolubility of Th in natural waters permit U to be available in precipitates from aqueous solutions and Th to be unavailable. Thus, any ²³⁰Th activity found later in such precipitates comes from radioactive decay of ²³⁸U and ²³⁴U. The growth of ²³⁰Th to secular equilibrium with U isotopes is a correct measure of the age of the sample, if the system remains closed since its formation. However, most of these carbonates are impure and

contain variable amounts of detrital material. This detritus consists mainly of clays. This material contributes significant, and usually unknown, quantities of natural isotopes from the ²³⁸U and ²³²Th decay chains to the chemical solution which is used to extract U and ²³⁰Th isotopes in the laboratory for dating purposes. It is thus necessary to apply a correction method to evaluate the isotope concentrations in the pure carbonate fraction of the contaminated carbonate.

There are several correction methods and all of them use the ²³²Th to evaluate the amount of detrital contamination of the impure carbonate (Ku and Liang, 1984; Schwarcz and Latham, 1989; Bischoff and Fitzpatrick, 1991; Kaufman, 1993). At the time of precipitation, the authigenic carbonate contains negligible amounts of ²³²Th and ²³⁰Th. This means that any ²³²Th found in a leachate of the carbonate must come from the detrital part of the impure carbonate. Different aliquots of an impure carbonate must have the same ²³⁰Th/²³²Th activity ratio at the time of precipitation of the carbonate. Along with ²³²Th, some ²³⁰Th is also

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leached from the detrital component into the solution, so that a correction for detrital ^{230}Th is necessary. Additionally, some U from the detritus could also be leached into the solution necessitating a correction for the U concentrations. [Allegre and Condomines \(1976\)](#) showed that if the U isotopes are in equilibrium and assuming that the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the fraction leached from the detrital material in the impure carbonate is the same as that in the detrital material, the time evolution of this activity ratio is given by the equation,

$$\begin{aligned} (^{230}\text{Th}/^{232}\text{Th})_{\text{L}} = & \left(^{230}\text{Th}/^{232}\text{Th} \right)_{\text{D}_0} e^{-\lambda_0 t} \\ & + (^{238}\text{U}/^{232}\text{Th})_{\text{L}} (1 - e^{-\lambda_0 t}), \end{aligned} \quad (1)$$

where L means the activity ratio in the leaching, D_0 the activity ratio in the detritus at the time of deposition and λ_0 the decay constant for ^{230}Th . In the following text, isotope ratios stand for activity ratios unless indicated otherwise.

The radioactive decay of ^{238}U and ^{232}Th are negligible for the time under consideration, thus their activity ratio can be considered constant in time. At $t = 0$, the time of precipitation, U and Th measurement of several leachates of the same impure carbonate will result in a horizontal line when plotting $^{230}\text{Th}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ activity ratios. After time t , the ^{230}Th activity concentration will grow due to the decay of U isotopes in the pure carbonate and, thus in the same plot the activity ratios in the several leachates will fall on a line with a slope $1 - e^{-\lambda_0 t}$. As time increases to values above $1/\lambda_0$, ^{230}Th will reach secular equilibrium with U isotopes. At this time, for each aliquot $^{230}\text{Th}/^{232}\text{Th} = ^{238}\text{U}/^{232}\text{Th}$ and the data points will fall along the so-called equiline, having a unit slope and passing through the origin. Thus, with time the slope of the isochron line will rotate from 0 to unity. This rotation occurs around a point called the equipoint which defines the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the detritus at the time of precipitation.

In the case of initial disequilibrium between U isotopes, the $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in leachates are described by the equation,

$$\begin{aligned} (^{230}\text{Th}/^{232}\text{Th})_{\text{L}} = & \left(^{230}\text{Th}/^{232}\text{Th} \right)_{\text{D}_0} e^{-\lambda_0 t} \\ & + (^{234}\text{U}/^{232}\text{Th})_{\text{L}} (1 - e^{-\lambda_0 t}). \end{aligned} \quad (2)$$

A plot of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ ratios in several leachates will allow the estimation of the age of the pure carbonate sample as well as the $^{230}\text{Th}/^{232}\text{Th}$ ratio in the detrital material at the time of the analysis.

[Schwarcz and Latham \(1989\)](#) proposed that an isochron could be constructed from leachates of the various aliquots (the L/L method), even though different fractions are extracted from the detrital material for each isotope. They showed that the

leachates would obey the linear relation,

$$\begin{aligned} (^{230}\text{Th}/^{232}\text{Th})_{\text{L}} = & \left(^{230}\text{Th}/^{234}\text{U} \right)_{\text{C}} \left(^{234}\text{U}/^{232}\text{Th} \right)_{\text{L}} \\ & + r_0/r_2 \left(^{230}\text{Th}/^{232}\text{Th} \right)_{\text{D}} \\ & - r_4/r_2 \left(^{230}\text{Th}/^{234}\text{U} \right)_{\text{C}} \left(^{234}\text{U}/^{232}\text{Th} \right)_{\text{D}}, \\ (^{234}\text{U}/^{232}\text{Th})_{\text{L}} = & \left(^{234}\text{U}/^{238}\text{U} \right)_{\text{C}} \left(^{238}\text{U}/^{232}\text{Th} \right)_{\text{L}} \\ & + r_4/r_2 \left(^{234}\text{U}/^{232}\text{Th} \right)_{\text{D}} \\ & - r_8/r_2 \left(^{234}\text{U}/^{238}\text{U} \right)_{\text{C}} \left(^{238}\text{U}/^{232}\text{Th} \right)_{\text{D}}, \end{aligned} \quad (3)$$

where r_0 , r_2 , r_8 and r_4 are fractions of ^{230}Th , ^{232}Th , ^{238}U and ^{234}U isotopes leached from the detritus into the solution. If relative fractions r_i/r_j are constant for coeval samples, a plot of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ activity ratios in leachates will define a line whose slope is the $^{230}\text{Th}/^{234}\text{U}$ ratio of the pure carbonate. Furthermore, a plot of $^{238}\text{U}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ in leachates will yield a slope of $^{234}\text{U}/^{238}\text{U}$ in the pure carbonate. Using the Bateman disequilibrium equation, the age of the pure carbonate samples is obtained.

We have applied the equations of [Allegre and Condomines \(1976\)](#) and of [Schwarcz and Latham \(1989\)](#) to study the behaviour of these isotopes in the detrital material when an artificial impure carbonate is dissolved for U/Th dating. In this study we evaluate the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio by both methods in a well-characterized sediment which could be considered as a typical detritus contained in an impure carbonate. Both methods are used to obtain the age of a pure carbonate in an artificially contaminated carbonate sample.

2. Experimental

The experiments were designed to evaluate the behaviour of detritus during the leaching of impure carbonates by applying the isochron technique. We used one natural detritus and a natural pure well-dated CaCO_3 , alone and in artificial mixtures. One set was designed to study the effects of sample pre-treatment on the detritus alone and a second set was used to examine the effect of acid attacks on both the carbonate and the detritus fractions in a mixture of constant proportions.

In all cases the samples were powdered and homogenized prior to the leaching. Cogenetic samples were dissolved with different nitric acid concentrations in order to have sufficient spread for isochron plots. Moreover, some of the samples were also heated at 900°C prior to the leaching ([Alcaraz-Pelegrina, 2003](#)). Once dissolved, the solution was filtered immediately to avoid possible absorption of thorium onto the detrital residue. Both, the leachates and residues were analysed for U and Th isotope concentrations. In leachates, iron carrier and known amounts of ^{232}U and ^{229}Th , for yield

determinations, were added prior to the precipitation of iron hydroxides. The precipitate was dissolved in 8 M HNO₃ and a solvent extraction method with tri-butyl-phosphate (TBP) was used to back-extract U and Th from dissolution into the organic phase (Martínez-Aguirre, 1991). Once separated, 20 ml of Xilene is mixed with the TBP and 1.5 M HCl as the inorganic phase is used to extract Th from the organic (TPB+Xilene) phase. Finally, U is back-extracted from the organic phase with distilled water and ready for electroplating. Some 1 ml of iron carrier is added to the Th fraction and precipitation of iron hydroxides is carried over. This precipitate is dissolved in 1:1 volume of 8 M HCl and concentrated HCl. As some U traces are also back-extracted with Th, an anion exchange resin (AG 1 × 8) is used for Th purification. A 4 cm length column of this resin is first conditioned with 8 M HCl. Then the solution is added to the column. The traces of U and Fe stay in the column and Th is collected in a beaker. Iron carrier is added to the solution and precipitation of iron hydroxides is again carried over. The precipitate is dissolved in nitric acid. A second column with the above resin, conditioned with 7 M nitric acid, is used to purify the Th fraction. The Th solution is added to the column. Iron and other impurities pass through the resin and Th stays. Th is finally collected by adding 2 M HCl to the column. This solution is ready for electroplating. Some 0.3 M NaSO₄ is added to final solutions, which are evaporated till dryness. Electroplating (Talvitie, 1972, Martínez-Aguirre, 1991) of U and Th is carried out during 1 h onto stainless steel planchets at 1.2 A. The planchets are finally measured by α -spectrometry.

The residues were placed in concentrated nitric acid and heated for several hours. This process was repeated several times with aqua regia. In each case the solution was taken to dryness prior to the next acid addition. Finally, the residues were treated with concentrated nitric acid until the insoluble residue colour changed to white or clear grey. At that moment, the solution was separated from residue and considered as the second leachate of the sample. This solution is analysed in the same way as the first leachate for U and Th isotopes.

3. Results and discussion

3.1. Acid treatment of detritus alone

For the first experiment, a bottom sediment sample from the Guadalquivir river at the South of Spain was used (Alcaraz-Pelegrina, 2003). This sediment represents a typical detrital component of impure surface carbonates as in the case of travertines and tufas. Five different aliquots were selected to evaluate the extraction capacity for U and Th isotopes when using different nitric acid concentrations. In each of the samples, U and

Th isotopes were measured in the first and the second leachates. Two of the samples were heated at 900 °C prior to the acid treatment. Leachates and residues were separated by centrifuging.

In Table 1, the specific activities for each of the U and Th isotopes in the first and second leachates are given, and of both leachates taken together, as the total extractable activity. Samples 4 and 5 had been heated for 3 h. As can be seen, the specific total activities for each isotope are approximately the same in all aliquots to within 1 – σ error ranges. However, those of the heated samples are slightly higher than in unheated ones. This result is in agreement with studies of Bischoff and Fitzpatrick (1991) which concluded that heating helps to promote U and Th isotope extraction with acid attack. As expected, the specific concentrations in the first leachates increased as the acid concentration increased (Alcaraz-Pelegrina, 2003). In Fig. 1, the specific concentration for each isotope is plotted against the acid concentration for the unheated samples. No linear relationship exists between acid concentration and activity concentration in these leachates. It seems that isotope concentration of the 7 M acid treatment is somewhat lower than expected. However, one must remember that the extraction time was different in each case and this could be the cause of the deviation from linearity. In Fig. 2, the activity concentrations normalized by time are plotted, along with those in heated samples, against acid concentration. It seems that deviation from linearity was effectively produced by differences in the length of time of the acid treatment and normalizing by time produces a linear relationship between acid concentration and extracted activity concentration for the unheated samples. As can be seen for all isotopes from the ²³⁸U decay chain, the activity concentration for each isotope in leachates 4 and 5 (previously heated) does not follow the same linear relationship as the unheated samples. The extracted concentrations are higher in the heated than in the unheated samples. In the case of ²³²Th, the extracted concentrations are the same for the heated and unheated samples. The extraction capacity depends only of the strength of the acid concentration used for the leaching.

Table 1 also lists the activity ratios in the first and second leachates as well as the total extractable. ²³⁸U and ²³⁴U are practically in equilibrium in all leachates and, as a consequence, they are also in secular equilibrium in the total extractable component. However, a slight increase of the ²³⁴U/²³⁸U activity ratio as the acid concentration increases can be observed. There is a clear difference in the behaviour between both Th isotopes. In fact, the ²³⁰Th/²³²Th ratio in the first leachate decreases as the acid concentration increases. This could be the result of a more efficient extraction of ²³²Th with respect to ²³⁰Th as the acid concentration increases. However, this effect cannot be seen in the

Table 1

U and Th isotope activities in mBq/g and activity ratios for first leachate (L₁), second leachate (L₂) and total extractable fraction when treating a sediment sample from the Guadalquivir river with different concentrations of nitric acid (see second column)

Sample	Description	²³⁸ U	²³⁴ U	²³⁰ Th	²³² Th	²³⁴ U/ ²³⁸ U	²³⁰ Th/ ²³² Th	²³⁰ Th/ ²³⁴ U	²³⁸ U/ ²³² Th	²³⁴ U/ ²³² Th
BT-1 (L ₁)	HNO ₃ 2 M, 2 h	4.24 ± 0.14	4.34 ± 0.14	5.45 ± 0.15	2.54 ± 0.09	1.024 ± 0.047	2.15 ± 0.10	1.256 ± 0.053	1.669 ± 0.081	1.709 ± 0.082
BT-1 (L ₂)		7.11 ± 0.17	6.81 ± 0.16	8.50 ± 0.26	18.5 ± 0.5	0.958 ± 0.032	0.459 ± 0.019	1.248 ± 0.048	0.384 ± 0.014	0.368 ± 0.013
BT-1(L ₁ + L ₂)		11.35 ± 0.22	11.15 ± 0.21	13.9 ± 0.3	21.0 ± 0.5	0.982 ± 0.027	0.662 ± 0.021	1.247 ± 0.036	0.540 ± 0.017	0.531 ± 0.016
BT-2 (L ₁)	HNO ₃ 4 M, 1.5 h	4.61 ± 0.13	4.84 ± 0.14	6.32 ± 0.16	3.46 ± 0.10	1.050 ± 0.042	1.827 ± 0.070	1.306 ± 0.050	1.332 ± 0.054	1.399 ± 0.057
BT-2 (L ₂)		6.37 ± 0.16	6.28 ± 0.16	6.70 ± 0.23	15.4 ± 0.5	0.986 ± 0.035	0.435 ± 0.021	1.067 ± 0.046	0.414 ± 0.017	0.408 ± 0.017
BT-2(L ₁ + L ₂)		10.98 ± 0.21	11.12 ± 0.21	13.02 ± 0.28	18.9 ± 0.5	1.013 ± 0.027	0.689 ± 0.023	1.171 ± 0.034	0.581 ± 0.019	0.588 ± 0.019
BT-3 (L ₁)	HNO ₃ 7 M, 1 h	4.66 ± 0.12	5.28 ± 0.13	6.64 ± 0.18	4.05 ± 0.12	1.133 ± 0.040	1.640 ± 0.066	1.258 ± 0.050	1.151 ± 0.045	1.304 ± 0.050
BT-3 (L ₂)		6.79 ± 0.17	6.80 ± 0.17	6.62 ± 0.22	15.2 ± 0.5	1.001 ± 0.035	0.435 ± 0.021	0.974 ± 0.041	0.447 ± 0.018	0.447 ± 0.018
BT-3(L ₁ + L ₂)		11.45 ± 0.21	12.08 ± 0.21	13.26 ± 0.28	19.3 ± 0.5	1.055 ± 0.027	0.687 ± 0.023	1.098 ± 0.030	0.593 ± 0.019	0.626 ± 0.020
BT-4 (L ₁)	Heated HNO ₃ 2 M, 2 h	6.74 ± 0.18	6.26 ± 0.17	5.96 ± 0.17	2.67 ± 0.09	0.929 ± 0.035	2.232 ± 0.099	0.952 ± 0.037	2.524 ± 0.109	2.345 ± 0.102
BT-4 (L ₂)		6.00 ± 0.18	5.55 ± 0.18	8.07 ± 0.22	16.62 ± 0.41	0.925 ± 0.041	0.486 ± 0.018	1.454 ± 0.062	0.361 ± 0.014	0.334 ± 0.014
BT-4(L ₁ + L ₂)		12.74 ± 0.25	11.81 ± 0.25	14.03 ± 0.28	19.29 ± 0.42	0.927 ± 0.027	0.727 ± 0.021	1.188 ± 0.035	0.660 ± 0.019	0.612 ± 0.019
BT-5 (L ₁)	Heated HNO ₃ 7 M, 1 h	7.42 ± 0.16	7.39 ± 0.16	7.98 ± 0.18	3.96 ± 0.10	0.996 ± 0.024	2.015 ± 0.068	1.080 ± 0.034	1.874 ± 0.062	1.866 ± 0.062
BT-5 (L ₂)		6.08 ± 0.17	6.05 ± 0.17	6.53 ± 0.18	17.59 ± 0.42	0.995 ± 0.039	0.371 ± 0.014	1.079 ± 0.042	0.346 ± 0.013	0.344 ± 0.013
BT-5(L ₁ + L ₂)		13.50 ± 0.23	13.44 ± 0.23	14.41 ± 0.25	21.55 ± 0.43	0.996 ± 0.024	0.669 ± 0.018	1.072 ± 0.026	0.626 ± 0.016	0.624 ± 0.016
BT		12.00 ± 1.07	11.92 ± 0.95	13.72 ± 0.47	20.01 ± 1.18	0.993 ± 0.119	0.686 ± 0.047	1.151 ± 0.100	0.600 ± 0.064	0.596 ± 0.059

The last line gives the mean values.

second leachate where all $^{230}\text{Th}/^{232}\text{Th}$ ratios are closely similar with a mean value of 0.686 ± 0.047 . No clear differences between heated and unheated samples can be observed either between U or Th isotopes.

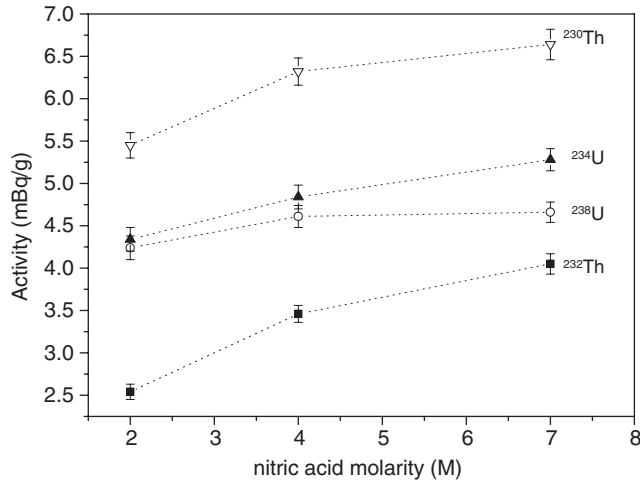


Fig. 1. U and Th isotope activities leached from Guadalquivir river sediment when treated with nitric acid of different concentrations, for unheated samples.

The differences in the ratios between U isotopes and ^{232}Th are also clear, in the first leachates and in the heated and unheated aliquots. The $^{238}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ ratios decrease as the acid concentrations increase, the highest values being observed in the heated samples. As in the case of the $^{230}\text{Th}/^{232}\text{Th}$ ratio, this fact must be due to a more efficient Th extraction when the acid concentrations increase. The ratios in the heated aliquots confirm again that heating of the sample promotes a higher extraction of U isotopes with an acid attack. All $^{238}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ ratios in the total extractable are closely similar with mean values of 0.600 ± 0.064 and 0.596 ± 0.059 , respectively.

Table 2 presents the fraction of each isotope which has been leached from the sediment per hour of acid treatment. These values have been plotted against the acid concentration in Fig. 3. As can be seen, the extraction efficiency of ^{238}U and ^{234}U is similar: higher in the case of heated samples and the efficiency increases when the acid concentration increases. For the three unheated samples there is a linear relationship between the extracted fraction and the acid concentration. However, the effect of heating greatly increases the extraction of both isotopes.

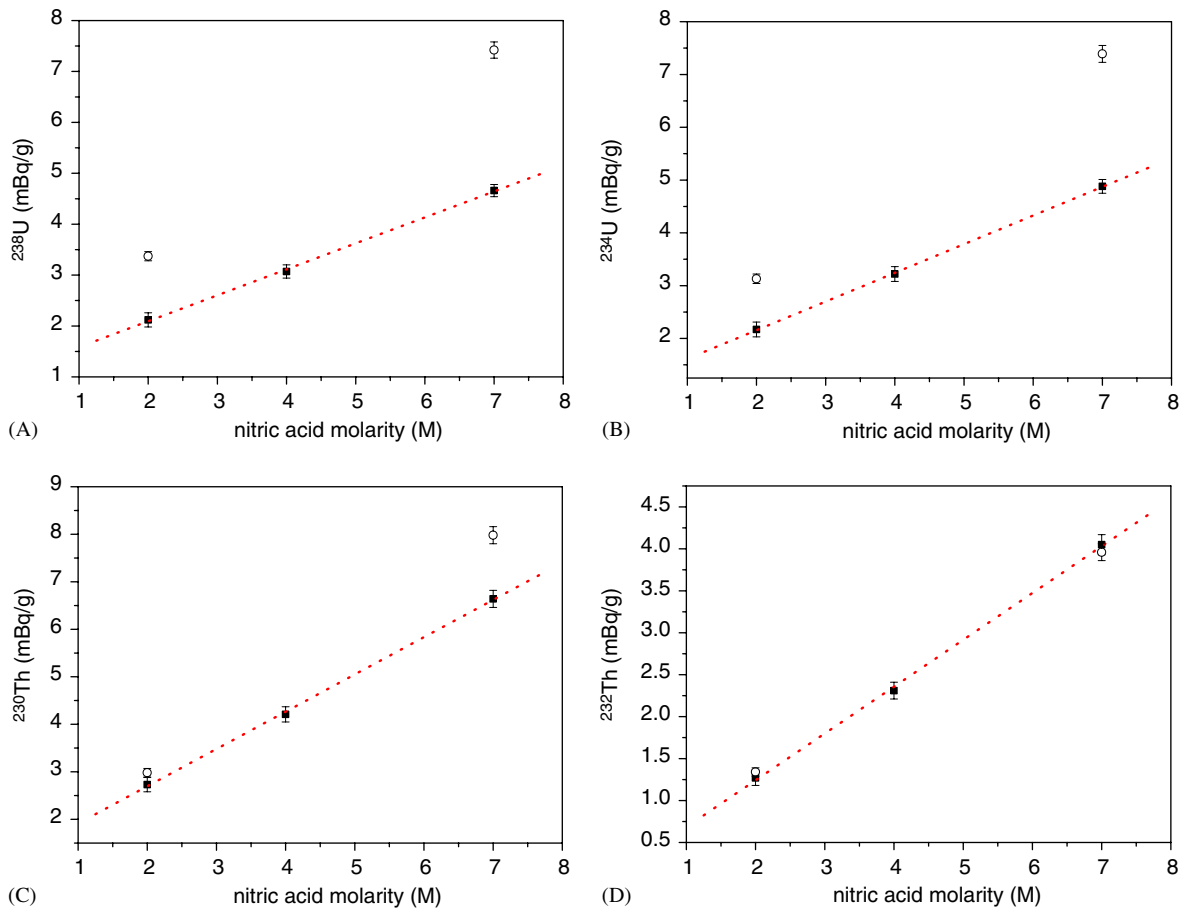


Fig. 2. U and Th isotope activities leached from the Guadalquivir river sediment per hour of treatment with nitric acid of different concentrations. Black squares are unheated samples and open circles are heated samples.

Table 2

Fraction of each isotope leached from the sediment per hour of acid treatment and ratios between extracted fraction for different isotopes used in the L/L method (Schwarcz and Latham, 1989)

Sample	r_8 (h^{-1})	r_4 (h^{-1})	r_0 (h^{-1})	r_2 (h^{-1})	r_8/r_2	r_4/r_2	r_0/r_2	r_0/r_4	r_8/r_4
BT-1	0.187 ± 0.007	0.195 ± 0.007	0.196 ± 0.007	0.060 ± 0.003	3.09 ± 0.18	3.21 ± 0.18	3.24 ± 0.18	1.01 ± 0.05	0.96 ± 0.05
BT-2	0.280 ± 0.010	0.290 ± 0.010	0.323 ± 0.011	0.122 ± 0.005	2.30 ± 0.11	2.38 ± 0.12	2.65 ± 0.13	1.11 ± 0.05	0.97 ± 0.05
BT-3	0.407 ± 0.013	0.437 ± 0.013	0.501 ± 0.017	0.210 ± 0.008	1.94 ± 0.10	2.08 ± 0.10	2.39 ± 0.12	1.15 ± 0.05	0.93 ± 0.04
BT-4	0.265 ± 0.009	0.265 ± 0.009	0.213 ± 0.008	0.069 ± 0.003	3.83 ± 0.21	3.84 ± 0.21	3.08 ± 0.17	0.80 ± 0.04	1.00 ± 0.05
BT-5	0.550 ± 0.015	0.550 ± 0.015	0.554 ± 0.016	0.184 ± 0.006	2.99 ± 0.13	2.99 ± 0.13	3.01 ± 0.13	1.01 ± 0.04	1.00 ± 0.04
Mean					2.83 ± 0.74	2.90 ± 0.69	2.87 ± 0.35	1.02 ± 0.14	0.97 ± 0.03

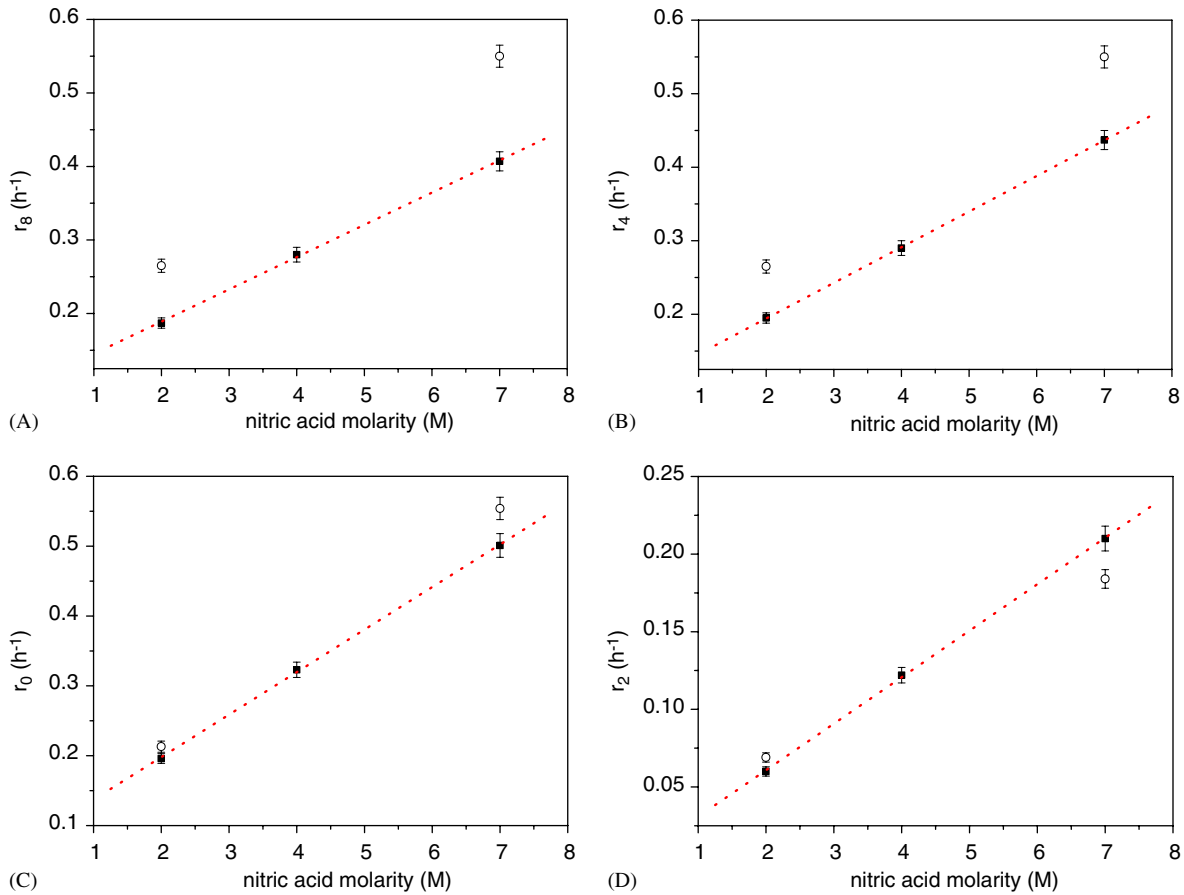


Fig. 3. Fraction of U and Th isotopes extracted from the sediment samples per hour of treatment with different nitric acid concentration. Black squares are unheated samples and open circles are heated samples.

In the case of ^{230}Th and ^{232}Th , the extracted fraction is higher for ^{230}Th than for ^{232}Th and, as in the case of the U isotopes, the extraction increases linearly with acid concentration. However, for Th isotopes there are no important differences between heated and unheated samples (BT-1 with BT-4 and BT-3 with BT-5), which means that the extracted activity depends mainly on the acid concentration used to dissolve the sample.

Accordingly, with the L/L method (Schwarcz and Latham, 1989), the fraction of each isotope extracted in each subsample may be different but there must be no

differential isotopic fractionation between different subsamples. Thus the ratios r_i/r_j must be equal in all subsamples (see Table 2). As can be seen, for the isotopes of the same decay chain, ^{238}U , ^{234}U and ^{230}Th , the ratios are practically unity without special differences between subsamples, given the mean values of 1.02 ± 0.14 and 0.97 ± 0.03 for r_0/r_4 and r_8/r_4 , respectively. This means that the detrital material was leached in the same relative proportion, independently of the treatment of the sample. The three isotopes from the ^{238}U decay chain are clearly extracted from the detritus

in a much higher proportion than the ^{232}Th , with only small differences between the subsamples. The higher extraction is related to the higher solubility of U isotopes and to the fact that ^{232}Th is the progenitor of the decay chain and thus, its mobility is much lower in comparison with ^{230}Th (Ivanovich and Harmon, 1992). Nevertheless, the differences between the samples are small and a constant value of 2.83 ± 0.74 , 2.90 ± 0.69 and 2.87 ± 0.35 can be used for r_8/r_2 , r_4/r_2 and r_0/r_2 ratios, respectively.

3.2. Acid treatment of detritus in presence of carbonate

In this section we describe the influence of the detrital material on the age of the carbonate. A sediment sample, BT, was mixed with a well-known pure carbonate (AL) and the L/L method (Schwarz and Latham, 1989) was used to obtain the carbonate age. The mixing proportion was 80% of pure carbonate and 20% of sediment sample, a significantly higher proportion of detrital material to what is usually found in natural impure carbonates.

The pure carbonate was previously dated by the U/Th method yielding an aged 14400 ± 700 a. The results for this sample are shown in Table 3. U specific concentrations in the pure carbonate are well above those in the sediment, whereas the opposite occurs in the case of Th isotopes, lower in the pure carbonate than in the sediment.

Five subsamples of the same homogenized impure carbonate were analysed. Samples A, B and C were leached in 2, 4 and 7 M nitric acid, respectively. Aliquots D and E were heated to 900°C for 3 h and then leached in 2 and 7 M nitric acid, respectively. The leachates were analysed for U and Th isotope activities. Table 3 shows the activity concentrations in mBq/g, the activity ratios and apparent ages for each sample as well as those in the pure carbonate sample (AL) and in the total extractable component of the sediment (BT).

Uranium isotope activities are quite similar in all subsamples and lower than in the pure carbonate. This

is due to the high uranium concentration in the pure carbonate with respect to the sediment sample. Thus, the detrital U contribution is quite small for all of them. The opposite occurs in the case of the Th isotopes. The activity concentration in leachates are a bit higher than in the pure carbonate, particularly for ^{232}Th . Except for sample ALBT-A, the Th activity concentrations increase as the acid concentrations increase and are higher in heated than in unheated samples. Evidently, lower U and higher ^{230}Th concentrations in leachates give apparent ages that are higher than the pure carbonate age (14400 ± 700 a). The $^{230}\text{Th}/^{232}\text{Th}$ ratios (see Table 3) are low, between 4 and 6, thus a correction method must be applied to obtain the age of the pure carbonate.

As the U and Th activities in the pure carbonate and in the pure detrital fraction are already known, it is possible to evaluate quantitatively the amount of each isotope in the detrital fraction that was incorporated into the solution during the leaching process. These results are shown in Table 4. Even when considering the large relative error, it seems that in presence of carbonates U and Th isotopes are leached from the detrital fraction in a higher proportion. This means that the presence of carbonate affects the extraction efficiency of isotopes from the detritus. However, the relative extraction fractions, r_i/r_j (see Table 4), show similar values within error margins in all aliquots and the mean values of these ratios are similar to those found in the leaching of detritus alone. Thus, we conclude that the L/L method can be used for dating purposes.

Fig. 4a shows the $^{230}\text{Th}/^{232}\text{Th}$ versus the $^{234}\text{U}/^{232}\text{Th}$ ratios in the leachates. According to the approach of Allegre and Condomines (1976) and using the least square method for fitting points, 0.1262 ± 0.0049 and 1.515 ± 0.143 were obtained for the slope and y-intercept of the line, respectively. From the slope and by using error propagation, an age of 14635 ± 794 a is obtained, in agreement with the previously obtained 14400 ± 700 a. However, the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the detrital material, 1.515 ± 0.143 , is in clear disagreement with the

Table 3

Specific activities of U and Th isotopes in mBq/g and activity ratios in leachates of artificial impure carbonate (ALBT-A to E), in the pure carbonate (AL) and in the sediment sample (BT), taken as mean values in Table 1

Sample	^{238}U	^{234}U	^{230}Th	^{232}Th	$^{238}\text{U}/^{232}\text{Th}$	$^{234}\text{U}/^{232}\text{Th}$	$^{230}\text{Th}/^{232}\text{Th}$	$^{230}\text{Th}/^{234}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	T (ka)
ALBT-A	20.6 ± 0.3	28.3 ± 0.4	5.26 ± 0.19	1.11 ± 0.05	18.6 ± 0.9	25.5 ± 1.2	4.74 ± 0.27	0.186 ± 0.007	1.374 ± 0.028	22.1 ± 0.9
ALBT-B	20.4 ± 0.4	28.7 ± 0.6	4.79 ± 0.17	0.77 ± 0.04	26.5 ± 1.5	37.3 ± 2.1	6.22 ± 0.39	0.167 ± 0.007	1.407 ± 0.040	19.7 ± 0.9
ALBT-C	20.5 ± 0.4	27.9 ± 0.6	4.92 ± 0.17	0.90 ± 0.04	22.8 ± 1.1	31.0 ± 1.5	5.47 ± 0.31	0.176 ± 0.007	1.361 ± 0.040	20.8 ± 0.9
ALBT-D	21.9 ± 0.4	29.2 ± 0.6	5.18 ± 0.18	1.04 ± 0.04	21.1 ± 0.9	28.1 ± 1.2	4.98 ± 0.26	0.177 ± 0.007	1.333 ± 0.037	21.1 ± 0.9
ALBT-E	20.6 ± 0.5	27.8 ± 0.6	5.37 ± 0.18	1.21 ± 0.05	17.0 ± 0.8	23.0 ± 0.9	4.44 ± 0.24	0.193 ± 0.008	1.350 ± 0.044	23.1 ± 1.0
AL	24.1 ± 0.6	32.5 ± 0.8	4.06 ± 0.17	0.07 ± 0.01	344 ± 50	464 ± 67	58.0 ± 8.6	0.125 ± 0.006	1.349 ± 0.047	14.4 ± 0.7
BT	12.00 ± 1.07	11.92 ± 0.95	13.72 ± 0.47	20.01 ± 1.18	0.600 ± 0.064	0.596 ± 0.059	0.686 ± 0.047	1.151 ± 0.100	0.993 ± 0.119	
UIISO								0.126 ± 0.018	1.476 ± 0.062	14.5 ± 2.0

Some activity ratios and nominal ages are also given. In last column results of the UIISO program (Ludwig, 1993) are also given.

Table 4
Same as Table 2 for acid leachates of the artificial impure carbonate

Sample	r_8	r_4	r_0	r_2	r_8/r_2	r_4/r_2	r_0/r_2	r_0/r_4	r_4/r_8
ALBT-A	0.586 ± 0.252	1.004 ± 0.333	0.751 ± 0.091	0.281 ± 0.020	2.1 ± 0.9	3.6 ± 1.2	2.7 ± 0.4	0.75 ± 0.26	1.71 ± 0.93
ALBT-B	0.497 ± 0.278	1.179 ± 0.387	0.576 ± 0.084	0.195 ± 0.015	2.6 ± 1.4	6.0 ± 2.0	3.0 ± 0.5	0.49 ± 0.18	2.37 ± 1.53
ALBT-C	0.542 ± 0.278	0.830 ± 0.385	0.624 ± 0.084	0.228 ± 0.016	2.4 ± 1.2	3.6 ± 1.7	2.7 ± 0.4	0.75 ± 0.36	1.53 ± 1.06
ALBT-D	0.998 ± 0.242	1.267 ± 0.366	0.679 ± 0.080	0.255 ± 0.022	3.9 ± 1.0	5.0 ± 1.5	2.7 ± 0.4	0.54 ± 0.17	1.27 ± 0.48
ALBT-E	0.503 ± 0.265	0.713 ± 0.353	0.746 ± 0.081	0.296 ± 0.026	1.7 ± 0.9	2.4 ± 1.2	2.5 ± 0.4	1.05 ± 0.53	1.42 ± 1.02
Mean					2.54 ± 0.83	4.14 ± 1.40	2.72 ± 0.18	0.72 ± 0.22	1.66 ± 0.43

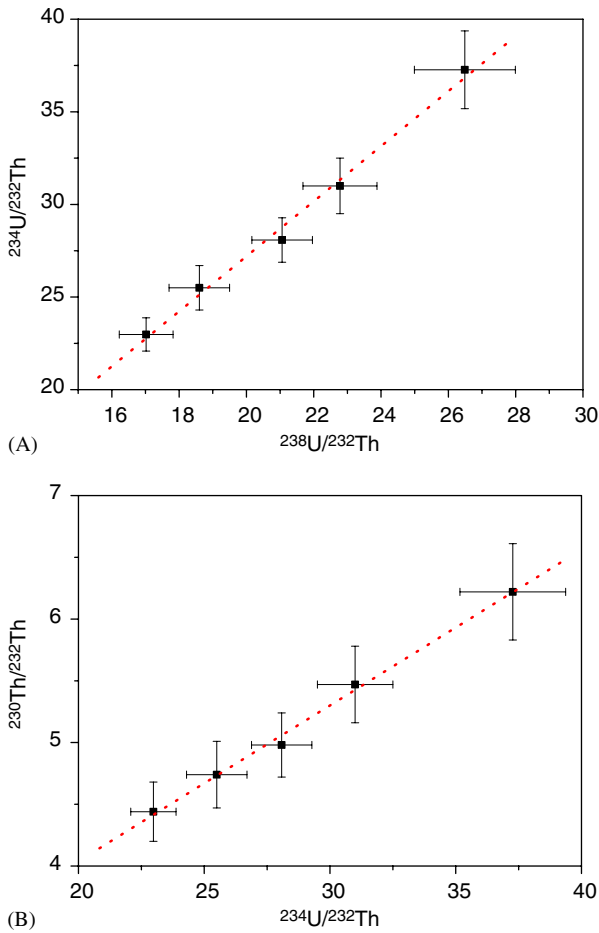


Fig. 4. Rosholt diagrams for artificial impure carbonate ALTB.

value obtained from the analysis of the detritus alone, 0.686 ± 0.047 . If the same values would have been obtained, they would have indicated that the activity ratio in the extracted fraction is the same as that in the detritus, that is $(^{230}\text{Th}/^{232}\text{Th})_{\text{D}} = (^{230}\text{Th}/^{232}\text{Th})_{\text{R}}$. Nevertheless in the previous section a $r_0/r_2 \neq 1$ was shown, meaning that both quantities have to be different. Thus, considering $(^{230}\text{Th}/^{232}\text{Th})_{\text{D}} = r_0/r_2 (^{230}\text{Th}/^{232}\text{Th})_{\text{R}}$, an extracted fraction ratio r_0/r_2 of 2.21 ± 0.26 is obtained, lower but similar to the values obtained both in the

analysis of the detritus alone (2.87 ± 0.35) and in the artificial impure carbonate (2.72 ± 0.18).

The L/L method has also been applied by using Rosholt diagrams. As in these diagrams both variables share the ^{232}Th isotope, a correlation exists between variables and thus accordingly with Ludwig and Titterton (1994) the error of each data point must be represented by ellipses of error. Table 3 shows activity ratios used in the UIISO program (Ludwig, 1993) for age determinations, and in Figs. 4a and b the Rosholt diagrams are shown. In the diagrams and for simplicity the data point errors have been represented as uncorrelated error. An age of 14500 ± 2000 a is obtained in agreement with the expected age of the pure carbonate sample. The large age error is mainly due to the low separation of the data in the plots, which in turn, is the result of the high detritus concentration in the samples. In contrast, the L/L method is based in a two-component mixture and both components, pure carbonate and pure detritus, can be included in the plots resulting in a much wider spread of the data points (see Fig. 5).

In Fig. 6, $^{230}\text{Th}/^{234}\text{U}$ are plotted against the $^{230}\text{Th}/^{232}\text{Th}$ ratios in the artificial mixed samples. As the $^{230}\text{Th}/^{232}\text{Th}$ ratios increase (lower amount of isotopes are extracted from the detritus), the $^{230}\text{Th}/^{234}\text{U}$ ratio decreases towards the value of the pure carbonate sample alone. As can be seen, the pure carbonate activity ratio is achieved when the $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in impure carbonate aliquots reach a value of about 20–25.

4. Summary

Two experiments were designed to evaluate the isotopic behaviour of detritus during the leaching of impure carbonates by applying the isochron technique. A natural detritus sample and a natural pure, well-dated carbonate were used.

In the first set of experiments, five aliquots of the detritus were treated with different nitric acid concentrations (2–7 M) and two of the samples were heated to

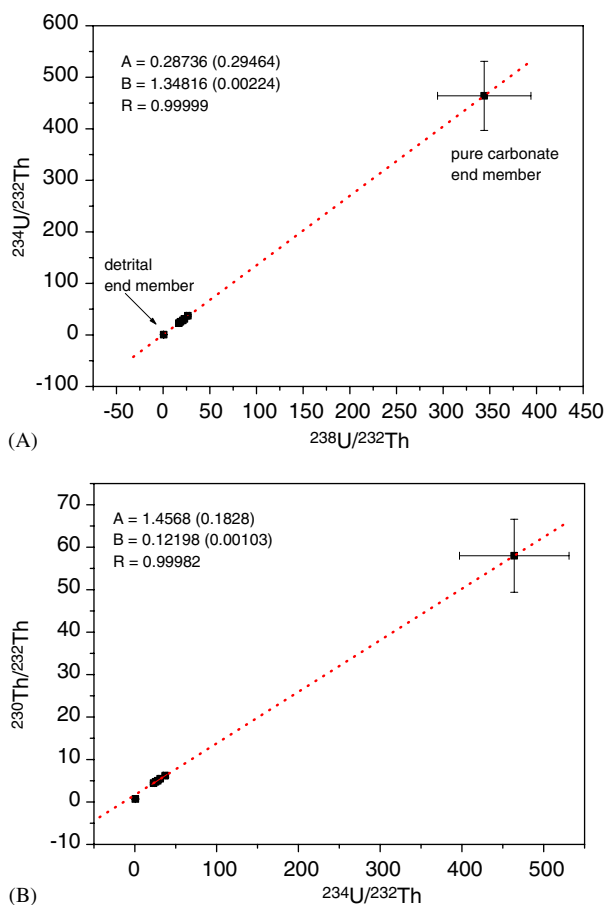


Fig. 5. Rosholt diagrams for sample ALTB including both end members: the pure carbonate and the pure detrital sample.

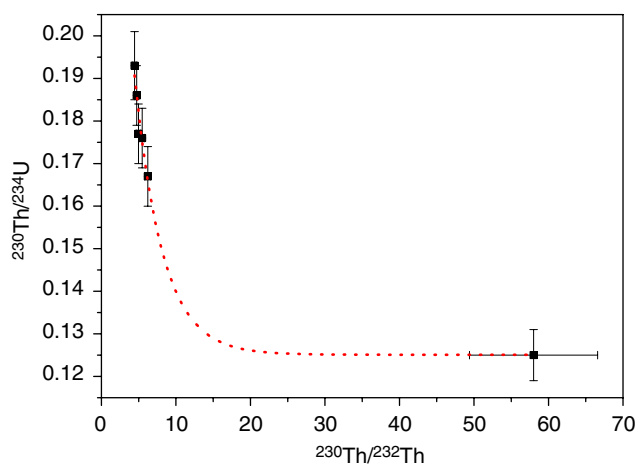


Fig. 6. $^{230}\text{Th}/^{234}\text{U}$ versus $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in subsamples of the artificial impure carbonate. The pure carbonate sample is also included.

900 °C to study pre-treatment effects in the isotope extraction from the detritus during the leaching of impure carbonates. For ^{234}U and ^{238}U , the fraction

extracted from the detritus behaved similarly; higher fractions were extracted from the heated samples and the extraction increases linearly with the acid concentration. For Th isotopes, the extracted fraction is higher for ^{230}Th than for ^{232}Th and, as in the case of U isotopes, the extraction efficiency increases linearly with acid concentration and no great differences between heated and unheated samples are obtained.

The validity of the L/L method for U/Th dating depends on the constancy of the ratios between extracted fractions for different isotopes. For the isotopes of the same decay chain, ^{238}U , ^{234}U and ^{230}Th , the extracted fraction ratios (r_i/r_j) are practically unity without differences between subsamples. Thus, for the ^{238}U decay chain there is neither isotopic nor elemental fractionation during the leaching process with different acid strengths. However, the isotopes of the U-decay chain are more efficiently extracted from the detritus than ^{232}Th , with small differences from one sample to another.

In the second experiment, the detritus was mixed with a well-dated pure carbonate to examine the effect of acid attacks on both the carbonate and the detritus fractions. As could be expected from the higher U concentration in the pure carbonate than in the detritus, the U isotope activities were quite similar in all leachates. Except for one of the leachates, the Th activities increased as the acid concentrations increased and were higher in the heated than in the unheated samples. In the presence of the carbonate, U and Th isotopes are extracted from the detritus in a higher proportion, but the ratios (r_i/r_j), remain constant within the relatively large error for each leachate of the artificial mixture, and their mean values were close to those found in the analysis of the detritus alone.

Due to the low $^{230}\text{Th}/^{232}\text{Th}$ ratios, a correction method must be applied to obtain the age of the pure carbonate (14.4 ± 0.7 ka). Using the equations of [Allegre and Condomines \(1976\)](#) an age of 14.6 ± 0.8 ka for the pure carbonate and a value for the extracted ratio fraction r_0/r_2 of 2.21 ± 0.26 , similar to that obtained with the analysis of isotopes either in the detritus alone (2.87 ± 0.35) and in the artificial impure carbonate (2.72 ± 0.18). The L/L method with Rosholt diagrams has been used and the UISO program gives an age of 14.4 ± 2.0 ka in accord with the age obtained in the analysis of the pure carbonate.

5. Conclusions

Different methods have been used to evaluate the isotopic and elemental fractionation in the detritus of artificially mixed impure carbonates. The data have shown that the extraction efficiency increased when the acid strength increased for every natural isotopes and

that it is similar for both U isotopes and higher for ^{230}Th than for ^{232}Th . Extraction efficiency ratios close to unity are obtained when evaluated between isotopes from the U decay chain and above unity when evaluated between the U decay chain isotopes and the ^{232}Th . However, these ratios remain constant, within the errors, for each leachate of the artificial mixture and thus, the conditions to apply the L/L method of [Schwarcz and Latham \(1989\)](#) hold. The L/L method has been applied to this artificial impure carbonate and the resulting age is in agreement with the age of the pure carbonate.

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