

U/Th dating of impure carbonates: $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in detrital material

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Abstract

In environmental age dating the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio is widely used as an indicator of detrital contamination. A clear relationship between this activity ratio and the carbonate sample's age has previously been demonstrated, whereby a detrital correction must be applied when the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of the leach drops to 20. We demonstrate that in some cases carbonate samples with $^{230}\text{Th}/^{232}\text{Th}$ well above 20 must be corrected, otherwise an overestimation of the sample's age is obtained. Evaluation of the relationship between $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ in the carbonate's aliquots will enable evaluation of the limit at which a carbonate can be considered pure or impure.

Keywords U/Th dating · Carbonates · Detrital material · Age corrections · Radio chronometry

Introduction

Isotopic imbalance between ^{230}Th and ^{234}U or ^{238}U has been widely applied to the dating of carbonate precipitates from aqueous solutions under a variety of environmental conditions [1]. The solubility of U in natural waters allows it to co-precipitate with precipitating solid, whereas Th, as an insoluble element, is unavailable for co-precipitation. Hence, the decay ingrowth, ^{230}Th , once the carbonate has been precipitated, supplies a method for age determination of geological systems. Dating of such systems, provided that the system has been closed since its formation and that ^{230}Th is not co-precipitated with the U, is straightforward, using the following Bateman Eq. (1) [2].

$$^{230}\text{Th}/^{238}\text{U} = \left((1 - e^{-\lambda_0 t}) + \left(\frac{^{234}\text{U}}{^{238}\text{U}} \right) - 1 \right) \left(\frac{\lambda_0}{\lambda_0 - \lambda_4} \right) (1 - e^{-(\lambda_0 - \lambda_4)t})$$

or

$$^{230}\text{Th}/^{234}\text{U} = \left(\frac{1}{\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right)} \right) (1 - e^{-\lambda_0 t}) + \left(1 - \left(\frac{^{238}\text{U}}{^{234}\text{U}} \right) \right) \left(\frac{\lambda_0}{\lambda_0 - \lambda_4} \right) (1 - e^{-(\lambda_0 - \lambda_4)t}) \quad (1)$$

In the Eq. (1), the activity ratios are at time t of sample measurement since sample precipitation and λ_0 and λ_4 are the decay constants for ^{230}Th and ^{234}U , respectively.

However, many of these carbonates are impure and can contain large amounts of detrital particles, inter-grown or cemented by the carbonates. This detrital material can contribute significant though undetermined amounts of Th and U, which during dissolution of the carbonate sample for U and Th analysis can be carried over into the leach. Thus, if significant ^{232}Th is present in the material to be dated, a correction for the ^{230}Th , ^{234}U and ^{238}U which must have accompanied the ^{232}Th needs to be made. All the various correction methods use ^{232}Th to indicate the degree of detrital contamination carried over into the leach. At the time of deposition, the pure carbonate has negligible amounts of ^{232}Th and ^{230}Th . Thus, any ^{232}Th found in the leach must be contributed by the detrital material. This material can also contain various amounts of ^{230}Th which must be corrected to obtain the amount in the pure carbonate. Additionally, some U from the detrital material can also carry over into the leach

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during dissolution of the sample, whereby a correction for this effect is also necessary.

A common approach is to analyse three or more cogenetic samples with variable $^{230}\text{Th}/^{232}\text{Th}$, $^{234}\text{U}/^{232}\text{Th}$ and $^{238}\text{U}/^{232}\text{Th}$ activity ratios. Rosholt [3] and Schwarcz and Latham [4] used an isochron technique for dating travertines and caliches in which ^{232}Th was used as the normalizing variable. Samples were leached with diluted acid (L/L technique), $^{230}\text{Th}/^{232}\text{Th}$ was plotted against $^{234}\text{U}/^{232}\text{Th}$ or $^{238}\text{U}/^{232}\text{Th}$ for each leach and the slope of the line connecting the pairs was considered as the $^{230}\text{Th}/^{234}\text{U}$ or $^{230}\text{Th}/^{238}\text{U}$ activity ratios in the pure carbonate end-member. A similar isochron with $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ is used to obtain the $^{234}\text{U}/^{238}\text{U}$ activity ratio in the pure carbonate. Once obtained, the activity ratios in the pure carbonate component of the calcite sample can be used in the above equation to obtain the sample's age.

High values of this activity ratio indicate high detrital contamination, so a detrital correction is necessary. Otherwise an overestimation of the sample's age is obtained. Bischoff and Fitzpatrick [5] suggested that detrital contamination is significant when the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio drops to 20; those with values above 20 may be considered pure carbonate samples and correction is not necessary. However, as we will show in some cases, even impure carbonate samples with $^{230}\text{Th}/^{232}\text{Th}$ well above 20 needs to be corrected for detrital contamination to obtain the real age of the samples, otherwise an overestimation of the respective sample age is obtained.

Moreover, because the CaCO_3 initially lacks ^{230}Th and all ^{232}Th has come from the detritus, all leaches must have the same initial $^{230}\text{Th}/^{232}\text{Th}$ as the detritus at the time of the carbonate's crystallization. Allegre and Condomines [6] showed that for the simple case in which ^{234}U and ^{238}U are in equilibrium, the thorium ratio of the various cogenetic samples is described by the Eq. (2)

$$^{230}\text{Th}/^{232}\text{Th} = (^{230}\text{Th}/^{232}\text{Th})_0 e^{-\lambda_0 t} + (^{238}\text{U}/^{232}\text{Th})(1 - e^{-\lambda_0 t}) \quad (2)$$

In the above Eq. (2), the $(^{230}\text{Th}/^{232}\text{Th})_0$ activity ratio is at the time of precipitation of the carbonate and the others are at the time of measurement of the sample.

Decay of ^{238}U and ^{232}Th is negligible for the time under consideration, so their activities and ratios are constant over time. At the time of crystallization, $t=0$, some cogenetic samples can have lower ^{230}Th activity than ^{238}U activity and ^{230}Th activity will consequently increase with time. Others may have ^{230}Th activity in excess of ^{238}U activity, and ^{230}Th will decrease with time. Both cases are described with the above Eq. (2). At $t=0$, a plot of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ for all cogenetic samples will show a horizontal line, with the y-intercept being the initial thorium ratio $(^{230}\text{Th}/^{232}\text{Th})_0$. After the time t , the same plot will show

data points on a line with a slope $(1 - e^{-\lambda_0 t})$. At $t \gg 1/\lambda_0$, $^{230}\text{Th}/^{232}\text{Th} = ^{238}\text{U}/^{232}\text{Th}$, representing secular equilibrium; the points will lie along a line with unit slope and passing through the origin. This means that the line rotates over time, starting from an initial slope of 0 and ending with a slope of unity. This rotation occurs around a point called the equipoint defining the initial $^{230}\text{Th}/^{232}\text{Th}$, which should be the initial value in the detritus [5]. In the event of initial imbalance between ^{234}U and ^{238}U , an equation similar to the one above, with ^{234}U instead of ^{238}U , will hold.

Twelve carbonate samples from the Rock of Gibraltar were analysed to conduct a study of its geological evolution. Samples GB01 to GB09 were collected in the same cave, St. Michael's Cave entrance, samples GB010 and GB011 at Forbes' Quarry and sample GB101 at Beefsteak Cave. The geological implications of dating such samples have already been published in Rodriguez-Vidal et al. [7]. Here we will present the study concerning the data obtained in the U/Th dating of the samples. Our paper only focuses on problems associated to dating, particularly two major problems. On the one hand, we will discuss the need for detrital correction in several carbonate samples in which the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of the leachate stays above 20 [5], to thereby avoid overestimation of the age sample. On the other, we will study the possibility of obtaining some interesting activity ratios in the detrital material included with the pure carbonate. This may enable us to evaluate the limit at which a carbonate could be considered a pure or impure carbonate.

Experimental

During development of the PaleoMed Project (see acknowledgements) focusing on the Rock of Gibraltar, numerous calcite samples were dated by the U/Th method. Most samples resulted as being pure carbonates ($^{230}\text{Th}/^{232}\text{Th}$ activity ratios well above 20) and the obtained ages were the ages expected by the researchers [7]. However, some of those sample results showed an age well above what was expected. Hence, even with the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio above 20, those samples were treated as impure carbonates. Indeed, different aliquots of those samples result in different nominal ages (Eq. 1), clearly confirming their impurity. Once corrected for their detrital material, the resulting ages were as expected [7]. In this paper we present this dating work.

Twelve calcite samples, collected at the Rock of Gibraltar, were used to study the effect of detrital material on determining the age of the respective calcite sample. The Rock of Gibraltar is a north-south peninsula; the eastern side is very steep while the western side has a gentler slope. The results of geomorphological studies of this rock can be seen in [7].

Calcite samples were powdered and homogenized using a hammer and mortar prior to dissolution in a solution 2 M

of nitric acid (HNO_3). For the solution HNO_3 , 69% purity and distilled water was used. After all the calcite dissolved, the residue was separated as soon as possible by centrifuging for 5 min at 4000 rpm in a Selecta Mixtasel centrifuge with 0.45 μm pore size Millipore filter 47 mm diameter filtration to eliminate all solid particles and thus minimize Th re-adsorption. The residue was discarded and the leach kept for further U and Th isotopes analysis. 1 ml of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mg/ml) as iron-carrier and well-known activities of ^{232}U and ^{229}Th (as U and Th tracers, calibrated and certified by CIEMAT, Spain), for yield determinations (both isotopes also alpha-emitters), were added before precipitation of iron hydroxides. The U and Th isotope precipitate with Fe hydroxides and the solution is discarded. The precipitate was dissolved in 20 ml 8 M HNO_3 and a solvent extraction technique in a decantation funnel (100 ml volume) with 5 ml of tri-butyl-phosphate (TBP MERCK pro analysis) as the organic compound was used to separate U and Th from iron and other actinides. Both phases are mixed by shaking for 5 min, followed by a 5-min rest until both phases are again separated. U and Th remain in the organic phase and the inorganic phase is discarded. This process is repeated twice with 10 ml of 8 M HNO_3 , to eliminate all Fe and other actinides that may have remained in the organic phase. The next step was to extract Th from this organic phase. For that purpose, 20 ml of Xylene (Panreac pro analysis) is added to the TBP and 15 ml 1.5 M HCl is used to separate Th from the organic phase. Both phases are mixed by shaking for 5 min followed by a 15-min rest until both phases are again separated. U remains in the organic phase whereas the Th is extracted in the inorganic phase. This is repeated twice to extract all Th from the organic phase. The Th fraction requires further purification and 15 ml of distilled water is finally used as the inorganic phase to back-extract U from the same organic phase, TBP + Xylene [8], shaking for 5 min followed by a 5-min rest. The process is repeated twice to extract as much U as possible. The U solution is then ready for electrodeposition onto a stainless-steel disk (see below).

0.5 ml of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mg/ml) is added to the Th fraction and a precipitation of iron hydroxides with ammonia solution 25% is carried out. This precipitate is dissolved in 5 ml of 8 M HCl and 5 ml of HCl. As some U traces are also back-extracted with Th, an anion exchange resin (BIO-RAD AG 1 \times 8, 100–200 mesh, hydrochloric form) is used for Th purification. A 4 cm long resin column (100 ml volume glass column 12 mm diameter with a 4 mm hole at the bottom) is conditioned twice with 20 ml of 8 M HCl and the solution is added to the column. U traces and iron stay in the column whereas Th passes through the resin and is collected in a beaker. Another 20 ml of 8 M HCl is added to the column to recover traces of Th. 0.5 ml of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mg/ml) is added to the solution and precipitation of iron hydroxides

along with the Th with ammonia solution 25% is again carried out. Further Th purification is necessary, using the same resin in a narrower column (25 ml volume glass column 6 mm diameter with a 2 mm hole at the bottom). 4 cm of the resin is conditioned twice with 10 ml of 7 M HNO_3 . The Th precipitation is dissolved with 2 ml of concentrated HCl plus 3 ml of 7 M HNO_3 and added to the column along with 2 more ml of 7 M HNO_3 . Iron and other impurities pass through the resin and Th remains. The resin is cleaned with another 20 ml of 7 M HNO_3 . Finally, Th is extracted from the resin with 20 ml of 2 M HCl [8]. This solution is ready for electrodeposition onto a stainless-steel disk.

1 ml of 0.3 M Na_2SO_4 is added to the U and Th final solutions to avoid deposition of U and/or Th on the beaker walls, evaporated until dry and dissolved with distilled 0.3 ml H_2SO_4 and 4 ml of distilled water. The pH is adjusted to 2.3–2.5 with ammonia solution 25%. The solution is added to the polyethylene electrolytic cell with 5 ml of H_2SO_4 1%. At the bottom of the electrolytic cell a 2 cm stainless-steel disk acts as the cathode and a platinum wire acts as the anode. The system is connected to a power supply. Electrodeposition [8, 9] of U or Th is carried out for 1 h at 1.2 amperes. One min before the hour, 1 ml of ammonia solution 25% is added to the solution. The disks are disconnected from the power supply and cleaned with acetone and distilled water. The U/Th disk is finally measured by alpha spectrometry with PIPS detectors in a CAMBERRA Alpha Spectrometer previously calibrated for energy and efficiency with a mixed alpha source of known activity.

Results and discussion

U and Th isotope concentrations and some activity ratios were obtained in twelve samples collected at the Rock of Gibraltar. The data were used on the one hand to evaluate the extent of Th contamination in impure carbonates with $^{230}\text{Th}/^{232}\text{Th}$ activity ratios above 20 [5], and on the other to evaluate the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the detrital material of the impure carbonates.

Aliquots with $^{230}\text{Th}/^{232}\text{Th}$ above 20

The activity concentration of U and Th isotopes in mBq/g and corresponding $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ activity ratios are presented in Table 1 for twelve carbonate samples, collected at the Rock of Gibraltar.

The results in Table 1 show that it is clear that except for sample GB06, which must be corrected for detritus ($^{230}\text{Th}/^{232}\text{Th}$ below 20), all the other samples seem to be pure carbonates, as their $^{230}\text{Th}/^{232}\text{Th}$ is above 20. Except for that

Table 1 Specific activities (mBq/g) and activity ratios in the analysis of 12 carbonate samples collected at the Rock of Gibraltar. It can be seen that, except in sample GB06, $^{230}\text{Th}/^{232}\text{Th}$ activity ratios are well above 20; they can thus be considered pure carbonate samples. In the last two columns the nominal age (obtained by Eq. 1) in ky and the $^{234}\text{U}/^{238}\text{U}$ activity ratio at the time of calcite precipitation are

| | ^{238}U | ^{230}Th | $^{234}\text{U}/^{238}\text{U}$ | $^{230}\text{Th}/^{234}\text{U}$ | $^{230}\text{Th}/^{232}\text{Th}$ | T (ky) | $(^{234}\text{U}/^{238}\text{U})_0$ |
|-------|------------------|-------------------|---------------------------------|----------------------------------|-----------------------------------|------------|-------------------------------------|
| GB01 | 5.57 (0.14) | 4.06 (0.14) | 0.974 (0.014) | 0.747 (0.032) | 298 (80) | 151 (14) | 0.960 (0.021) |
| GB02 | 2.90 (0.09) | 1.15 (0.07) | 1.047 (0.027) | 0.379 (0.024) | 29.9 (6.8) | 51.5 (4.2) | 1.054 (0.031) |
| GB03 | 2.69 (0.06) | 1.59 (0.05) | 1.067 (0.020) | 0.551 (0.021) | 164 (37) | 86.1 (4.9) | 1.085 (0.025) |
| GB04 | 7.02 (0.13) | 5.06 (0.15) | 0.997 (0.012) | 0.723 (0.025) | 699 (221) | 140 (10) | 0.995 (0.017) |
| GB05 | 3.06 (0.06) | 2.32 (0.06) | 1.045 (0.018) | 0.725 (0.025) | 119 (18) | 138 (9) | 1.066 (0.027) |
| GB06 | 3.93 (0.23) | 3.00 (0.10) | 1.031 (0.064) | 0.741 (0.049) | 10.5 (0.7) | 145 (20) | 1.046 (0.097) |
| GB07 | 3.38 (0.08) | 1.36 (0.04) | 1.023 (0.022) | 0.394 (0.015) | 35.8 (4.1) | 54.3 (2.7) | 1.027 (0.026) |
| GB08 | 3.05 (0.06) | 1.02 (0.03) | 1.052 (0.017) | 0.319 (0.012) | 154 (38) | 41.5 (1.8) | 1.058 (0.019) |
| GB09 | 2.82 (0.07) | 2.21 (0.06) | 1.021 (0.023) | 0.767 (0.028) | 552 (13) | 157 (13) | 1.032 (0.036) |
| GB010 | 1.82 (0.07) | 1.29 (0.06) | 1.239 (0.052) | 0.571 (0.034) | 28.8 (5.7) | 88.7 (7.9) | 1.306 (0.067) |
| GB011 | 2.00 (0.04) | 0.39 (0.02) | 1.159 (0.024) | 0.168 (0.008) | 40.2 (9.3) | 19.9 (1.1) | 1.168 (0.025) |
| GB101 | 6.28 (0.15) | 4.96 (0.16) | 1.104 (0.022) | 0.715 (0.029) | 37.1 (4.5) | 132 (10) | 1.151 (0.032) |

sample, Bateman equations were used to obtain the age of the carbonate samples. The results, as well as the $^{234}\text{U}/^{238}\text{U}$ activity ratio in the pure carbonate at the time of deposition, are also presented in Table 1.

Except for three samples (GB01, GB04 and GB101) with higher activity concentrations, probably precipitated from waters with higher U content, U concentration range from 2 to 4 mBq/g, no significant differences were observed between the three locations. However, the samples at Forbes's Quarry have U concentrations slightly lower than the samples from St. Michael's cave and a sample collected at Beefsteak Cave (GB101) is one of the samples with the highest activity concentrations, 6.3–6.9 mBq/g for each isotope, respectively. The similarities and differences are more evident in the $^{234}\text{U}/^{238}\text{U}$ activity ratios at the time of deposition (column 7). All samples collected at St Michael's Cave clearly contain both U isotopes in secular equilibrium, whereas in the others there is a slight excess of ^{234}U . The similarities and differences must be related to the

also given. For error determination, propagation of errors was used (for example for ^{238}U activity concentration the equation used was $^{238}\text{U} = (N_{238}/N_{232})^{232}\text{U}$, where N_{238} and N_{232} are the alpha counts for ^{238}U and ^{232}U , respectively and ^{232}U the added activity of the U tracer)

activity ratio in the waters from which the carbonate was precipitated.

As the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in sample GB06 was below 20, it was considered an impure carbonate and correction for its detrital material was thus necessary. Several aliquots (from the same original homogenized sample) were prepared by dissolving with different HNO_3 concentrations (from 2 to 8 M), from 100 to 250 ml depending on the sample's mass; the results are shown in Table 2. As expected, different acid concentrations yield different activity ratios. The LL method and Rosholt diagrams (see Fig. 1) were thus used for detrital correction and the activity ratios and age of the pure carbonate obtained using the ISOPLOT program (3D plot) [10]. These results are also presented in Table 2. As expected, the age of the pure carbonate (70 ky), once corrected, clearly shows that when the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio drops to 20, detrital material correction is necessary.

As stated above, the $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in Table 1, above 20, indicate that those samples can be considered pure

Table 2 Specific activities (mBq/g), activity ratios and nominal age in ky (using Eq. 1) in the analysis of five aliquots of carbonate sample GB06. The data error was obtained by error propagation. Samples

| GB06 | ^{238}U | ^{230}Th | $^{234}\text{U}/^{238}\text{U}$ | $^{230}\text{Th}/^{234}\text{U}$ | $^{230}\text{Th}/^{232}\text{Th}$ | T (ky) | $(^{234}\text{U}/^{238}\text{U})_0$ |
|------|------------------|-------------------|---------------------------------|----------------------------------|-----------------------------------|----------|-------------------------------------|
| 1 | 3.93 (0.23) | 3.00 (0.10) | 1.031 (0.064) | 0.741 (0.049) | 10.5 (0.7) | 145 (20) | 1.046 (0.097) |
| 2 | 3.65 (0.07) | 3.44 (0.11) | 1.082 (0.018) | 0.871 (0.031) | 6.52 (0.32) | 210 (22) | 1.147 (0.032) |
| 3 | 4.22 (0.10) | 4.56 (0.16) | 1.119 (0.027) | 0.966 (0.041) | 6.34 (0.40) | 298 (67) | 1.275 (0.062) |
| 4 | 3.63 (0.14) | 3.16 (0.10) | 1.115 (0.045) | 0.781 (0.039) | 8.29 (0.52) | 158 (17) | 1.178 (0.070) |
| 5 | 4.83 (0.09) | 3.62 (0.12) | 1.073 (0.016) | 0.699 (0.027) | 8.64 (0.55) | 127 (9) | 1.105 (0.023) |
| ISOP | | | 1.029 (0.035) | 0.476 (0.051) | | 70 (11) | 1.035 (0.043) |

were dissolved with different nitric acid concentrations (2–8 M). The last line shows the results of the corrected activity ratios and age of the pure carbonate sample obtained using the ISOPLOT program [10]

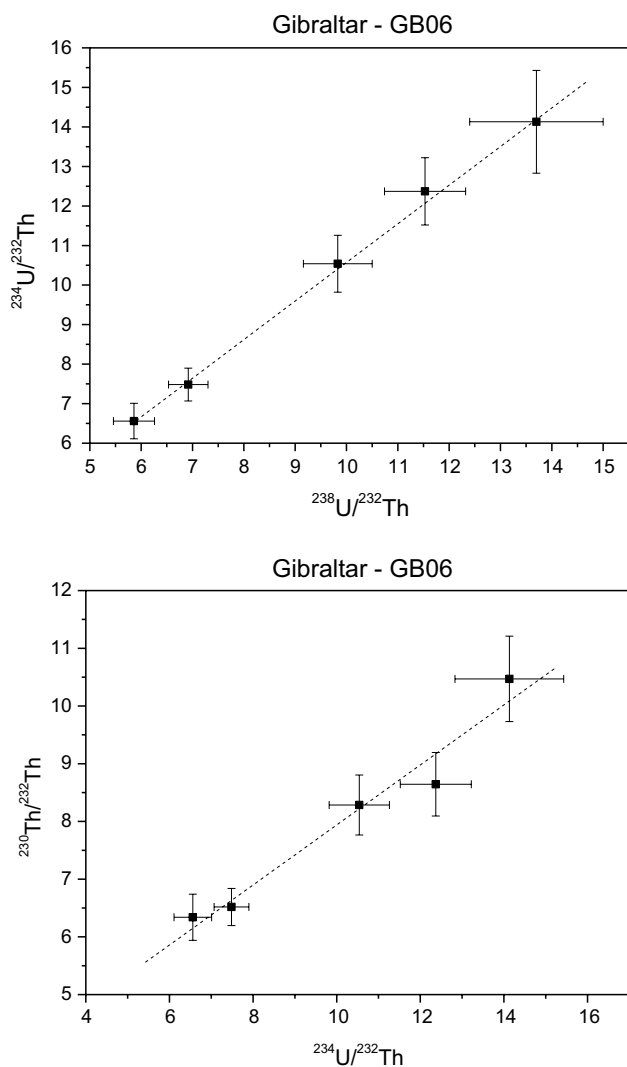


Fig. 1 Rosholt diagrams for sample GB06

carbonate, so correction is not necessary. This would mean that all aliquots of a same sample, with activity ratio above 20, should result in the same age.

However, when comparing the sample ages with their stratification profile [7], the ages of samples GB02, GB010 and GB101 do not fit their position and it seems they should be younger. To verify their ages, several respective aliquots (from the same original sample) were analysed by dissolving with different nitric acid concentration, as in sample GB06; the results are shown in Table 3. As can be seen in the table, the activity concentrations are different in each aliquot; the exceptions are the U concentration in GB02 and GB010, quite similar in each aliquot. Differences in U and Th concentrations are quite evident in sample GB101. These facts should indicate the extraction of different U and Th isotope activities from the detrital material contained in the carbonate samples. To verify this fact, in Figs. 2, 3 and 4 Rosholt diagrams for each sample are presented. Rosholt diagrams show a linear relationship between activity ratios in the several aliquots of each sample; this means that samples GB02, GB010 and GB101 cannot be considered pure carbonate samples and their age must be corrected. The ISOPLOT program (3D plot) was also used to obtain the real age of these samples and the results are shown in Table 4.

As can be seen, in the case of sample GB010 the differences between aliquots are small considering the error in the data. However, it seems that only aliquot 3, with the highest $^{230}\text{Th}/^{232}\text{Th} \cong 100$, has the age of the sample (see Table 4). Results from aliquots of samples GB02 and GB101, with aliquots with different nominal ages, show the clear need to correct the activity concentrations to obtain the real age of the pure carbonate. Indeed, the corrected ages (see Table 4) are clearly lower than those obtained in the aliquots. Only for the high $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the aliquot (67 in

Table 3 Specific activities (mBq/g), activity ratios and nominal age (Eq. 1) in ky in different aliquots of samples GB02, GB010 and GB101. The different aliquots were dissolved with different concentrations of HNO_3 (2–8 M). The data errors were obtained by error propagation

| | ^{238}U | ^{230}Th | $^{234}\text{U}/^{238}\text{U}$ | $^{230}\text{Th}/^{234}\text{U}$ | $^{230}\text{Th}/^{232}\text{Th}$ | T (ky) | $(^{234}\text{U}/^{238}\text{U})_0$ |
|--------------|------------------|-------------------|---------------------------------|----------------------------------|-----------------------------------|------------|-------------------------------------|
| <i>GB02</i> | | | | | | | |
| 1 | 2.90 (0.09) | 1.15 (0.07) | 1.047 (0.027) | 0.379 (0.024) | 30 (7) | 51.5 (4.2) | 1.054 (0.031) |
| 2 | 3.09 (0.10) | 1.11 (0.06) | 1.069 (0.028) | 0.335 (0.021) | 37 (9) | 44.1 (3.4) | 1.078 (0.032) |
| 3 | 3.15 (0.10) | 0.93 (0.04) | 1.048 (0.026) | 0.282 (0.015) | 67 (14) | 35.9 (2.3) | 1.053 (0.029) |
| 4 | 3.79 (0.08) | 1.49 (0.07) | 1.039 (0.019) | 0.378 (0.019) | 24 (4) | 51.3 (3.2) | 1.046 (0.021) |
| <i>GB010</i> | | | | | | | |
| 1 | 1.82 (0.07) | 1.29 (0.06) | 1.239 (0.052) | 0.571 (0.034) | 28.8 (5.7) | 88.7 (7.9) | 1.306 (0.067) |
| 2 | 1.80 (0.04) | 1.21 (0.05) | 1.182 (0.030) | 0.570 (0.027) | 10.6 (1.2) | 89.2 (6.4) | 1.234 (0.039) |
| 3 | 1.75 (0.05) | 1.12 (0.08) | 1.247 (0.043) | 0.512 (0.040) | 108 (31) | 75.6 (8.3) | 1.305 (0.053) |
| <i>GB101</i> | | | | | | | |
| 1 | 6.28 (0.15) | 4.96 (0.16) | 1.104 (0.022) | 0.715 (0.029) | 37.1 (4.5) | 132 (10) | 1.151 (0.032) |
| 2 | 5.34 (0.11) | 4.91 (0.14) | 1.130 (0.028) | 0.814 (0.028) | 27 (2) | 172 (14) | 1.211 (0.030) |
| 3 | 6.67 (0.14) | 6.00 (0.19) | 1.151 (0.020) | 0.782 (0.030) | 28.6 (2.7) | 156 (13) | 1.234 (0.031) |
| 4 | 3.97 (0.08) | 4.01 (0.15) | 1.148 (0.021) | 0.883 (0.038) | 18.7 (2.0) | 210 (26) | 1.266 (0.038) |

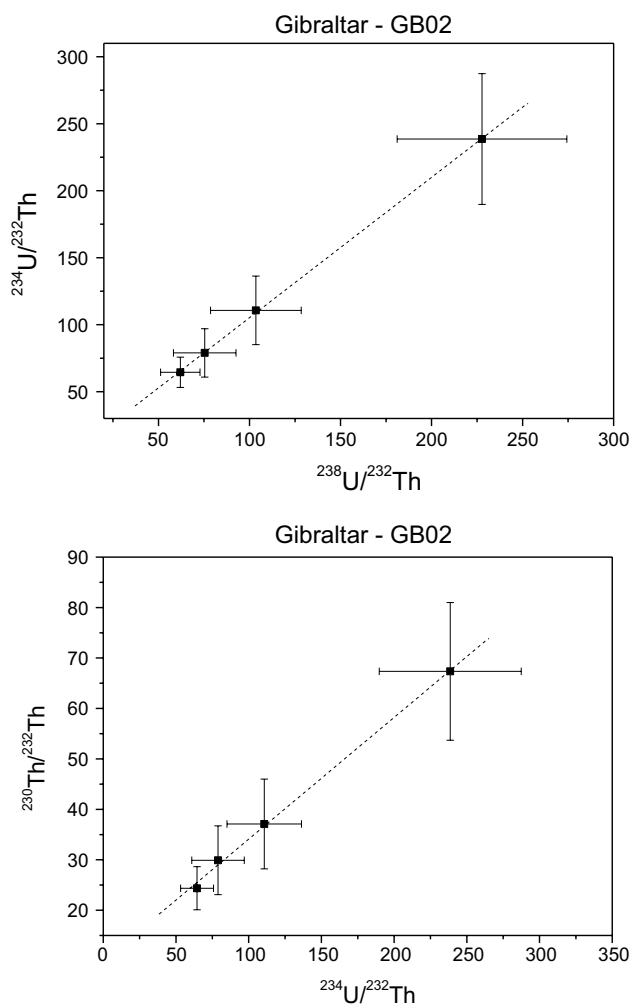


Fig. 2 Rosholt diagrams for sample GB02

sample GB02) does the uncorrected age agree with the corrected age (see Table 4). In the case of sample GB101 all uncorrected ages are overestimated. In Fig. 5, the $^{230}\text{Th}/^{234}\text{U}$ activity ratios versus the $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the aliquots for each sample (including sample GB06) are plotted. As can be seen, for sample GB06, a constant $^{230}\text{Th}/^{234}\text{U}$ activity ratio is obtained for $^{230}\text{Th}/^{232}\text{Th}$ at about 20. However, for the other three samples constancy is obtained for $^{230}\text{Th}/^{232}\text{Th}$ activity ratios well above 100. This means we need to be careful when considering a carbonate sample as pure or impure when dating is required.

$^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the detritus

It is interesting to obtain activity ratios in the detrital material, particularly the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in this material at the time of deposition. All aliquots of an impure carbonate

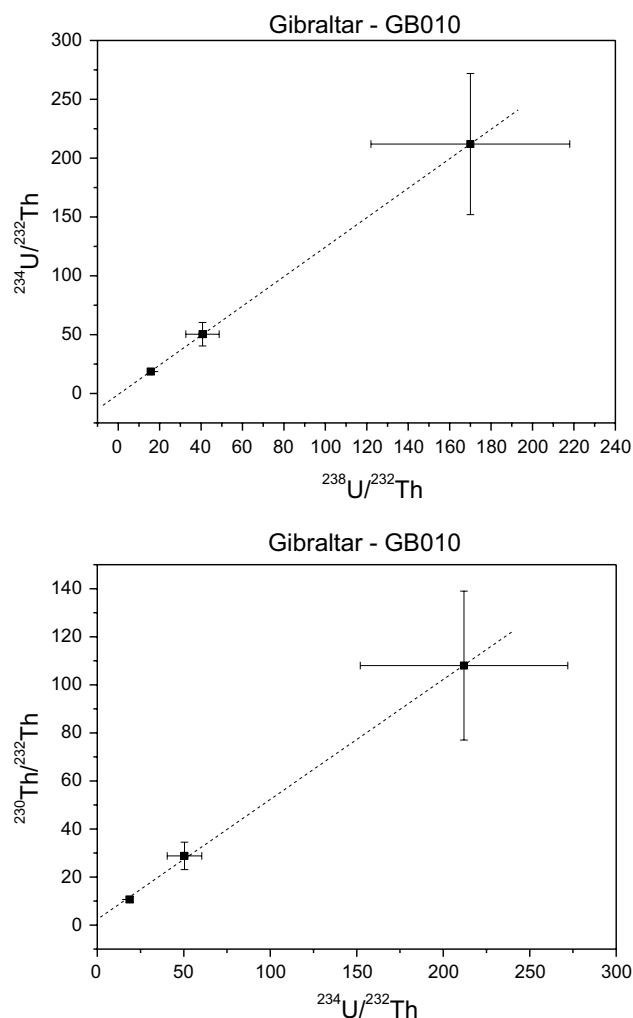


Fig. 3 Rosholt diagrams for sample GB010

sample share the same detrital material and consequently the same value of this activity ratio. We applied several methods to evaluate this activity ratio in the above impure carbonates.

First as we already know the samples' age, obtained using the L/L method and the activity ratios in leachates of each aliquot, it is possible by using the SL (single leach) method [1, 11] to determine the actual and initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the detrital material for each aliquot. This method considers that the detrital material contributes negligible amounts of both uranium isotopes to the leach of the sample and that the ^{230}Th in it comes from that in the pure carbonate along with part of the ^{230}Th of detrital material which is also extracted together with ^{232}Th . The method presumes that the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in extracted fractions is the same as in the actual detrital material. The actual activity ratio is the activity ratio at the time of deposition, corrected by the ^{230}Th decay. Thus,

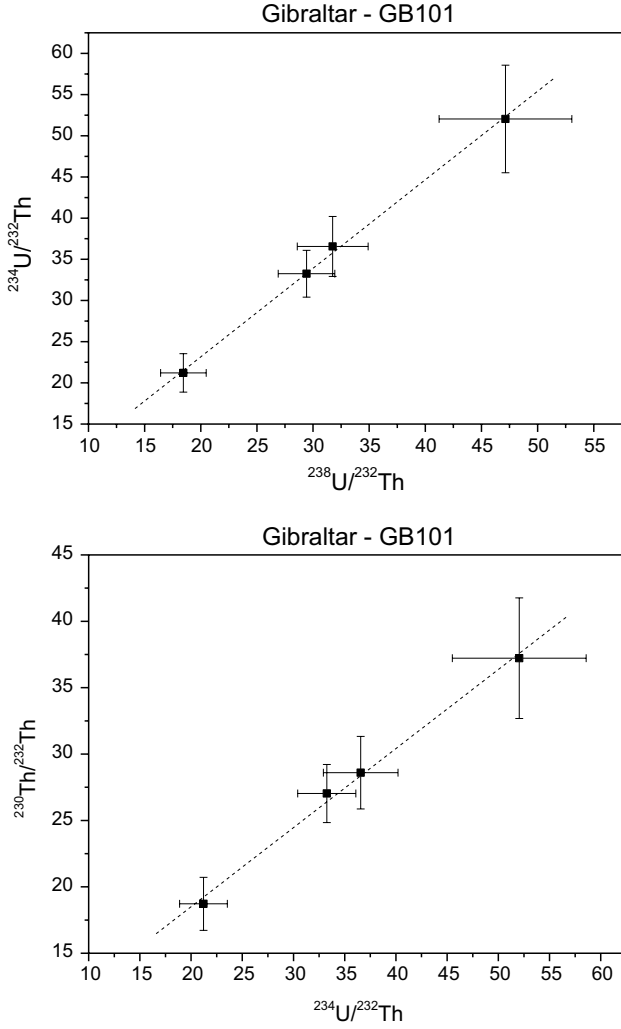


Fig. 4 Rosholt diagrams for sample GB101

Table 4 Results obtained in samples GB02, GB010 and GB101, considered impure carbonates using the L/L method and the ISOPLOT program (3D plot) [10]

| Sample | $^{234}\text{U}/^{238}\text{U}$ | $^{230}\text{Th}/^{234}\text{U}$ | T (ky) | $(^{234}\text{U}/^{238}\text{U})_0$ |
|--------|---------------------------------|----------------------------------|-------------|-------------------------------------|
| GB02 | 1.060 (0.035) | 0.245 (0.026) | 30.5 (3.5) | 1.066 (0.038) |
| GB010 | 1.258 (0.043) | 0.532 (0.040) | 79.8 (8.4) | 1.323 (0.054) |
| GB101 | 1.094 (0.034) | 0.604 (0.058) | 98.8 (15.5) | 1.124 (0.045) |

$$\begin{aligned}
 ^{238}\text{U}_C &= ^{238}\text{U}_L \\
 ^{234}\text{U}_C &= ^{234}\text{U}_L \\
 ^{230}\text{Th}_C &= ^{230}\text{Th}_L - ^{232}\text{Th}_L \left(^{230}\text{Th}/^{232}\text{Th} \right)_D e^{-\lambda_0 t}
 \end{aligned} \quad (3)$$

The subscript C means the concentration in the pure carbonate, L in the leachate of the impure carbonate and D in the detrital material of the impure carbonate.

By introducing these equations in the Bateman dating equation it is possible to obtain a general equation between activity ratios in the leachates, the $^{230}\text{Th}/^{232}\text{Th}$ in the detrital material and t , the time of deposition. Hence, for each aliquot, given that its age is already known, it is possible to calculate the initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the detrital material. These results are shown in Table 5. As the detrital material is the same in all aliquots of the same impure carbonate, the activity ratio in the detrital material can be considered as the mean value of all aliquots.

In such a Table, it can be seen that generally (except sample GB010) the actual and initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in aliquots of the same impure carbonate are practically constant and a mean value can be used. This activity ratio is clearly lower in the case of sample GB06. A large discrepancy between aliquots of sample GB010 was obtained, and thus a mean value cannot be considered.

Second as described by Allegre and Condomines [6], at $t=0$ (time of deposition), a plot of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ for all cogenetic samples would show a horizontal line, with the y-intercept being the initial thorium ratio $(^{230}\text{Th}/^{232}\text{Th})_0$. After time t , the same plot will show data points on a line with a slope $(1 - e^{-\lambda_0 t})$. At $t \gg 1/\lambda_0$, $^{230}\text{Th}/^{232}\text{Th} = ^{238}\text{U}/^{232}\text{Th}$ representing secular equilibrium; the points will lie along a line with unit slope and passing through the origin. This means that the line rotates over time, starting from an initial slope of 0 and ending with a slope of unity. This rotation occurs around a point called the equipoint, defining the initial $^{230}\text{Th}/^{232}\text{Th}$, which should be the initial value in the detritus [5]. In the case of initial disequilibrium between ^{234}U and ^{238}U , an equation similar to the one above, with ^{234}U instead of ^{238}U , will hold. Thus, in the event of secular equilibrium between uranium isotopes, a plot of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ activity ratios of the aliquots will yield a line (isochron) that will cut the equiline line at a point (equipoint); the horizontal line cutting the same point will provide the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio at the time of deposition in the detrital material. Furthermore, the y-intercept of the isochron line will show the $^{230}\text{Th}/^{232}\text{Th}$ at the current time; thus, from both data the time of deposition can also be obtained. If there is no equilibrium, the same can be obtained by switching $^{238}\text{U}/^{232}\text{Th}$ for $^{234}\text{U}/^{232}\text{Th}$. These plots are presented in Figs. 6, 7, 8 and 9 for samples GB06, GB02, GB010 y GB101, and the results of the y-intercepts of the isochron and horizontal lines are respectively presented in Table 6.

Rather high $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in detrital material from samples GB02 and GB101, well above 10 for the initial value, were obtained and about three times lower for the other two samples (GB06 and GB010). Considering that the correction for sample GB010 was quite small, it seems that the limiting ratio at which contaminations affect a sample's age must be related to the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio

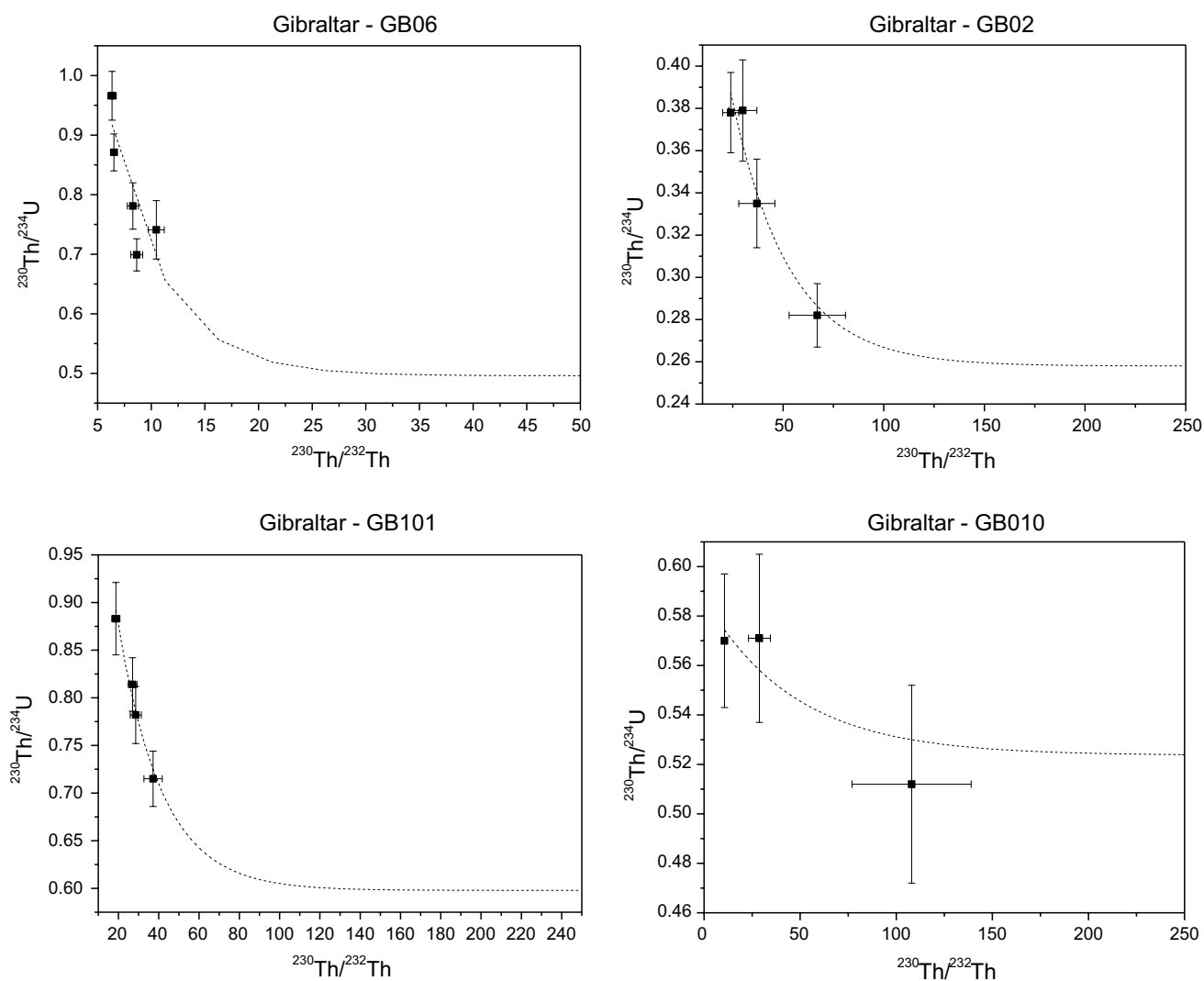


Fig. 5 $^{230}\text{Th}/^{234}\text{U}$ versus $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in samples GB06, GB02, GB101 and GB010

Table 5 Activity ratios in the detrital material for aliquots of impure carbonates GB06, GB02, GB010 and GB101. Results are obtained by using SL method Eq. (3) and the ages previously calculated with the L/L method and the ISOPLOT program [10]

| Sample | $^{230}\text{Th}/^{232}\text{Th}_D$ | $^{230}\text{Th}/^{232}\text{Th}_{D_0}$ | $^{230}\text{Th}/^{232}\text{Th}_D$ | $^{230}\text{Th}/^{232}\text{Th}_{D_0}$ |
|---------|-------------------------------------|---|-------------------------------------|---|
| GB06-1 | 2.93 | 5.59 | GB02-1 | 10.5 |
| 2 | 3.73 | 7.12 | 2 | 9.90 |
| 3 | 3.19 | 6.08 | 3 | 8.76 |
| 4 | 3.25 | 6.19 | 4 | 8.53 |
| 5 | 2.72 | 5.19 | | |
| Mean | 3.16 (0.38) | 6.03 (0.76) | Mean | 9.42 (0.94) |
| GB010-1 | 2.11 | 4.39 | GB101-1 | 6.86 |
| 2 | 0.758 | 1.58 | 2 | 6.37 |
| 3 | -4.4 | -9.25 | 3 | 5.73 |
| | | | 4 | 5.83 |
| Mean | | | Mean | 6.20 (0.52) |
| | | | | 15.4 (1.3) |

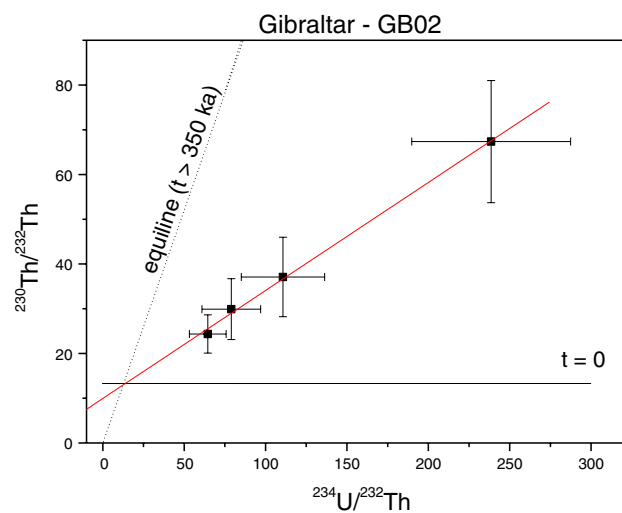
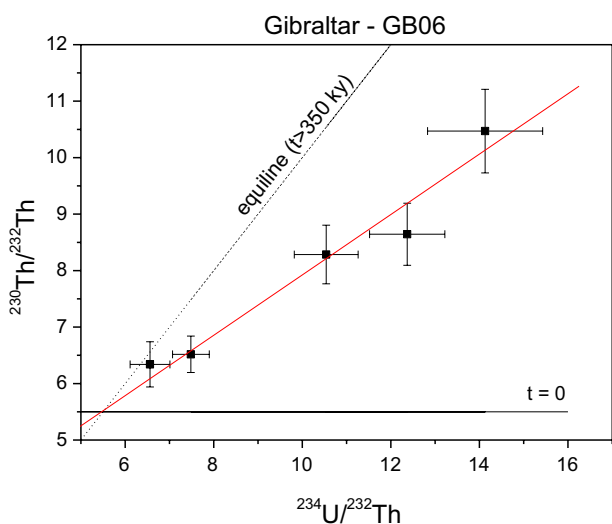
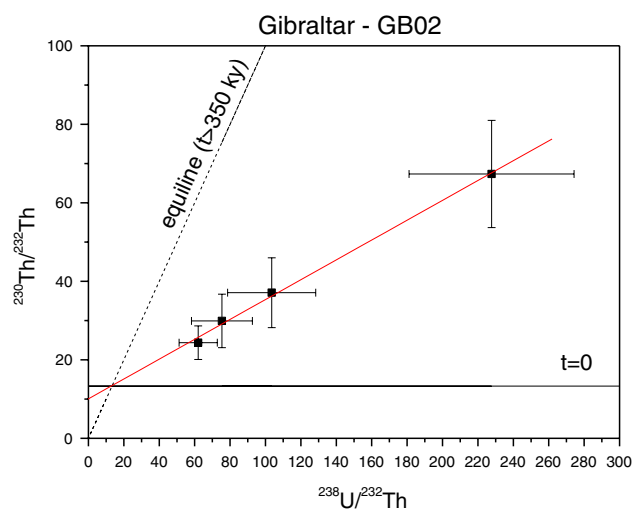
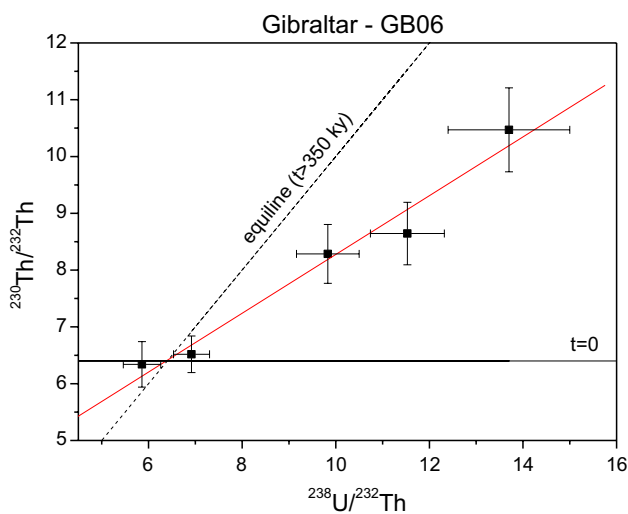


Fig. 6 $^{230}\text{Th}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ (a) and $^{234}\text{U}/^{232}\text{Th}$ (b) activity ratios in sample GB06. At $t=0$, cogenetic samples will fall along a horizontal line. This line would rotate over time and at secular equilibrium all points will lie along a line with unity slope and passing through the origin (equiline). The y-intercept of the horizontal line provides the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the detrital material originally included in the carbonate sample

Fig. 7 Same as Fig. 6 but for sample GB02

in the detrital material. High activity ratios would produce different ages in leachates with $^{230}\text{Th}/^{232}\text{Th}$ activity ratios about 20.

Comparing the data in Tables 5 and 6, the $^{230}\text{Th}/^{232}\text{Th}$ activity ratios obtained by both methods agree quite well and the age of the carbonates obtained through the equi-point is the same as that obtained by applying the L/L method. Furthermore, it has now been possible to determine the activity ratios in the case of sample GB010 and

the age obtained agrees with that obtained by applying the L/L method.

The study has shown the possibility of evaluating the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in detrital material of impure carbonates at the present time, at the time of precipitation with the carbonate. These activity ratios furthermore provide a method to obtain the age of the sample by using Eqs. (2) and (3) with a similar result.

Conclusions

Analyses of U and Th isotopes in carbonate samples from the Rock of Gibraltar were carried out to obtain their age using the U/Th method. The data on $^{230}\text{Th}/^{232}\text{Th}$ activity ratios showed, barring one sample, values well above 20,

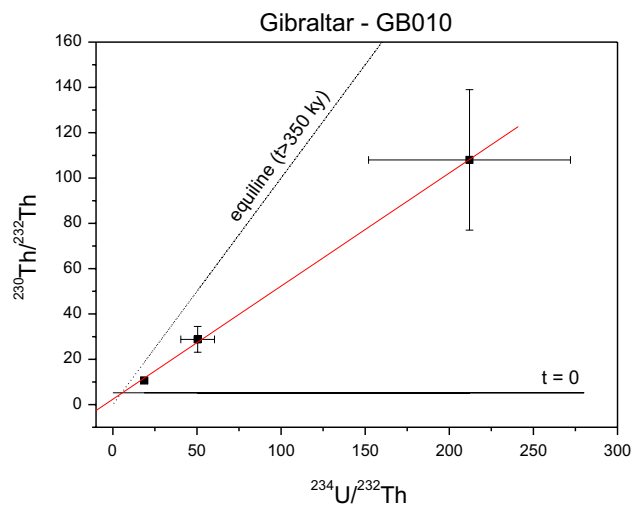
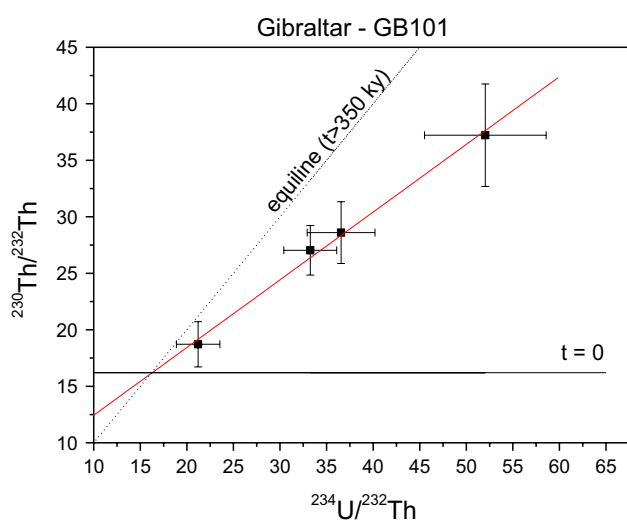
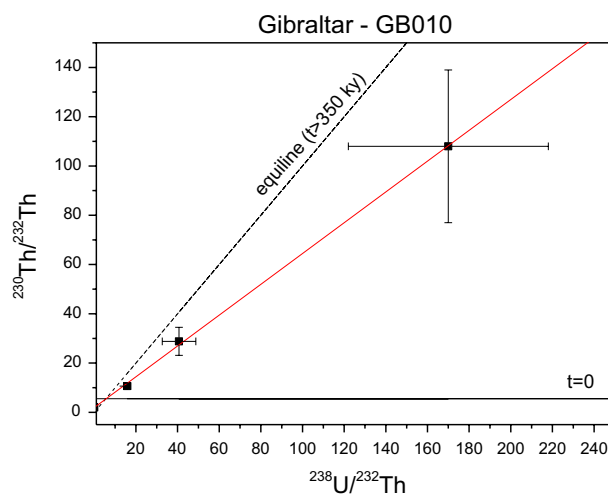
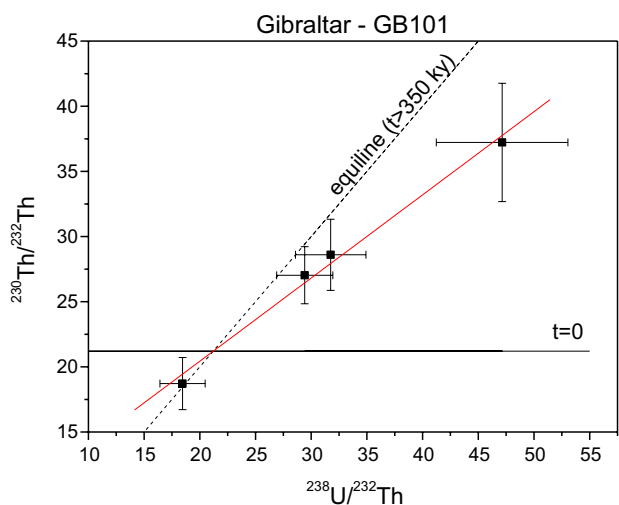


Fig. 8 Same as Fig. 6 but for sample GB101

and in principle they were thus considered pure carbonate samples. However, age results from several aliquots of two samples (GB02 and GB101) showed a clear need to correct the activity concentrations due to the detrital material contained to obtain their real age, even when $^{230}\text{Th}/^{232}\text{Th}$ activity ratios are well above 20. In fact, the corrected ages are clearly lower than those obtained in the different aliquots. Only for high $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in aliquots (67 in sample GB02) does the uncorrected age agree with the corrected age. In the case of sample GB101, all uncorrected ages are overestimated, above the corrected age. The $^{230}\text{Th}/^{234}\text{U}$ versus $^{230}\text{Th}/^{232}\text{Th}$ activity ratio plots shows that the constant $^{230}\text{Th}/^{234}\text{U}$ activity ratio in sample GB06 (originally considered to be impure carbonate) is obtained for $^{230}\text{Th}/^{232}\text{Th}$ around 20. However, for the other

Fig. 9 Same as Fig. 6 but for sample GB010

Table 6 $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the detrital material of impure carbonates GB06, GB02, GB010 and GB10 [6]. In the last column the age in ky of the samples, obtained with actual and initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratios (Eq. 2), are also shown. See Figs. 6, 7, 8 and 9

| Sample | $^{230}\text{Th}/^{232}\text{Th})_D$ | $^{230}\text{Th}/^{232}\text{Th})_{D_0}$ | T (ky) |
|--------|--------------------------------------|--|--------|
| GB06 | 2.74 | 5.5 | 75.6 |
| GB02 | 9.94 | 13.3 | 31.6 |
| GB010 | 2.38 | 5.2 | 84.8 |
| GB101 | 6.4 | 16.2 | 101 |

three samples the constancy is obtained for $^{230}\text{Th}/^{232}\text{Th}$ activity ratios well above 100. We must be very careful deciding if a carbonate samples is pure or impure.

We have found that the $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in detrital material obtained by two different methods are

similar. Furthermore, the sample ages obtained via the equipoint and the L/L method also result as being the same. It was hence possible to determine this activity ratio in the case of sample GB010; the age obtained agrees with the one obtained by applying the L/L method.

We also found that the limit at which detritus correction is necessary and thus the limiting ratio at which contamination affects a sample's age must be related to the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the detrital material. High activity ratios would produce different ages in leachates with $^{230}\text{Th}/^{232}\text{Th}$ activity ratios around 20.

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