U/Th dating of carbonate deposits from Chafarinas Islands, Spain

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Abstract The Chafarinas Islands are a group of volcanic outcrops off the north coast of the African continent. Quaternary deposits and calcrete formations cover most of the islands' planed surface, mainly on Rey Francisco I Island. Uranium-series ages are presented for a geological section with 18 m of detrital deposits and calcrete layers. Calcretes consist of impure carbonate; the leach/leach (L/L) method was therefore used to obtain $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios in the pure authigenic carbonate fraction to obtain ages of the samples. Resulting ages range from 14 to 80 ka. Except for one sample at the bottom of the age sequence, with the youngest age, all others have ages that agree with their stratigraphic location. Ages obtained using the L/L method were also compared with the method of Allegre and Condomines (Earth Planet Sci Lett 28:395–406, 1976) and with a more recent method (Ludwig and Paces Geochim Cosmochim Acta 66:487–506, 2002, Sharp et al. Quat Res 59:139–150, 2003, Haase-Schramm et al. Geochim Cosmochim Acta 68:985–1005, 2004). The latter two methods were also used to estimate isotopic composition of the detrital component in the impure carbonate and model a more realistic age for the anomalous sample. Minimal uranium isotope activity ratio differences imply that environmental conditions between 25 and 60 ka remained relatively uniform and that a major change may have occurred ~ 80 ka ago.

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Introduction

Isotopes from the ^{238}U decay chain have been widely used to evaluate the time when certain geological systems were initially formed and to study their evolution over time. In particular, isotopic disequilibrium between ^{230}Th and ^{234}U has been used to date carbonate precipitated from natural water. The solubility of U combined with the insolubility of Th in natural waters permit U to be incorporated in precipitates from aqueous solutions, whereas initial Th is not present in pure authigenic cements. Any ^{230}Th activity found later in such precipitates is thus derived from the radioactive decay of ^{238}U and ^{234}U. The systematic increase in ^{230}Th toward secular equilibrium with U isotopes accurately reflects the age of the sample, if the system has remained close to isotope exchange since its formation. However, many carbonates formed in near-surface environments, particularly those precipitated from continental natural waters, are impure and contain variable amounts of detrital material, consisting mainly of clays. When impure carbonate is dissolved for U and Th analysis, the detrital component contributes significant and usually unknown quantities of isotopes from the ^{238}U and ^{232}Th decay chains. It is thus necessary to apply a correction method to evaluate isotope concentrations in the pure carbonate fraction of the impure carbonate, in order to obtain an accurate age for the samples.

Correction for the presence of initial ^{230}Th, ^{234}U and ^{238}U from the detrital component is usually made by using the ^{232}Th concentration as an index of detritus content. Direct measurement of the U–Th isotopic composition of the

detrital component may be difficult if the detrital particles are too fine to separate mechanically or if there is substantial variation in the U–Th isotopic composition of the detrital component. At the time of precipitation, the pure authigenic carbonate component contains negligible amounts of ^{232}Th and ^{230}Th. This means that any ^{232}Th found in a leachate from the carbonate must come from the detrital part of the impure carbonate. If the detrital component has a single, uniform U–Th isotopic composition at the time of precipitation of the impure carbonate (i.e. constant U/Th and ^{230}Th/^{232}Th activity ratio), mathematical techniques that assume simple two-component mixing between a ^{232}Th-free component (authigenic cement) and a ^{232}Th-bearing component (detritus) are often employed [9, 14, 5, 8].

Allegre and Condomines [4] developed a method for dating volcanic rocks. However, Bischoff and Fitzpatrick [5] proposed the use of their method for dating impure carbonate, as the principles of radioactive decay are the same for impure carbonates and for mineral solidifying from a melt. They [4] showed that if U isotopes are in equilibrium and the initial ^{230}Th/^{232}Th activity ratio in all fractions leached from an impure carbonate is equal to that in the detrital material, the time evolution of this activity ratio is given by the equation:

$$\left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{L}} = \left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{D}_\text{o}} e^{-\lambda_\text{o} t} + \left(^{238}\text{U}/^{232}\text{Th}\right)_{\text{L}} \left(1 - e^{-\lambda_\text{o} t}\right), \quad (1)$$

where L means the activity ratio in the leachate, D_o the activity ratio in the detritus at time of deposition and λ_o the decay constant for ^{230}Th. At $t = 0$, the time of precipitation, U and Th measurement of several leachates from the same homogenized impure carbonate result in a horizontal line when plotting ^{230}Th/^{232}Th versus ^{238}U/^{232}Th activity ratios. After time t, the ^{230}Th activity concentration grows, due to the decay of U isotopes in the pure carbonate; thus in the same plot the activity ratios in the several leachates will fall on a line with a slope $1 - e^{-\lambda_\text{o} t}$. As time increases to values above $1/\lambda_\text{o}$, for each aliquot ^{230}Th/^{232}Th $= {}^{238}$U/^{232}Th and the data points will fall along the so called equiline: having a unit slope and passing through the origin. Isochrons evolving at different values of t rotate around a point called the equipoint which defines the ^{230}Th/^{232}Th activity ratio in the detritus at the time of precipitation.

If U isotopes are in disequilibrium, the ^{230}Th/^{232}Th activity ratios in leachates are described by the equation:

$$\left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{L}} = \left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{D}_\text{o}} e^{-\lambda_\text{o} t} + \left(^{234}\text{U}/^{232}\text{Th}\right)_{\text{L}} \left(1 - e^{-\lambda_\text{o} t}\right). \quad (2)$$

A plot of ^{230}Th/^{232}Th versus ^{234}U/^{232}Th ratios in several leachates will allow estimation of the ^{230}Th/^{234}U activity

ratio of the pure carbonate sample as well as the ^{230}Th/^{232}Th ratio in the detrital material at the time of analysis. Even considering that the ^{230}Th/^{232}Th activity ratio in the detritus is probably different from the activity ratio in the detritus part leached from the impure carbonate, the above equation can also be used, though the $\left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{D}_\text{o}}$ activity ratio must be changed by a factor r_0/r_2, with r_0 and r_2 being the fractions of ^{230}Th and ^{232}Th respectively extracted from the detritus into the solution during the leaching process. Hence:

$r_0/r_2 \left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{D}_\text{o}}$ instead of $\left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{D}_\text{o}}$.

An isochron approach involving total dissolution of several presumably cogenetic samples is often used [5, 13], considering that the detritus is different in each cogenetic sample. However, the fundamental requirement of a cogenetic sample suite is often difficult or impossible to verify before analysis of the total sample. Other correction methods involving isochrons arising from the analysis of several leachings of different aliquots from the same impure carbonate have been also used [17]. They proposed that an isochron can be constructed from leachates of the various aliquots from a homogenized sample (the L/L method) even though different fractions are extracted from the detrital material for each isotope. They showed that the leachates will obey the linear relation:

$$\left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{L}} = \left(^{230}\text{Th}/^{234}\text{U}\right)_{\text{C}} \left(^{234}\text{U}/^{232}\text{Th}\right)_{\text{L}} + r_0/r_2 \left(^{230}\text{Th}/^{232}\text{Th}\right)_{\text{D}} - r_4/r_2 \left(^{230}\text{Th}/^{234}\text{U}\right)_{\text{C}} \left(^{234}\text{U}/^{232}\text{Th}\right)_{\text{D}} \quad (3a)$$

$$\left(^{234}\text{U}/^{232}\text{Th}\right)_{\text{L}} = \left(^{234}\text{U}/^{238}\text{U}\right)_{\text{C}} \left(^{238}\text{U}/^{232}\text{Th}\right)_{\text{L}} + r_4/r_2 \left(^{234}\text{U}/^{232}\text{Th}\right)_{\text{D}} - r_8/r_2 \left(^{234}\text{U}/^{238}\text{U}\right)_{\text{C}} \left(^{238}\text{U}/^{232}\text{Th}\right)_{\text{D}} \quad (3b)$$

r_0, r_2, r_8 and r_4 being the 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 [3] a plot of ^{230}Th/^{232}Th versus ^{234}U/^{232}Th activity ratios in leachates will define a line whose slope is the ^{230}Th/^{234}U ratio of the pure carbonate. Furthermore, a plot of ^{234}U/^{232}Th versus ^{238}U/^{232}Th in leachates will yield a slope of ^{234}U/^{238}U in the pure carbonate. Using the Bateman disequilibrium equation, the age of the pure carbonate sample is obtained.

Over the last several years the analysis of several leachates has become unusual in the dating of impure carbonates, mainly due to differential fractionation in the leachates and to the chemical complexity of the analysis. If differential fractionation occurs, activity ratio values from

different leachates would not define a line and activity ratios in the pure carbonate will therefore not be obtained. The L/L method equations can nevertheless also be used in total dissolution of different aliquots of cogenetic samples. These samples must have different activity ratios in the detritus, which is difficult to ascertain prior to the analysis of the sample.

More recently, several approaches have been developed to date carbonates regardless of the amount of respective detrital material content [11, 18, 6]. Those carbonate samples with sufficiently high ratios of authigenic ^{230}Th to allogenic ^{230}Th present within the detrital component require small corrections for the detrital U and Th isotopes. So they assume that even approximate assumptions about the U–Th isotopic composition of the detritus enable useful precision in their calculated ^{230}Th/U age. They considered that analysis of a single complete sample is equivalent to determine a two-point isochron age, except that the second point on the isochron is defined by estimated isotope ratios with realistic errors assigned to the estimate (^{234}U/^{238}U = ^{230}Th/^{238}U = 1.0 ± 0.1 and ^{232}Th/^{238}U = 1.21 ± 0.60 in [11, 18] and ^{232}Th/^{238}U = 0.271 ± 0.027 in [6]).

Although the latter correction method was supposedly developed for samples with high ^{230}Th/^{232}Th activity ratios, i.e. nearly pure carbonates, if the assumed activity ratios are those in the real detritus it may be used even in very dirty carbonates. Samples from the Chafarinas Islands present high detrital material content. Thus, in this case an estimate of activity ratios in the detritus would probably (except in the case where the estimate is actually the real activity ratios in the detritus) give wrong ages and very different corrected ages for every subsample from the same impure carbonate. However, assuming that the pure detritus activity ratios must lie on the same isochron line as the several leachates from an impure carbonate [6, 3], Osmond diagrams have been used to estimate activity ratios in detrital material from the Chafarinas Islands samples.

The purpose of this study was to evaluate the above different correction methods for U–Th dating on carbonate deposits from the Chafarinas Islands. We will also use these correction methods to obtain and discuss some interesting activity ratios in the detritus of such impure carbonates, particularly ^{230}Th/^{232}Th activity ratio.

Samples and radiochemical methods

The Chafarinas Islands are located off the north coast of Morocco about 50 km east of Melilla and 4 km north of Cape Agua (35.1826° N latitude, −2.4240° longitude; Fig. 1). The small islands are formed from volcanic rocks from the Upper Miocene to Pliocene ages. Quaternary
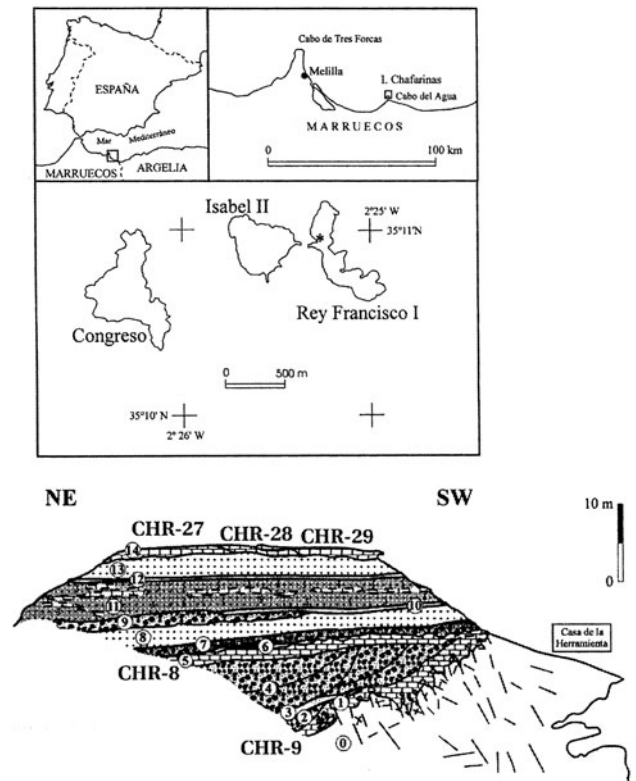

Fig. 1 Map of the Chafarinas Islands off the north coast of Africa. Locations of samples collected at Rey Francisco I Island are also shown. *Circled* numbers from 0 to 14 are the stratigraphic levels at Rey Francisco I Island, as described by Rodríguez-Vidal et al. [15]

surface deposits including calcrete cover most of the surface area, especially on Rey Francisco I, the easternmost island. A geological description of the islands can be found in Rodríguez-Vidal et al. [15]. Five samples of calcrete were collected from an 18-m-thick section of surface deposits constituting the most complete stratigraphic sequence in the northern part of the island. Sample CHR-9 was taken from the base of the sequence, sample CHR-8 from its middle and samples CHR-27, CHR-28 and CHR-29 from the uppermost calcrete layer, which appears to have lateral evolution (NE-SW) with older samples situated to the NE. All samples of calcrete contain substantial amounts of detrital material, greater than 20 % by weight, with the highest percentages in samples CHR-8 and CHR-9, of around 40 %.

Bulk samples were crushed and homogenized and then separated in several aliquots [2]. Aliquots from the same bulk sample would therefore share the same detritus and have the same activity ratios for the detrital component. The aliquots were dissolved in different nitric acid concentrations (2–8 M) in order to totally dissolve the carbonate and to extract different isotopic concentrations from the detrital material. These leachates were separated as quickly as possible from the residue and stored for U and Th analysis.

The residue remaining from one aliquot was also analyzed for U and Th isotopes. It was digested alternatively in concentrated nitric acid and aqua regia and in each step the solution was taken to dryness at high temperature (it can last from 7 to 10 days). The very small final white or clear grey residue was separated by centrifuging and filtration and discarded and the solution was added to the initial leachate for U and Th analysis. These samples were considered as totally dissolved samples. Additional residue samples were also analyzed in the same way.

Iron carrier (FeCl$_3$) and known amounts of highly purified ^{232}U and ^{229}Th isotope tracers, for yield determinations, were added to the acid solutions prepared from weak or strong acid leaching. Iron hydroxides, along with dissolved U and Th, were precipitated and then separated from the solutions. A solvent extraction method was used to separate U from Th isotopes by first dissolving the iron precipitate in 8 M HNO$_3$, and then adding tributyl-phosphate (TBP) to back-extract both uranium and thorium from solution into the TBP phase. Once the TBP phase was separated from the aqueous phase, 20 ml of Xilene was mixed with the TBP phase. Th was extracted from the organic phase using 1.5 M HCl as the inorganic phase. Finally, uranium was extracted from the organic phase

Table 1 U and Th isotopes activity concentrations (mBq/g) and some activity ratios of samples colleted at Rey Francisco I Island (Chafarinas Islands)

Sample	^{238}U	^{234}U	^{230}Th	^{232}Th	^{234}U/^{238}U	^{230}Th/^{234}U	^{230}Th/^{232}Th	T (ky)
CHR8: level 5								
CHR8-1	11.7 ± 0.6	16.2 ± 0.8	14.0 ± 1.2	13.9 ± 1.2	1.385 ± 0.028	0.861 ± 0.084	1.105 ± 0.020	182 ± 43
CHR8-2	7.62 ± 0.30	11.7 ± 0.5	8.73 ± 0.71	5.69 ± 0.47	1.533 ± 0.020	0.747 ± 0.067	1.533 ± 0.032	133 ± 22
CHR8-R	28.6 ± 1.0	28.4 ± 1.0	40.3 ± 1.5	57.1 ± 2.0	0.990 ± 0.032	1.421 ± 0.070	0.705 ± 0.018	
CHR9: level 1								
CHR9-1	5.02 ± 0.34	7.12 ± 0.47	9.81 ± 0.87	11.3 ± 1.0	1.420 ± 0.051	1.378 ± 0.153	0.867 ± 0.015	>350
CHR9-2	5.39 ± 0.15	9.76 ± 0.24	4.17 ± 0.14	4.04 ± 0.14	1.809 ± 0.050	0.427 ± 0.018	1.032 ± 0.035	57.8 ± 3.1
CHR9-3	5.33 ± 0.19	9.97 ± 0.30	4.47 ± 0.16	3.87 ± 0.14	1.872 ± 0.066	0.448 ± 0.021	1.156 ± 0.042	61.3 ± 3.6
CHR9-4	5.27 ± 0.17	9.87 ± 0.26	4.52 ± 0.16	4.08 ± 0.15	1.874 ± 0.058	0.458 ± 0.020	1.107 ± 0.038	63.1 ± 3.6
CHR9-5	2.65 ± 0.09	4.47 ± 0.13	3.63 ± 0.14	4.02 ± 0.15	1.688 ± 0.046	0.812 ± 0.038	0.903 ± 0.026	152.4 ± 13.9
CHR9-R	7.28 ± 0.39	7.92 ± 0.41	24.8 ± 1.1	30.0 ± 1.2	1.088 ± 0.071	3.136 ± 0.211	0.828 ± 0.031	
CHR9-T	5.08 ± 0.21	6.28 ± 0.22	14.7 ± 0.6	17.6 ± 0.6	1.236 ± 0.067	2.344 ± 0.134	0.835 ± 0.044	>350
CHR27: level 14, NE								
CHR27-1	4.16 ± 0.10	5.43 ± 0.12	3.80 ± 0.11	3.30 ± 0.10	1.304 ± 0.029	0.700 ± 0.026	1.152 ± 0.032	122 ± 8
CHR27-2	4.36 ± 0.13	5.68 ± 0.16	3.98 ± 0.11	3.84 ± 0.11	1.303 ± 0.037	0.699 ± 0.028	1.036 ± 0.026	122 ± 8
CHR27-3	4.42 ± 0.10	5.46 ± 0.11	3.71 ± 0.15	3.94 ± 0.15	1.237 ± 0.025	0.730 ± 0.024	1.034 ± 0.022	133 ± 8
CHR27-4	4.55 ± 0.09	5.85 ± 0.11	4.39 ± 0.17	3.82 ± 0.15	1.286 ± 0.022	0.745 ± 0.024	1.104 ± 0.023	137 ± 8
CHR27-5	4.58 ± 0.14	5.89 ± 0.17	4.34 ± 0.13	3.46 ± 0.11	1.285 ± 0.039	0.736 ± 0.030	1.251 ± 0.035	134 ± 10
CHR27-6	4.44 ± 0.11	5.70 ± 0.13	4.30 ± 0.13	3.57 ± 0.11	1.284 ± 0.029	0.755 ± 0.028	1.204 ± 0.033	141 ± 10
CHR27-R	12.9 ± 0.4	12.2 ± 0.4	20.5 ± 0.6	34.4 ± 1.0	0.943 ± 0.031	1.682 ± 0.074	0.596 ± 0.013	
CHR27-T	5.34 ± 0.11	6.34 ± 0.12	6.05 ± 0.12	7.50 ± 0.17	1.187 ± 0.033	0.954 ± 0.026	0.807 ± 0.024	265 ± 28
CHR28: level 14 Intermediate								
CHR28-1	5.56 ± 0.13	7.11 ± 0.16	3.95 ± 0.13	5.02 ± 0.15	1.278 ± 0.026	0.555 ± 0.022	0.787 ± 0.021	84.8 ± 4.8
CHR28-2	4.92 ± 0.11	6.01 ± 0.13	3.73 ± 0.12	4.88 ± 0.15	1.221 ± 0.022	0.620 ± 0.024	0.764 ± 0.020	101 ± 6
CHR28-3	5.53 ± 0.13	7.01 ± 0.16	4.53 ± 0.14	6.05 ± 0.18	1.268 ± 0.025	0.647 ± 0.025	0.749 ± 0.018	107 ± 7
CHR28-R	11.6 ± 0.5	11.1 ± 0.5	13.9 ± 0.5	25.8 ± 0.8	0.955 ± 0.045	1.255 ± 0.068	0.540 ± 0.014	
CHR28-T	7.07 ± 0.16	8.11 ± 0.17	6.44 ± 0.16	10.2 ± 0.2	1.147 ± 0.035	0.794 ± 0.026	0.632 ± 0.021	161.6 ± 11.7
CHR29: level 14 SW								
CHR29-1	4.06 ± 0.10	5.24 ± 0.12	3.05 ± 0.10	4.30 ± 0.14	1.290 ± 0.027	0.582 ± 0.024	0.709 ± 0.020	90.7 ± 5.6
CHR29-2	3.09 ± 0.08	3.94 ± 0.10	2.71 ± 0.09	4.26 ± 0.13	1.277 ± 0.032	0.686 ± 0.028	0.635 ± 0.017	119 ± 8
CHR29-3	4.07 ± 0.09	5.23 ± 0.12	3.19 ± 0.10	4.60 ± 0.14	1.284 ± 0.023	0.610 ± 0.023	0.693 ± 0.016	95.3 ± 7.5
CHR29-4	4.62 ± 0.13	6.09 ± 0.16	3.41 ± 0.11	5.09 ± 0.15	1.316 ± 0.036	0.560 ± 0.023	0.670 ± 0.019	85.6 ± 5.1
CHR29-R	11.2 ± 0.5	11.3 ± 0.5	14.2 ± 0.5	26.7 ± 0.8	1.012 ± 0.046	1.253 ± 0.065	0.532 ± 0.013	

The sample number followed by L means a leachate, R a residue of a leachate, while T means total samples, obtained by the addition of dissolved residue to the leachate. In column 9 nominal ages obtained by directly using the Bateman disequilibrium equation are also shown. Errors are $1 - \sigma$

using distilled water. The uranium fraction is ready for electroplating after solvent extraction, while the thorium fraction needs further purification as some traces of uranium are also extracted with the thorium. Thorium purification used anion exchange resin (AG1 × 8 hydrochloric form) conditioned in HCl 8 M. A second Th purification was necessary using the same resin conditioned in HNO_3 7 M.

Purified U and Th solutions were transferred onto stainless steel disks after adding 1 ml of 0.3 M $NaSO_4$ and electroplating at 1.2 A for 1 h. Radioactivity of ^{229}Th, ^{230}Th, ^{232}Th, ^{232}U, ^{234}U and ^{238}U were measured by decay counting in an alpha spectrometer system equipped with PIPS detectors [19]. Moderate-to-high recovery yields and well resolved spectra provide analytically reliable results.

Results and discussion

Table 1 shows the U and Th isotope activity concentrations as well as several activity ratios in each leachate (L), in the analyzed residue (R) and in the total dissolved sample (T) obtained by adding the dissolved residue to the leachate. The data's $1 - \sigma$ error is also included. Uncorrected ages calculated from measured ^{230}Th/^{234}U and ^{234}U/^{238}U activity ratios using the U-series disequilibrium age equation (Appendix A of [7]) are given for each sample separately. The ^{238}U activity concentrations range from 2.65 to 11.7 mBq/g in leachates, with the highest concentration in sample CHR-8, whereas most of the others are in the 4–5 mBq/g range. Residues tend to have higher ^{238}U activity concentrations than leachates from the same bulk
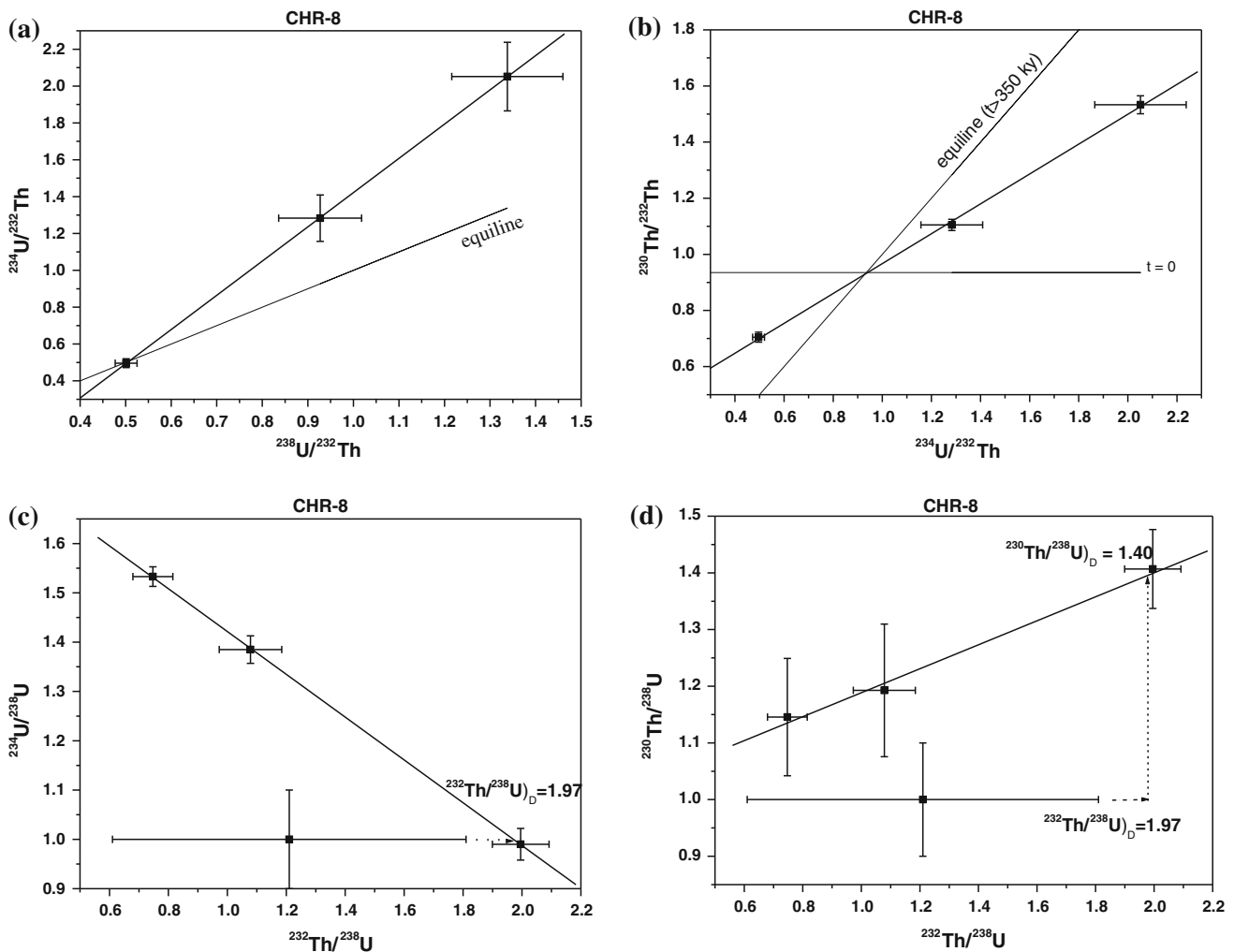

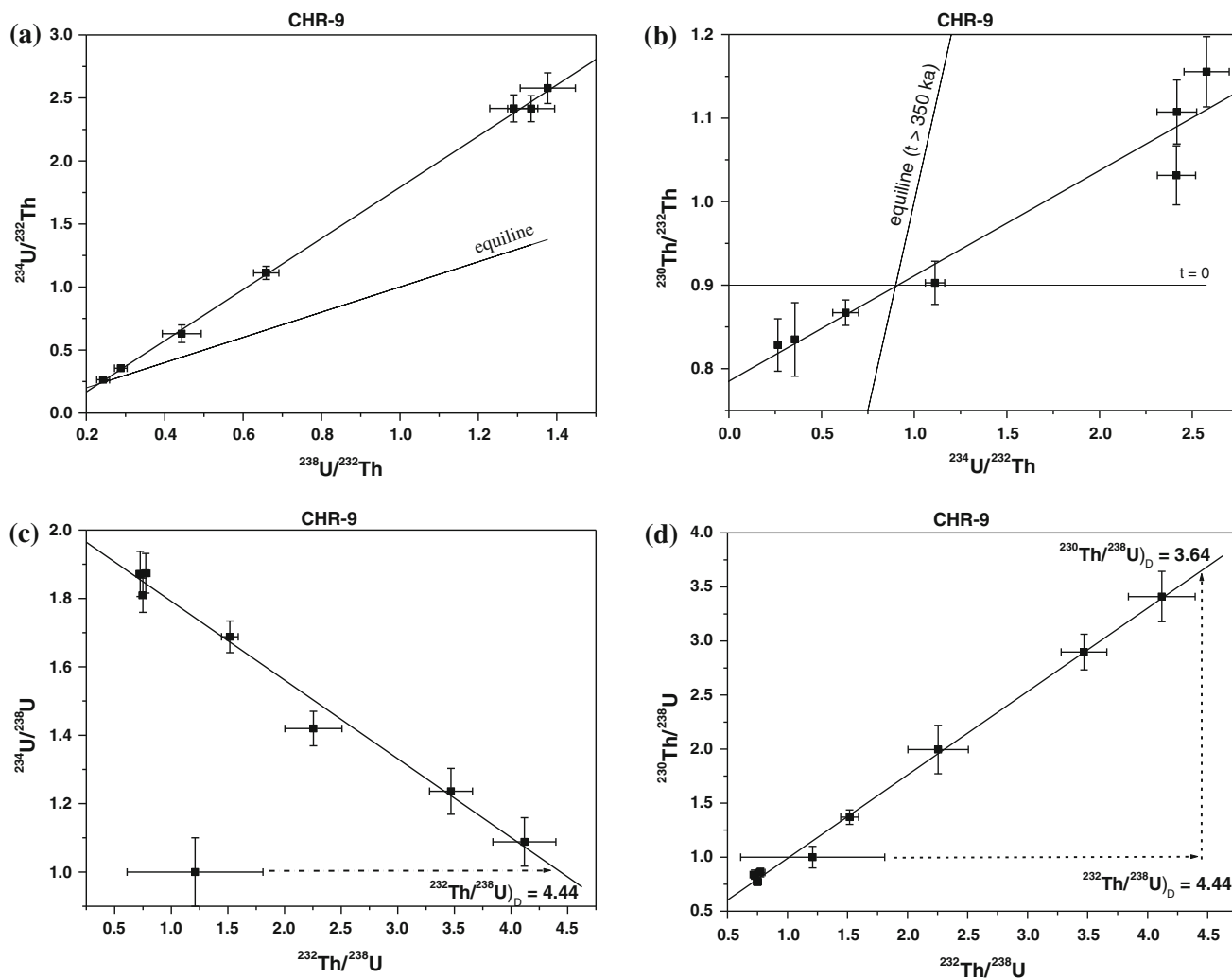
Fig. 2 Results for sample CHR-8. **a** ^{234}U/^{232}Th versus ^{238}U/^{232}Th data points. The equiline at which both uranium isotopes are in equilibrium is also shown. **b** ^{230}Th/^{232}Th versus ^{234}U/^{232}Th data points. The equiline or line at which ^{230}Th is in equilibrium with ^{234}U and the line at which ^{230}Th/^{232}Th remains constant and the same as its value at the time of precipitation are also shown. **c, d** Osmond diagrams for CHR-8 sample. The assumed [6] isotope ratios in the detrital (^{234}U/^{238}U = ^{230}Th/^{238}U = 1±0.1 and ^{232}Th/^{238}U = 1.21 ± 0.60) have been included as an example. Assuming secular equilibrium between both uranium isotopes in the detritus, the lines were used to obtain the ^{232}Th/^{238}U (**c**) and ^{230}Th/^{238}U (**d**) activity ratios in the detritus

Fig. 3 Results for sample CHR-9. **a** $^{234}U/^{232}Th$ versus $^{238}U/^{232}Th$ data points. The equiline at which both uranium isotopes are in equilibrium is also shown. **b** $^{230}Th/^{232}Th$ versus $^{234}U/^{232}Th$ data points. The equiline or line at which ^{230}Th is in equilibrium with ^{234}U and the line at which $^{230}Th/^{232}Th$ remains constant and the same as its value at the time of precipitation are also shown. **c, d** Osmond diagrams for CHR-9 sample. The assumed [6] isotope ratios in the detrital ($^{234}U/^{238}U = {}^{230}Th/^{238}U = 1\pm0.1$ and $^{232}Th/^{238}U = 1.21 \pm 0.60$) have been included as an example. Assuming secular equilibrium between both uranium isotopes in the detritus, the lines were used to obtain the $^{232}Th/^{238}U$ (**c**) and $^{230}Th/^{238}U$ (**d**) activity ratios in the detritus

sample, with the highest concentration again from sample CHR-8. This difference between leachates and residues is more evident in the case of Th isotopes. Leachates have ^{230}Th and ^{232}Th activity concentrations that are lower than or similar to those for U, however residues have Th isotope activity concentrations well above those for U in the same samples. Again the highest Th activity concentrations are found in sample CHR-8. A high percentage of detrital materials in these samples as well as higher Th concentration in the residues gives high $^{230}Th/^{234}U$ activity ratios, which results in overestimation of ages even though uncorrected ages for different leachates of the same sample are similar. These overestimated ages are corroborated by the values of the $^{230}Th/^{232}Th$ activity ratios in every aliquot (see Table 1). The results of the $^{230}Th/^{232}Th$ activity ratio

in the residues, below unity, show values below those in the leachates. As expected, $^{234}U/^{238}U$ activity ratios in residues are lower than those in the leachates. $^{234}U/^{238}U$ activity ratios from the leachate represents preferentially dissolved carbonates which might have $^{234}U/^{238}U > 1$ as inherited from the water they precipitated from. For leachates, measured uranium isotope activity ratios range 1.1–1.3 for samples CHR-27, CHR-28 and CHR-29, and higher for samples CHR-8, 1.4–1.5, and CHR-9, 1.5–1.8. As expected, residue samples have $^{234}U/^{238}U$ activity ratios either close to the secular equilibrium value of 1.0. For the $^{230}Th/^{232}Th$ activity ratios, leachates have values ranging from 0.7 to 1.5 whereas residues have lower values, consistent with the higher Th/U values present in the detrital component compared to pure carbonate.
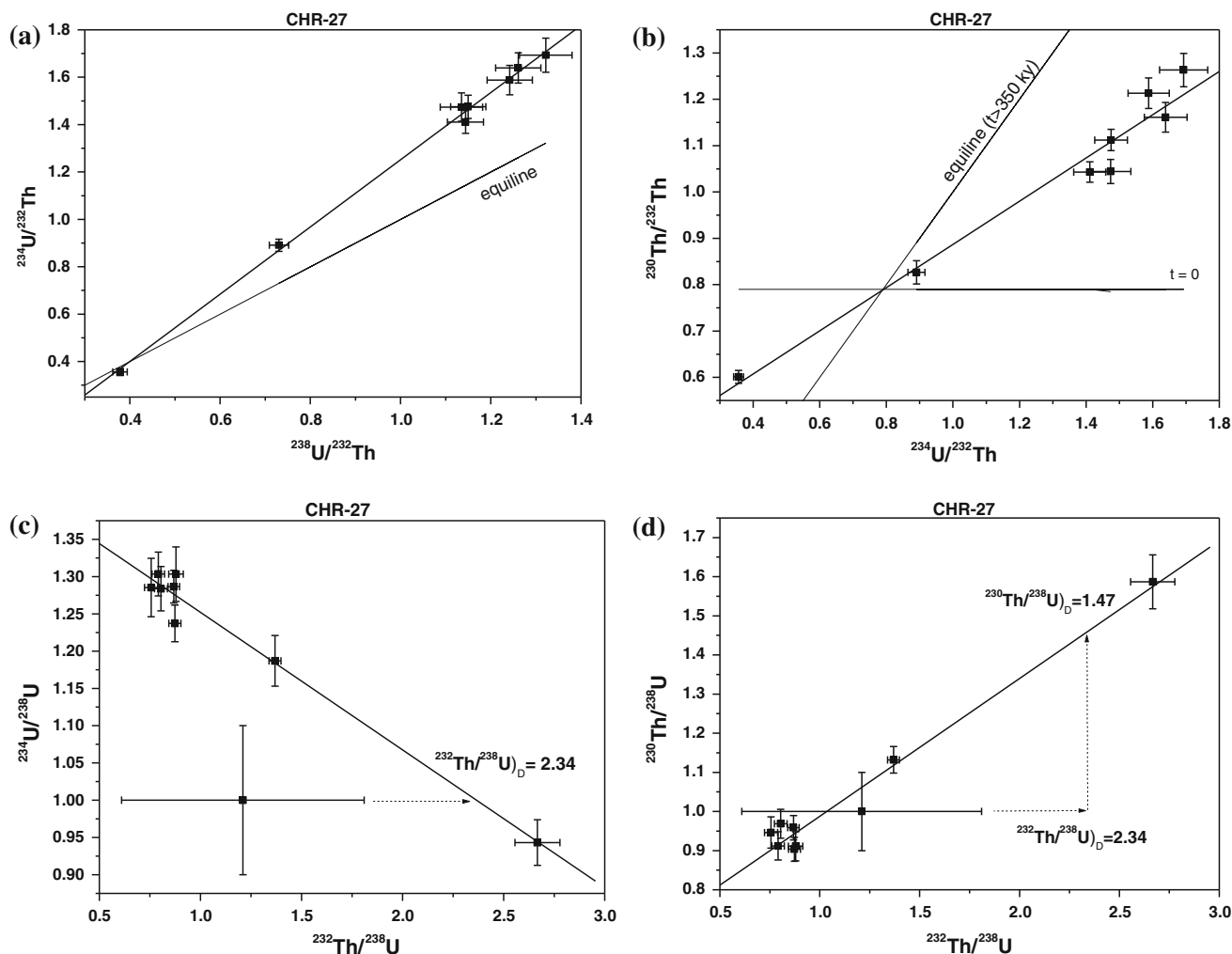
(a) CHR-27 — $^{234}U/^{232}Th$ versus $^{238}U/^{232}Th$, with equiline labelled.

(b) CHR-27 — $^{230}Th/^{232}Th$ versus $^{234}U/^{232}Th$, with equiline ($t > 350$ ky) and $t = 0$ line labelled.

(c) CHR-27 — $^{234}U/^{238}U$ versus $^{232}Th/^{238}U$, with $^{232}Th/^{238}U)_D = 2.34$ labelled.

(d) CHR-27 — $^{230}Th/^{238}U$ versus $^{232}Th/^{238}U$, with $^{230}Th/^{238}U)_D = 1.47$ and $^{232}Th/^{238}U)_D = 2.34$ labelled.

Fig. 4 Results for sample CHR-27. **a** $^{234}U/^{232}Th$ versus $^{238}U/^{232}Th$ data points. The equiline at which both uranium isotopes are in equilibrium is also shown. **b** $^{230}Th/^{232}Th$ versus $^{234}U/^{232}Th$ data points. The equiline or line at which ^{230}Th is in equilibrium with ^{234}U and the line at which $^{230}Th/^{232}Th$ remains constant and the same as its value at the time of precipitation are also shown. **c, d** Osmond diagrams for CHR-27 sample. The assumed [6] isotope ratios in the detrital ($^{234}U/^{238}U = {}^{230}Th/^{238}U = 1 \pm 0.1$ and $^{232}Th/^{238}U = 1.21 \pm 0.60$) have been included as an example. Assuming secular equilibrium between both uranium isotopes in the detritus, the lines were used to obtain the $^{232}Th/^{238}U$ (**c**) and $^{230}Th/^{238}U$ (**d**) activity ratios in the detritus

For illustration purposes only, 2D Rosholt-type diagrams for each sample are shown (a, b) in Figs. 2, 3, 4, 5 and 6. Activity ratios in the ^{232}Th-free, pure carbonate end member were calculated using a 3D-isochron fit with Isoplot [10, 12], along with the age, initial $^{234}U/^{238}U$ activity ratio and regression statistics (MSWD and probability of fit; Table 2). Generally, the ages range from 14.1 ± 1.5 ka for sample CHR-9 to 76 ± 11 ka for sample CHR-8. As commented above, samples CHR-27, CHR-28 and CHR-29 were taken at the top of the series in a calcrete layer that seems to have lateral evolution with older samples situated at NE positions [15]. The ages obtained support this model because sample CHR-29 was situated in the SW position and it has the youngest age, 25.3 ± 2.9 ka (agreeing with the other ^{14}C date of 20.3 ± 0.3 ka), whereas CHR-27 was situated in the NE position and has the oldest age,

62.9 ± 2.9 ka, with CHR-28 situated in an intermediate position and having an intermediate age, 33.4 ± 2.6 ka. The $^{234}U/^{238}U$ activity ratio at the time of deposition in this time interval is constant (1.538 ± 0.038 as the mean value). This could indicate that during this time period (25–63 ka) climate conditions did not change and that the samples were precipitated in the same conditions and probably from similar waters. Sample CHR-8 was situated some meters below the surface and as expected is older than samples from the top layer, at 76 ± 11 ka. Sample CHR-9 was taken at the bottom of the stratigraphic section and was expected to be the oldest sample. However, the age obtained was only 14.1 ± 1.5 ka, which is younger rather than older than the overlying horizons. The $^{234}U/^{238}U$ initial activity ratios in both samples (CHR-8 and CHR-9) are higher than those of samples CHR-27 to
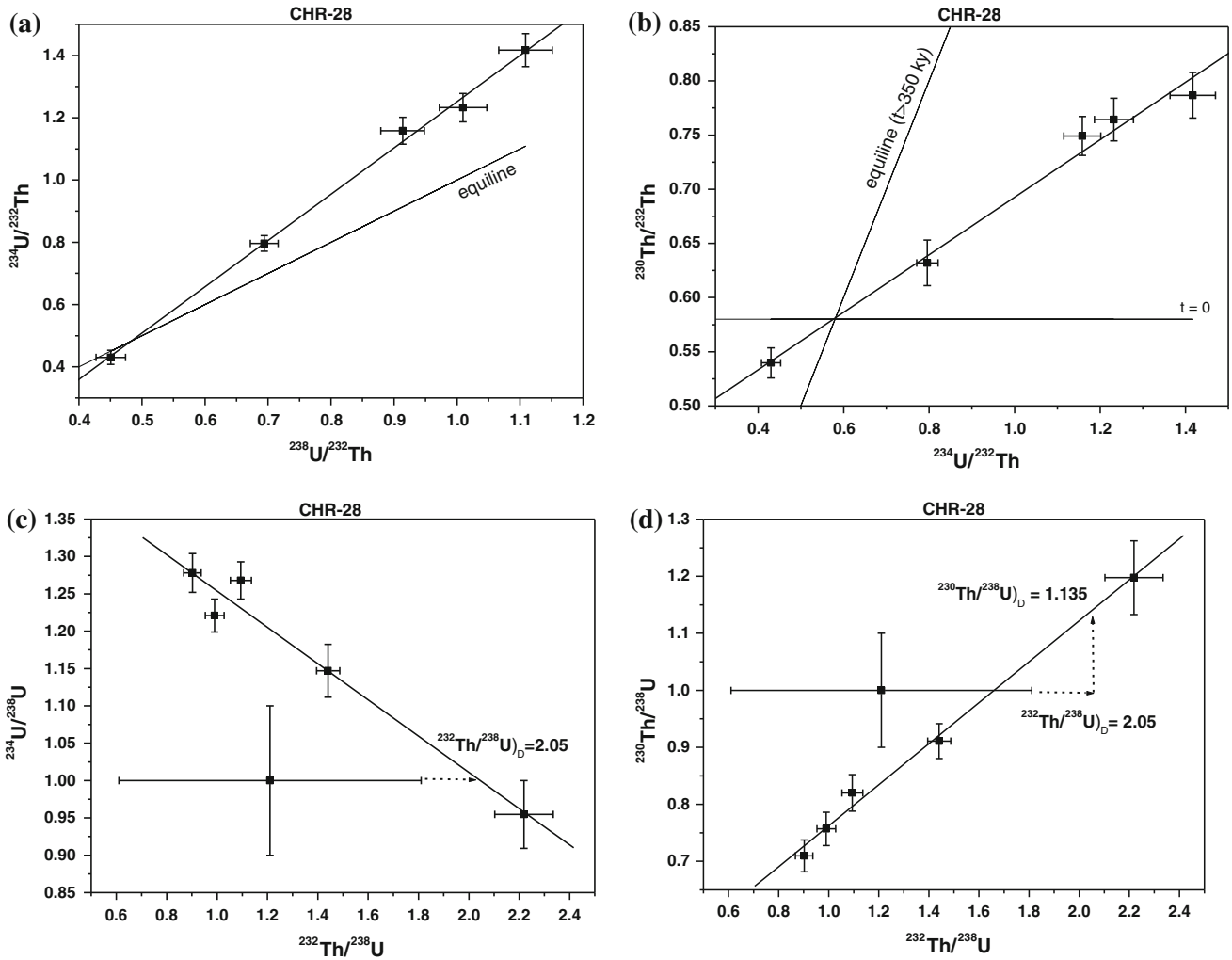
Fig. 5 Results for sample CHR-28. **a** ^{234}U/^{232}Th versus ^{238}U/^{232}Th data points. The equiline at which both uranium isotopes are in equilibrium is also shown. **b** ^{230}Th/^{232}Th versus ^{234}U/^{232}Th data points. The equiline or line at which ^{230}Th is in equilibrium with ^{234}U and the line at which ^{230}Th/^{232}Th remains constant and the same as its value at the time of precipitation are also shown. **c, d** Osmond diagrams for CHR-28 sample. The assumed [6] isotope ratios in the detrital (^{234}U/^{238}U = ^{230}Th/^{238}U = 1±0.1 and ^{232}Th/^{238}U = 1.21 ± 0.60) have been included as an example. Assuming secular equilibrium between both uranium isotopes in the detritus, the lines were used to obtain the ^{232}Th/^{238}U (**c**) and ^{230}Th/^{238}U (**d**) activity ratios in the detritus

CHR-29 and quite similar to each other, with 2.056 ± 0.006 as the mean value. This fact may indicate that the precipitation conditions of both samples were different from the uppermost calcrete layer samples. This could eventually be associated to the rapid and sudden warm-humid event 5.1 at 79–80 ka that affected the northern part of Africa [1, 16]. Nevertheless, sample CHR-9 at least seems to have behaved as an open system for U and/or Th isotopes since its formation, as discussed below.

As can be observed in Rosholt diagrams (Figs. 2, 3, 4, 5, 6a, b), both residue and total samples follow the same isochron line as the leachates and they have thus been included in the age calculations. Following Allegre and Condomines [4] as ^{234}U and ^{238}U are clearly in disequilibrium, by using

Eq. 2 and Rosholt diagrams (Figs. 2b, 3b, 4b, 5b, 6b) it is possible to obtain the ^{230}Th/^{232}Th activity ratios at present and at deposition time in the detritus. The results are shown in columns 2 and 3 of Table 3. Column 4 of this Table also shows the ages obtained by using the time evolution equation, considering that the ^{232}Th concentration remains constant during the period of time considered. The age errors were evaluated by error propagation. Even considering that the ages have a relatively high error, the results are similar to those obtained using the equations of the L/L method [17]. More interesting are the results obtained for the present day ^{230}Th/^{232}Th activity ratio in the detritus (see column 2 of Table 3). Except for sample CHR-9, all the others have similar values for this activity ratio with a mean
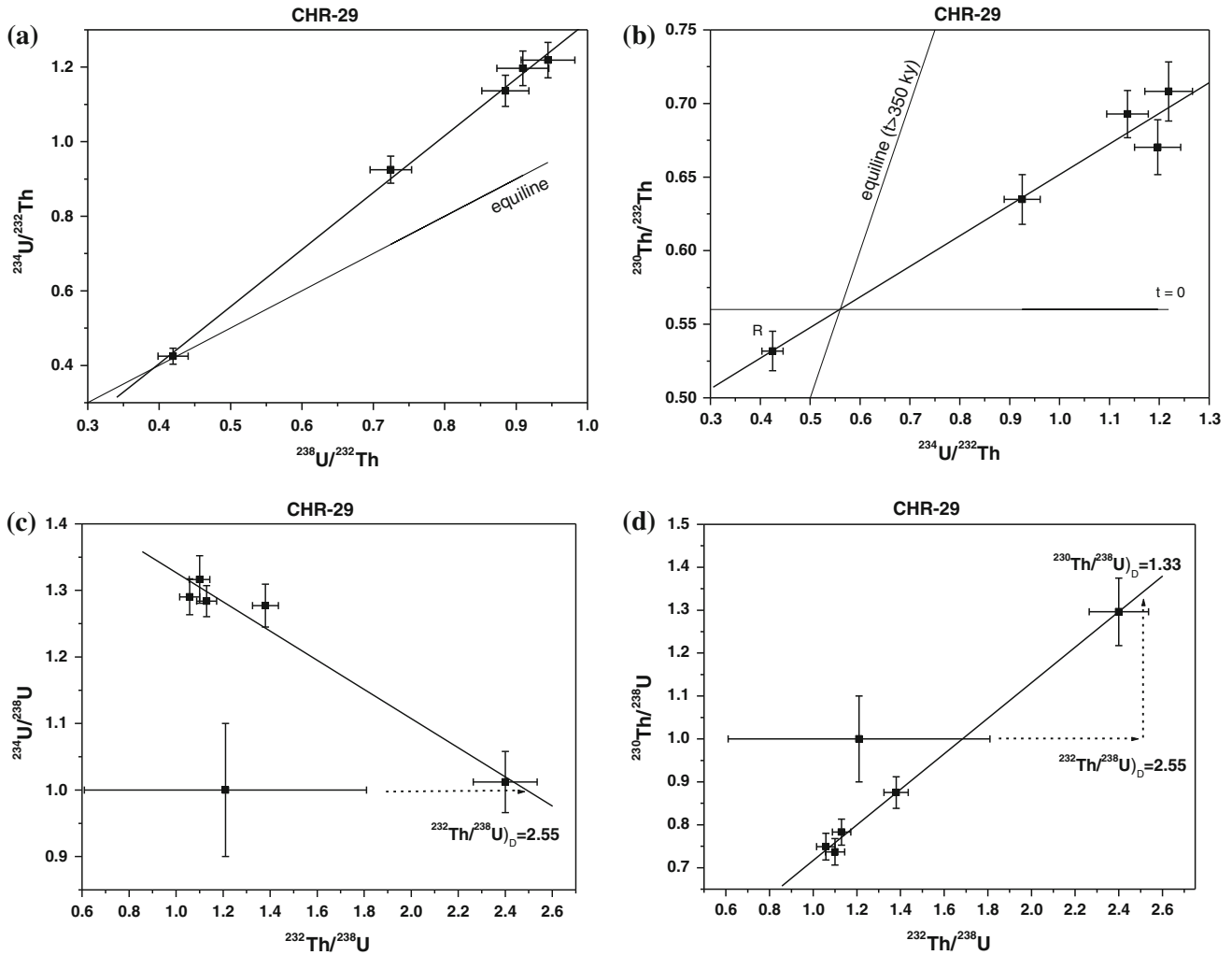
Fig. 6 Results for sample CHR-29. **a** $^{234}U/^{232}Th$ versus $^{238}U/^{232}Th$ data points. The equiline at which both uranium isotopes are in equilibrium is also shown. **b** $^{230}Th/^{232}Th$ versus $^{234}U/^{232}Th$ data points. The equiline or line at which ^{230}Th is in equilibrium with ^{234}U and the line at which $^{230}Th/^{232}Th$ remains constant and the same as its value at the time of precipitation are also shown. **c, d** Osmond diagrams for CHR-29 sample. The assumed [6] isotope ratios in the detrital ($^{234}U/^{238}U = {}^{230}Th/^{238}U = 1\pm0.1$ and $^{232}Th/^{238}U = 1.21 \pm 0.60$) have been included as an example. Assuming secular equilibrium between both uranium isotopes in the detritus, the *lines* were used to obtain the $^{232}Th/^{238}U$ (**c**) and $^{230}Th/^{238}U$ (**d**) activity ratios in the detritus

value of 0.429 ± 0.017. Sample CHR-9 has a clearly higher value of the same activity ratio. It seems that either the original detrital material in this sample is different from that in the other samples or that an increase of ^{230}Th concentration in the detritus has been occurring since sample formation. Indeed, if the present-day value in the detritus is taken as the mean value in the other samples (0.429 ± 0.017) and the initial value as that in Table 3 (0.890 ± 0.043), then the time t since its formation results as being 79.2 ± 6.8 ka, more in agreement with its expected age

A different analytical approach for dating calcrete was used by Ludwig and Paces [11] and Sharp et al. [18] and for nearly pure samples of lacustrine aragonite by Haase-Schramm et al. [6]. These authors targeted small samples of relatively pure carbonate with high U/Th ratios that require only small corrections for initial ^{230}Th from a detrital component. They assumed that in those samples with sufficiently high ratios of authigenic ^{230}Th to allogenic ^{230}Th present within the carbonate, a small correction for the detrital U and Th isotopes is required. They assumed that the analysis of a single sample is equivalent to determining a two-point isochron age, except that the second point on the isochron is defined by a detrital component assumed to be in radioactive secular equilibrium (i.e., $^{234}U/^{238}U = {}^{230}Th/^{238}U = 1.0$) with $^{232}Th/^{238}U$ activity ratio of $\sim 1.21 \pm 0.60$ for silicate material [11, 18] or 0.271 ± 0.027 for detritus that included substantial

Table 2 The ^{234}U/^{238}U and ^{230}Th/^{238}U activity ratios in the pure carbonate component of each sample and their ages obtained with the ISOPLOT program [10] are given

Sample	^{234}U/^{238}U	^{230}Th/^{238}U	T (ka)	$(^{234}$U/^{238}U$)_o$	MSWD	Pr. of fit
CHR8	1.852 ± 0.064	0.971 ± 0.122	76 ± 11	2.053 ± 0.079	0.030	0.97
CHR9	2.019 ± 0.046	0.247 ± 0.025	14.1 ± 1.5	2.059 ± 0.048	0.747	0.68
CHR27	1.432 ± 0.027	0.645 ± 0.025	62.9 ± 2.9	1.514 ± 0.032	1.140	0.33
CHR28	1.491 ± 0.046	0.401 ± 0.030	33.4 ± 2.6	1.539 ± 0.050	0.835	0.54
CHR29	1.524 ± 0.060	0.320 ± 0.035	25.3 ± 2.9	1.562 ± 0.065	0.728	0.63

The ^{234}U/^{238}U activity ratio at the time of deposition (5th column) was obtained by using the disequilibrium equation with the activity ratio at the time of measurement and the age of the sample. In last two columns the MSWD and the probability of fit of the fitted line are also given

amounts of marine carbonate [6]. Error assigned to the assumed detrital component is propagated throughout the age calculation and the result is low in total errors for samples with low ^{232}Th/^{238}U, or has very large errors for samples with high ^{232}Th/^{238}U. This approach could be used for more impure carbonates if the assumed activity ratios were identical to those in the real detrital component. We will use this approach to evaluate some activity ratios in the detrital material and compare the results with data previously obtained.

Figures 2, 3, 4, 5 and 6c, d show the Osmond diagrams for each Chafarinas Islands sample. In each of these figures the assumed isotope ratios for the detrital component (^{234}U/^{238}U = ^{230}Th/^{238}U = 1±0.1 and ^{232}Th/^{238}U = 1.21 ± 0.60) were included. As can be seen, data for the assumed detrital component do not fall on the regression line defined by the leachate, residue and total samples. It is probable that the pure detrital end-member has ^{234}U/^{238}U activity ratios close to secular equilibrium values (indeed, the residue samples have a ^{234}U/^{238}U activity ratio close to unity) and the value ^{234}U/^{238}U = 1.0 ± 0.1 is considered a realistic value. It is therefore probable that the value 1.21 assumed for the ^{232}Th/^{238}U activity ratio of the pure detrital end-member is not accurate. If the regression line has real age meaning, and the detrital component has a ^{234}U/^{238}U activity ratio of unity, an estimate of the true value for the ^{232}Th/^{238}U activity ratio in the detritus can be obtained (see Figs. 2c, 3c, 4c, 5c, 6c). These estimates are also shown in Table 3 as $(^{232}$Th/^{238}U$)_D$ (column 5). These values of the $(^{232}$Th/^{238}U$)_D$ activity ratios can be used to determine (see Figs. 2d, 3d, 4d, 5d, 6d) values for the $(^{230}$Th/^{238}U$)_D$ and $(^{230}$Th/^{232}Th$)_D$ activity ratios in the pure detrital end-member by noting where the $(^{232}$Th/^{238}U$)_D$ value intersects the regression line (see columns 6 and 7 from Table 3). The ^{230}Th/^{232}Th activity ratio in the residue (column 7 of Table 3) is obtained by dividing ^{230}Th/^{238}U by ^{232}Th/^{238}U, i.e. column 6 by column 5.

Data in Table 3, except for results from sample CHR-9, show $(^{232}$Th/^{238}U$)_D$ activity ratios in the pure detrital end-member of around 2, with a mean value of 2.23 ± 0.27 and $(^{230}$Th/^{238}U$)_D$ activity ratios also similar to each other and

with a mean value of 1.33 ± 0.14. However, for sample CHR-9 both activity ratios have values higher than in the rest of the samples, 4.42 ± 0.58 and 3.63 ± 0.46, respectively. The high error bars in the activity ratios do not allow a clear conclusion. However, sample CHR-9 seems to have a ^{230}Th/^{232}Th activity ratio higher than in the other samples and clearly very high ^{232}Th/^{238}U and ^{230}Th/^{238}U activity ratios in comparison with the rest of the samples, confirming that a probable migration of uranium from the detritus into the carbonate as well as an increase of ^{230}Th in the detritus have occurred. This increase, due to the low Th mobility in the environment, may be due to α-recoil processes after ^{234}U decay in the carbonate.

To confirm the anomaly of sample CHR-9 in Fig. 7, activity ratios in the detrital component were plotted. In Fig. 7a, the ^{230}Th/^{232}Th activity ratios were plotted against the age ($e^{\lambda t}$) of the samples. As can be observed in such figure, except for sample CHR-9 all samples follow a linear trend agreeing with the decay of ^{230}Th excess in the detritus over time. The linear data fit gives a ^{230}Th/^{232}Th activity ratio at present time value of 0.42 ± 0.03, similar to the mean value in Table 3 (column 2). If a value of ^{230}Th/^{232}Th activity ratio of 0.89 is considered for sample CHR-9, its corresponding age should be 81.5 ka, again in agreement with its stratigraphic location. Moreover, in Fig. 7b, ^{230}Th/^{232}Th versus ^{238}U/^{232}Th activity ratios in the detritus for all samples is plotted. Again, sample CHR-9 does not follow the same trend as the other samples. If the above value of the ^{230}Th/^{232}Th activity ratio for sample CHR-9 is used in the linear fit obtained with the rest of the samples, a value of the ^{238}U/^{232}Th activity ratio in the detritus of 0.68 for sample CHR-9 is obtained. This value corresponds to a ^{230}Th/^{238}U activity ratio in the detrital component of sample CHR-9 of 1.21, similar to the values in Table 3 (column 6).

The results for the anomalous sample (CHR-9), i.e. very low ^{230}Th/^{238}U activity ratio in the pure carbonate and a high value in the detrital component, compared to the other samples, seem to show a migration of uranium from the detrital component into the carbonate. Moreover, if the age of this sample is around 79 ka, its present day ^{234}U/^{238}U

Table 3 Activity ratios in the detritus component of the samples obtained by using Allegre and Condomines [4] equation (columns 2, 3 and 4) and by Ludwig and Paces [11] approach (columns 5, 6 and 7). See text

| Samples	$(^{230}\text{Th}/^{232}\text{Th})_{present}$	$(^{230}\text{Th}/^{232}\text{Th})_{initial}$	T (ka)	$(^{232}\text{Th}/^{238}\text{U})_D$	$(^{230}\text{Th}/^{238}\text{U})_D$	$(^{230}\text{Th}/^{232}\text{Th})_D$
CHR-8	0.436 ± 0.005	0.966 ± 0.020	86.3 ± 18.9	1.97 ± 0.32	1.40 ± 0.21	0.710 ± 0.157
CHR-9	0.756 ± 0.023	0.890 ± 0.043	17.6 ± 7.2	4.42 ± 0.58	3.63 ± 0.46	0.821 ± 0.150
CHR-27	0.406 ± 0.050	0.776 ± 0.108	70.2 ± 20.1	2.34 ± 0.36	1.47 ± 0.15	0.628 ± 0.115
CHR-28	0.426 ± 0.013	0.586 ± 0.021	34.5 ± 0.5	2.05 ± 0.44	1.14 ± 0.16	0.555 ± 0.144
CHR-29	0.447 ± 0.018	0.567 ± 0.026	25.9 ± 6.6	2.55 ± 0.58	1.33 ± 0.24	0.523 ± 0.151
Mean	0.429 ± 0.017			2.23 ± 0.27	1.33 ± 0.14	0.596 ± 0.097
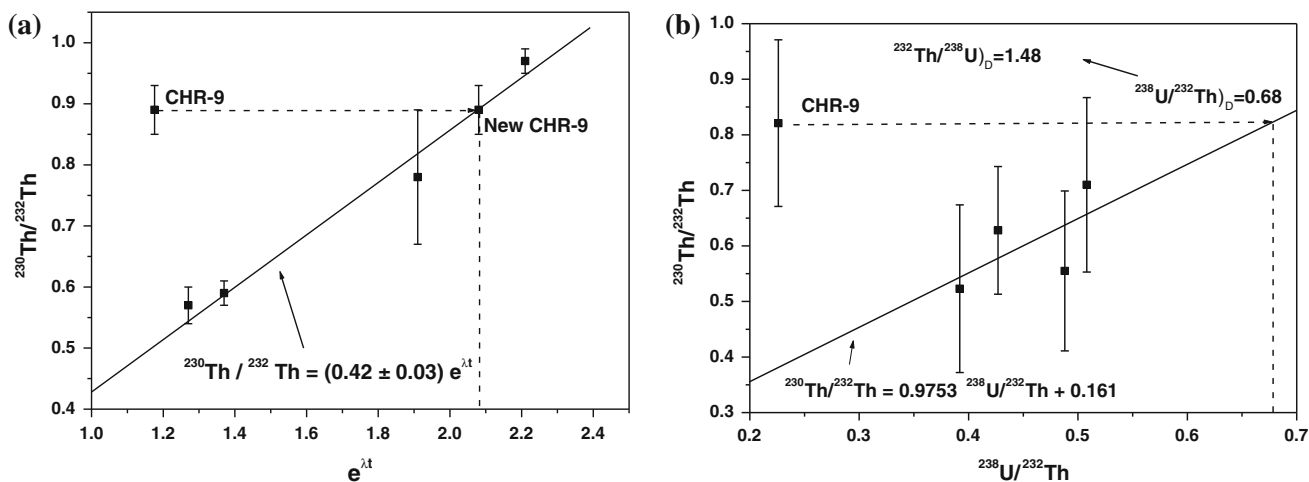
Fig. 7 a $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the detrital component versus the age of the carbonate (column 3 in Table 3) and **b** $^{230}\text{Th}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ activity ratios in the detrital components (data from columns 7 and the inverse of column 5 in Table 3). In both figures results of the fitted regression line are also shown

activity ratio should be 1.65 instead of 2.02. This outcome could be interpreted as a preferential leaching of ^{234}U (relative to ^{238}U) from the detrital component into the carbonate.

Furthermore, the activity ratios obtained in the detritus material indicate that we must be very careful when considering average values of those activity ratios for dating purposes, even in relatively pure carbonates. It is necessary to study those activity ratios in detritus from the specific areas under study.

Conclusion

The uranium-series method was applied to continental carbonate deposits from the Chafarinas Islands. All treated samples were impure carbonates and the L/L method was used to obtain activity ratios in carbonate fraction. Ages obtained range from 23 to 80 ka BP and are consistent with stratigraphic positions of the samples analysed. Initial activity ratios for uranium isotopes indicate that no changes in environmental conditions occured in the 25–60 ka BP

period and that a change occurred 80 ka ago. However, an anomalous age was obtained for one of the samples, which should be the oldest but results as being the youngest.

Use of the Allegre and Condomines [4] method gave the present-day $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the detrital component of the samples. With the exception of the sample with anomalous age, the activity ratio results as being the same for all the others, with a mean of 0.429 ± 0.027. This fact may be the effect of a ^{230}Th ejection, after ^{234}U α-decay, from the carbonate into the detritus since sample precipitation, resulting in an age below its real age. By considering for this sample the same present-day $^{230}\text{Th}/^{232}\text{Th}$ activity ratios in the residue, an age of 79.2 ± 6.8 ka is obtained. This age is in accordance with its stratigraphic location (see Fig. 1).

The anomalous activity ratios in this sample are also confirmed in the values of the $^{230}\text{Th}/^{238}\text{U}$ and $^{232}\text{Th}/^{238}\text{U}$ activity ratios obtained using Osmond diagrams and the approach of Ludwig and Paces [11], Sharp et al. [18] and Haase-Schramm et al. [6]. The rest of the sample shows a constancy of both activity ratios, whereas the anomalous sample has values between 2 and 3 times higher. The

results might confirm that a leaching of uranium isotopes (preferentially ^{234}U) from the detrital component into the carbonate has been occurring. These activity ratios clearly differ from the mean earth estimation proposed by Ludwig and Paces [11] and Sharp et al. [18]. Their two-point isochron approach must thus be used very carefully.

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