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## Method Development for $^{234}\text{U}$ and $^{230}\text{Th}$ Determination and Application to Fossil Deep-Water Coral and Authigenic Carbonate Dating from the Campos Basin - Brazil

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Foi desenvolvido um método para determinação de  $^{234}\text{U}$  e  $^{230}\text{Th}$  empregando uma separação por extração cromatográfica seguida por medidas com ICP-MS quadrupolar (ICP-QMS). Para carbonatos autigênicos, uma segunda etapa de separação, por cromatografia de troca-iônica em meio nítrico, foi incluída. Esses métodos foram aplicados a sete amostras de fósseis de corais de águas profundas e duas amostras de carbonato autigênicos do talude continental da Bacia de Campos. As idades determinadas para as amostras de fósseis de corais variaram entre 9-202 kanos com uma incerteza de 1%, consistente com os valores determinados pela datação com  $^{14}\text{C}$ , bem como com as idades  $^{230}\text{Th}/^{234}\text{U}$  determinadas por FIAS-ICP-QMS. Uma das amostras de carbonato autigênico analisada apresentou uma idade de aproximadamente 80 kanos. A outra amostra apresentou uma razão  $^{230}\text{Th}/^{234}\text{U}$  próximo do equilíbrio e fora da faixa de aplicação do método.

A  $^{234}\text{U}$  and  $^{230}\text{Th}$  determination method based on an extraction chromatographic separation followed by ICP-MS with quadrupole (ICP-QMS) was developed. For authigenic carbonates, a second separation step with ion exchange chromatography in a  $\text{HNO}_3$  solution was added. These methods were applied to seven fossil deep-water coral and two authigenic carbonate samples from the continental slope of the Campos Basin - Brazil. The ages determined for the fossil corals samples from the same sediment core ranged from 9 to 202 ky with a 1% uncertainty, consistent with the values determined by  $^{14}\text{C}$  dating and with those determined by  $^{230}\text{Th}/^{234}\text{U}$  using flow injection coupled to an ICP-QMS. One of the authigenic carbonates analyzed presented an age of approximately 80 ky. The other sample exhibited a  $^{230}\text{Th}/^{234}\text{U}$  activity ratio close to equilibrium and out of the application range of the method.

**Keywords:**  $^{230}\text{Th}/^{234}\text{U}$  dating, ICP-MS, fossil deep-water corals, authigenic carbonates

### Introduction

The Brazilian continental margin contains substantial hydrocarbon reserves and thus has been the subject of research related to biostratigraphy, paleoecology and paleoceanography. Sequences of appearing and disappearing fossil deep-water corals have been found in sediments sampled from the Campos Basin continental slope.<sup>1</sup>

Deep-water fossil corals could serve as records with high temporal resolution for the reconstruction of rapid changes in past ocean circulation.<sup>2</sup> The earth's climate changes rapidly on the geological time scale, and the bottom

of the sea plays an important role as a paleoceanographic record.<sup>3,4</sup> Some authors have suggested that the deep-water corals are well suited to the study of rapid climate change.<sup>2,5,6</sup> Past deep circulation patterns have been reconstructed using high-resolution records of deep-water corals obtained by  $^{14}\text{C}$  or U/Th dating.

According to Miller,<sup>7</sup> seabed hydrocarbon seeps have been widely used as an indicator of deep hydrocarbon accumulations. Detailed study of the geochemical, geological and geochronological aspects of seep-related features can provide important information on the origin, evolution and thermal processes of hydrocarbon migration, thus contributing to a better understanding of petroleum systems.

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Over the past few years, several studies on the underwater environment and fossil records rocks have emphasized the importance of carbonate formation associated with the age of hydrocarbon seepage and microbial activity.<sup>8</sup> Because authigenic carbonate precipitation most commonly results from anaerobic methane oxidation, its carbon source is petrogenic and thus conventional  $^{14}\text{C}$  dating is not applicable. However, several studies have demonstrated the applicability of the  $^{230}\text{Th}/^{234}\text{U}$  method for these purposes.<sup>9-11</sup>

Depending on the sample age, the  $^{230}\text{Th}$  activity can be low, which causes a high uncertainty in age determination by radiochemical methods, even after long counting times. Thus,  $^{230}\text{Th}/^{234}\text{U}$  in these samples (corals and authigenic carbonates) can be determined using mass spectrometry.<sup>12-15</sup>

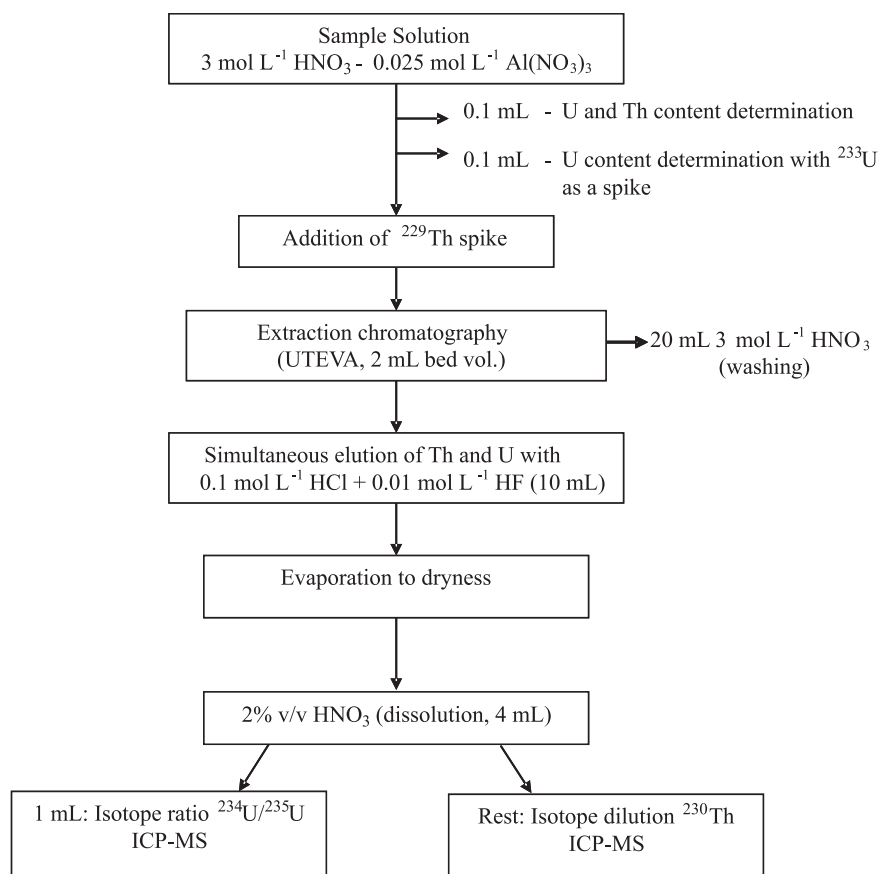
In this work, the  $^{230}\text{Th}/^{234}\text{U}$  determination method by ICP-MS was performed by the Institute for Radioprotection and Dosimetry/Brazilian Nuclear Commission (IRD/CNEN), using on-line chemical separation (FIAS) employing UTEVA cartridges (Eichrom Co.).<sup>16</sup> The method had to be adapted for application to samples of authigenic carbonates, because low chemical yields were observed, probably due to large amounts of iron.

The aim of the present work is to develop an analytical method for  $^{230}\text{Th}/^{234}\text{U}$  dating of authigenic carbonate and deep-water coral samples with improved precision and accuracy over the on-line separation (FIAS) method currently used by the IRD/CNEN. The calculated ages were compared with values obtained by other techniques, such as  $^{14}\text{C}$  dating by mass spectrometry coupled to a particle accelerator (AMS) by the Laboratory of the University of California (USA) and  $^{230}\text{Th}/^{234}\text{U}$  dating with a flow injection system coupled to an ICP-QMS method by the Institute for Radioprotection and Dosimetry (Brazil).

## Experimental

The seven fossil coral and two authigenic carbonate samples, which originated from the continental slope of the Campos Basin - Brazil, were obtained from Petrobras.

To remove the U and Th fractions on the coral samples carried by the Fe-Mn coatings and clay particles, mechanical cleaning was first performed, followed by ultrasonic washing with  $1\text{ mol L}^{-1}\text{ HNO}_3$  for 20 min. A second chemical cleaning procedure adapted from



**Figure 1.** Method for  $^{234}\text{U}$  and  $^{230}\text{Th}$  determination - fossil coral samples.

Lomitschka and Mangini<sup>12</sup> was then performed. One gram of cleaned coral sample was ground in an agate mortar and dissolved in 30 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub>. When some residue remained, it was dissolved completely with an acid mixture composed by HNO<sub>3</sub> plus HF, evaporated to eliminate HF, and the obtained residue re-dissolved with 3 mol L<sup>-1</sup> HNO<sub>3</sub> and reserved for its U and Th content determination by ICP-QMS. These results were used to correct the  $^{234}\text{U}$  and  $^{230}\text{Th}$  values on the carbonate phase for the detritic contribution by applying the  $^{232}\text{Th}$  concentration on the carbonate phase and the U/Th ratio on the residual phase. Thorium-230 and  $^{234}\text{U}$  concentrations on the leaching solution were determined according to the method illustrated in Figure 1. The  $^{230}\text{Th}$ ,  $^{234}\text{U}$  and  $^{238}\text{U}$  values, corrected for the detritic contribution, were used to calculate the coral ages according to equation 3.

The external layer of the authigenic carbonate samples was removed, and the remaining part was ground in an agate mortar and sieved into four fractions < 170, 170-80, 80-42 and 42-24 mesh. One gram of each fraction was leached with 7 mol L<sup>-1</sup> HNO<sub>3</sub> in order to yield the carbonate phase. The remaining residual fraction was totally dissolved with HNO<sub>3</sub> plus HF mixture, and then  $^{238}\text{U}$  and  $^{232}\text{Th}$  were determined by ICP-QMS. The  $^{230}\text{Th}$ ,  $^{232}\text{Th}$ ,  $^{234}\text{U}$  and  $^{235}\text{U}$  results on the carbonate phase were used to construct both Rosholt and Osmond isochrones<sup>17</sup> and to obtain the  $^{230}\text{Th}/^{234}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  activity ratios. The results obtained using these two different approaches were applied to equation 3.

The uranium and thorium elemental and isotope determinations were performed using a Perkin-Elmer ELAN 6000 ICP-QMS instrument using the conditions described in Table 1. The  $^{233}\text{U}$  and  $^{229}\text{Th}$  spikes used are traceable to BIPM and were diluted according to the Radionuclides Metrology Section of the Institute for Radioprotection and Dosimetry (SEMRA/IRD).

Mass bias was corrected by applying equation 1, where  $\beta$  was determined from NIST CRM U020A (1 ng mL<sup>-1</sup>) analysis and equation 2:<sup>18</sup>

$$R_{\text{Corrected}}^{x/y} = R_{\text{Measured}}^{x/y} (\text{mass}_x/\text{mass}_y)^\beta \quad (1)$$

$$\beta = \frac{\ln(R_{\text{Standard}}^{a/b}/R_{\text{Measured}}^{a/b})}{\ln(\text{mass}_a/\text{mass}_b)} \quad (2)$$

To reduce the mass discrimination effect, the  $^{234}\text{U}/^{235}\text{U}$  isotope ratio was measured instead of the  $^{234}\text{U}/^{238}\text{U}$  isotope ratio. To calculate the  $^{234}\text{U}/^{238}\text{U}$  isotope ratio, the measured  $^{234}\text{U}/^{235}\text{U}$  isotope ratio was multiplied by the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio (0.0072526). To calculate the  $^{230}\text{Th}/^{234}\text{U}$  mass concentration ratio, the obtained  $^{230}\text{Th}$  concentration was divided by the product of the  $^{234}\text{U}/^{238}\text{U}$  isotope ratio

**Table 1.** Instrument and data acquisition settings for Perkin-Elmer ELAN 6000 ICP-MS

Instrument settings			
RF power	1.05 kW		
Nebulizer	Ultrasonic with membrane desolvator (USN) Cross flow (CFN)		
Sampler cone	Nickel, 1.1 mm orifice diameter		
Skimmer cone	Nickel, 0.9 mm orifice diameter		
Argon flow rates			
Plasma gas	15 L min <sup>-1</sup>		
Auxiliary gas	1.2 L min <sup>-1</sup>		
Nebulizer gas	1.02 L min <sup>-1</sup> (CFN) 1.21 L min <sup>-1</sup> (USN)		
Ultra-sonic nebulizer settings			
Sample uptake rate	1.5 mL min <sup>-1</sup>		
Heating temperature	140 °C		
Cooling temperature	3 °C		
Membrane desolvator heating temperature	160 °C		
Sweep gas flow rate	2.0 L min <sup>-1</sup>		
Data acquisition settings			
Acquisition mode	Peak hopping		
Read delay	40 s (USN) 30 s (CFN)		
Atom ratio measurements			
Monitored isotopes	$^{234}\text{U}$ , $^{235}\text{U}$	$^{233}\text{U}$ , $^{238}\text{U}$	$^{229}\text{Th}$ , $^{230}\text{Th}$
Sweeps/replicates	400	60	100
Replicates	3	6	6
Dwell time	75 ms/50 ms	50 ms/50 ms	25 ms/25 ms
Total time of analysis	150 s	36 s	30 s
Concentration measurements			
Monitored isotopes	$^{238}\text{U}$ and $^{232}\text{Th}$		
Sweeps/replicates	20		
Replicates	3		
Dwell time	50 ms		
Total time of analysis	3 s		
Integration type	Average		

multiplied by the  $^{238}\text{U}$  mass concentration. To obtain the  $^{230}\text{Th}/^{234}\text{U}$  activity ratio, the calculated mass concentration ratio was multiplied by the ratio of the specific activities of the isotopes in question.

The  $^{234}\text{U}/^{238}\text{U}$  and  $^{230}\text{Th}/^{234}\text{U}$  activity ratios were calculated. Based on the obtained values, the ages were determined according to equation 3,<sup>19</sup>

$$^{230}\text{Th}/^{234}\text{U} = \frac{1 - e^{-\lambda_{230}t}}{^{234}\text{U}/^{238}\text{U}} + \left(1 - \frac{1}{^{234}\text{U}/^{238}\text{U}}\right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}}\right) (1 - e^{-(\lambda_{230} - \lambda_{234})t}) \quad (3)$$

where  $\lambda_{230}$  is the  $^{230}\text{Th}$  decay constant and,  $\lambda_{234}$  is the  $^{234}\text{U}$  decay constant.

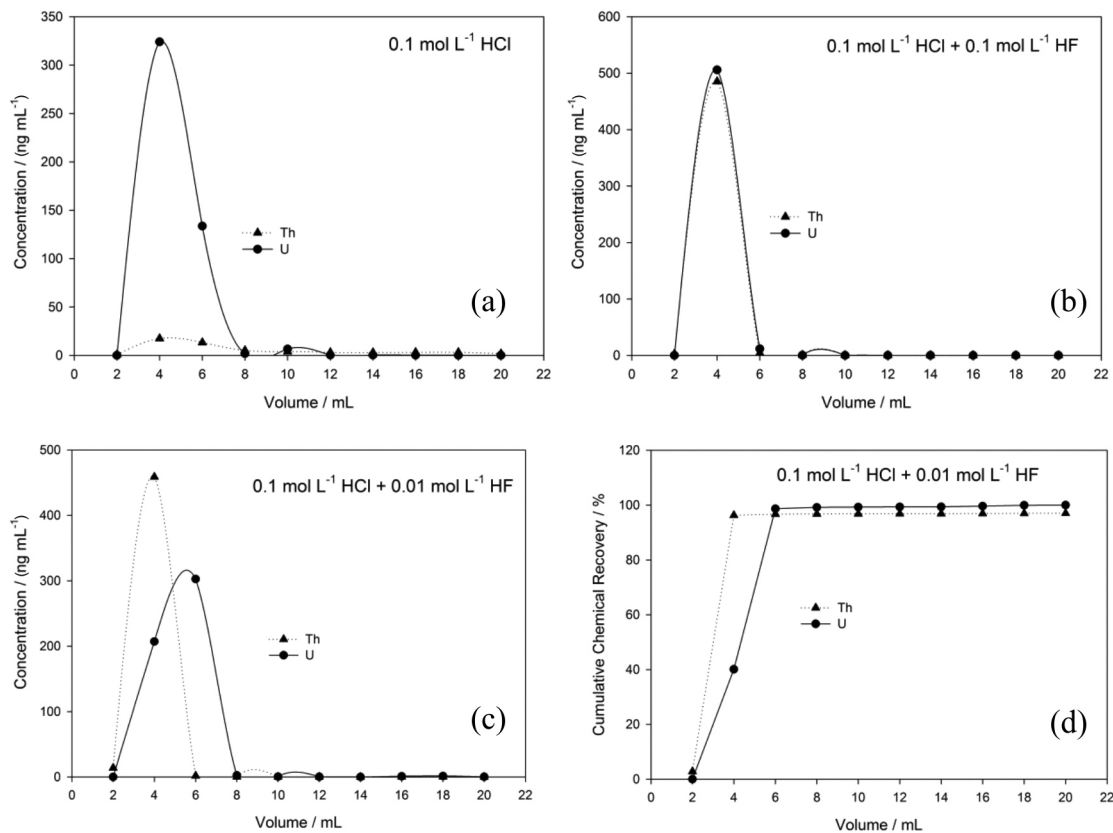
The developed methods were tested for  $^{234}\text{U}$  and  $^{230}\text{Th}$  determinations of the NIST SRM 4357 standard reference ocean sediment material. Three 2 g aliquot samples were used for each method.

## Results and Discussion

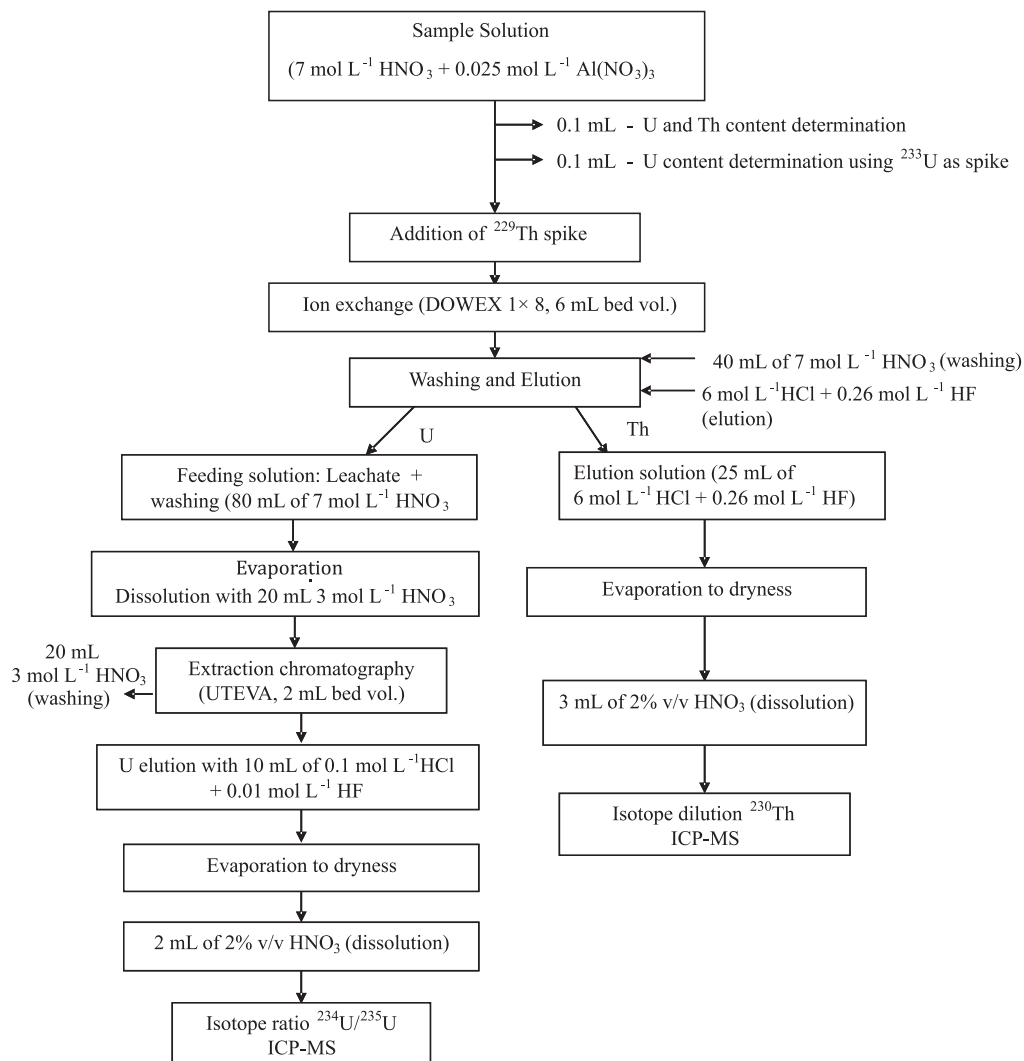
For accurate  $^{234}\text{U}$  and  $^{230}\text{Th}$  determination in the fossil coral and authigenic carbonate samples, a separation procedure was needed to eliminate the main matrix elements and to obtain a sample solution with a chemical composition similar to that of standards.<sup>20</sup> An off-line separation procedure was applied based on extraction chromatography with 2 mL UTEVA (Eichrom Co.) columns<sup>21-26</sup> (Figure 1). The elution curves of U and Th with 0.1 mol L<sup>-1</sup> HCl, 0.1 mol L<sup>-1</sup> HCl + 0.1 mol L<sup>-1</sup> HF, and 0.1 mol L<sup>-1</sup> HCl + 0.01 mol L<sup>-1</sup> HF, were tested. The feed solution (40 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.025 mol L<sup>-1</sup> Al(NO<sub>3</sub>)<sub>3</sub>) was added to 1000 ng of U<sub>nat</sub> and 1000 ng of Th<sub>nat</sub>. Based on the obtained results (Figure 2), 10 mL of 0.1 mol L<sup>-1</sup> HCl + 0.01 mol L<sup>-1</sup> HF was used as the U and Th eluent to avoid higher HF concentrations and to obtain 100% recovery for both elements. This condition ensures that Th and U are quantitatively retained and eluted during separation from the matrix. The U and Th decontamination factors (DF) from Ca, Fe, Al, Mg and Sr, which are representative of the major matrix elements, are shown in Table 2. The obtained decontamination factors are considered satisfactory, because they are equal to or greater than 10<sup>3</sup>.<sup>27</sup>

Due to the low thorium chemical yield obtained, the initial tests with authigenic carbonate samples revealed the need for a matrix separation step before chromatographic extraction with the UTEVA column (Figure 3). Based on previous work (Godoy *et al.*<sup>28</sup>), ion exchange chromatography with DOWEX 1X8 was tested. Using 40 mL of 7 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.025 mol L<sup>-1</sup> Al(NO<sub>3</sub>)<sub>3</sub> as feed solution containing 1000 ng of U and 1000 ng of thorium, the elution curves of Th with 6 mol L<sup>-1</sup> HCl + 0.26 mol L<sup>-1</sup> HF, 1 mol L<sup>-1</sup> HCl + 0.26 mol L<sup>-1</sup> HF and 0.1 mol L<sup>-1</sup> HCl + 0.26 mol L<sup>-1</sup> HF were determined. Based on the obtained results (Figure 4), 25 mL of 6 mol L<sup>-1</sup> HCl + 0.26 mol L<sup>-1</sup> HF was chosen as the Th eluent. Thorium was strongly adsorbed, whereas uranium was not retained by the DOWEX 1X8 resin and instead was distributed between the feed and washing solutions. Both solutions were collected together for U determination, followed by a second separation step with UTEVA columns similar to that applied for the coral samples.

The obtained  $^{234}\text{U}$  and  $^{230}\text{Th}$  concentrations for the NIST SRM 4357 certified reference marine sediment sample using both methods are shown in Tables 3 and 4. The results are within the confidence interval for both isotopes. For these samples, the  $^{230}\text{Th}$  achieved accuracy (2.8 and 2.2%),



**Figure 2.** Uranium and thorium elution curves from 4 cm UTEVA columns: a) 0.1 mol L<sup>-1</sup> HCl, b) 0.1 mol L<sup>-1</sup> HCl + 0.1 mol L<sup>-1</sup> HF, c) 0.1 mol L<sup>-1</sup> HCl + 0.01 mol L<sup>-1</sup> HF, d) Cumulative chemical recovery applying 0.1 mol L<sup>-1</sup> HCl + 0.01 mol L<sup>-1</sup> HF.

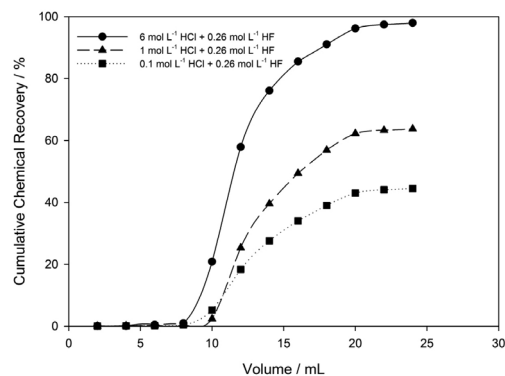


**Figure 3.** Method for  $^{234}\text{U}$  and  $^{230}\text{Th}$  determination - authigenic carbonate samples.

**Table 2.** Achieved decontamination factors

Element	Decontamination factor
Ca	$5.7 \times 10^3$
Fe	$3.8 \times 10^3$
Al	$3.1 \times 10^3$
Mg	$9.9 \times 10^2$
Sr	$4.3 \times 10^3$

by applying this off-line separation method are better than those obtained by Godoy *et al.*,<sup>16</sup> whose values were above 10%, but within the 95% confidence interval of the certified value. The  $^{230}\text{Th}$  precisions (1.9 and 3.1%) are similar to that (1.5%) reported by Godoy *et al.*<sup>16</sup> Although  $^{234}\text{U}$  does not have a certified reference value, the precision and accuracy values for this isotope using the proposed method were similar to those using on-line methods.<sup>16</sup>



**Figure 4.** Thorium elution curves using 6 mL DOWEX 1X8 columns.

For the fossil deep-water corals samples from Campos Basin, the  $^{230}\text{Th}/^{234}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  activity ratios as well as the calculated ages are shown in Table 5. Taking into account the peak areas, the residual fraction contribution and the uncertainty related to the spikes, the uncertainties

**Table 3.**  $^{230}\text{Th}$  and  $^{234}\text{U}$  activity values for NIST SRM 4357 certified reference marine sediment sample using the method for coral samples

Radionuclide	Reference Value / (Bq kg <sup>-1</sup> )	CI <sup>a</sup> (95%) / (Bq kg <sup>-1</sup> )	Meanvalue <sup>b</sup> / (Bq kg <sup>-1</sup> )	Precision / %	Accuracy / %
$^{234}\text{U}$	12 <sup>c</sup>	9-15	12.79 ± 0.82	6.4	6.6
$^{230}\text{Th}$	12.0	9.6-14.4	12.33 ± 0.45	3.6	2.8

<sup>a</sup>Confidence interval. <sup>b</sup>Data represent the average ± 1.96 SD of three replicates. <sup>c</sup>Value not certified.

**Table 4.** Authigenic carbonate samples

Radionuclide	Reference Value / (Bq kg <sup>-1</sup> )	CI <sup>a</sup> (95%) / (Bq kg <sup>-1</sup> )	Meanvalue <sup>b</sup> / (Bq kg <sup>-1</sup> )	Precision / (%)	Accuracy / (%)
$^{234}\text{U}$	12 <sup>c</sup>	9-15	12.29 ± 0.86	7.2	2.4
$^{230}\text{Th}$	12.0	9.6-14.4	12.27 ± 0.74	6.2	2.2

<sup>a</sup> Confidence interval. <sup>b</sup> Data represent the average ± 1.96 SD of three replicates. <sup>c</sup> Value not certified.

**Table 5.**  $^{230}\text{Th}/^{234}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  activity ratios and calculated ages of the fossil coral samples

Sample	$^{230}\text{Th}/^{234}\text{U}$ Activity ratio <sup>a</sup>	$^{234}\text{U}/^{238}\text{U}$ Activity ratio <sup>b</sup>	Age / ky
5	0.0913 ± 0.0057	1.1660 ± 0.0330	10.3892 ± 0.0057
30	0.0799 ± 0.0020	1.1513 ± 0.0127	9.04032 ± 0.00070
44	0.1227 ± 0.0064	1.1507 ± 0.0281	14.1966 ± 0.0076
47	0.1188 ± 0.0046	1.1783 ± 0.0207	13.7114 ± 0.0038
68	0.1925 ± 0.0104	1.1725 ± 0.0332	23.130 ± 0.021
87	0.1167 ± 0.0104	1.1710 ± 0.0289	13.492 ± 0.018
238	0.8551 ± 0.0421	1.0569 ± 0.0270	202.1 ± 2.0

<sup>a</sup>Data represent the average ± 4.30 SD of three ICP-MS readings. <sup>b</sup>Data represent the average ± 4.30 SD of three ICP-MS readings.

associated with coral were about 1%. Table 6 shows the fossil coral ages determined using the proposed method, with the previous method based on flow injection, and by  $^{14}\text{C}$  AMS dating at the University of California, Irvine, United States. To verify if there were statistically significant differences between the obtained results by the three methods, ANOVA tests were applied, as shown in Table 7. Because the calculated F (0.50) value was lower than the critical F (3.89) value, no significant differences were found among the three methods.

The authigenic carbonate samples contained detritic contamination not only at the surface, but throughout

**Table 6.** Ages of fossil corals based on different methods

Coral Sample	Age / ky		
	This work ICP-MS (batch)	IRD ICP-MS (flow injection)	Univ. California $^{14}\text{C}$ -AMS
5	10.39	10.91	10.93
30	9.04	8.4	11.14
44	14.20	14.87	14.98
47	13.71	14.71	11.12
68	23.13	26.07	22.97
87	13.49	13.13	
238	202.1		

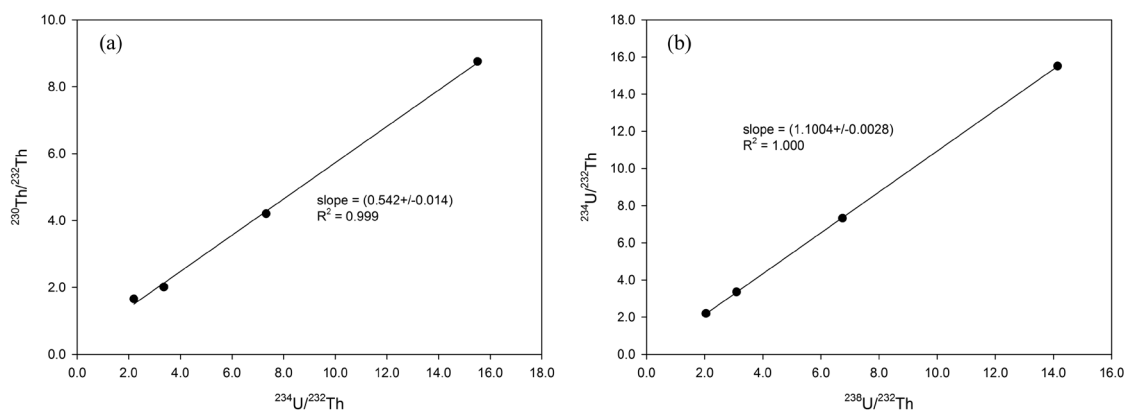
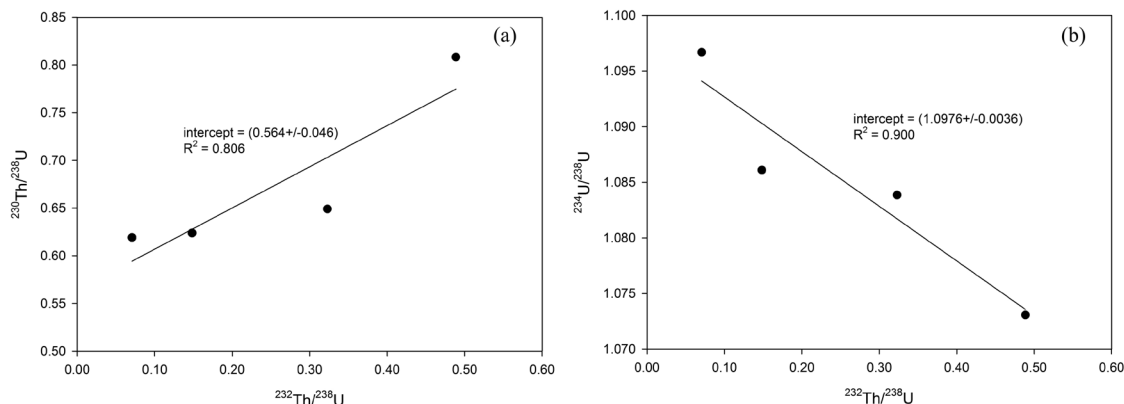
the entire sample. Therefore, usual cleaning procedures, such as mechanical and chemical removal of the surface layers, did not generate a final sample with a low  $^{232}\text{Th}$  content, as observed for the coral samples (range of ng g<sup>-1</sup>). The procedure described by Ku<sup>29</sup> was applied with sample fractionation by size to generate independent sub-samples. Based on the obtained results, two different isochrons were constructed:  $^{230}\text{Th}/^{232}\text{Th}$  vs.  $^{234}\text{U}/^{232}\text{Th}$  and  $^{234}\text{U}/^{232}\text{Th}$  vs.  $^{238}\text{U}/^{232}\text{Th}$  for the Rosholt plots (Figure 5) and  $^{230}\text{Th}/^{238}\text{U}$  vs.  $^{232}\text{Th}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  vs.  $^{232}\text{Th}/^{238}\text{U}$  for the Osmond plots (Figure 6). The  $^{230}\text{Th}/^{234}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  activity ratios were obtained using the slopes of the Rosholt plots and the intercepts of the Osmond plots. The obtained values were statistically equivalent: (0.542 ± 0.014)  $^{230}\text{Th}/^{234}\text{U}$  and (1.1004 ± 0.0028)  $^{234}\text{U}/^{238}\text{U}$  and (0.564 ± 0.046)  $^{230}\text{Th}/^{234}\text{U}$  and (1.0976 ± 0.0036)  $^{234}\text{U}/^{238}\text{U}$  for the Osmond and Rosholt plots, respectively. Applying these results to equation 3, the age of this authigenic carbonate sample was (83.6 ± 0.1) ky according to the Osmond plot and (88.8 ± 0.1) ky based on the Rosholt plot. According to Ludwig,<sup>17</sup> the Osmond plot provides a more realistic value for samples with a high  $^{232}\text{Th}$  content. Furthermore, because  $^{232}\text{Th}$  and  $^{234}\text{U}$  each appear in both of the isochrons, the results of the regressions are correlated



**Table 7.** Test and least significant difference between the methods at 95% confidence level

This work (1)	IRD flow injection (2)	Univ. California- Irvine AMS (3)	1-2	2-3	1-3
10.39	10.91	10.93	-0.52	-0.02	-0.54
9.04	8.4	11.14	0.64	-2.74	-2.10
14.20	14.87	14.98	-0.67	-0.11	-0.78
13.71	14.71	11.12	-1.00	3.59	2.59
23.13	26.07	22.97	-2.94	3.10	0.16
13.49	13.13				
			Mean		
			SD		
			GM		
			SSF	2	
			SSE	12	
			MSF		
			MSE		
			$F_{\text{calc}}$	$F_{\text{crit}}$	3.89
			LSD <sup>a</sup>		

<sup>a</sup>LSD = Least Significant Difference.

**Figure 5.** Rosholt plots for authigenic carbonate.**Figure 6.** Osmond plots for authigenic carbonate samples.

in a complex way. However, these correlations are never taken into account when calculating the ages or age-errors. Therefore, a simultaneous solution using all three of the ratios for the modified Osmond ratios is needed to generate

a regression for an isochron line in three dimensions. The calculated age, determined using Isoplot 3.7 software,<sup>17</sup> used to construct the 3D  $^{232}\text{Th}/^{238}\text{U}$ - $^{230}\text{Th}/^{238}\text{U}$ - $^{234}\text{U}/^{238}\text{U}$  isochron was  $(78.66 \pm 0.17)$  ky.



The other authigenic carbonate sample yielded a  $^{230}\text{Th}/^{234}\text{U}$  value close to one. Consequently, the corresponding age was not calculated, indicating that it is close to or older than 300 ky.

## Conclusions

Two  $^{234}\text{U}$  and  $^{230}\text{Th}$  determination methods based on extraction chromatographic separation followed by ICP-QMS measurements were developed. These methods were validated for fossil deep-water corals and authigenic carbonates by using certified reference marine sediment.

Samples of fossil corals from the same sediment core and from authigenic carbonates were analyzed and dated. The obtained fossil coral ages agree with other values determined using  $^{230}\text{Th}/^{234}\text{U}$  flow injection separation coupled to ICP-QMS and with  $^{14}\text{C}$ -AMS.

The developed methods are equivalent in terms of precision and more accurate than the previously applied method based on flow injection separation coupled to an ICP-QMS. In addition, the proposed method has the following advantages: final solution free of salts and with a chemical composition similar to ICP-QMS standard solutions, less accumulation of salts in the interface of the equipment (skimmer and sampler cones) and applicability to more complex matrices, such as authigenic carbonates.

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