



^{234}U and ^{230}Th determination by FIA-ICP-MS and application to uranium-series disequilibrium in marine samples

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Abstract

A ^{234}U and ^{230}Th determination method based on an extraction chromatographic separation on a flow injection system coupled to a quadruple ICP-MS was developed. Two-milliliter UTEVA (Eichrom Co.) cartridges were applied as separation tool and ^{236}U and ^{229}Th as spikes. Loading and washing steps were carried out in 3 M HNO_3 solution and 0.05 M ammonium oxalate applied to elute both uranium and thorium. The method was applied initially to the IAEA-327 soil reference sample and NIST SRM 4357 ocean sediment reference material, with the obtained ^{234}U and ^{230}Th concentrations in agreement with the reference levels. Samples from a deep-sea sediment core (2450 m water depth) were analyzed and based on $^{230}\text{Th}/^{234}\text{U}$ dating, a mean sedimentation rate of 3.3 cm ky^{-1} was calculated. Samples from two sediment layers were also dated by ^{14}C -AMS and the observed ages agree with the $^{230}\text{Th}/^{234}\text{U}$ results.

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1. Introduction

Sea level changes, induced by climatic forcing have been the single most prominent factor in controlling economic accumulations of sand in deep waters since the Late Cenozoic (Posamentier et al., 1988). Thus, understanding the Pleistocene climatic fluctuations and their controls on sedimentation is of key importance for the formulation of analogue models that can then be applied to oil-bearing sands in deep water (Viana et al., 1998).

Biostratigraphy is a key ingredient of this process. For the Quaternary, the presence and the frequency of certain planktonic foraminifera indicative of cold or warm waters are used to monitor past climatic changes and to bracket glacial and interglacial periods (Ericson and Wollin, 1968). These climatic induced faunal changes need to be calibrated to an absolute timescale in order to be used as a dating tool. In general, this is achieved by calibrating these faunal changes with the SPECMAP oxygen isotope curve tuned to the Earth's orbital cycles (Imbrie, 1985). However, many faunal datums are not coeval with boundaries of oxygen isotopic stages. Thus, independent absolute dating is necessary.

In his work Vicalvi (1997) validated, through dating with ^{14}C , his biostratigraphic zonation for the period of up to 40,000 years. Since 40,000 years represents a practical limit of the ^{14}C technique, alternatives need to be applied, as the dating based on the pair $^{230}\text{Th}/^{234}\text{U}$, which encloses periods of up to 350,000 years (Thomson et al., 1999; Veeh et al., 2000). Additionally, as the biostratigraphy is based on a sequence of appearing/disappearing of certain species, the loss of intervals of the sediment core due to mass wasting, so common in slope sediments, makes impracticable the dating after this point, as exemplified in the Bu-91/GL-07 core (Vicalvi, 1997). Beyond the range of radiocarbon, $^{230}\text{Th}/^{234}\text{U}$ dating represents an important tool.

Additionally, the dating with $^{230}\text{Th}/^{234}\text{U}$ can be useful for the understanding of other existing events in Campos Basin:

- Dating of authigenic carbonate nodules resultant of methane exudation, found in sediment cores layers (Kowsmann and Carvalho, 2002);
- Dating of deep-sea fossil corals. Sediment cores collected in this region have shown cycles of corals growth, with the appearance of fossil corals at different sediment layer depths. Dating of these fossil corals can help in the interpretation of these past cycles and contribute for the studies of the existing living corals.

One of the great disadvantages of the U and Th determination by alpha spectrometry, in this type of sample, is the large counting time necessary to achieve a good statistics and, consequently, a lower associated uncertainty. A way to face this difficulty is the use of the mass spectrometry, in particular, of the plasma inductively coupled mass spectrometry (ICP-MS). The ICP-MS technique is more adequate for the determination of ^{232}Th (1.39×10^{10} years) and ^{238}U (4.47×10^9 years), long-lived radionuclides, but it can be applied, successfully, in the determination of ^{230}Th (7.52×10^4 years) and ^{234}U (2.48×10^5 years), particularly, if associated with a pre-concentration stage. This pre-concentration can be carried out on-line using a flow injection system (FIAS) connected to the ICP-MS. In particular, for the determination of U and Th by FIA-ICP-MS, the resins developed by the company Eichrom are quite popular (Lee and Lee, 2001; Pietruzka et al., 2002).

Therefore, the aim of the present work was to develop an analytical method, faster than the alpha spectrometry, designed for the application of the $^{230}\text{Th}/^{234}\text{U}$ dating of authigenic

carbonate and deep-water sediments samples, taking into account the required accuracy and precision, and compare the calculated ages with those derivatives of the application of others techniques as the bio-stratigraphy.

The results of the dating of a 4.4-meter-long piston core (982100096), retrieved in water depths of 2425 m in the Campos Basin, SE Brazil, is also discussed. The core underwent a bio-stratigraphic zonation by Vicalvi (1997) based on the Ericson and Wollin (1968) method.

2. Material and methods

The uranium and thorium elemental and isotopes determinations were performed using a Perkin–Elmer ELAN 6000 ICP-MS. For the uranium and thorium separation, the system was coupled to a Perkin–Elmer flow injection system with a sample changer (Fig. 1). ^{236}U and ^{229}Th were used as spikes (Isotope Products Laboratories) and UTEVA (Eichrom Technologies Inc.) 2-mL cartridges were applied as a tool for uranium and thorium concentration and matrix separation. About 10 mL sample solution (3 M HNO_3) is pumped through the cartridge, follows a washing step, also with 3 M HNO_3 , and uranium and thorium are eluted together using a 0.05 M ammonium oxalate solution, as shown in details in Table 1. Table 2 shows the Perkin–Elmer ELAN 6000 ICP-MS operation conditions, when coupled to the flow-injection system.

The method was tested for ^{234}U and ^{230}Th determination applying it to the IAEA-327 standard reference soil sample, 31.9 Bq kg^{-1} ^{234}U and 34.1 Bq kg^{-1} ^{230}Th , and to the NIST SRM 4357 standard reference ocean sediment material, 12 Bq kg^{-1} ^{234}U and 12.5 Bq kg^{-1} ^{230}Th . Four 1-g aliquot IAEA-327 samples and six 3-g aliquot NIST SRM 4357 samples were taken and completely dissolved by $\text{HNO}_3/\text{HF}/\text{HClO}_4$ and tetraborate fusion of the remaining residue.

Samples taken from the PETROBRAS deep-sea sediment core 9821096 (water depth 2450 m) were obtained. One-gram aliquots were analyzed for ^{234}U and ^{230}Th as described for the soil reference sample. Additional aliquot was taken for the determination of ^{238}U and ^{232}Th , as described by Godoy et al. (2004), after leaching with 3 M HNO_3 and after the total dissolution of the remaining residues.

Two samples from different depths (53 and 121 cm), on the ^{14}C dating range, were sent to the Keck-CCAMS facility, from the Earth System Science Department, University of California, Irvine, for sample preparation and analysis, using the accelerator mass spectrometry (AMS) technique (Tuniz et al., 1998).

To measure ^{14}C on an AMS system using carbonaceous starting materials, carbon was chemically separated from the original sample (CO_2 production from a chemically clean sample), converted to graphite targets (Vogel et al., 1984), and loaded into the ion-source.

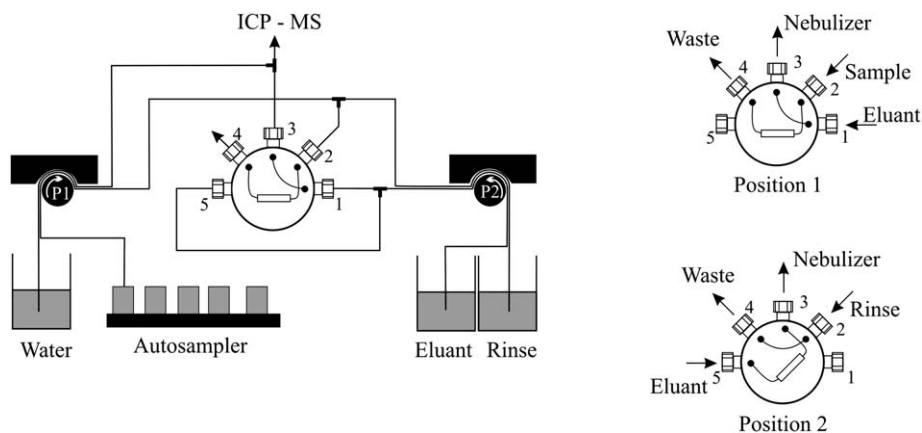


Fig. 1. Flow injection system with the sample changer, showing also the tubing connections according to the applied valve position.

Table 1
Applied uranium and thorium on-line separation schema

Step	Read	Time (s)	Pump 1 (rpm)	Pump 2 (rpm)	Valve position	Observation
Pre-sample		60		60	1	HNO ₃ 3 M
Loading		99	80		1	HNO ₃ 3 M
Washing		30		60	1	HNO ₃ 3 M
Elution start		20		120	2	(NH ₄) ₂ C ₂ O ₄ 0.05 M
Elution reading	Yes	40		120	2	(NH ₄) ₂ C ₂ O ₄ 0.05 M
Column washing 1		60		120	2	(NH ₄) ₂ C ₂ O ₄ 0.05 M
Column washing 2		60		60	1	HNO ₃ 3 M
Post-sample		30	60		2	H ₂ O

At the AMS prep-laboratory, carbon dioxide is produced from pre-leached carbonate samples by acid hydrolysis using 85% phosphoric acid in disposable septum-sealed reactors. The CO₂ produced is cryogenically purified inside a vacuum line, transferred into Pyrex tubes attached to individual reactors and reduced to graphite, using hydrogen at 550 °C over pre-baked iron powder (Santos et al., 2004). The graphite (plus-iron) targets are pressed into aluminum sample holders and loaded into an ion-source wheel. The ratios of ¹⁴C/¹²C and ¹³C/¹²C are measured on the AMS system.

The Keck-CCAMS facility operates a compact AMS system (National Electrostatic Corporation (0.5 MV 1.5SDH-2)). Precisions of 2–3‰ are achieved routinely based on scatter in results for multiple aliquots of a primary standard. Accuracy is determined from the deviation of secondary standards from the known values and is usually not higher than 3‰ (Southon et al., 2004). The total procedural blank for this set of samples was determined to be 0.10 ± 0.03 pMC (equivalent to 55 ka yr BP) from multiple measurements of ¹⁴C-free calcite.

3. Results and discussion

Six blank samples, including the ²³⁶U and ²²⁹Th spikes, were analyzed and, based on the observed results, a detection limit of 0.35 and 0.05 mBq g⁻¹ for ²³⁰Th and ²³⁴U, respectively, for 1 g sample, was achieved. These detection limits seems to be adequate for a future ²³⁰Th/²³⁴U dating of fossil corals (Lomitschka and Mangini, 1999; Stirling et al., 1995).

The isobaric interference of ²³⁵UH on the ²³⁶U peak area was investigated. The 239 mass/charge ratio peak area represents the ²³⁸UH formation and can be used to monitor this UH

Table 2
Perkin–Elmer SCIEX ELAN 6000 ICP-MS operation conditions, when coupled to the flow-injection system

RF Power	1050 W
Plasma gas flow rate	17 L min ⁻¹
Auxiliary gas flow rate	1.2 L min ⁻¹
Nebulizer gas flow rate	0.9 L min ⁻¹
Scan mode	Peak hopping transient
Lens scanning	Enabled
Detector mode	Dual-pulse and analog
Dwell time	30 ms
Sweeps/Readings	1
Readings/Replicate	300
No. of replicates	1
Resolution	0.7 amu at 10% peak maximum
Signal processing	Spectral peaks integrated

interference. For the applied conditions, the ^{235}U formation represents only $3.2 \times 10^{-3}\%$ of the ^{235}U peak area that is negligible comparing to the ^{236}U added, this result is similar to that reported by Hollembach et al. (1995), $6 \times 10^{-3}\%$.

The ^{234}U and ^{230}Th obtained values for the IAEA-327 standard reference soil sample are shown in Table 3. The ^{234}U is in agreement with the certificate value while ^{230}Th showed a tendency to lower values. The ^{230}Th determination was repeated and the same mean value was obtained. Comparing the ^{238}U certificate and the measured ^{234}U and ^{230}Th values, one could say that there is a radioactive equilibrium in the ^{238}U series in this soil sample. A second reference material was taken, NIST SRM 4357, and the ^{234}U and ^{230}Th obtained values are shown in Table 4. It can be seen that ^{230}Th is in good agreement with the certified value. Despite of the fact that ^{234}U be only a reference value but not certified, also for this radionuclide an agreement is observed. A possible reason for the different ^{230}Th performance observed with the IAEA and the NIST reference samples is the number of accepted values used for the establishment of the certified value, ten and eighteen respectively. The achieved uncertainty for both radionuclides is similar to that expected for mass spectrometric measurements of these radionuclides (Chen et al., 1992).

For the 98210096 sediment core, the obtained $^{230}\text{Th}_{\text{total}}$, $^{234}\text{U}_{\text{total}}$, ^{238}U and ^{232}Th elemental concentration in the carbonate phase and $^{238}\text{U}/^{232}\text{Th}$ elemental ratio in the residual phase, as well as the calculated $^{230}\text{Th}_{\text{excess}}$ are shown in Table 5. The $^{238}\text{U}/^{232}\text{Th}$ ratio increases with the depth showing a higher detrital contribution for older ages. Two samples were re-analyzed, 32 and 94 cm, and, as can be seen in both cases, the results were essentially equals. The $^{230}\text{Th}_{\text{excess}}$ was calculated according to the equation (1):

$$\begin{aligned} ^{230}\text{Th}_{\text{excess}} = & ^{230}\text{Th} - ^{230}\text{Th}_{\text{residual}} - ^{230}\text{Th}_{\text{authigenic}} = ^{230}\text{Th} - 0.0124 \times \text{Th}_{\text{carbonate}} \\ & \times (\text{U/Th})_{\text{residual}} - [({}^{234}\text{U} - 0.0124 \times \text{Th}_{\text{carbonate}} \times (\text{U/Th})_{\text{residual}}) \\ & \times 1.45 \times (e^{-\lambda_{234}t} - e^{-\lambda_{230}t})] \end{aligned} \quad (1)$$

where $^{230}\text{Th}_{\text{excess}} = ^{230}\text{Th}$ originating in the seawater, attached to the suspended particles and deposited in the sea floor (Bq kg^{-1}); $^{230}\text{Th} = ^{230}\text{Th}$ total content determined experimentally (Bq kg^{-1}); $^{230}\text{Th}_{\text{residual}} = ^{230}\text{Th}$ belonging to the so-called residual phase of the sediment, as clay materials, normally, associated to a terrigenous origin—therefore, supposed to be in secular equilibrium with ^{238}U (Bq kg^{-1}); $^{230}\text{Th}_{\text{authigenic}} = ^{230}\text{Th}$ build-up due to an excess of ^{234}U , in relation to ^{238}U , observed in the carbonate phase of the sediment (Bq kg^{-1}); $0.0124 = ^{238}\text{U}$ specific activity ($\text{Bq mg}_{\text{U-238}}^{-1}$); $\text{Th}_{\text{carbonate}} = ^{232}\text{Th}$ content in the carbonate phase ($\text{mg}_{\text{Th-232}} \text{kg}^{-1}$); $(\text{U/Th})_{\text{residual}} = ^{238}\text{U}/^{232}\text{Th}$ mass concentration ratio in the residual phase ($\text{mg}_{\text{U-238}} \text{mg}_{\text{Th-232}}^{-1}$); $\lambda_{234} = ^{234}\text{U}$ decay constant $= 2.84 \times 10^{-3} \text{ky}^{-1}$; $\lambda_{230} = ^{230}\text{Th}$ decay constant $= 9.19 \times 10^{-3} \text{ky}^{-1}$; t = sediment layer age, which was estimated based on the foraminifera dates (Table 6).

Since the complete sediment core was not available, but some reference dates, the $^{230}\text{Th}_{\text{excess}}$ inventory was calculated as proposed by Oldfield and Appleby (1984), equation (2). The

Table 3
Standard reference soil sample IAEA-327 obtained results for ^{234}U and ^{230}Th , values in Bq kg^{-1} ($n = 4$)

Radionuclide	Reference value	95% confidence interval	Mean value	SD
^{234}U	31.9	30.4–33.4	30.73	0.56
^{230}Th	34.1	32.4–35.8	31.52	0.65

Table 4

Standard reference soil sample NIST SRM 4357 obtained results for ^{234}U and ^{230}Th , values in Bq kg^{-1} ($n = 6$)

Radionuclide	Reference value	95% confidence interval	Mean value	SD
^{234}U	12	9–15	12.38	0.61
^{230}Th	12.0	9.6–14.48	13.83	0.21

calculated $^{230}\text{Th}_{\text{excess}}$ inventory was a factor of two higher than that obtained using the ^{230}Th flux to bottom sediments ($F_{230\text{Th}}$) according to Huh and Kadko (1992), showing a sediment focusing. A constant $^{230}\text{Th}_{\text{excess}}$ concentration was observed for the first 30 cm and the core description, performed by geologists from PETROBRAS, shows also this mixing layer. Therefore, it was necessary also to include this factor on the age calculation. The mean residence time in the mixing zone was estimated in 18.8 kyears and its $^{230}\text{Th}_{\text{excess}}$ inventory in 2.8 Bq cm^{-2} .

$$t = 18.8 + \ln(I_o/(I + \Delta I))/\lambda_{230}$$

$$I_o = ^{230}\text{Th}_{\text{excess}} \text{ total inventory (Bq cm}^{-2}\text{);}$$

$$I = ^{230}\text{Th}_{\text{excess}} \text{ inventory below the sediment depth taken into account (Bq cm}^{-2}\text{);}$$

$$\Delta I = \text{mixing layer } ^{230}\text{Th}_{\text{excess}} \text{ inventory (Bq cm}^{-2}\text{).}$$

Fig. 2 shows the obtained sediment layer depth versus CRS age profile, together with the foraminifera datum. The $^{230}\text{Th}/^{234}\text{U}$ age error bar represents the 95% expanded uncertainty, being the ^{239}Th and ^{236}U spikes uncertainties (3.5%) the main contributions to it. A mean sedimentation rate of $(3.35 \pm 0.08) \text{ cm ky}^{-1}$ was obtained similar to the mean sedimentation rate

Table 5

Obtained $^{230}\text{Th}_{\text{total}}$, $^{234}\text{U}_{\text{total}}$, ^{238}U and ^{232}Th elemental concentration in the carbonate phase and the $^{238}\text{U}/^{232}\text{Th}$ elemental ratio in the residual phase, as well as the calculated $^{230}\text{Th}_{\text{excess}}$ (values in Bq kg^{-1} or mg kg^{-1} , accordingly)

Sediment layer depth (cm)	$^{230}\text{Th}_{\text{total}}$	$^{234}\text{U}_{\text{total}}$	$^{238}\text{U}_{\text{carb}}$	$^{232}\text{Th}_{\text{carb}}$	$(^{238}\text{U}/^{232}\text{Th})_{\text{res.}}$	$^{230}\text{Th}_{\text{excess}}$
5	87.7	27.8	0.75	1.91	0.15	84.3
10	83.7	26.9	0.94	3.62	0.18	75.5
32a	98.4	32.6	0.67	4.05	0.17	89.8
32b	105.0	37.5				96.4
53	73.7	32.7	0.84	3.95	0.18	64.8
74	47.7	26.8	0.61	3.00	0.23	39.1
94a	42.4	35.3	1.06	2.88	0.22	34.5
94b	43.0	27.4				35.2
94c	45.9	28.3				38.1
121	40.4	41.7	1.41	3.97	0.23	29.1
165	44.1	33.2	1.11	1.74	0.22	39.3
185	43.8	31.3	0.92	1.94	0.22	38.5
211	38.7	34.4	1.27	3.73	0.26	26.5
248	41.7	31.9	0.73	2.89	0.23	33.4
274	40.6	37.6	1.01	2.40	0.24	33.5
323	38.9	22.1	1.00	3.27	0.26	31.7
354	51.2	28.5	1.26	3.96	0.27	40.8
374	58.2	17.8	0.92	2.14	0.24	44.9
393	49.1	18.9	0.56	5.11	0.27	42.8
418	64.4	64.1	3.25	7.27	0.32	35.8

Table 6
98210096 sediment core foraminifera ages and estimate sedimentation rates between datum

Sed. layer depth (cm)	Foram. based age (ky)	Interval sed. rate (cm ky ⁻¹)
20	11	
70	40	1.7
185	84	2.6
385	127	4.6
433	160	1.5

calculated using the foraminifera ages. Two samples were taken for ¹⁴C dating, one just below the mixing layer and the other closer to the ¹⁴C dating limit (~40 ka yrs BP). The uncalibrated ¹⁴C ages from both samples are also shown in Fig. 2 and a very good agreement among the results of both techniques is observed. In order to test the CRS hypothesis, the ²³⁰Th_{excess} flux between layers of known ages, based on the ¹⁴C dating, was calculated, according to Oldfield and Appleby (1984), and compared to the integrated flux for the whole core. The obtained value was in range of ±20% of the ²³⁰Th_{excess} flux integrated for the whole core, showing the use of the CRS model to be valid for this particular sediment core.

The foraminifera dates are based on the ratio between cold and warm water species and the last occurrence datum (LAD) of some species, which depend on salinity and temperature, and tend to be transgressive in time and space. For example, the *Pulleniatiana obliquiloculata* LAD subdivides biozone Y of Ericson and Wollin (1968) into Y1 and Y2. According to Prell and Damuth (1978), the Y1/Y2 boundary varies from 60 ky in the Gulf of Mexico, to 50 ky in the Caribbean Sea, to 35 ky in the Equatorial Atlantic. Vicalvi (1997) established an age of 42–40 ky for this datum in the South Atlantic, based on ¹⁴C dating.

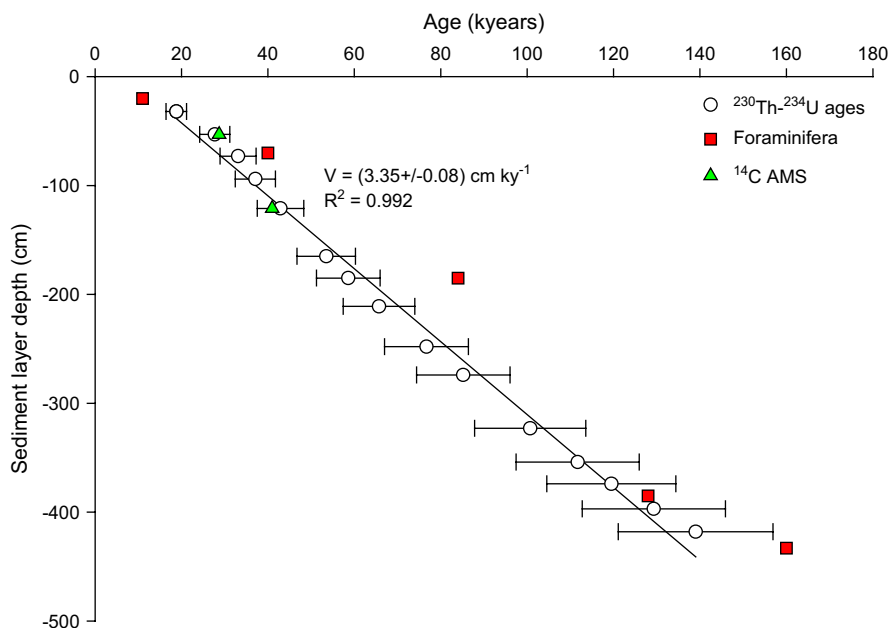


Fig. 2. 98210096 sediment core obtained ²³⁰Th/²³⁴U ages, un-calibrated ¹⁴C ages and foraminifera dates for comparison (error bars = 95% expanded uncertainty associated to the ²³⁰Th/²³⁴U ages).

The X/W biozone boundary of Ericson and Wollin (1968) was dated by U-Th method at 127 ky (Slowey et al., 1996). The age of 84,000 years, which defines the limit between biozones Y and X of Ericson and Wollin (1968), was calculated by Damuth (1975) for two Equatorial Mid-Ocean Ridge cores, assuming a constant sedimentation rate between the Holocene (11,000 years) and the 127,000-year datum.

For the present sediment core, the 11,000-year datum is in the mixing zone and therefore cannot be considered here. For the sediment level corresponding to the 40,000-year datum an age of 30 ky was calculated, which could also be due to the influence of the mixing layer. Considering the 40,000 and the 127,000 datum, and assuming a constant sedimentation rate, the 84,000 datum should correspond to a sediment depth of 230 cm, discrepant from the depth observed in Table 5, and closer to the value calculated using the results from the present work (254 cm). For the 127,000 year datum at 385 cm, the observed difference from the age of 117 ky, calculated by applying a sedimentation rate of 3.3 cm ky^{-1} (Fig. 2) is less than 10%, which seems to be quite reasonable, taking into account the all the uncertainties related to the foraminifera ages.

4. Conclusions

A ^{234}U and ^{230}Th determination method based on an extraction chromatographic separation on a flow injection system coupled to a quadruple ICP-MS was developed. Based on 1-g samples, detection limit of 0.35 and 0.05 mBq g^{-1} for ^{230}Th and ^{234}U was achieved, respectively. The method was validated by means of standard reference samples and both ^{234}U and ^{230}Th were in agreement with the reference values.

Samples from a deep-sea sediment core (2450 m water depth) were analyzed and, based on $^{230}\text{Th}/^{234}\text{U}$ age determinations, a mean sedimentation rate of 3.3 cm ky^{-1} was calculated. Samples from two sediment layers were also dated by ^{14}C -AMS and the observed ages agree with the $^{230}\text{Th}/^{234}\text{U}$ results. Large differences between $^{230}\text{Th}/^{234}\text{U}$ and attributed ages for foraminifera zonal boundaries were observed for specific datums, in particular for those not well tied to the oxygen isotopic stratigraphy, as for example, the Y/X biozone boundary. This indicates the necessity of additional efforts such as presented here, aiming at validating the Quaternary biostratigraphy in the South Atlantic.

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