„BABEŞ-BOLYAI” UNIVERSITY
CLUJ-NAPOCA

Faculty of Environmental Science and Engineering

URANIUM SERIES DISEQUILIBRIUM DATING

- PhD Thesis Summary -

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Introduction

Uranium series dating methods are used on large scale with multiple applications, especially U/Th dating method due to the large interval ages that can be estimated with it. The main applications of U-Th dating method include sea-level oscillations, paleoclimatology and archaeology (Richards et al., 1994, Henderson and Slowey, 2000; Cheng et al., 2000, Onac and Lauritzen 1996; Haase-Schramm et al., 2004; Schellmann et al., 2004; Schwarcz and Rink, 2001).

The motivation of this paper is represented by the implementation of the U / Th dating method methodology in the alpha spectrometry laboratory of the Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca.

The thesis was divided into six chapters.

Chapter 1 presents the laws that govern the radioactive decay of natural radioactive decay chains.

Chapter 2 is a brief description of the uranium disequilibria dating methods including the U / Th dating method methodology.

In Chapter 3 is described the sample preparation methodology for subsequent analysis techniques by coupled plasma mass spectrometry and also by alpha spectrometry. The experimental results obtained for the yield optimization and separation efficiencies of U and Th with different separation methods can be found in this chapter.

Chapter 4 describes the methods used for U and Th isotopes measurements used in this paper. In the first part of the chapter the alpha spectrometry method is presented, and also some experimental data obtained by using protection films against alpha detector contamination. The second part of the chapter describes the methodology used for MC-ICPMS followed by illustration of the experimental data obtained for the calibration of the U and Th spike.

In Chapter 5 the results obtained by U / Th dating method of analysis of various samples taken from Croatia, Bahamas, Sardinia and various islands of the Mediterranean Sea are presented. For each set of samples various aspects of U/Th dating method are discussed.

The final part of the thesis, represented by chapter 6, consists of the presented results general conclusions

1. Radioactive series

Nuclear physics was born with the discovery of the radioactivity, by chance, in 1896, by Henri Becquerel.

If in 1904 only twenty natural radioactive elements were known, in 1912 their number increased to thirty, and now, more than 1.200 radionuclides and more than 257 stable isotopes are known.

Radioactivity is defined as a property of nuclei to decay by spontaneous emission of radiation: alpha (α), beta (β), gamma (γ) or electron capture from inner layers (Muscalu, 1975).

The nucleus decay probability in time is independent of external factors, all the atoms of the same species having the same decay probability. If N is the total number of nuclei, and dN the number of nuclei that decay during the time dt:

$$dN = -\lambda N\, dt \qquad (1.1)$$

where: - dt – the period (time) needed for the nuclei dN to decay;

- λ – radioactive constant.

Thus, the radioactive decay law can be defined (Cosma and Jurcut, 1996; Ivanovich and Harmon, 1982):

$$N = N_0 e^{-\lambda t} \qquad (1.2)$$

where: - N – number of radioactive nuclei remaining after time t;

- N_0 – initial radioactive nuclei number

The half-life ($T_{1/2}$) is the time period in which the initial radionuclides number drops to half due to radioactive decay.

The activity is usually measured in Becquerels, 1Bq being the equivalent of a decay for second. Curie is another measure unit tolerated, (1Ci) is defined as a gram of radium activity equivalent (1 Ci = 3.7 1010 Bq).

The first radiation experiments were performed using deviations in electric and magnetic fields. Thus, were determined the types of radiation emitted by radioactive substances (Daraban, 2006):

a) Alpha radiation (α) – composed of nuclei of ${}^4_2\mathrm{He}$; it can be absorbed by an aluminum foil thick as several micrometres.

b) Beta radiation (β) – composed of light particles (electrons or positrons); it can be absorbed by an aluminium foil with a thickness of 1 mm.

c) Gamma radiation (γ) – highly penetrating, is not deflected by a magnetic or an electric.

In 1903 Villard and Rutherford have established that alpha radiation consist in a double ionisated helium nucleus (He^{++}), by deflecting the radionuclides radiations in a magnetic (Daraban, 2006).

A defining characteristic of alpha radiation is low penetration ability in solids and liquids, which is within the micron range, but in air, the penetration is of centimetres order (Dărăban, 2006).

The radioactive series can be classified into three series (natural series), genetically independent, and one artificially obtained serie (table 1.1) (Ivanovich and Harmon, 1984).

Series name	Type	Final nucleus	Series first nuclide	$T_{1/2}$ (years)
Thorium	4n	^{208}Pb	^{232}Th	$1.41\ 10^{10}$
Uranium	4n+2	^{206} Pb	^{238}U	$4.47\ 10^{9}$
Actinium	4n+3	^{207}Pb	^{235}U	$7.04\ 10^{8}$
Neptunium	4n+l	^{209}Bi	^{257}Np	$2.14\ 10^{6}$

Table 1.1. –Radioactive series (Cosma and Jurcuț, 1996).

The uranium series is the longest radioactive series known.

Although in many undisturbed natural materials, the activities between products of their radioactive nuclei have reached secular equilibrium, this equilibrium being the basis of one of the most important dating methods (U-Pb), some exceptions can be found, because of the different chemical processes and isotopic fractionation of natural materials. These natural fractionation processes are the foundation of the uranium series disequilibria dating methods.

2. Methodology used in uranium series disequilibria dating

In any natural material containing uranium which was not disrupted for tens of millions years, between the parent radionuclide and his descendants a secular equilibrium has been established.

However, when a sedimentary deposit is formed, many geochemical processes occur and can cause isotopic fractionation of the elements, triggering a state of imbalance between parent nuclides and his daughters.

If no changes or if there are no other mechanisms of migration of radionuclide after the initial deposit, it is possible, in principle, at this stage of equilibrium, to determine the event age by measuring radionuclide levels in the system.

Thus, uranium series disequilibria dating methods are based on uranium activity and its successors measurements (Ivanovich and Harmon, 1982).

There are two main reasons for dating geological and archaeological environment (Van Calsteren and Thomas, 2006):

1. A precise age for a bone or a deposit may be the basis of our understanding of its meaning by establishing its archaeological and geological context.
2. The time-span between two dates of samples that were deposited under different conditions makes it possible to calculate the rate of change and may indicate the process that caused the change.

However, very few radiometric methods are able to date events in the range 300 ka - 1000 ka (Cosma and Văsaru, 1998; Ivanovich and Harmon, 1982; Onac, 2004).

Uranium series disequilibrium dating include a range of techniques involving many different nuclides. These methods can be divided into two distinct categories (Ivanovich and Harmon, 1982):

1. Methods that rely on uranium accumulation daughters (daughters deficiency methods): $^{230}Th/^{234}U$, $^{231}Pa/^{235}U$, He/U.
2. Methods based on nuclide decay intermediates (daughters excess methods): $^{234}U/^{238}U$, ^{230}Th excess, ^{231}Pa excess , $^{230}Th/^{232}Th$, $^{231}Pa/^{230}Th$, ^{234}Th, $^{228}Th/^{232}Th$, ^{210}Pb.

Of these, the most widely used dating methods are: $^{230}Th/^{234}U$ şi ^{210}Pb.

Basically all radiometric dating methods should be based on certain assumptions and arguments, and for their validity and consistency checks are needed. For the uranium series disequilibrium dating methods, the assumptions and arguments depends on samples to be dated and also on the source area of the samples. Thus, there are general criteria that can be applied to uranium series disequilibrium dating methods (Ivanovich and Harmon, 1982):

1. There must be a measurable amount of uranium in the sample.
2. For the daughters deficiency dating methods no daughters should be present at initial time, nor have entered into the system over time. Otherwise, some corrections must be made for the initial daughter presence in the sample.
3. The dated sample must be in a closed system, no nuclides migration related to the sample should exist.

2.1. U/Th dating method

The most used uranium series disequilibrium dating method is the U / Th method. This is applicable to many materials, which are subject to certain assumptions about the analyzed system, speleothems being some of the most used materials (Condomines et al., 2003, Lundstrom, 2003; Bourdon and Sims, 2003, Edwards et al., 2003, Richards and Dora, 2003).

Speleothems are composed of mineral material and usually are formed in caves as a result of driping groundwater. U released into groundwater through various rock alteration, comes to be precipitated with calcite in speleothems while the insoluble thorium remain fixed to soil components.

Thus, they form a system containing U and no Th. Over time, ^{234}U decays in the ^{230}Th, and for the system initial moment determination the U/ Th ratio measurement is needed (Richards and Dora, 2003; Onac, 2004).

If the system remains undisturbed for several million years, a secular equilibrium state between ^{238}U and ^{230}Th is reached, since the half-life of the parent isotope is greater than theyr daughters.

The return to the secular equilibrium state of the U series, in a closed system, from the initial state of disequilibrium, can be described by a function of time using the decay constants if (Richards and Dora, 2003):

1. the intermediates decay products present at the system formation time can be corrected or they were absent from the system,
2. from the system formation time no isotopic exchange took place with the environment.

The method is based on the natural separation of U from Th, resulting a radioactive disequilibrium state in the U series. U and Th have a tetravalent form in lithosphere, but in oxidizing conditions U becomes soluble forming complex hexavalent combinations. In contrast to U, Th is absorbed by clay or co-precipitated with various salts, it can be transported only ismall quantities of particles which contains Th. Thus, U and Th in underground environments are precipitated with CaCO3 while their followers are absent (Onac, 2004; Van Calsteren and Thomas, 2006; Richards and Dora, 2003).

If the sample does not contain ^{230}Th at the initial moment of the closed system, then ^{230}Th/^{234}U ratio is given by (Ivanovich and Harmon, 1982):

$$\frac{^{230}Th}{^{234}U} = \frac{1-e^{-\lambda_{230}t}}{^{234}U/^{238}U} + \left(1 - \frac{1}{\frac{^{234}U}{^{238}U}}\right)\frac{\lambda_{230}}{(\lambda_{230}-\lambda_{234})}\left(1 - e^{-(\lambda_{230}-\lambda_{234})t}\right) \qquad (2.1)$$

In practice, the age range that can be determined with this method is up to about 350 ka-600 ka (depending on the isotopic ratios measuring method).

To determine the initial ^{230}Th, , ^{232}Th is measured and used as an initial ^{230}Th concentration index, considering the ^{232}Th found as incorporated at the system formation time with the initial ^{230}Th (Kaufman, 1993; Richards şi Dorale, 2003, Schwarcz şi Latham, 1989) .

Usually the ratio ^{232}Th /^{230}Th used for this correction is in context with the sample (Richards and Dora, 2003), continental crust U concentrations being in the range from 0.1 to 6 mg / g in crustal rocks, the Th / U ratio being ~ 3.5 (Wedepohl, 1995).

For a complete ^{230}Th initial the isochrone correction methodology is used associated with total sample dissolution. Although many methods have been developed to determine the initial Th fraction, the total dissolution method and the subsequent isochrone methodology is the one that examines all fractions of Th. (Luo and Ku, 1991, Bischoff and Fitzpatrick, 1991; Ludwig, 2003, Ku and Liang, 1984; Schwarz and Latham, 1989; Alcaraz Pelegrin, 2005).

Although using a TIMS instrument, where isotopes of interest measurements are sequential, peak tail correction are necessary, analytical uncertainties of ~ 5 ‰ are present for U and Th measurements, ages uncertainties are improved from ± 10 to ± ka 2 ka for a carbonate sample age of 120 ka and an uncertainty of 10 ka for a sample of 300 ka, uncertainties much smaller in comparison with alpha spectrometry results. Lately, MC-ICPMS use is more frequent, replacing TIMS for high precision measurement of U and Th isotopes and in many cases surpassing the results obtained with TIMS (Goldstein and Stirling, 2003).

3. Sample preparation

3.1. Carbonates sample preparation for subsequent analysis by MC-ICP-MS and / or alpha spectrometry

High precision measurements of radioactive isotopes (alpha spectrometry, high-resolution mass spectrometry), sample preparation is crucial for achieving concluding results. For both methods mentioned chemical separation of the interest elements is required.

For alpha spectrometry, due to alpha emitters radionuclides with near energies (10-20 keV) some peaks are overlapping in the spectrum, making the interest isotope concentration determination impossible. Therefore a chemical separation is needed before spectroscopic analysis.

The chemical separation role is to isolate the interest elements from the sample to minimize interference between multiple alpha emitters present.

The measurement of samples using alpha spectrometry requires the sample deposition on a plate made of different materials. Film thickness deposition is very important because the thicker it is wider peaks are going to be obtained in the alpha spectrum. This thickness is determined both by the of deposition and by the separation methods.

In the case of high-resolution mass spectrometry (MC-ICP-MS) can cause interference with other isotopes or other compounds, obtaining incorrect results due to reduced separation efficiency. This problem is known as the "Matrix effect". A good separation maintains plasma conditions for good control of mass fractionations and also maintains clean the instrument components.

The reparation of radioactive elements (U and Th)

Radioactive elements separations are based on the traditional elements separation methods: precipitation, ion exchange and solvent extraction. A recent method which began to be used on a large scale since the 90s is extraction chromatography (Lehto and Hou, 2011).

The usual method in which ion exchange resins are used to separate uranium and thorium is ion exchange chromatography. These resins are placed in a plastic or glass column and are then treated with an appropriate solution, usually an acid with the same concentration of the solution in which the sample. This solution has a corresponding volume to the column resin and is transferred to the column. In most cases, matrix elution is performed with the same acid with the same concentration of the solution of the sample form. In this way, all radionuclides not detained are washed from the column resin. Radionuclides of interest, those who were detained in the column can be eluted with various acids which typically have low concentrations. During elution, concentration and eluent composition can be varied so that retained elements can be selectively separated (Lehto and Hou, 2011).

If large are used, the use of co-precipitation method with Fe is suggested, because in this way the chromatographic columns will not be overloaded with sample, preventing low yield results and matrix traces in the final solution.

The analytical procedure is described in the literature and is based on U and Th concentration from the sample by dissolving it in different acids, followed by co-precipitation of these radioactive elements with iron hydroxide. Further, U and Th are separated from Fe by extraction with ether and radioactive elements of interest are then separated using ion exchange resins (Gascoyne, 1977; Schwarcz, 1979; lvanovich and Harmon, 1982; Lauritzen and Mylroie , 2000).

Extraction chromatography is one of the most appropriate techniques for separating radioactive elements as liquid-liquid extraction selectivity combined with ease of the use of chromatographic columns. Resins used in this paper, based on this principle, are TRU and UTEVA.

The principle of extraction chromatography has three major components: an inert support, stationary phase and mobile phase. The inert support usually consists of porous silica or organic polymer. As the stationary phase, liquid extracts made from one or more components are used. The mobile phase is usually an acid (nitric acid or hydrochloric acid), but complex solutions (oxalic or hydrofluoric acid) are usually added to increase selectivity or for a better ions elution.

Compared with the method involving ion exchange resins, extraction chromatography offers two major advantages: the use of smaller amounts of acids and a much shorter procedure duration.

As ion exchange resins, using extraction chromatography may arise for related matrix problems especially for large samples that can over-load the columns. To avoid these problems, a co-precipitation with iron before chemical separation is suggested, or the sample may be passed twice through separation columns (Potter et al., 2005).

Some negative effects of these extracts have been reported, for samples analysis by TIMS (thermal ionisation mass spectrometry) and by ICPMS. These negative effects are attributed to the presence of small amounts of organic matter in the final sample solutions (Goldstein and Stirling, 2003). To eliminate these effects organic matter may be treated with hydrogen peroxide and nitric acid (Potter et al., 2005).

Electrodeposition

The adequate electrodeposition for alpha spectrometry analysis must be thin and uniform to obtain high-resolution spectra. This technique is the most widely used method for producing alpha sources (Tsoupko-Sitnikov et al., 2000, Garcia-Torano, 2006, Bajo and Eikenberg, 1999).

Alpha sources obtained by electrodeposidion are prepared by depositing the element of interest on a metal substrate, represented by cathode electrodeposition cell (stainless steel plate), while the anode is a platinum wire (Lee et al., 2000; Oliveira and Carvalho, 2006).

3.1.1. U and Th separation efficiency for carbonates. Matrix effect

After the radioactive elements separation, the resulting solution should be as pure as possible; the presence of several elements in relatively high concentrations or the presence of organic matter can greatly affect the quality of analytical isotopic measurements by ICP-MS (Becker, 2007; Pietruszka and Reznik, 2008 , Douville et al., 2011).

Due to the matrix may occur mass dependent matrix discrimination that adversely affect accurate isotopic ratios measurements by ICP-MS.

After uranium separation from a carbonate sample two solutions are obtained, one containing uranium, high purity, and the second containing the sample matrix. After measuring the U solution are obtained certain values for the U isotopic ratios. If different U isotopic ratios are obtained by adding a quantity of the matrix solution into the high purity U solution we can say that the matrix effect is observed.

The most common disposing methods of this effect are improving the chemical separation, sample dilution, sample introduction system modifications, optimizing operating instrument parameters, methods that are described by Agatemor and Beauchemin, 2011 and by Lehn et al. , 2003. Most mechanisms that occur in plasma are not well understood and therefore have the interferences related to matrix effect are not always well disposed or corrected. Due to these factors, for the carbonates samples is recommended to remove any traces of matrix by improving separation of radioactive elements to avoid matrix effects.

3.2. Uranium and thorium separation methods for carbonates samples for subsequent analysis by MC-ICP-MS. Choosing the best method.

Samples analysis and preparation was made at the Bristol University, England, and Bristol Isotope Group laboratories.

For the small carbonates samples (50-1000 mg) analysis was used a Thermo-Finnigan MC-ICP-MS instrument, with double spray of quartz and a Cetac Aridus. This instrument has a RPQ filter and dynode multiplier for high sensitivity measurements of uranium series.

All reagents used in experimental studies were ultra-pure or super-pure grade.

3.2.1. Yield investigation and optimization

a) U and Th separation methods using ion exchange resins

The used separation method for the two radioactive elements by ion exchange chromatography of small samples (50-200 mg) presented in this paper is similar to that described by Chen 1986 and Chen and Wasserburg, 1981, and was named generic method 1 Dowex resin ..

The uranium and thorium separation yield is one of the most important parameters. Optimizing the yield is necessary for applications where a pre-concentration of the interest radioactive element is not possible or the sample is found in small quantities (i.e. U / Th dating).

For 36 carbonates samples, with masses of about 0.1 g each, was used method 1 (Dowex). The yields are shown in Figure 3.4.

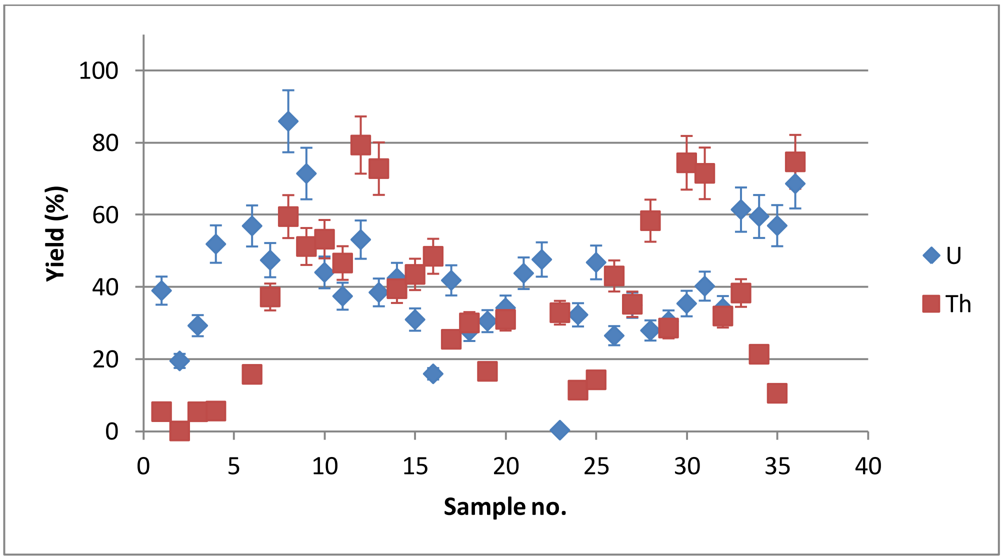

Figure 3.4. Method 1 yield for 36 samples.

The yield is relatively small, with an average of 41% for U and 36% for Th. Th is the most important for U / Th dating measurements and to reduce the final uncertainties the yield should be as high as possible.

To improve the method 1 yield various changes were applied (increased eluent volume, different eluting steps); the proposed method was named modified method 1. Also, to reduce the costs, the U usual eluent (HBr) was replaced with ultra pure water, the results are presented in Figure 3.5. for U and 3.6. for Th.

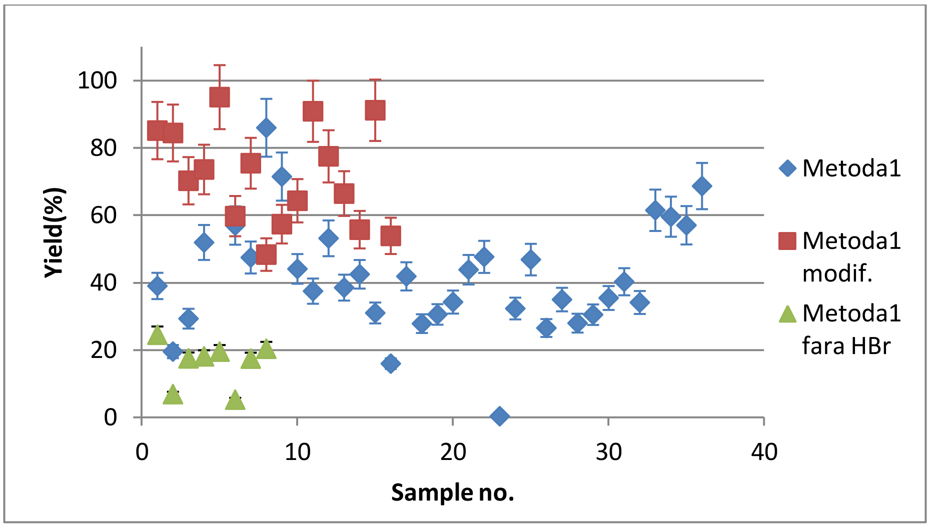

Figure 3.5. Method 1 and modified method 1 U yields.

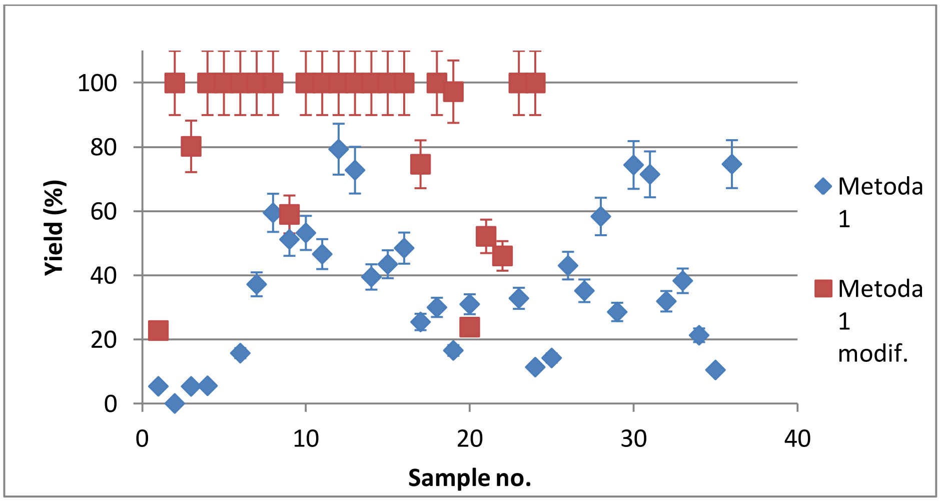

Figure 3.6. Figure 3.5. Method 1 and modified method 1 Th yields.

Because larger volumes of eluents were used for U and Th in modified method 1 compared to method 1, the yield average increased significantly, from 41% to 70% for U and from 36% to 95% for Th

The method used to separate radioactive elements by ion exchange chromatography for relatively large samples (0.9 g - 1g), includes a Fe co-precipitation to remove most of the sample matrix and is similar to that described by Ma et al., 2012.

Fe co-precipitation method was used on carbonates samples, the yields are presented in Figure 3.7.

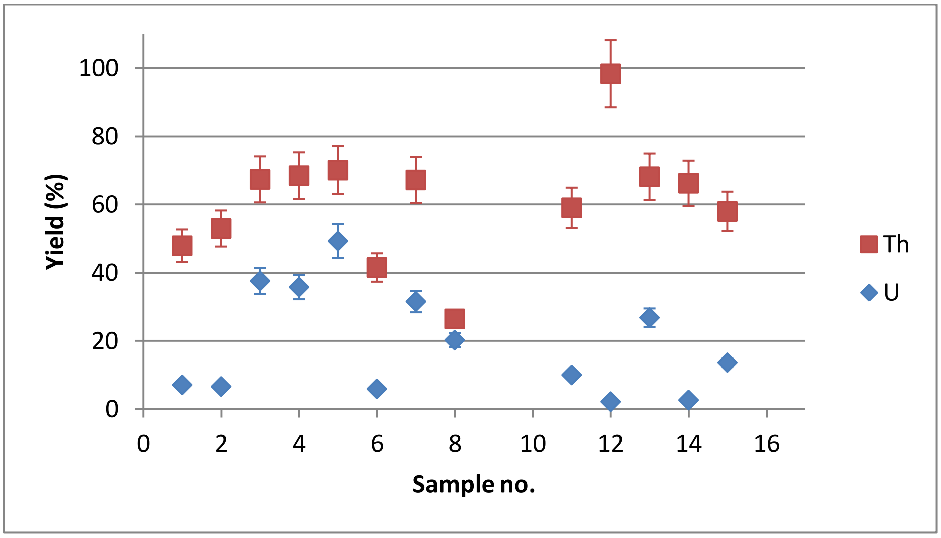

Figure 3.7. Fe co-precipitation method yields.

The yields are relatively low, requiring a calibration for this method to optimize the degree of recovery.

b.) U and Th separation using methods based on extraction chromatography resins. TRU spec resin

The methods used (for analyzing small carbonates samples 50-200 mg) is similar to that described by Potter et al. 2005, and were named TRU - method 1 and TRU - method 2.

Two columns calibrations for each method were done. Because for the second method were obtained higher yields, TRU - method 2 was used on carbonates samples, , with masses of about 0.1 g. For two of these were used 50-100 µm TRU spec resin and the other two samples, 100-150 µm TRU spec resin. The obtained yields are shown in Figure 3.8.

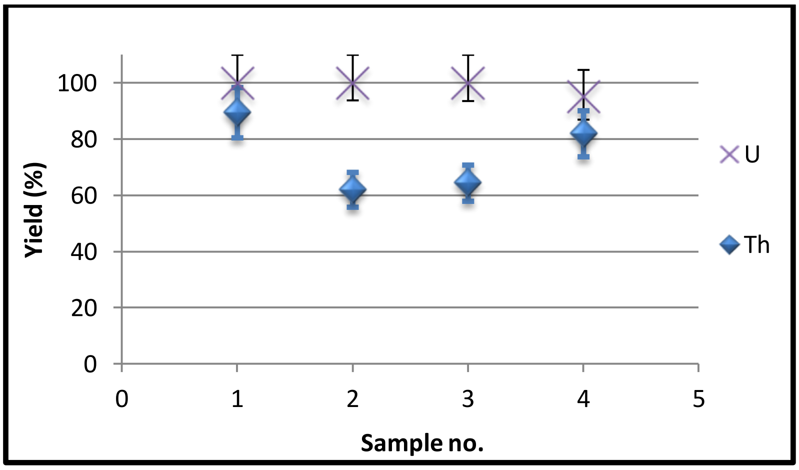

Figure 3.8. Tru resin yields

(1 and 2 for 100-150 µm, 3,4 for 50-100 µm)

The 100-150 µm TRU resin yields were 100% for U and 76% for Th and 50-100 µm TRU resin yields were 98% for U and 73% for Th.

Another type of resin that is based on extraction chromatography are UTEVA resins. The method used is well described by Potter et al. 2005 and was named UTEVA-.

The method was applied for U and Th separation from 15 carbonates samples with masses of about 0.1 g; the yields obtained are shown in Figure 3.9.

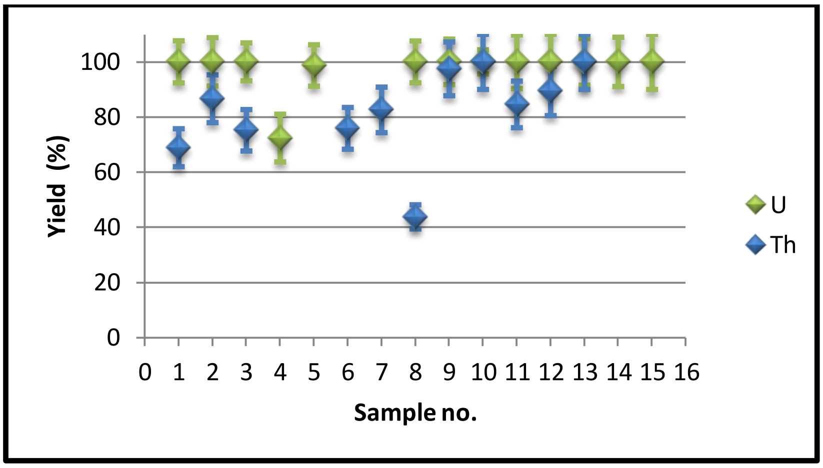

Figure 3.9. UTEVA method 1 yields.

The yield average obtained for U was 97% and 82% for Th.

To optimize the yield of the method various changes were applied, the proposed method was called UTEVA method 2. The obtained yields for the proposed method are shown in Figure 3.10.

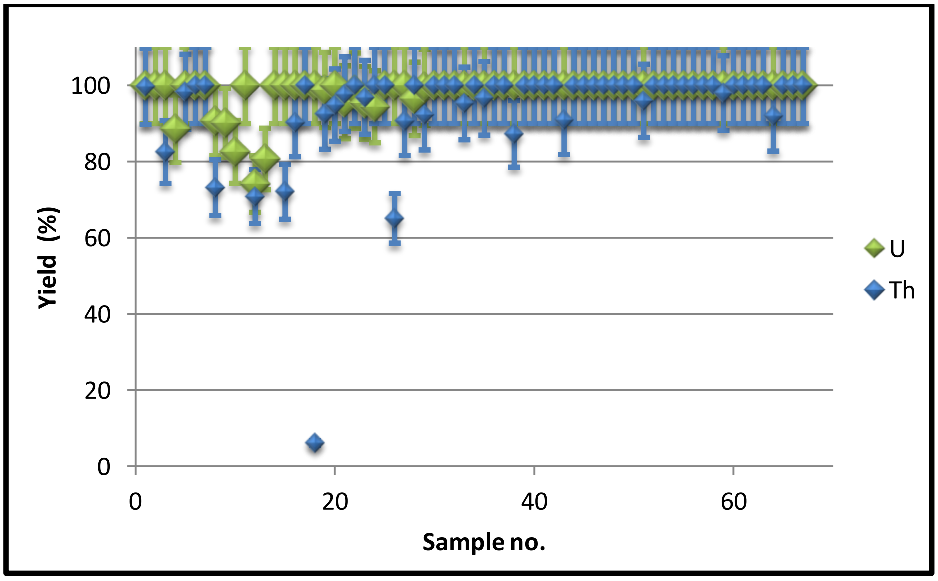

Figure 3.10. UTEVA method 2 yields.

The yield average for U is 98% and 95% for Th. Changes to the original method led to higher yields enough for the most demanding U and Th analysis.

To choose the best method the following parameters must be taken into account: separation efficiency, degree of recovery, time demanding. The separation efficiency is discussed in the next section.

As time demanding, UTEVA resin method is most rapid method tested, followed by TRU spec resin method, co-precipitation with Fe method, the method that requires the most time is method 1 (Dowex resin / Bio Rad) .

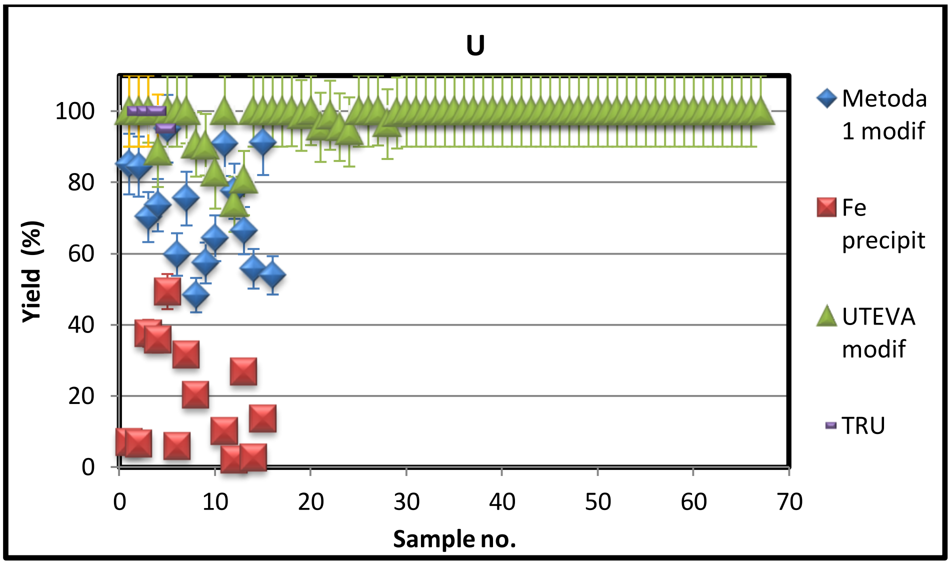

Figure 3.11: U yields fro the different separation methods used.

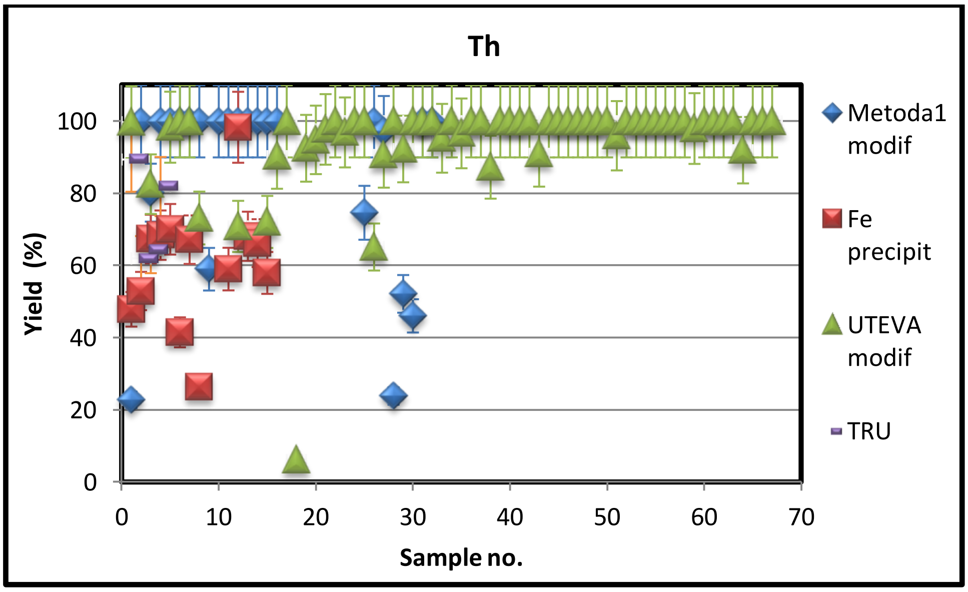

Figure 3.12 Th yields from the different separation methods used.

From the yields point of view UTEVA resins modified method is superior to other three methods investigated, as it can be seen in Figure 3.11 and Figure 3.12.

3.2.2. Radioactive elements separation efficiency form carbonate matrix and matrix effect

One of the most important parameters of a separation is the method's efficiency. Remaining traces of carbonate samples matrix found in the analyzed solution by ICPMS, can lead to erroneous results.

Different U and Th separation methods have been tested, the results suggesting the most efficient separation method being the UTEVA resin method. Due to this conclusion, the UTEVA resins method 2 was used for reproducibility tests.

A calcite sample was powdered, homogenized and divided into 4 subsample with different masses: subsample 1 - 0.1 g subsample 2 - 0.5 g subsample from 3 - 0.1 g subsample 4 - 0.1 g. UTEVA resin method 2 was use for U and Th separation from the mentioned subsamples, in two different days. The results are illustrated in the figures below.

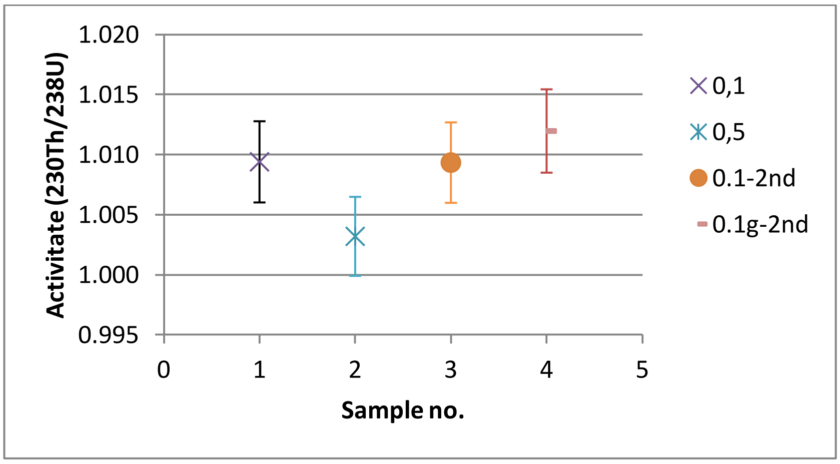

Figure 3.13. UTEVA method reproducibility.

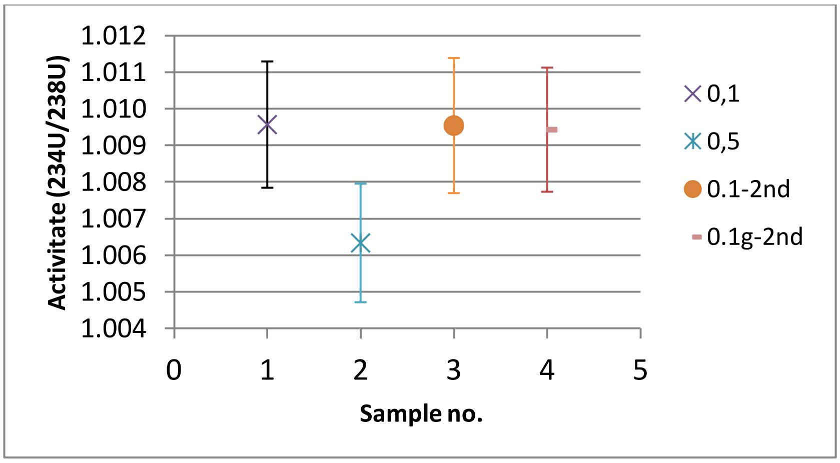

Figure 3.14. UTEVA method reproducibility.

Subsample 2 is the only one that tends towards an incorrect value, although the values are within the uncertainties range of the other results. This is the subsample with the largest amount of carbonates matrix and was probably not washed well enough.

It can be concluded that UTEVA separation method 2 for samples with a maximum mass of 0.1 g has sufficiently good separation efficiency, high yields and requires a relatively short working time.

3.3. Sample preparation methods for alpha spectrometry analysis

3.3.1. Uranium and thorium separation using ion exchange resins

Samples preparation and analyses were made in the alpha spectrometry and radiochemistry laboratory from the Faculty of Environmental Science and Engineering, Babes Bolyai University, Cluj.

Analyses were performed with an ORTEC Soloist alpha spectrometer with PIPS (Passivated Implanted Planar Silicon) detector, of 1200 mm^2 size, which has a resolution of 19 keV, and data acquisition was performed using ASPEC-927 Dual Multichannel analyzer . All chemicals used were of analytical grade. The ion exchange resins used were Dowex AG type 1x8 (100-200 mesh).

The chemical interest element yield after the separation from the sample matrix is very important for all subsequent analysis methods, and by varying the separation parameters the interest element varies. To obtain optimum parameters for U separation were used different conditionings of resins and different temperatures for different eluent concentrations.

U solution, of known activity, was prepared by dissolving uranil nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (99.99%, purchased from Merck Company) in 9M HCl. In this way uranil nitrate was converted to the hydrochloride form. This solution was used as a standard solution to check the influence of different methods of resins pre-treatment (2 methods) and various eluents influence on the degree of recovery.

To check the selectivity of the procedures followed a solution of Th with well known activity was preparated. 12 samples were prepared from solution U, adding to each an amount of Th solution equivalent to 1 Bq / sample.

Samples obtained after elution were electrodeposited on stainless steel plates, which were analyzed by alpha spectrometer. In Figure. 3.15. an alpha spectrum obtained is shown.

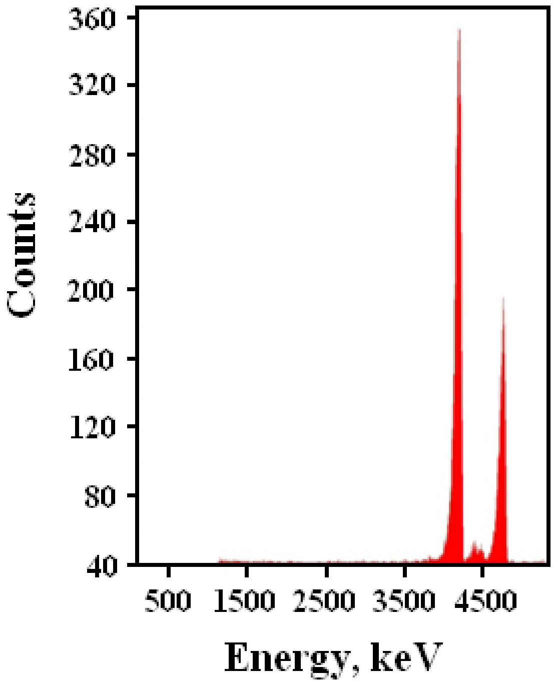

Figure 3.15. Alpha spectrum obtained (Nita et al., 2011).

The main energies of U isotopes are: ^{238}U - 4196 keV, ^{234}U - 4777 keV, and ^{235}U - 4679 keV. In Figure 38 it can be seen the three isotopes mentioned. ^{238}U if ^{234}U peaks are not equal, so isotopes are not in secular equilibrium as it should and we can say that uranium is depleted uranium.

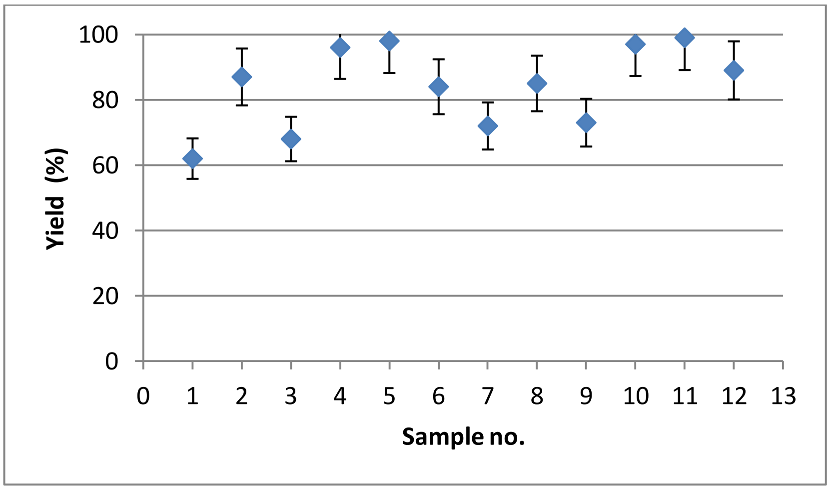

Figure 3.16. Yields obtained for different resin conditioning and for different U eluents.

For the second resin conditioning method (sampls 7-12) used higher yields were obtained (comparated with the first method – samples 1-6) . The highest yield was obtained for sample 11, for which elution was used 0.1 M HCl at room temperature, while the lowest yield was obtained for sample 7, for which elution was used 0.05 M HCl brought to the boiling point.

Since for both conditioning methods the best results were obtained for the elution with 0.1 M HCl at room temperature (samples 1 and 7), and the lowest yield for 0.05 M HCl brought to the boiling point (samples 5 and 7) we conclude that the eluent concentration (although the difference is relatively small) and its temperature influences the U recovery.

Different resins conditionings appear not to be a dominant yield parameter, the difference between the two yields results sets being small.

Not traces of Th were found, Th main isotope energies are: ^{232}Th – 4007 keV, 3952 keV and ^{230}Th – 4682 keV, 4615 keV, which suggests a good separation of U from Th.

For radioactive elements separation from the carbonates matrix that are analyzed by alpha spectrometry are commonly used large samples (5-50g) due to relatively low limit detection of alpha spectrometer. The method is similar to those described by Holmgren et al., 1994, Anderson and Fleer, 1982, Gascoyne, 1992.

U and Th spectra obtained for environmental carbonates samples are illustrated in Figure 3.17. and 3.18.

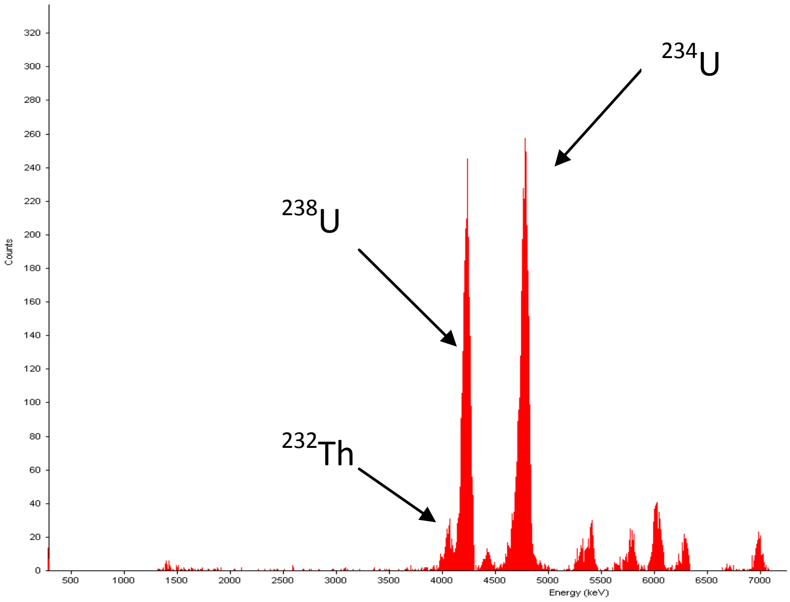

Figure 3.17. U alpha spectrum obtained

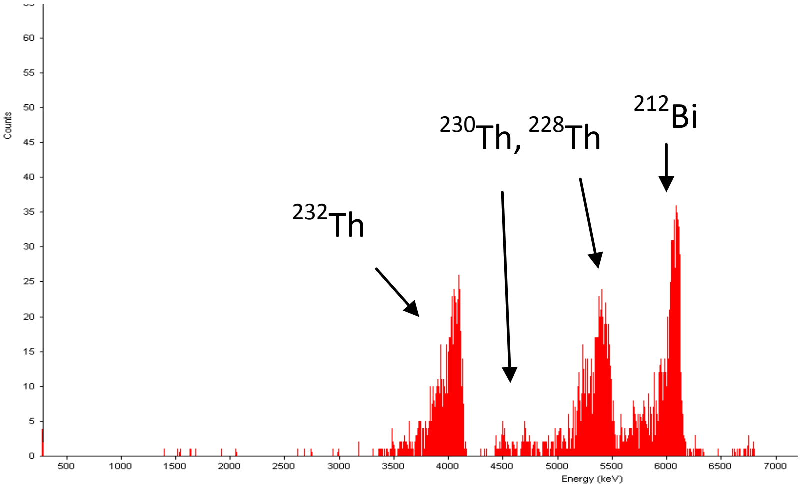

Figure 3.18. Th alpha spectrum obtained

Spectra obtained suggest a relatively good sample preparation. If in the U spectrum Th traces can be seen, in Th spectrum no U traces are observed, the spectra haveing an acceptable resolution.

U and Th efficiency separation optimization and electrodeposition improving requires a future in detail study.

3.3.2. Electrodeposition

Sample analysis by alpha spectrometry involves the interest element electrodeposition onto a metal plate. To get a good resolution spectrum the electrodeposition should have a thin film form.

For U electrodeposition different methods with various dominant parameters are described in the literature (Amol Salar et al, 2006; Maya et al, 2004): the electrolyte type, electrode material and shape, surface quality cathode, anode form, electrodeposition timing.

Usually electrodepositions are done on stainless steel plates at a current of 1.5 A.

The used method is to add a few drops of Na_2SO_4 to each sample (in solution) to prevent adsorption to glass walls. Samples are brought to dryness by evaporation on a hotplate, resulting residue being dissolved in 10 ml of 0.075M H_2SO_4. With H_2SO_4 and NH_4OH sample solutions are brought to pH 2.2. A solution of Na_2SO_4 is used as electrolyte, for an easily controlled pH during electrodeposition. A few drops of thymol blue 0.04% is added to each sample. Platinum anode is placed at a distance of 1 cm from the cathode. One minute before the elecrodeposition end 1 ml of NH_4OH is added. After elecrodeposition the plate is washed with distilled water.

A result of an electrodeposition with the mentioned method is the alpha spectrum shown in Figure 3.19.

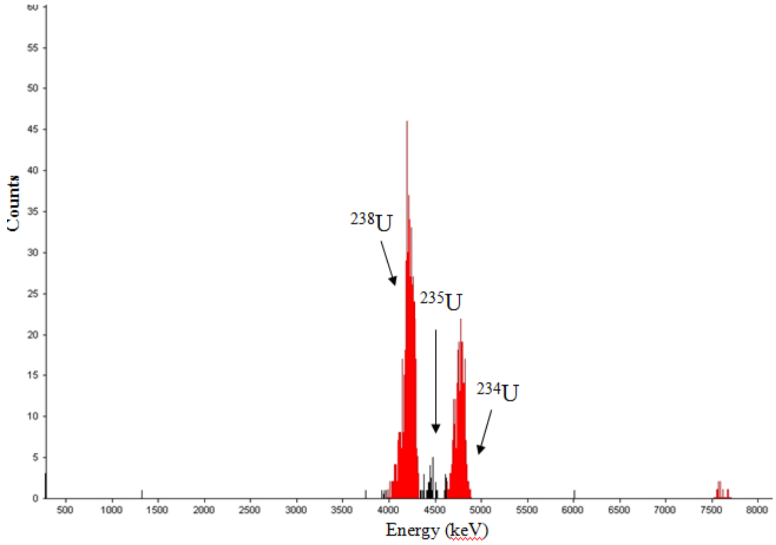

Figure 3.19. Alpha spectrum obtained from a U sample electrodeposition

The advantages of the used method are high resolution spectra, high yield, good reproducibility and the method’s simplicity.

4. Radioactive isotopes measurements with disequilibria dating applications

Although several methods for radioactive isotopes measurements are used, in dating, the most used are alpha spectrometry, TIMS and MC-ICPMS.

4.1. Alpha spectrometry

The alpha spectrometer used for the measurements presented in this paper was ORTEC Soloist with PIPS detector (Passivated Implanted Planar Silicon) with a 900 mm^2 1200 mm^2 size, which has a 19 keV resolution. The data acquisition was performed using ASPEC-927 Dual Multichannel analyzer.

To determine the U / Th ratios frequently alpha spectrometry methods are used. Some radionuclides of this couple are overlapping in the alpha spectrum (alpha particles emissions with very close energies), so a U and Th chemical separation is nedded, which is a indispensable inconvenience (Cosma and Jurca , 1996, Garcia-Torano, 2006).

Alpha spectrometry applications requiring extremely good control in the preparation of chemical alpha sources, which often are the electrodepositions of the interest element on a stainless steel plate (Bickel et al., 2000).

Alpha sources optimal geometry is a "infinitely thin" film deposited on a flat surface for alpha spectra resolution to be as good as possible (Goldstein and Stirling, 2003).

The alpha detector and the source / sample are placed in vacuumed cell, because of the average short alpha particles path in air (Yu et al., 2003), and also because of the radon presence and other parameters that may disturb the measurements.

A typical alpha spectrometry system consists of detector, preamplifier, high resolution amplifier, multichannel analyzer and data acquisition system.

Most times the alpha spectrometer is connected to a computer that displays the spectrum with the pulses.

One of the most important alpha spectrometry applications are the nuclear decay measurements, for decay probability deduction of alpha emitting radionuclides (Garcia-Torano et al., 2005; Garcia-Torano, 1998; Dayras and Chauvin, 2004; Garcia-Torano, 2000 , Sibbens and Denecke, 2000).

4.1.1. Alpha detectors protection using formvar films

For high precision measurements, using alpha spectrometry, silicon detectors contamination with recoil nuclei is a sensitive issue, especially for sources containing radioisotopes which have short half-lifes, or their daughters have short half-lifes. Contamination can occur when sample radionuclides the can strike the detector and accumulate in the surface layer. Through their decay, the background will increase, leading to measurement decreased sensitivity (Van der Wijk, 1987, Van der Wijk, et al., 1987; Vainblat et al., 2004).

Recoil nuclei contamination cannot be avoided nor with the best alpha source preparation also cleanning the contaminated detector does not help too much because recoil nuclei usually penetrate its surface layer. Thus the options are: periodic detector replacement or contamination prevention.

Due to the relatively high difference between alpha particles and recoil nuclei a thin film may be placed between the detector and the source, thin enough to allow alpha particles to pass while the recoil nuclei are stopped by it.

The film production is a simple process and the principle is the formvar films deposition on glass and after the removal away from the surface, being kept on a frame. The films producing method is well described by Van der Wijk (1987).

The use of formvar protective film effects were studied (produced in our laboratory) against alpha recoil nuclei detector contamination.

A source was measured with the formvar film placed between the detector and the source, then no film was used. This protocol was repeated for several films, resulting in different energies for alpha particles. From energy differences was obtained different energy for each formvar film.

When an alpha particle passes through a thin film, loses energy due to the interaction of atoms with alpha particle film, the film having a "stopping power".

The experimental results suggest a decrease in peak energy with film number increasing analysis used, thus as the peak power is higher the energy shift is smaller. Thus, the higher the peak energy is, the lower the energy shift is. A decrease in peak-height offset by an increase in their thickness was observed, peak area not being significantly affected. The main parameter affected by the use of protective films is resolution, which degrades by about 7%.

4.2. Mass spectrometry (MC-ICPMS)

Inductively coupled plasma mass spectrometry using multiple detectors (collectors) technique was developed by combining the ionization efficiency of ICP with the magnetic mass selector, equipped with multiple Faraday cups to get precise determination of the isotopic composition of high ionization potential elements that are difficult to analyze by TIMS (Rehkämper, 2007).

The advantages of MC-ICPMS compared to TIMS includes high ionization efficiency, a smaller amount of required sample, input higher speed and quickly samples / standards change possibility, and thereby the potential to use "standard-sample bracketing " procedure. Major disadvantages are higher background than TIMS, interference possibility, higher mass fractionation, but all these can be corrected (Pereira et al., 2010, Nebel-Jacobsen et al., 2005).

The sample is ionized argon plasma induced by a high-frequency electric field (plasma torch). High temperature plasma of about 10000 K, can ionize completely hard to ionized elements (hafnium, thorium) by thermal emission. The element to be ionized is first atomized and then ionized. This is a plasma sprayed as an aerosol, or if using laser ablation is released directly into the plasma. Mass fractionation is between one twentieth of a percentage for easy element (boron), and a percentage for heavy elements. Mass fractionation correction is made using isotopic ratios similar element as internal standard because mass fractionation is due only to isotope mass, being independent of the isotope chemical properties. (Allegre, 2008).

Samples analysis results presented in this paper was done by using a Thermo-Finnigan instrument MC-ICPMS with Cetac Aridus.

Correction and calculus

All data are corrected for background, contributions tail, SEM non-linearity, isotopic fractionation, differences measurement due to various collectors (SEM-Faraday cup), and also of the spike contribution, using spreadsheets (Excel) created by members of BIG (Bristol Isotope Group), and linked to Isoplot (BGC's Visual Basic Add-in for Microsoft's Excel).

Uncertainties related to sample mass, tracer mass, measured isotope ratio, spike calibration, standard isotopic ratios, half-lifes, are propagated using a Monte Carlo procedure to determine the final interest isotopes activities ratios uncertainties (Hoffmann et al. 2007).

4.2.1. ^{236}U şi ^{229}Th spike calibration

Added tracer isotopic ratios to the sample must be known as precisely as possible. U / Th tracer calibration can be done by two methods. The first method is to simply measure the isotopic ratios of the tracer. The second method consists in measuring a sample of U / Th which is in secular equilibrium with the first daughters, to which was added a known quantity of tracer. Thus, the tracer is calibrated according to isotopic activities ratios of the used solution (238U/234U = 234U/230Th = 1).

A tracer solution (^{236}U şi ^{229}Th) with unknown isotopic composition, isotope ratio and isotope concentrations was calibrated. An overview of isotopic composition is shown by Figure 4.1., which is a scan type measurement.

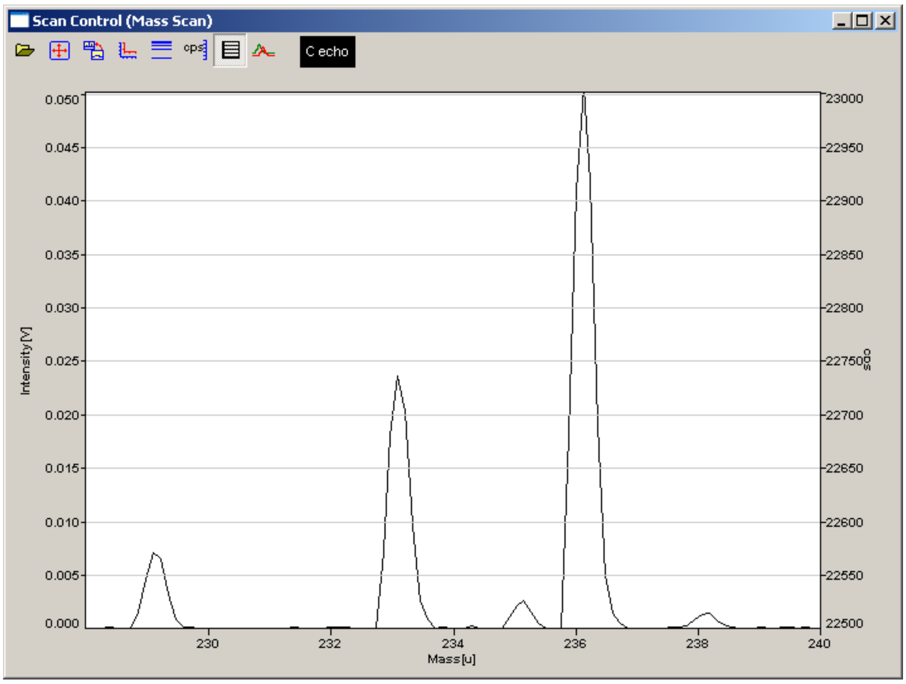

Figure 4.1. Isotope intensities according to their atomic mass.

5. Obtained ^{234}U-^{230}Th dating method experimental results

Samples preparation and analysis were made at Bristol University, England, and Bristol Isotope Group laboratories.

Samples analysis was used a Thermo-Finnigan MC-ICP-MS instrument, with double spray of quartz and a Cetac Aridus. This instrument has a RPQ filter and dinod multiplier for high sensitivity measurements of uranium series.

All reagents used in experimental studies were ultra-pure or super-pure grade.

All data are corrected for background contributions, tail contributions, SEM non-linearity, isotopic fractionation, differences measurement due to various collectors (SEM-Faraday cup), and also of the spike contribution, using spreadsheets (Excel) created by members of BIG (Bristol Isotope Group), and linked to Isoplot (BGC's Visual Basic Add-in for Microsoft's Excel).

5.1 MC-ICPMS U-Th age determinations on altered submerged speleothems from Croatia

For sea levels variations determinations in time, numerous samples were analyzed using different indicators. Some of the most valuable samples used are speleothems from the current flooded caves.

Eastern coast of the Adriatic Sea was formed during the late Pleistocene- early Holocene by flooding the existing karst area, including many caves (Suricata et al., 2005).

We have attempted to date two deep submerged speleothems (POG-1, -53.0 m; POG-2, -35.6 m) from a coastal cave from Poganika cave, Šolta, Croatia, to supplement the previous sea level work from this coast (Surid et al., 2005, 2009) that focuses on the last glacial period. Both samples are heavily encrusted with marine overgrowths and were sampled in situ. POG-1 demonstrates open system behavior and cannot be dated reliably. POG-2 has finite ages ~ 308 ka and appears to have grown very rapidly (~ 800 a).

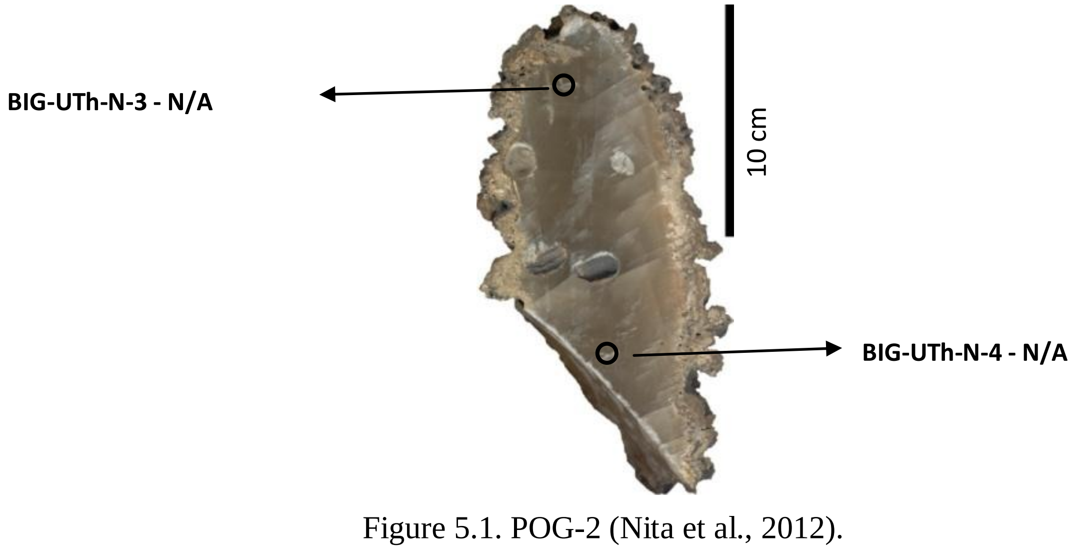

Figure 5.1. POG-2 (Nita et al., 2012).

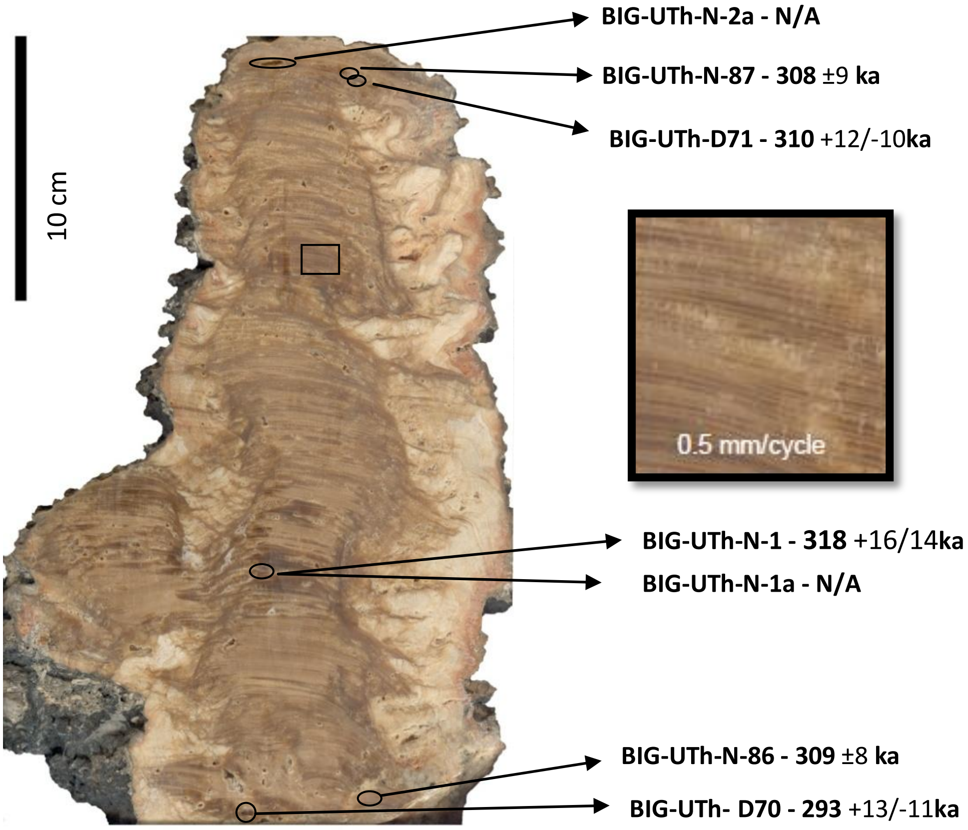

Figure 5.2. POG-1 (Niță et al., 2012).

The sample is illustrating dense, brown calcite core with well-preserved growth layers. While numerous MC-ICPMS U-Th determinations indicate that there are finite ages of ~ 310 ka at the top and base of the sample and potentially very rapid growth, minor reversals (and inconsistent initial $^{234}U/^{238}U$ ratios are a cause for concern and warrant further investigation).

Low sea level at ~308 ka (based on growth at -53 m below present sea level and uncorrected for GIA) is consistent with the timing of high sea levels based on closed system coral ages from Henderson Atoll (Andersen et al, 2010) - 307 ka for MIS 9.1, the fall of global sea levels to < -40 m based on Red Sea δ18O data (tuned to EPICA Dome C) (Rohling et al, 2009), ages of submerged speleothems from the Bahamas (Hoffmann et al, 2007).

5.2. New data on some speleothems from the Bahamas

A speleothem from Bahamas, taken from -18.1 m, which was analyzed by alpha spectrometry and TIMS by Richards et al, 1994, was reanalysed for new information on the estimated ages, with the possibility to have missed the first layer. For the first layer dating subsample quantities used were decreased, and analyzed with MC-ICPMS.

Since the interest age is within the first layer, only from the first ~ 2 mm of the sample, subsamples were taken. For a better control of the sampling procedure the was divided into 3 sections: Bahamas I, II E Bahamas, Bahamas II F, after removing the detritical layer

Each subsample was scraped, having about 0.2 mm in the sample growth direction

Detritical component corrections were made initially to the crustal average value ($^{232}Th/^{238}U$) of 1.34 ± 0.67, observing questionable results. To verify these results the adjacent coeval subsamples, taken from the first layer of the sample, were used for a isochrone plot. Thus, a correct value was obtained for the first substrate detritical component (^{230}Th/^{232}Th = 17.5 ± 6.9), performing the necessary corrections (Richards et al., 2012).

For the rest of the subsamples a second isochrone was built, obtaining a value for the detritical 230/232 of 12.7 ± 8.8.

An illustration of the large difference in age estimates obtained with the two corrections can be seen in the figure below.

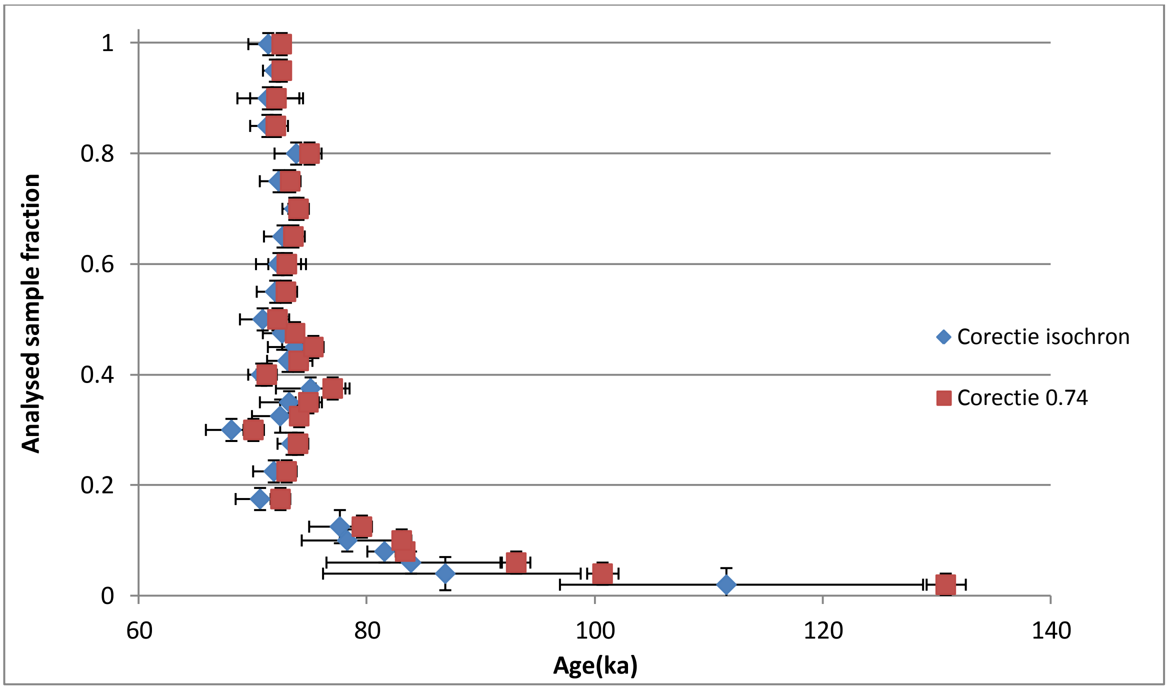

Figure 5.3. Differences between the two common methods of initial Th correction for sample GB-89-25-5C.

The results suggest a first relatively old age. If ages obtained for BIG-uth-N-154, 155, 165 (first three ages in Figure 5.3.) are questionable due to the difference between them and the rest of the ages obtained and the large associated uncertainties, high consistency is observed for the following ages of interest (BIG-uth-N 179 191 156). Thus, the first age of the sample can be estimated in the range ~ 82 ka ≤ GB-89-25-5C <~ 129 ka, having a very high probability of being between ~ 82 ka ≤ GB-89-25-5C ≤ ~ 83 ka.

The results are consistent with Richards et al, 1994, Li et al., 1989, Lundberg and Ford, 1994, the estimated ages obtained can be considered an extension of the results obtained by Richards et al, 1994, from ~ 79.4 to ~ 82.5 ka ka.

For the analyzed sample the detritical component corrections determined by isochrones contribution to the final age uncertainties are very high suggesting a more thorough future study to minimize these uncertainties.

5.3. The mammals evolution on islands related samples age estimation

Small mammals evolution in small environments over time is a topic widely studied because dwarf and gigantism phenomenon is closely related to restricted areas of habitat of various mammals. Phenomena usually occur on islands, hence the term "island rule" which refers to the phenomenon of miniaturization of large animals and gigantism of small animals. (Raia and Meri, 2006; Lister, 1993, 2009, Foster, 1964; Van Den Bergh et al., 2008, Richards et al., 2012). Thus fossil dating to be represented on a time scale is crucial.

Samples from different islands of the Mediterranean were collected and analyzed as part of a NERC funded project, among others, on the evolution of island dwarfism mammals. Over 70 ages were estimated but only interest sample dating methodology is presented. For discussions on the mammals evolution further investigations needed.

Dating samples with bone inclusions.

Samples with fossil inclusions are very important because of direct estimated age report with the interest inclusion.

Unlike calcite, bones behave as open systems. A living bone has a few ppb of U, while the one that was in contact with different natural environments can contain from 1 to 100 ppm U adsorbed from the environment (soil, etc.) (Pike and Pettitt, 2003). Thus, the calcite being in direct contact with a bone may lose U, and the estimated age being incorrect. By the stratigraphcal dating U concentrations of related subsamples can be compared and determine if the subsample has been contaminated.

Different samples were analyzed for age estimation and for an age range classification of the bone inclusions.

Dirty samples.

Initial Th correction is very important because applied as a slightly wrong used value correction can lead to very different age from reality, depending on the concentration of the detritical component. Thus, the isochrone methodology is applied for a good initial Th estimation.

We attempted to date the three samples that had a high detrital component, taken from the same area. Samples were composed of detrital components (clay and other inclusions) cemented by carbonates. Two of these samples showed thin layers of calcite.

Eight subsample were taken for dating, three calcite subsamples and five cemented material subsamples (CL).

For the initial Th correction an isochrone was plotted assuming that all samples have the same age. Thus, the detritical component obtained value $^{230}Th/^{232}Th=0.531+/- 0.039$.

But it is possible that the two types of material have been deposited at different times, separated by a unknown period of time, thin calcite layers may be a further intrusion into cement material. Thus, for each type of material an isochrone was plotted.

For CL was obtained a detritical component value $^{230}Th/^{232}Th = 0.44 + / -11$ and is significantly less than that obtained by isochronous for all samples.

For calcite was obtained a detritical component value $^{230}Th/^{232}Th = 0.74+/-0.16$, being the same value as the mean bulk earth used for initial Th correction. But the value obtained is different from the other two correction values obtained for detritical component, suggesting that the different materials have different ages.

Results sutain the importance of the right correction method for initial Th. Although initially it was assumed that all samples have the same age, subsequently was illustrated the two different materials (calcite and CL) could be deposited at different times, possibly CL samples have different ages or different detritical component due to the obtained ages inconsistency. A further study is needed to establish the initial Th values and the correct ages, due to insufficient stratigraphy information and insufficient subsamples.

Old ages.

U/Th dating method ability for materials with old agea was studied. Ages were estimated between 389 ka and 807 ka and observed that generally with age increasing their uncertainties are increasing. Thus, the dating method ability hardly exceeds the threshold of 600 ka age that remain relevant (finite age uncertainties), there are cases in which positive infinite ages with uncertainties can be useful.

6. Conclusions

U and Th separation methods using ion exchange resins were optimized for MC-ICPMS methods and alpha spectrometry analysis. For extraction chromatography, TRU and UTEVA resins separation methods were studied and optimized.

The use of formvar protection films have been studied against alpha recoil nuclei detector contamination. Different energy displacements and peak resolutions decreases were observed in sites the analyzed alpha spectra, according to used film thickness.

Using MC-ICPMS a spike with unknown composition, concentration and isotope ratio was calibrated, to be used later for U series daring.

Over 120 samples were analyzed, with over 100 estimated ages, for different applications.

The analyzed Croatian, Bahamas samples, with sea levels importance, are consistent with the literature. Furthermore the Bahamas samples results are an extension of the data obtained by Richard et al., 1994.

The research related to the mammals evolution on islands, the presented samples were divided into three categories to illustrate the methodology used for different types of samples. Thus, the ages obtained should be analyzed further to determine both their consistency and their relevance.

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