The potential of ingrowth ^{226}Ra as a new dating tool for late Holocene carbonate deposits

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Introduction

One of the most common methods for dating carbonate deposits, such as speleothems or calcareous sinter deposits, is the $^{230}Th/U$-disequilibrium method. However, substantial detrital contamination may represent a major problem for radiometric dating. This is especially true for young samples, such as the calcareous sinter deposits from Roman aqueducts used in this study. The high ^{232}Th content, which is an indicator for the amount of detrital contamination, leads to elevated U/Th-ages and generally larger uncertainties, which limit the potential of such young samples for paleoclimate reconstructions. Figure 1 shows $^{230}Th/U$-ages for seven carbonate deposits from aqueducts from Cordoba (VC1, VC2), Dor (DOR1), Naxos (NX09, NX14), Béziers and Jerash. The, for detrital contaminated, uncorrected ages are without exception too old for the corresponding time period during which the carbonate was deposited. Although the corrected ages fit within error in the correct time period, the associated errors are quite large and show the limitations of the $^{230}Th/U$-disequilibrium method for paleoclimate reconstruction from young and dirty samples.

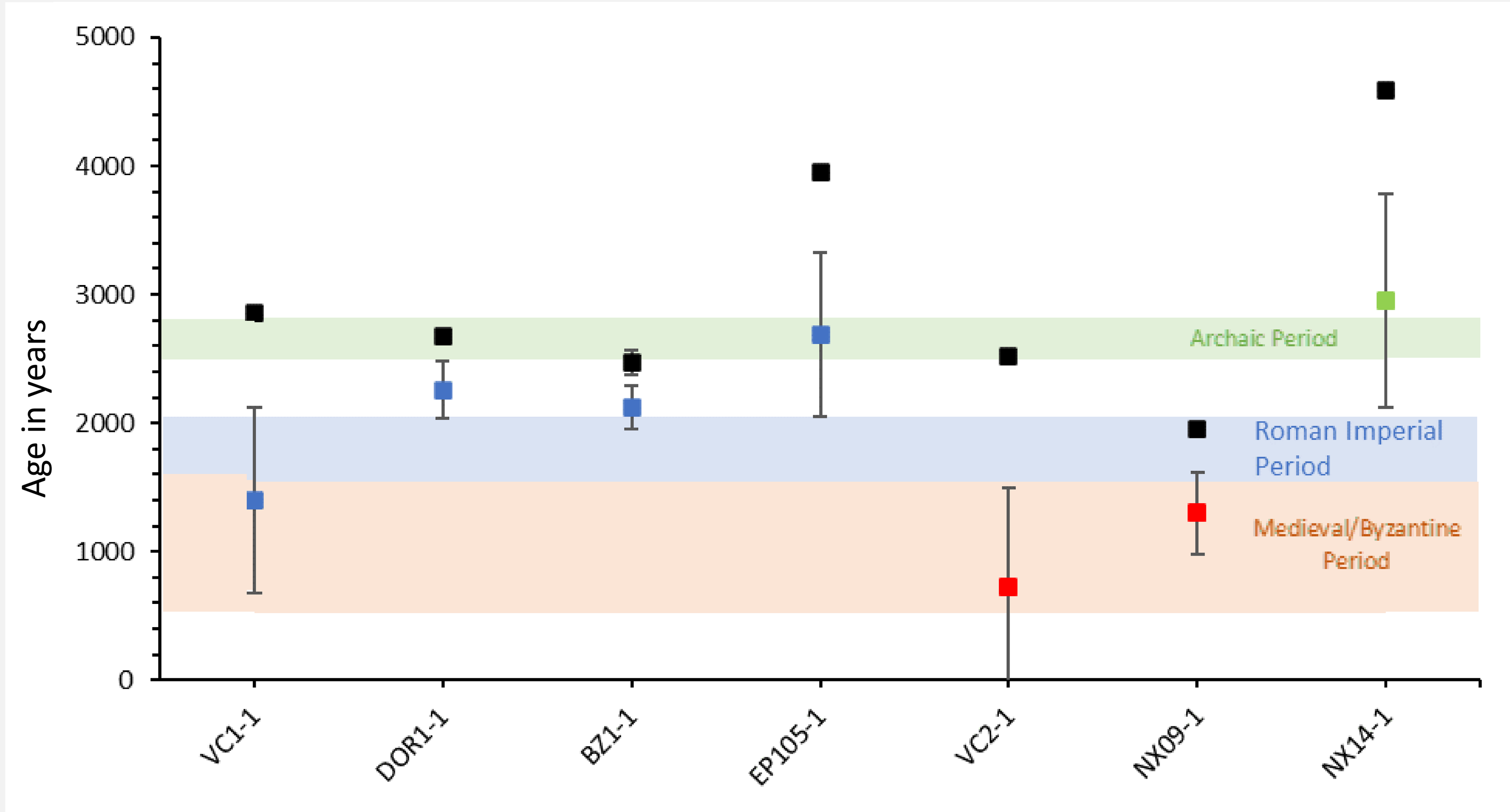

Figure 1: $^{230}Th/U$-ages for different carbonate samples from Aqueducts. Black squares indicate for detrital contamination uncorrected ages. Blue squares indicate the corrected ages for samples deposited during the Roman Imperial Period, while red and green squares are the corrected ages from samples from the Medieval/Byzantine and Greek Archaic Period respectively. For the correction of the ages it is assumed, that the $^{232}Th/^{238}U$ weight ratio of the detritus represents the average ratio in the upper continental crust and that ^{238}U, ^{234}U and ^{230}Th are in secular equilibrium (e.g. Wedepohl, 1995).

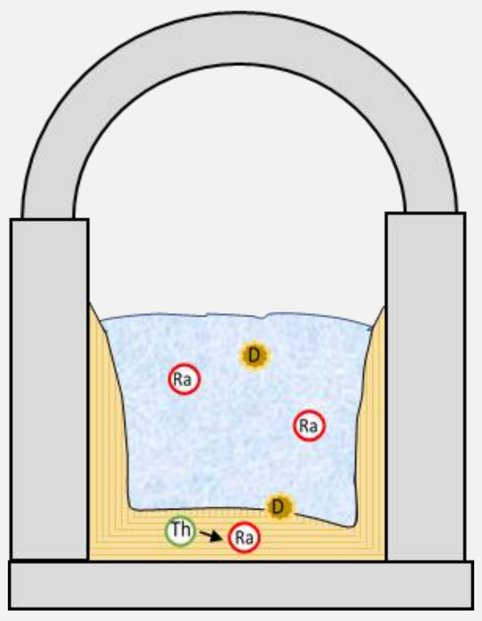

Figure 2: Schematic of an aqueduct channel with carbonate deposits on the floor and walls of the channel. The three possible sources of ^{226}Ra (detrital, ingrowth and excess) are also indicated.

Radium in terrestrial carbonates

In general, there are three possible sources of ^{226}Ra in terrestrial carbonate deposits:

- Excess ^{226}Ra, which is present in the water and incorporated during the formation of the deposit
- Detrital ^{226}Ra associated with clay and other detrital material present in the carbonate
- Ingrowth ^{226}Ra from the radioactive decay of its parent ^{230}Th.

To make use of ingrowth ^{226}Ra as a new dating tool it is necessary to correct the amount of ^{226}Ra in the sample for its excess and detrital components. The excess component is corrected using Ba and the detrital component is corrected using the ^{232}Th present in the sample.

Calculation of the $^{226}Ra/U$-age

The $^{226}Ra/U$-age is calculated based on Bateman´s solution for a system of differential equations (Bateman, 1908). The first part of the equation is given in the following:

$$\frac{^{226}Ra}{^{238}U} = 1 + \frac{\lambda_{230} * \lambda_{226} * \left(\frac{^{234}U}{^{238}U} + 1\right)}{(\lambda_{234} - \lambda_{230}) * (\lambda_{234} - \lambda_{226})} + \cdots \qquad \text{(Eq. 1)}$$

λ denotes the decay constant in years for the different members of the decay chain starting with ^{238}U. The equation considers the amount of ingrowth ^{226}Ra coming from its parent ^{230}Th over time, which itself is dependent on the decay of ^{238}U and ^{234}U as well as the decay from ^{226}Ra to ^{222}Rn. To calculate the age of a sample the corrected $^{226}Ra/U$ and $^{234}U/^{238}U$ ratios are needed. The model calculations to obtain these ratios are based on the work of Ludwig and Titterington (1994). We adapted their calculations to the ^{226}Ra-^{232}Th-Ba-system to find the best-fit line for a three-dimensional isochron diagram.

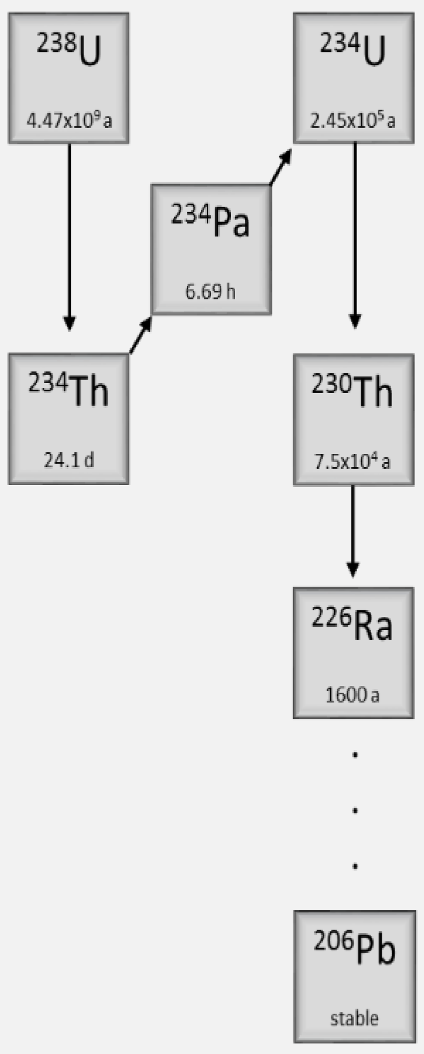

Figure 3: Decay chain of ^{238}U

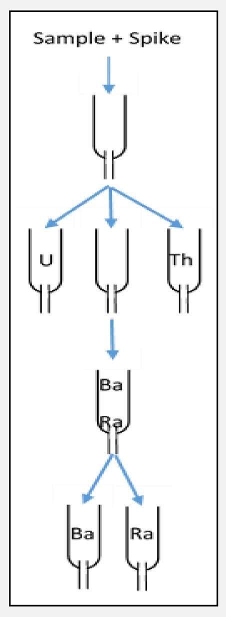

Figure 4: Schematic of column chromatography for the separation of U, Th, Ra and Ba

Chemical separation

Separation of U, Th, Ra and Ba is done from one single aliquot of sample material with column chromatography.

This allows for a direct comparison of the traditional $^{230}Th/U$-ages and the novel $^{226}Ra/U$-ages from the same aliquot of sample material.

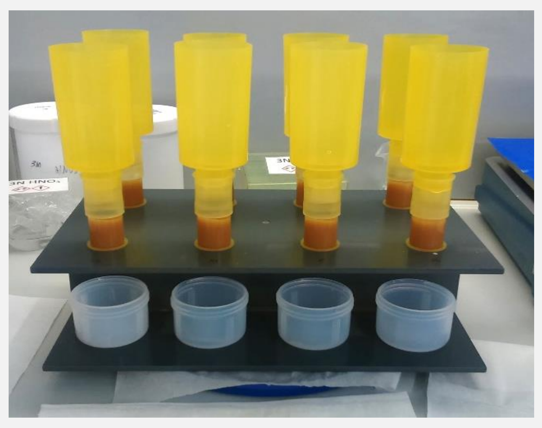

Figure 5: Setup for chemical separation

Results

Model simulations show that the system is influenced by the amount of ^{232}Th and U in the sample, like it is the case for the traditional $^{230}Th/U$-dating:

- High ^{232}Th content leads to elevated ages and larger errors
- Low ^{232}Th coupled with high U content leads to smaller errors
- High ^{232}Th content overprints the effect of high U content

Besides the amount of Th and U, the system is also influenced by the amount of Ra and Ba present in the sample:

- High excess Ra content leads to elevated ages
- High Ba content leads to elevated ages

Another important aspect in the accuracy of the obtained model ages is the analytical error. Model simulations indicate, that $^{226}Ra/U$-ages are less influenced by

- Larger analytical error in Th
- Larger analytical error in U

than the traditional $^{230}Th/U$-ages and that

- Larger analytical errors in Ra and Ba

play only a minor role for the uncertainty of the model ages.

First rough measurements of the aqueduct carbonates indicate very low excess ^{226}Ra content for all the samples, while the amount of Ba is varying from sample to sample. The relatively low U-content and high ^{232}Th content make these samples challenging to date for the traditional $^{230}Th/U$-method, as well as the novel $^{226}Ra/U$-approach. The next step is the comparison of the model results with the data obtained from the samples.

References

Bateman H. (1908): The solution of a system of differential equations occurring in the theory of radio-active transformations. Proc. Cambridge Phil. Soc., 15, 423-427.
Ludwig K. R. and Titterington D. M. (1994):Calculation of 230Th/U ischrons, ages, and errors. Geochim. Cosmochim. Acta, 58, 5031-5042.
Wedepohl, K. H. (1995): The composition of the continental crust. Geochim. Cosmochim. Acta, 59(7), 1217-1232.

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