

THE $^{230}\text{Th}/^{234}\text{U}$ DISEQUILIBRIUM DATING OF CAVE TRAVERTINES

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The age of a "pure" calcite speleothem can be determined from the ratio of the ^{230}Th to ^{234}U contents. The straightforward age determination is upset if thorium or uranium bearing detrital contaminants are present in the calcite. The importance and possibility of correcting for detrital contamination is discussed and examples given of the magnitude of the corrections for particular samples from the Petralona cave in North Greece.

1. Introduction

The precipitation of calcium carbonate from cave waters may be accompanied by the deposition of a small proportion of uranium (say, up to 5 ppm) but should be free from thorium [1]. Thus, if neither uranium nor thorium migrate into or out of the calcite deposit, the formation of ^{230}Th (half-life 75200 y) by the decay of ^{234}U (half-life 247000 y) can provide a measure of the age of the deposit. This dating technique has had considerable application [2]. The sample of travertine of interest is processed chemically to extract the thorium and the uranium contents as thin deposits for alpha particle spectrometry to determine the activities of the relevant isotopes. Many travertines of interest contain detrital material inseparable from the calcite, so that when the travertine sample is processed chemically the detritus may contribute thorium and uranium. Some procedures have been adopted or proposed to deal with this contamination [2]. The thorium from the detritus will contain both ^{230}Th and ^{232}Th and so the alpha particles from the latter can provide a measure of the ^{230}Th contribution from the detritus if the $^{230}\text{Th}:^{232}\text{Th}$ ratio can be measured for the detrital material [3]. If several samples from the same travertine deposit with different degrees of detrital contamination are available the $^{230}\text{Th}:^{234}\text{U}$ content ratio may be plotted against the $^{232}\text{Th}:^{234}\text{U}$ content ratio as a measure of detrital thorium contamination. Extrapolation to zero ^{232}Th content can then provide the $^{230}\text{Th}:^{234}\text{U}$ ratio for the pure calcite [4]. Commonly the calcium carbonate is dissolved in nitric acid as the first step in the chemical processing and any insoluble residue (due to detritus) is

discarded. It is during this process that thorium and uranium may be leached from the detritus and so possibly lead to an error in age determination. In the present work the detrital residue was dissolved in another reagent and was also analysed for thorium and uranium content. A correction was then applied on the assumption that the ratio of thorium to uranium leached from the detritus when dissolving the calcium carbonate is the same as in the detrital residue [5]. Thus a correction can be made when there is no reason to assume a common age for several samples and so when an extrapolation approach, such as proposed by Schwarcz [2], is not possible. Travertine samples from the Petralona cave in North Greece were investigated. Ages corrected from the detrital residue analysis are compared with uncorrected ages and with ages corrected by the simpler procedure [3] of assuming that only detrital thorium is significant.

2. Experimental procedure

The thorium and uranium were chemically separated from the calcium carbonate of the travertine sample along the lines used previously [1] with improvement to the thorium extraction efficiency as proposed by Harmon [6]. The chemical procedure is summarised in the flow diagram, fig. 1. The thorium and uranium extraction efficiencies were taken into account by spiking the calcium carbonate solution with a weak ^{228}Th and ^{232}U solution of known composition. Thin deposits of thorium and uranium were formed by evaporation on stainless steel discs. The yields of the different isotopes were determined by alpha particle spectroscopy using a silicon surface barrier detector of surface area 350 mm^2 at a distance of 8 mm from the sample and with an energy resolution of 47 keV fwhm. Typical alpha par-

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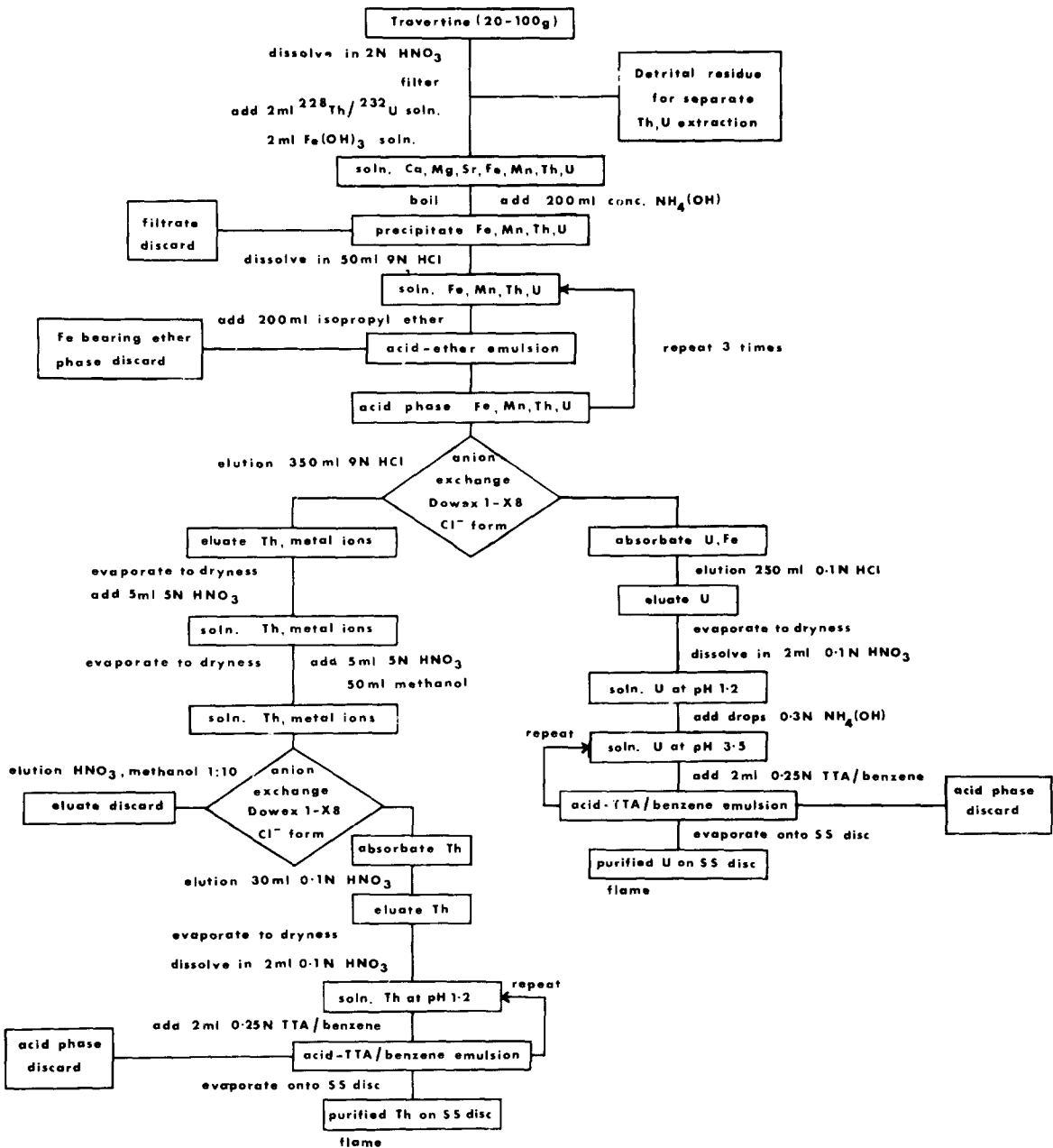


Fig. 1. Flow diagram of the thorium and uranium chemical extraction procedure.

ticle energy spectra are shown in fig.2. From such spectra, knowing the $^{228}\text{Th} : ^{232}\text{U}$ activity ratio for the spike solution, the age t of a "pure" calcium carbonate travertine can be determined from,

$$\frac{^{230}\text{Th}}{^{234}\text{U}} = \frac{^{238}\text{U}}{^{234}\text{U}} (1 - e^{-\lambda_{230}t}) + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left(1 - \frac{^{238}\text{U}}{^{234}\text{U}} \right) [1 - e^{-(\lambda_{230} - \lambda_{234})t}],$$

where $^{230}\text{Th}/^{234}\text{U}$ and $^{238}\text{U}/^{234}\text{U}$ are the measured activity ratios and λ_{230} and λ_{234} are the decay constants for ^{230}Th and ^{234}U alpha decay respectively. Such an analysis gives the uncorrected ages in table 1. Of course if the alpha particle energy spectra indicate the presence of ^{232}Th then there is some detrital contamination and the possibility of error in the deduced age.

The first approach [3] to correcting for detrital ^{230}Th indicated by the presence of ^{232}Th was to estimate the

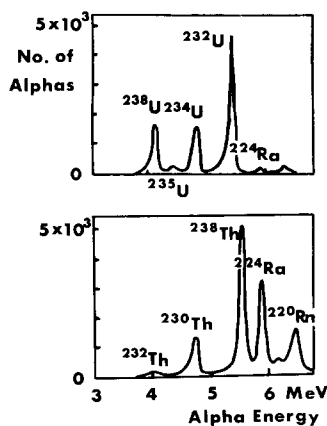


Fig. 2. Typical alpha particle energy spectra.

^{230}Th activity appropriate to the dating of the calcite from,

$$^{230}\text{Th} = ^{230}\text{Th}_{\text{obs}} - \left(\frac{^{230}\text{Th}}{^{232}\text{Th}} \right)_i ^{232}\text{Th}_{\text{obs}} e^{-\lambda_{230}t},$$

where $(^{230}\text{Th}/^{232}\text{Th})_i$ is the activity ratio for the detritus when incorporated into the travertine on formation. Because of the long half-life of ^{232}Th (1.48×10^{10} y) the activity ratio $(^{230}\text{Th}/^{232}\text{Th})_i$ is assumed to be the same as in present day detrital samples. Ages determined in this way are identified as "initial Th only correction" in

table 1. However this correction takes account only of ^{230}Th present in the detritus at the time of formation of the travertine and not of ^{230}Th formed by the decay of ^{234}U in the detritus.

More information on the thorium and uranium content of the detrital component of the travertine was sought by analysis of the nitric acid insoluble residue from the dissolution of the calcium carbonate. The residue was completely dissolved in a mixture of HClO_4 and HF acids and the thorium and uranium extracted as in fig. 1 for alpha particle spectroscopy to determine the ^{230}Th , ^{232}Th , ^{234}U and ^{238}U activities of the detrital residue. It was assumed that the ratio of thorium to uranium leached from the detritus when dissolving the calcium carbonate is the same as in the detrital residue. It follows from this assumption that the ^{230}Th , ^{234}U and ^{238}U activities for use in dating the calcite are given by,

$$^{230}\text{Th} = ^{230}\text{Th}_o - ^{232}\text{Th}_o \left(^{230}\text{Th}_d / ^{232}\text{Th}_d \right),$$

$$^{234}\text{U} = ^{234}\text{U}_o - ^{232}\text{Th}_o \left(^{234}\text{U}_d / ^{232}\text{Th}_d \right),$$

$$^{238}\text{U} = ^{238}\text{U}_o - ^{232}\text{Th}_o \left(^{238}\text{U}_d / ^{232}\text{Th}_d \right),$$

where the suffix "o" refers to the activities observed from dissolution of the calcite and the suffix "d" to the activities determined from dissolution of the detrital residue. Ages deduced from such corrected activities are identified in table 1 as "Th/U correction".

The detrital material in the travertines investigated was predominantly clay. The relevant activities leached from a clay sample by weak nitric acid, as used to

Table 1
 $^{230}\text{Th}/^{234}\text{U}$ disequilibrium ages of travertine deposits from the Petralona cave, Greece.

Sample	P-ARST	P-1B	P-4-1	P-15A	P-12 top	P-13
Th p.p.m. ^a	0.18	0.53	0.19	0.14	0.91	0.73
U p.p.m. ^a	0.24	0.72	0.53	0.68	0.75	2.70
$(^{230}\text{Th}/^{234}\text{U})_{\text{obs}}$	0.63 ± 0.04	0.79 ± 0.09	0.79 ± 0.05	0.87 ± 0.08	0.95 ± 0.05	0.98 ± 0.05
$(^{230}\text{Th}/^{234}\text{U})_{\text{corr}}$	0.49 ± 0.06	0.68 ± 0.10	0.76 ± 0.06	^b	0.78 ± 0.04	0.78 ± 0.04
$(^{234}\text{U}/^{238}\text{U})_{\text{obs}}$	1.2 ± 0.1	1.3 ± 0.1	1.128 ± 0.004	1.07 ± 0.03	1.27 ± 0.05	1.32 ± 0.03
$(^{234}\text{U}/^{238}\text{U})_{\text{corr}}$	1.8 ± 0.3	4.0 ± 0.6	1.34 ± 0.06	^b	1.17 ± 0.05	1.66 ± 0.16
$(^{230}\text{Th}/^{232}\text{Th})_{\text{obs}}^{\text{c}}$	3.0	4.4	49.0	13.8	3.0	15.0
Age (10^3 y)						
uncorrected	104^{+13}_{-11}	152^{+43}_{-32}	160^{+23}_{-19}	213^{+80}_{-46}	250^{+50}_{-35}	270^{+60}_{-40}
$(^{230}\text{Th}/^{232}\text{Th})_i^{\text{d}}$	1.25	1.25	2.08	1.25	1.44	1.6
Age (10^3 y)						
initial Th only						
correction	73^{+16}_{-15}	128^{+51}_{-40}	137^{+26}_{-23}	204^{+85}_{-50}	200^{+55}_{-40}	260^{+60}_{-40}
Age (10^3 y)						
Th/U correction	75^{+12}_{-11}	105^{+25}_{-21}	140^{+23}_{-20}	^b	155^{+20}_{-16}	150^{+15}_{-13}

^a Accuracy approximately $\pm 3\%$.

^b No detrital residue in this case.

^c Accuracy approximately $\pm 5\%$.

^d The initial thorium isotope ratio was taken to be equal to the value measured for relevant detritus.

Table 2
The leaching of thorium and uranium from clay by weak nitric acid.

	$\frac{^{230}\text{Th}}{^{232}\text{Th}}$	$\frac{^{234}\text{U}}{^{238}\text{U}}$	Th (p.p.m.) (accuracy +50%)	U (p.p.m.)	$\frac{\text{Th}}{\text{U}}$
From filtrate solution in weak nitric acid	1.5 ± 0.2	0.8 ± 0.3	1.1	0.3	3.5 ± 0.2
From dissolution of the residue	1.6 ± 0.2	1.0 ± 0.3	24.5	8.1	3.1 ± 0.2
From dissolution of all of a sample of the clay	1.6 ± 0.3	1.2 ± 0.3	28.4	8.8	3.2 ± 0.2

dissolve the calcium carbonate were compared with the activities found in the nitric acid insoluble residue and in a sample of the original clay, as shown in table 2. Within the limited accuracy of such measurements the Th/U ratios were the same in the leached, residue and total samples, as were the $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios. It is also encouraging in relation to the correction procedure that the amounts of thorium and uranium leached from the clay by the nitric acid were quite small.

3. Discussion

Inspection of table 1 shows the importance of correcting for thorium and uranium leached from detritus for travertine samples from the Petralona cave, the corrections ranging from a few percent to almost a factor of two. Ku et al. [7] also dissolved the detrital residue in $\text{HF}-\text{HClO}_4$ reagent, analysed it for thorium and uranium content and devised a correction scheme on the assumptions that initially the calcium carbonate contains negligible amounts of ^{230}Th and ^{232}Th or that it has a $^{230}\text{Th}:^{232}\text{Th}$ ratio similar to that in the detritus, that secular equilibrium exists in the detritus and that in the acid leaching of the detritus no fractionation of the thorium isotopes occurs. Their scheme differs from the present one in that preferential leaching of thorium or of uranium from the detritus is allowed for and secular equilibrium is assumed whereas the present scheme assumes the thorium and uranium to be leached from the detritus in proportion to their content in the detritus and avoids the assumption of secular equilibrium. Schwarcz [2] has proposed a scheme which avoids either of these assumptions about the detrital contribution of thorium and uranium but which requires the analysis of the carbonate and the detrital residue from a number of samples of travertine of common age, each sample providing by chance a different degree of detrital con-

tamination so that extrapolation to zero contamination is possible.

Unfortunately no independent check on the corrected ages in table 1 is available. Similar ages would not be expected for most of the samples since they came from different parts of the cave and from different travertine layers. However it is encouraging to note that samples P-4-1 and P-12 top both came from the top layer of travertine at positions separated by about 5 m. Their uncorrected ages are quite different while their corrected ages agree as might be expected for the same layer of travertine deposit.

An account, including further dating work, of the anthropological and archaeological significance of the Petralona cave dates is in preparation.

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