REFLECTIONS ON THE $^{230}$Th/U DATING OF DIRTY MATERIAL

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Abstract: High correlation coefficients between the activity ratios of the uranium and thorium isotopes common for the „isochron” approach of $^{230}$Th/U dating of dirty material mask the requirement to check for closed-system conditions of uranium in addition to the detrital correction of $^{230}$Th/U ages. The difficulty to calculate standard deviations of $^{230}$Th/U dates derived by the „isochron” approach complicates the problem. The methodical reasons are discussed. Closed-system conditions are checked by the $^{234}$U/$^{238}$U – $^{230}$Th$^{238}$U AR plot which can also be used to carry out least-squares fitted detrital correction of $^{230}$Th/U ages of dirty material.

1. PRACTICE OF $^{230}$Th/U DATING OF DIRTY MATERIAL

The idealized model for $^{230}$Th/U dating is based on two assumptions:

1. Terrestrial material (e.g. speleothem) contained solely uranium immediately after its formation and was free of („detrital”) thorium.

2. The dated material had behaved as a closed system for uranium through the time of aging.

During aging $^{234}$U has decayed to $^{209}$Th (supported, radiogenic) and the $^{230}$Th/$^{234}$U activity ratio (AR; indicated by angular brackets in equations) has risen from 0 at the zero age towards the maximum of unity at infinite age. The conventional $^{230}$Th/U age $A$ is given by

$$ \left[ \frac{^{234}U}{^{230}Th} \right] = \left[ \frac{^{238}U}{^{234}U} \right] \left( 1 - e^{-\lambda_{230}A} \right) + \left( 1 - \frac{^{238}U}{^{234}U} \right) $$ \hspace{1cm} (1.1)

The $\lambda$‘s stand for the decay constants of the corresponding uranium and thorium isotopes (Ivanovich and Harmon, 1992). The confidence interval of $A$ is calculated with Eq. (1.1) using modified ARs

$$ +\sigma A \Rightarrow \left[ ^{234}U - \sigma^{234}U \right] / \left[ ^{230}Th' + \sigma^{230}Th' \right] $$

$$ -\sigma A \Rightarrow \left[ ^{234}U + \sigma^{234}U \right] / \left[ ^{230}Th' - \sigma^{230}Th' \right] $$ \hspace{1cm} (1.2)

Natural material differs from the ideal (pure) one. During a short period of formation detrital thorium usually becomes admixed with an initial $^{230}$Th/$^{232}$Th AR (also called initial $Th$ index $f_i$). This unsupported $^{230}$Th decays, while the activity of the supported $^{230}$Th increases. The activity of $^{230}$Th' is calculated from the measured total $^{230}$Th activity ($=Th' + Th'*$) using Eq. (1.3) (Kaufman and Broecker, 1965). The difference between the uncorrected $^{230}$Th/U age calculated from the total $^{230}$Th activity, and the detritus-corrected $^{230}$Th/U age calculated from $^{230}$Th' increases with Th index or the $^{232}$Th activity growth, decreasing the age and uranium content of the sample. Standard deviation of the detritus-corrected $^{230}$Th/U age is obtained analogously to the method described above for the $^{230}$Th/U age. $\sigma^{230}$Th' is obtained by applying error propagation to Eq. (1.3). Commonly, $\sigma^{230}$Th and $\sigma^{230}$Th' do not differ too much.

$$ \left[ ^{230}Th_{total} \right] = \left[ ^{230}Th' \right] + \left[ \frac{^{230}Th}{^{232}Th} \right] / \left[^{232}Th \right] $$

$$ = \left[ ^{230}Th' \right] + 4f_i \left[ ^{232}Th \right] $$ \hspace{1cm} (1.3)

In most cases, $f_i$ (or the present value $f$) is not known but sometimes arbitrary chosen to be Unity. The initial thorium index $f_i$ at the time of formation ranges from 0.5 to more than 10. As a result detritus-corrected $^{230}$Th/U ages are regularly erroneous if the uncorrected and detritus-corrected $^{230}$Th/U ages deviate more than 10 %. This is an often case (Ivanovich and Harmon, 1992).

The described situation should be elucidated by an example. I dated two marl layers in one sediment profile in the Gobi Desert, China, applying the total sample dissolution (TSD) method (Kaufman, 1993). The individual $^{230}$Th/U ages are compiled in Table 1 for two assumed thorium–index values – Zero and Unity – and the actual one determined by the „isochron” approach which will be described later. The obtained $^{230}$Th/U ages widely deviate from each other. It is obvious that the thorium index $f$ must be very accurately known.

The „isochron” approach (Ku and Liang, 1984) directly yields detritus-corrected $^{230}$Th/U ages. The basic assumption is that that the detrital thorium with an initial
230Th/232Th, AR is admixed in deviating proportions into the newly formed material.

Dividing Eq. (1.3) by the [232Th] activity and multiplying the first term on the right side [230Th] by [234U/232U] AR we obtain the equation of a straight line (Fig. 1).

\[
\left(\frac{230}{232}\text{Th}\right) = \left(\frac{230}{232}\text{Th}\right)_0 + f \cdot e^{-\lambda t}
\]

(1.4)

The slope of the straight mixing line („isochron”) in the plot of 230Th/232Th AR versus 234U/232Th AR („isochron” plot; Fig. 1) equals the actual 230Th/234U AR which is the crucial parameter to calculate 230Th/U ages (Eq. (1.1)). The intersection of the „isochron“ on the Y axis yields the present 230Th/232Th AR or the present thorium index f. The ARs of material with little detrital thorium plots on the right and those of impure material on the left side of the graph. Usually the so-called „isochron“ approach is applied for which three or, better, many more thorium and uranium isotope activity ratios (AR) of coeval samples must be determined. The „isochron“ approach for 230Th/U dating is widely applied for dirty material. A wealth of papers has been published, for instance, on the 230Th/U dating of impure carbonate.

In papers on „isochron“-derived 230Th/U ages seldom the standard deviations are given though a DOS Shell program by Ludwig and Titterington (1994) is available. Reservations may exist due to the theoretical complexity of the developed maximum likelihood algorithm. Another problem may be the growing distance to DOS programs.

This complexity is the result of the erroneous activity ratios on both axes which are, according to Eq. (1.4), correlated to each other with the common denominator [232Th]

(correlation coefficient r ≠ 0). The correlation coefficient r of two AR of 230Th/232Th and 234U/232Th (Eq. (1.1)) is given by

\[
r = \frac{\sigma_{[234U]230Th} \cdot \sigma_{[232Th]}^2 + \sigma_{[232Th]} \cdot \sigma_{[234U]}^2}{\sigma_{[234U]230Th} \cdot \sigma_{[232Th]}^2 + \sigma_{[232Th]} \cdot \sigma_{[234U]}^2}
\]

(1.5)

In most case studies AR data fit the „isochron“ better than statistically expected (Fig. 2).

For the case of a common nominator of two isotope ratios the least-squares method (for Rb/Sr dating) was applied by York (1966, 1967 and 1969), Brooks et al. (1968) and Wendt (1986). The method by York (1966 and 1969) is the most generalized one and also applicable to 230Th/U dating. It allows both numerator and denominator to have largely differing standard deviations. The method by Brooks et al. (1968) presupposes that the standard deviations of the measured activity ratios are inversely correlated to each other (r = –1; York 1969). The method by Wendt (1986) is only valid if the confidence intervals of the ARs do not exceed certain ranges which is seldom the case for uranium and thorium activities.

The effect of the common nominator (232Th activity) to the calculation of detritally corrected 230Th/U ages is elucidated by one example. Table 2 shows the 230Th/U ages with their standard deviations, obtained by means of different methods to calculate 230Th/U ages by the „isochron” approach with data determined from a fen-peat profile Dierkshausen (York, 1966; Wendt, 1986; Geyh, 1994). Two cases are distinguished. In the Case A the measured standard deviations of the 230Th activity was applied, in Case B σ[232Th] = 0 was chosen. The confidence intervals of the „isochron” 230Th/U ages applying the actual standard deviations of the 230Th/232Th are > 19,000 yr while those for the assumed σ[232Th] = 0 are smaller by a factor of three.
The small sigma values are reasonable though not correct as they were calculated with an assumed standard deviation of $^{232}\text{Th}$ AR of Zero. The decisive parameter for calculating $^{230}\text{Th}/\text{U}$ ages is, however, the $^{230}\text{Th}/^{234}\text{U}$ AR which is not related to the $^{232}\text{Th}$ activity. The $^{232}\text{Th}$ activity becomes, however, implemented into the calculation if the $^{230}\text{Th}/^{234}\text{U}$ AR from dirty material is determined by the „isochron” approach – using the plot $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$.

Apart from the described problem to correct for the detrital contamination it remains to check whether the dated samples behaved as a closed system for uranium. Authors of papers describing their results of the „isochron” approach from tufa, travertine, calcarete and peat often claim that correlation coefficients larger than 0.98 – 0.99 confirm the reliability of the obtained $^{230}\text{Th}/\text{U}$ ages without an evident and manifest explanation. Exaggerated correlation coefficients for the dots in the „isochron” plot mean that their actual scatter is smaller than expected from the standard deviations of the ARs (Fig. 2).

2. EXPERIENCE GATHERED WITH THE „ISOCHRON” METHOD

There are three crucial problems which have not yet been thoroughly discussed:

1. Usually exaggerated correlation coefficients of the $^{230}\text{Th}/^{232}\text{Th}$ AR and $^{234}\text{U}/^{232}\text{Th}$ AR contradict Gaussian statistics.

2. Checks for closed-system conditions of uranium as a key presupposition for $^{230}\text{Th}/\text{U}$ dating. They are not made if high correlation coefficients are found as usual. Ivanovich and Harmon (1992) recommended for this purpose the application of the evolution plot $^{234}\text{U}/^{230}\text{U}$ AR versus $^{230}\text{Th}/^{234}\text{U}$ AR (Fig. 3). Data dots from coeval samples of the same origin form a narrow cluster if closed system conditions have behaved for uranium. However, the corresponding ARs from impure material do not form a cluster.

3. The application of the „isochron” approach requires measurements of uranium and thorium activities of many samples with a wide range of $^{230}\text{Th}/^{232}\text{Th}$ ARs or of detrital contamination. Under natural conditions, rocks with a relatively uniform petrologic composition may not fulfill this prerequisite, and the ARs form only one narrow cluster. Such a cluster does not allow to determine an accurate slope of the straight „isochron”. Discarding arbitrarily dots is no solution as any slope and $^{230}\text{Th}/^{232}\text{Th}$ AR may be obtained. Reliable $^{230}\text{Th}/\text{U}$ ages cannot be determined although the correlation coefficient is large.

Ludwig and Titterington (1994) therefore request to carry out at least six of the costly uranium and thorium isotope-analyses.

3. SOLUTION OF SOME PROBLEMS

The search for the reason why exaggerated standard deviations of the „isochron” $^{230}\text{Th}/\text{U}$ ages are common came to fruition in the theory of the „artificial isochrons” (Butler, 1982; Dodson, 1982). It is based on the „spurious” or „zero” correlation already recognized by Pearson in 1896.

„Zero” correlation

The ratio of unrelated variables with the same standard deviations divided by a common denominator of the same size yield a „zero” correlation of $> 0.5$. If the standard deviations differ from the coefficient „zero”, correlation increases to $> 0.75$. This explains why more or less all correlation coefficients are close to Unity if the least-squares fit of the „isochron” approach for both the thorium and uranium activity ratios was applied. Therefore, the common interpretation of authors that a high correlation coefficient evidences perfect fulfillment of the two presuppositions of the „isochron” approach is wrong. Instead, high r values are the result of exaggerated standard deviations due to „zero” correlation.

As the uranium and thorium activity ratios measured radiometrically or by TIMS are usually widely scattered, any correction for the „zero” correlation (Chayes, 1949 & 1971) cannot be applied. Such a calculation theoretically compensates for the increase of the correlation coefficient due to the „zero” correlation. As a result, the actual confidence interval of the least-squares fitted „isochron” $^{230}\text{Th}/\text{U}$ cannot be reliably estimated.

My solution was (Geyh, 1994) to estimate the present $^{230}\text{Th}/^{232}\text{Th}$ AR with exaggerated standard deviation ($\pm f \pm \sigma f$) using the „isochron” approach (York, 1966). This confidence interval is used for error propagation of

![Fig. 3. $^{234}\text{U}/^{230}\text{U} – ^{230}\text{Th}/^{238}\text{U}$ plot for the check of closed or open system conditions after Ivanovich and Harmon (1992).](image-url)
Eq. (1.3). This way was considered as acceptable since the contribution of the detrital correction to the total standard deviation of the $^{230}\text{Th}/U$ age is usually small. Single $^{230}\text{Th}/U$ ages of coeval samples with an „isochron“-derived, detritus correction (Eq. (1.1) and (1.3)) are finally checked with the $\chi^2$ test (Eq. (3.6)). The weighted mean and its standard deviation are calculated if the dates fit the test. This confidence interval approximates the true age of the dated material. In the already mentioned example from the Gobi Desert the present Th index was of 0.438 ± 0.006. The final $^{230}\text{Th}/U$ date is 54.3 ± 2.1 kyr which remains in good agreement with the actual scatter of the data of ± 2.3 kyr.

$$\chi^2 = \sum_{i=1}^{n} \left( \frac{A_i - \overline{A}_{\text{mean}}}{\sigma_i} \right)^2$$

(3.6)

This method was applied for $^{230}\text{Th}/U$ dating of seven well-known sites with Eemian peat in Europe (Geyh et al., 1997). At least four samples with different detritus contamination were collected and analyzed from each site. The „isochron“ $^{230}\text{Th}/U$ ages and the mean of the „isochron“-derived detritus-corrected $^{230}\text{Th}/U$ ages are compiled in Table 3. The confidence intervals of the „isochron“ $^{230}\text{Th}/U$ ages are up to six times larger than the actual scatter of the dates (Gaussian statistics). Only the standard deviations of „isochron“-derived detritally corrected $^{230}\text{Th}/U$ dates (Geyh, 1994; Table 3) reflect the actual scatter of the $^{230}\text{Th}/U$ ages calculated by the Gaussian statistics. The wide confidence intervals of the „isochron“ $^{230}\text{Th}/U$ ages would even not allow to distinguish peat grown during the Eemian interglacial period (about 125 kyr) and the Brörup interstadial period (about 85 kyr). The plot $^{230}\text{Th}/^{232}\text{Th}$ AR versus $^{234}\text{U}/^{232}\text{Th}$ AR yields for every site perfect least-squares fits with a correlation coefficient >0.95.

Table 3. „Isochron“ $^{230}\text{Th}/U$ ages, in years, and „isochron“-derived detritally corrected $^{230}\text{Th}/U$ dates of European Eemian peat (Geyh et al., 1997).

<table>
<thead>
<tr>
<th>Site</th>
<th>„Isochron“ age</th>
<th>± $\sigma$ A</th>
<th>Isochron-derived detrital-corrected $^{230}\text{Th}/U$ age</th>
<th>± $\sigma$ A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dierkhausen</td>
<td>109,400</td>
<td>+ 30,300</td>
<td>111,400</td>
<td>± 3700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 23,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Großweil</td>
<td>113,900</td>
<td>+ 19,400</td>
<td>112,900</td>
<td>± 6500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 16,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hamburg qee 1</td>
<td>105,350</td>
<td>+ 20,550</td>
<td>102,800</td>
<td>± 5250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 17,250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nieselach</td>
<td>120,900</td>
<td>+ 6,450</td>
<td>113,450</td>
<td>± 1875</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 6,100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pfefferbichl</td>
<td>111,750</td>
<td>+ 5,350</td>
<td>111,750</td>
<td>± 2325</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 5,100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hinte</td>
<td>116,250</td>
<td>+ 32,200</td>
<td>111,350</td>
<td>± 8175</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 24,700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beerenmösl</td>
<td>111,700</td>
<td>+ 46,140</td>
<td>109,400</td>
<td>± 5350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 32,230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poisson statistics</td>
<td>109,370</td>
<td>+ 10,260</td>
<td>111,460</td>
<td>± 3360</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 9,550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gaussian statistics</td>
<td>112,750</td>
<td>± 4,970</td>
<td>110,290</td>
<td>± 3580</td>
</tr>
</tbody>
</table>

Ludwig and Titterington (1994) developed the maximum likelihood algorithm to estimate standard deviation of the $^{230}\text{Th}/U$ age. The introduction of the error correlation $r_r$ of the $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ ARs overcomes the problem of the „zero“ correlation. It is given by

$$r_r = \frac{\sigma_{^{230}\text{Th} / ^{232}\text{Th}}} {\sqrt{2 \times \sigma_{^{230}\text{Th} / ^{232}\text{Th}} \times \sigma_{^{234}\text{U} / ^{232}\text{Th}}}}$$

(3.7)

$r_r$ is a function of the standard deviations of the ARs interrelated by a common nominator and the unrelated AR. The success of both approaches is reflected from the data compiled in Table 4. My approach seems to deliver the smallest standard deviations.

The least-squares fitted detrital correction and check for closed-system conditions

The success of my approach to determine „isochron“-derived detritally corrected $^{230}\text{Th}/U$ ages stimulated reflections whether the „isochron“ approach is necessary. The $^{230}\text{Th}/^{232}\text{Th}$ AR and $^{234}\text{U}/^{232}\text{Th}$ AR of coeval dirty samples always yield widely scattering dots (Fig. 4). The dots move to the left applying detrital correction (Kaufman and Broecker, 1965) with iteratively rising values of the thorium index. The movement is the faster,
the higher is the detrital contamination. Finally, the dots form the narrowest cluster with a minimum width if the detrital correction is done with the present $^{230}\text{Th}/^{232}\text{Th}$ AR of the detrital contamination. It can be estimated by the „isochron” approach. The width of the cluster widens again if the thorium index is further increased.

I applied this method to the ARs of two marl layers in the Gobi Desert, China. The $^{230}\text{Th}/^{238}\text{U}$ AR was detritally corrected with iteratively rising thorium index. I started with $f = 0$ and used an increment of 0.01. The width of the cluster of the dots approached its minimum at $f = 0.44$ (Fig. 5). The „isochron” approach delivered $f = 0.0438 \pm 0.0006$. According to Fig. 5 the minimum scatter of the dots gives a reason for doubts whether all samples behaved as closed systems. In any case the „isochron” plot for the two marl layers (Fig. 6) with a correlation coefficient of $>0.99$ do not give any indication for that.

This iterative least-squares fitting to estimate the present $^{230}\text{Th}/^{232}\text{Th}$ AR of the detrital contamination has several advantages over the „isochron” approach:

1. The resulting present thorium index allows simple error-propagation calculation as well as avoidance of any complication related to the „zero” correlation.
2. This approach can also be applied to samples with relatively homogenous detrital contamination. In such cases the thorium and uranium isotope activity ratios form a cluster in the „isochron” plot and do not allow estimation of a reliable slope of the „isochron”.
3. This approach does not require more than two sets of ARs. Indeed, the precision of the $^{230}\text{Th}/^{238}\text{U}$ AR used for the calculation of the $^{230}\text{Th}/^{238}\text{U}$ date increases with a rising number of analytical results.
4. The $^{234}\text{U}/^{238}\text{U} - ^{230}\text{Th}/^{232}\text{Th}$ plot directly allows a check for closed-system conditions of uranium. A narrow cluster of the dots obtained after detrital correction with the present $^{230}\text{Th}/^{232}\text{Th}$ AR of the detrital contamination evidences closed-system conditions.

The chosen example demonstrates that the plot $^{234}\text{U}/^{238}\text{U} - ^{230}\text{Th}/^{232}\text{Th}$ may have relatively low sensitivity to indicate mobilization of uranium within a profile. Data dots of samples with indications for uranium mobilization still form relatively narrow clusters but often with a vertical eccentricity. Hence, the plot seems to deliver at least a qualitative indication on open-system
conditions for uranium. But this is better than that of the „isochron“ plot. Additional information may be obtained from plots of the uranium concentration, the $^{234}\text{U}/^{238}\text{U}$ AR, and the $^{230}\text{Th}/\text{U}$ ages versus the depth of a profile. Sometimes trends become visible which allow to identify processes as preferential leaching or accumulation of $^{234}\text{U}$. Models may allow quantitative estimates of the uranium balance if seeping groundwater did not remove uranium from the profile.

4. CONCLUSIONS

Precise $^{230}\text{Th}/\text{U}$ ages of impure materials (carbonates, peat) are obtained applying the least-squares fitted detrital correction of $^{230}\text{Th}/\text{U}$ ages. The applied $^{234}\text{U}/^{238}\text{U} - ^{230}\text{Th}^{*}/^{238}\text{U}$ AR plot delivers the present $^{230}\text{Th}^{*}/^{232}\text{Th}$ AR of the detrital contamination and at least a qualitative indication for closed-system conditions of uranium. The reliability of the corrected $^{230}\text{Th}^{*}/\text{U}$ ages is checked applying the $\chi^2$ test. This new approach is applicable to homogeneously contaminated dirty material and requires minimum two uranium and thorium isotope determinations. Hence, the method is less costly though the precision of the final $^{230}\text{Th}/\text{U}$ date rises with the square root of the number of analyses. As shown, in conclusion, the determination of $^{230}\text{Th}^{*}/\text{U}$ dates of impure material and the check of the reliability of these results is still open for further methodical improvements.

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