Three new ways to calculate average (U–Th)/He ages

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Abstract

Traditionally the "average" age of multiple (U–Th)/He analyses has been calculated as the arithmetic mean age. This paper presents three alternative methods: (a) in analogy with the fission track method, the pooled age is calculated by adding the respective U, Th and He abundances of several grains together, thereby generating one "synthetic" multi-grain measurement; (b) the isochron age is the slope of helium concentration versus present-day helium production; (c) the central age is computed from the geometric mean U–Th–He composition. Each of these methods is more appropriate than the arithmetic mean age in certain applications. The pooled age is useful for comparing single-grain with multi-grain analyses, while the isochron age can be used to detect "parentless helium". The central age is the most accurate and statistically robust way to calculate a sample average of several single-grain analyses because U, Th and He form a ternary system and only the central age adequately captures the statistics of this compositional data space. Fortunately, the expected difference between the arithmetic mean age and the central age is relatively small, less than 1% if the external age reproducibility is better than 15% (1σ). Finally, the (U–Th)/He age equation is visualized on a ternary diagram to illustrate that the α-ejection correction should be applied before, and not after age calculation, in order to avoid a partial linearization of the age equation. Including Sm as a fourth parent element precludes a straightforward visualization of the age equation on a two-dimensional plot. Nevertheless, the pooled, isochron and central age methods can be easily generalized to the case of (U–Th–Sm)/He dating. To facilitate the calculation of the central age, a web-based calculator is provided at http://pvermees.andropov.org/central.

1. Introduction

Radiogenic helium-geochronology is based on a summed set of differential equations:

$$\frac{d[\text{He}]}{dt} = -\sum_{i=1}^{n} \frac{d[\text{P}_i]}{dt} \quad \text{with}: \frac{d[\text{P}_i]}{dt} = -\lambda_i[\text{P}_i] \qquad (1)$$

where t=time, [He]=helium abundance, [P_i]=abundance of the ith parent nuclide and λ_i=decay constant of this nuclide (for $1 \le i \le n$). Despite the simplicity of Eq. (1), there are several ways to solve it, three of which will be discussed in Section 2. A linear approximation is accurate to better than 1% for ages up to 100 Ma, which can be considered satisfactory in comparison with the external reproducibility of (U–Th)/He dating (20–

30%; e.g., Stock et al., 2006). Nevertheless, most researchers rightly decide to calculate an exact age by numerical iteration. This paper raises the point that the accuracy gained by doing so is easily lost by two common practices: (1) performing the α-ejection after, rather than before age calculation and (2) using the arithmetic mean age to summarize a dataset of several single-grain measurements. After Section 3 presents two similarly biased alternatives to the arithmetic mean age that are appropriate for specific applications, Section 4 introduces the central age as the most accurate way to compute average (U–Th)/He ages. The accuracy gained by using the central age instead of the arithmetic mean age is comparable to that gained by iteratively solving the (U–Th)/He age equation instead of using the linear approximation. The only cost of the new procedure is computational complexity. To facilitate the calculations, they are implemented in an online calculator (http://pvermees.andropov.org/central) and illustrated on a published dataset of inclusion-bearing apatites. Finally, Section

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5 presents a generalized method to calculate central ages for datasets that also include a fourth radioactive parent, ^{147}Sm.

2. Calculating single-grain ages: many ways to skin a cat

Ten naturally-occuring long-lived α-emitting radionuclides exist on Earth: ^{144}Nd, ^{147}Sm, ^{148}Sm, ^{152}Gd, ^{174}Hf, ^{186}Os, ^{190}Pt, ^{232}Th, ^{235}U and ^{238}U. For the purpose of helium-thermochronology, all but the heaviest three of these nuclides can often be neglected because of their low abundance and low helium-yield. For example, only one α-particle is produced per ^{147}Sm, whereas six to eight are formed in the Th and U decay series. Further simplification is possible because the present-day ^{238}U/^{235}U-ratio is constant in the solar system (=137.88; Steiger and Jäger, 1977). Therefore, the ingrowth of helium with time (t) can be written as a function of the elemental U, Th and He abundances or concentrations:

$$[He] = \left(8\frac{137.88}{138.88}\left(e^{\lambda_{238}t} - 1\right) + \frac{7}{138.88}\left(e^{\lambda_{235}t} - 1\right) \right)$$
$$\times [U] + 6\left(e^{\lambda_{232}t} - 1\right)[Th] \quad (2)$$

with λ_{232}, λ_{235} and λ_{238} the decay constants of ^{232}Th, ^{235}U and ^{238}U, respectively. Eq. (2) has no analytical solution but is easy to solve iteratively. However, for young ages ($t \ll 1/\lambda_{235}$), a reasonably accurate linear approximation also exists:

$$t = \frac{[He]}{P} \quad (3)$$

with P the present-day helium production rate:

$$P = \left(8\frac{137.88}{138.88}\lambda_{238} + \frac{7}{138.88}\lambda_{235} \right)$$
$$\times [U] + 6\lambda_{232}[Th] \quad (4)$$

The accuracy of this solution will be discussed in Section 4. Besides being easy to implement, the linear age equation is useful for illustrative purposes and opens up some new applications which will be discussed in Section 3.

Meesters and Dunai (2005) introduced an alternative direct solution to the (U–Th)/He age equation:

$$t = \frac{1}{\lambda_{wm}} \ln\left(1 + \frac{\lambda_{wm}}{P}[He] \right) \quad (5)$$

with λ_{wm} the weighted mean decay constant:

$$\lambda_{wm} = \frac{\left(8\frac{137.88}{138.88}\lambda_{238}^2 + \frac{7}{138.88}\lambda_{235}^2 \right)[U] + 6\lambda_{232}^2[Th]}{P} \quad (6)$$

As shown by Meesters and Dunai (2005) and in Section 4, this solution is remarkably accurate for all practical applications.

3. Multi-grain ages

Eqs. (2–6) can be used to calculate (U–Th)/He ages from individual U, Th and He measurements, but do not explain how to calculate the "average" value of multiple analyses. Traditionally,

the average has been estimated by the arithmetic mean of the single-grain ages. This section will introduce two alternative methods for calculating average ages, and the next section will add a third. Each of these new methods is more appropriate than the arithmetic mean age in specific applications.

3.1. The pooled age

Helium can be extracted from the host grain either in a resistance furnace or by laser-heating in a micro-oven (House et al., 2000). In the former, but sometimes also in the latter case, it may be necessary to analyze multiple mineral grains together (e.g., Persano et al., 2007). "Pooling" several grains boosts the signal strength and sometimes averages out α-ejection correction errors caused by zoning and mineral inclusions. Vermeesch et al. (2007) introduced the "pooled age" as the best way to compare multiple single-grain ages with one or more multi-grain ages, or to compare two sets of multi-grain ages with each other (Fig. 1). The pooled age is calculated by adding the respective U, Th and He abundances (in moles) of several measurements together, thereby generating one "synthetic" multi-
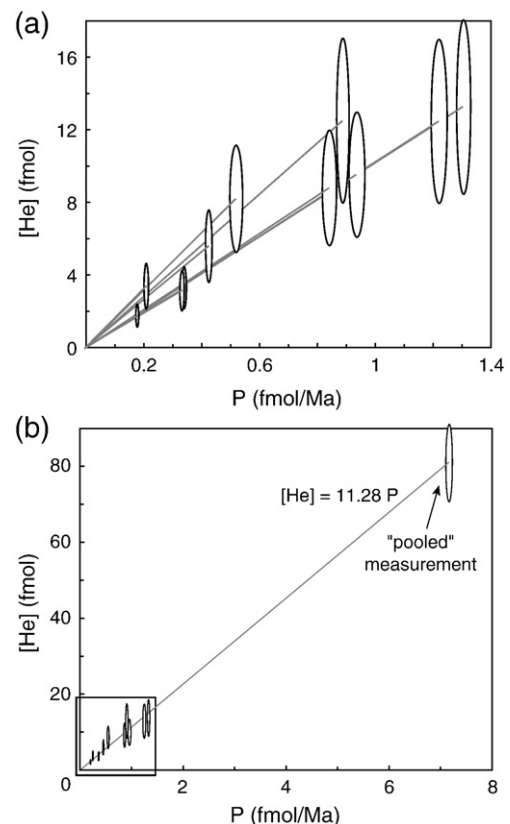

Fig. 1. Linearized (U–Th)/He diagram with a subset of the HF-treated inclusion-bearing apatite data of Vermeesch et al. (2007). 30% uncertainty (2σ) was added to the helium abundances to account for α-ejection correction induced scatter (Vermeesch et al., 2007). (a) According to the linear age equation, (U–Th)/He ages are given by the slopes of lines connecting each (P,[He])-point with the origin; (b) the "pooled" age is a "synthetic multi-grain age" calculated from the summed production rates and helium abundances of all the measurements. The box in 1.b marks the outline of 1.a. The pooled age of the sample is 11.28±0.14 Ma.

grain measurement. The age of the pooled measurement can then be calculated using any of the equations given in Section 2.

An obvious disadvantage of pooling compositional data is that the resulting age is biased to the high U, Th or He compositions. Because such bias can be associated with anomalous grains affected by radiation damage or implanted helium, the pooled age may be wrong by effectively giving extra weight to outliers. However, these objections are also true for standard multi-grain analyses, which cannot be avoided when dating small, young, or U–Th-poor grains (e.g., Persano et al., 2007). In short, the pooled age must be used for and only for averaging multi-grain aliquots.

3.2. The (U–Th)/He isochron

The previous section showed that (U–Th)/He data can be visualized on a two-dimensional plot of helium abundance or concentration versus-production (Fig. 1). To calculate a pooled age, it is important that [U], [Th] and [He] are elemental abundances, expressed in moles. If the data are recast in units of concentration, some of the bias towards high U–Th-grains disappears and the He–P diagram can be used to define a (U–Th)/He isochron. This is an unconstrained linear fit through a series of single-grain (P,[He]) measurements.

For an application of the isochron method, consider the U–Th rich mineral inclusions in apatite which are often held responsible for erroneously old (U–Th)/He ages, because they produce "parentless" He. This problem can be detected with the (U–Th)/He isochron. In the absence of mineral inclusions, the isochron goes through the origin (P=[He]=0). However, in the presence of α-emitting inclusions, the isochron is either not defined or does not go through the origin. For example, consider the worst-case scenario of an α-emitting zircon inclusion contained in an apatite without U and Th. The inclusion ejects He into the surrounding apatite that is measured following degassing by heating with a laser or in a resistance furnace. However, the zircon inclusion will not dissolve in the concentrated HNO_3 that is commonly used to digest apatites prior to U–Th analysis. Therefore, the apparent (U–Th)-production of such a sample is zero, and its isochron does not go through the origin of the [He]–P diagram.

Vermeesch et al. (2007) solved the parentless helium problem by dissolution of the apatite and its inclusions in hot HF. The effectiveness of this technique is illustrated by comparing an inclusion-rich sample from Naxos using the traditional HNO_3 method with an HF-treated aliquot of the same sample. The latter defines a well-constrained (U–Th)/He isochron with zero intercept, whereas the former does not (Fig. 2). Calculation of the isochron age, including error propagation, can easily be done using the Isoplot Excel add-in (Ludwig, 2003).

4. U–Th–He as a ternary system

The age-Eqs. (2), (3) and (5) do not specify the measurement units of [U], [Th] and [He]. These can be expressed in moles or moles/g, but they can also be non-dimensionalized by normalization to a constant sum: $[U'] \equiv [U]/([U]+[Th]+[He])$, $[Th'] \equiv [Th]/([U]+[Th]+[He])$ and $[He'] \equiv [He]/([U]+[Th]+[He])$ so that $[U']+[Th']+[He']=1$. Therefore, U, Th and He

form a ternary system, can be plotted on a ternary diagram, and are subject to the peculiar mathematics of the ternary dataspace. In a three-component system $(A+B+C=1)$, increasing one component (e.g., A) causes a decrease in the two other components (B and C). Another consequence of so-called data closure is that the arithmetic mean of compositional data has no physical meaning (Weltje, 2002).

4.1. Plotting the (U–Th)/He age equation on ternary diagrams

Following the nomenclature of Aitchison (1986), the ternary diagram is a 2-*simplex* (Δ_2). The very fact that it is possible to plot ternary data on a two-dimensional sheet of paper tells us that the sample space really has only two, and not three dimensions. As a solution to the compositional data problem, Aitchison (1986) suggested to transform the data from Δ_2 to $\mathbb{R}^2$ using the logratio transformation. After performing the desired ("traditional") statistical analysis on the transformed data in $\mathbb{R}^2$, the results can be transformed back to Δ_2 using the inverse logratio transformation (Fig. 3). Implementation details about the logratio transformation will be given in Section 4.3.

Ternary diagrams and logratio plots are useful tools for visualizing U–Th–He data and the (U–Th)/He age equation.
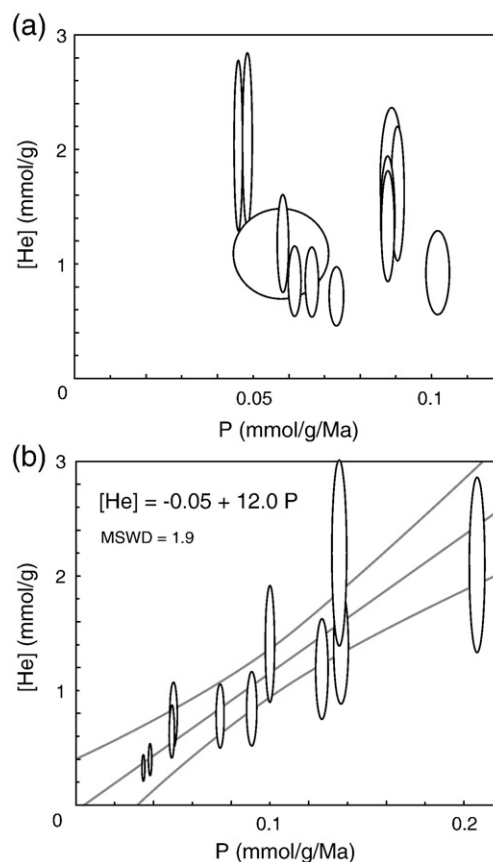

Fig. 2. (U–Th)/He isochron plots for inclusion-bearing apatites from Naxos, Greece (Vermeesch et al., 2007). (a) HNO_3-treated apatites do not plot on a line, indicating "parentless helium" caused by undissolved mineral inclusions containing "missing" U and Th; (b) HF-treated apatites from the same sample do form a well-defined isochron intersecting the origin, indicating that all parent and daughter nuclides are accounted for. The isochron age is 12.0±4.2 Ma.
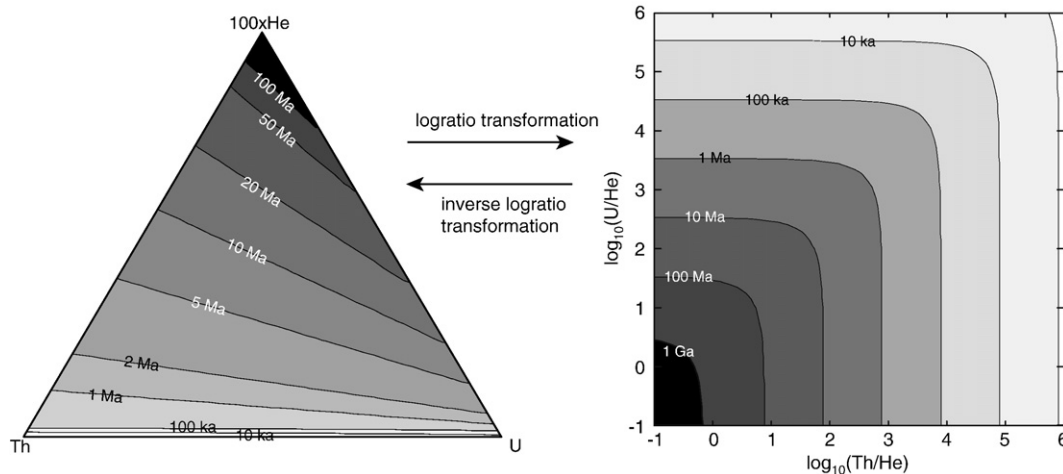
Fig. 3. Ternary U–Th–He data can be mapped to two-dimensional logratio-space without loss of information.

Thus, it can be shown that the linear age equation is accurate to better than 1% for ages up to 100 Ma (Fig. 4.a) whereas the equation of Meesters and Dunai (2005) reaches the same accuracy at 1 Ga (Fig. 4.b). Fig. 4.c represents a warning against applying the α-ejection correction after, rather than before the age calculation. This causes a partial "linearization" of the age equation and results in a loss of accuracy. For example, dividing an uncorrected (U–Th)/He age by an α-retention factor F_t of 0.7 results in a misfit that is 30% of the linear age equation misfit. To take full advantage of the accuracy of the exact age equation, one must divide [He] by F_t *before* calculating the (U–Th)/He age.

4.2. The central age

The logratio transformation is useful for more than just the purpose of visualization. It provides a fourth and arguably best way to calculate the average age of a population of single-grain (U–Th)/He measurements. The central age is calculated from the "average" U–Th–He composition of the dataset, where "average" is defined as the geometric mean of the single-grain U, Th and He measurements. The geometric mean of compositional data equals the arithmetic mean of logratio transformed data.

How important is the difference between the arithmetic mean age and the central age? To simplify this question, consider the special case of a sample with only one radioactive parent, say Th. Assume that $W = \ln([\text{He}]/[\text{Th}])$ is normally distributed with mean μ and standard deviation σ. Using the linearized age equation for clarity, the central age t_c is given by:

$$t_c = Ce^\mu \tag{7}$$

with $C = 1/(6\lambda_{232})$ for Th. Using the first raw moment of the lognormal distribution (Aitchison and Brown, 1957), the arithmetic mean age t_m is:

$$t_m = Ce^{\mu + \sigma^2/2} \tag{8}$$

so that the relative difference between t_m and t_c is:

$$\frac{t_m - t_c}{t_c} = e^{\sigma^2/2} - 1 \tag{9}$$

Using the second central moment of the lognormal distribution (Aitchison and Brown, 1957), the variance of the single-grain ages is given by:

$$\sigma_t^2 = C^2 \left(e^{\sigma^2} - 1\right)e^{2\mu + \sigma^2} \tag{10}$$

Plotting $(t_m - t_c)/t_c$ versus σ_t/t_c reveals that the central age is systematically younger than the mean age. Fortunately, the difference is small. For example, for a typical external reproducibility of ~25% (e.g. $\sigma_t/t = 11\%$ for Stock et al., 2006), the expected difference is <1% (Fig. 5). Finally, it is interesting to note that the geometric mean of the lognormal distribution equals its median. Therefore, the central age asymptotically converges to the median age. However, typical numbers of replicate analyses are not sufficient for this approach to be truly beneficial.

4.3. Application to HF-treated Naxos apatites

We now return to the sample of HF-treated inclusion-bearing apatites from Naxos that was previously used to illustrate the pooled and isochron age (Figs. 1 and 2). The raw data and the different steps of the central age calculation are given in Table 1. We will now walk through the different parts (labeled a, b and c) of this table.

(a) The upper left part of Table 1 lists the U, Th and He abundances of 11 single-grain analyses. Their respective single-grain ages (t) were calculated using the exact age equation, even though the linear age approximation (Eq. (3)) is accurate to better than 0.1% for such young ages (Fig. 4.a). The pooled U, Th and He abundances are obtained by simple summation of the constituent grains. Note that the helium abundances are corrected for α-ejection prior to being pooled. A nominal $\sigma = 15\%$ statistical uncertainty is associated with F_t, assuming randomly distributed mineral inclusions (Vermeesch et al., 2007). The pooled abundances were normalized to unity to facilitate comparison with the geometric mean composition (see below).

(b) To calculate the isochron age, the abundances are first rescaled to units of concentration (e.g. in nmol/g). This removes the bias towards large grains, which can dominate the pooled age calculation. The α-production rate P is given by Eq. (4). The linear regression (Fig. 2) was done
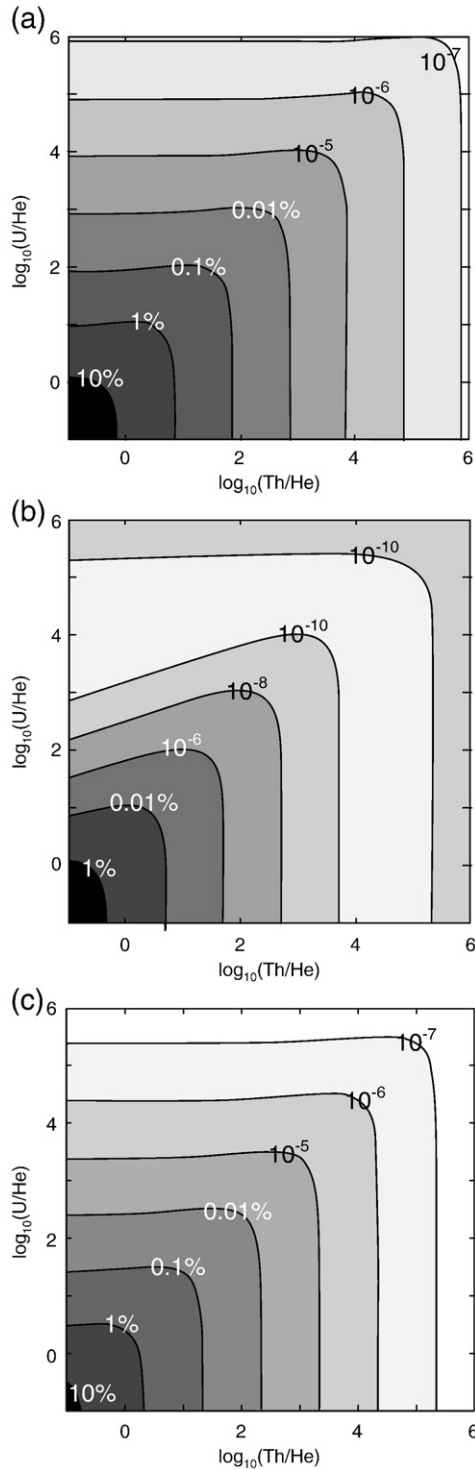
(a)

(b)

(c)

Fig. 4. (a) Relative misfit of the linear approximation (Eq. (3)) to the exact age equation (Eq. (2)); (b) misfit of the direct solution of Meesters and Dunai (2005) (Eq. (5)); (c) misfit caused by making the α-ejection correction after the age calculation (with F_t=0.7).
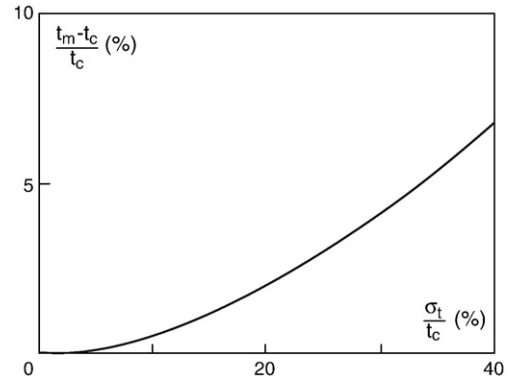
Fig. 5. Expected difference between the mean age t_c and the central age t_m plotted against the relative spread of the single-grain ages.

using Isochron 3.0 (Ludwig, 2003), yielding a slope of 12.0 ±4.2 Ma with an intercept of −0.05±0.45 nmol/g He.

(c) Central ages are somewhat more complicated to calculate than arithmetic mean ages, pooled ages or isochron ages. Therefore, these calculations will be discussed in more detail. First, transform each of the n single-grain analyses to logratio-space (Fig. 6):

$$V_i = \ln\left(\frac{[U_i]}{[He_i]}\right), W_i = \ln\left(\frac{[Th_i]}{[He_i]}\right) \quad (11)$$

For $i=1,...,n$. Note that this transformation can be done irrespective of whether the U, Th and He measurements are expressed in abundance units or in units of concentration. Following standard error propagation, the (co)variances of these quantities are estimated by:

$$\hat{\sigma}_{V_i}^2 = \left(\frac{\sigma U_i}{U_i}\right)^2 + \left(\frac{\sigma He_i}{He_i}\right)^2, \hat{\sigma}_{W_i}^2 = \left(\frac{\sigma Th_i}{Th_i}\right)^2 + \left(\frac{\sigma He_i}{He_i}\right)^2, \text{cov}_{V_i,W_i} = \left(\frac{\sigma He_i}{He_i}\right)^2 \quad (12)$$

Next, calculate the arithmetic mean of the logratio transformed data:

$$\bar{V} = \frac{1}{n}\sum_{i=1}^{n} V_i, \bar{W} = \frac{1}{n}\sum_{i=1}^{n} W_i, \quad (13)$$

With the following (co)variances:

$$\hat{\sigma}_{\bar{V}}^2 = \frac{1}{n^2}\sum_{i=1}^{n} \hat{\sigma}_{V_i}^2, \hat{\sigma}_{\bar{W}}^2 = \frac{1}{n^2}\sum_{i=1}^{n} \hat{\sigma}_{W_i}^2, \text{cov}_{\bar{V},\bar{W}} = \frac{1}{n^2}\sum_{i=1}^{n}\text{cov}_{V_i,W_i} \quad (14)$$

Note that Eq. (14) only propagates the internal (i.e. analytical) uncertainty, and not the external error. Single-grain (U–Th)/He ages tend to suffer from overdispersion with respect to the formal analytical precision for a number of reasons (Fitzgerald et al., 2006; Vermeesch et al., 2007). Therefore, it may be better to use an alternative equation propagating the external error:

$$\hat{\sigma}_{\bar{V}}^2 = \frac{\sum_{i=1}^{n}\left(V_i - \bar{V}\right)^2}{n(n-1)}, \hat{\sigma}_{\bar{W}}^2 = \frac{\sum_{i=1}^{n}\left(W_i - \bar{W}\right)^2}{n(n-1)}, \quad (15)$$

$$\text{cov}_{\bar{V},\bar{W}} = \frac{\sum_{i=1}^{n}\left(V_i - \bar{V}\right)\left(W_i - \bar{W}\right)}{n(n-1)}$$

Table 1

Step-by-step data reduction of the Naxos dataset of 11 inclusion-bearing apatites (with an arithmetic mean age of 11.58±0.20 Ma)

Samplename	MF1	MF2	MF4	MF5	MF6	MF7	MF8	MF9	MF10	MF11	MF12	Pooled	Normalized	Geommean
U (fmol)	588.2	874.4	294.3	595.9	645.1	867.2	221.9	225.9	131.1	356.9	107.0	4907.9	0.614343	0.598444
1se	6.9	7.6	3.5	7.7	8.4	8.9	2.6	2.3	2.0	6.8	1.5	19.7	0.001663	0.001535
Th (fmol)	451.3	628.0	156.4	260.3	370.2	374.2	163.5	136.3	130.3	203.5	126.0	3000.0	0.375517	0.391507
1se	7.0	11.1	2.6	4.3	7.0	5.0	2.8	2.0	2.0	4.6	2.4	17.7	0.001667	0.001537
He (fmol)	9.571	9.752	4.270	6.970	6.909	10.636	2.020	2.356	1.995	6.420	1.014	–	–	–
1se	0.086	0.091	0.069	0.104	0.088	0.108	0.065	0.066	0.065	0.082	0.061	–	–	–
Ft	0.77	0.74	0.78	0.80	0.73	0.85	0.65	0.79	0.59	0.79	0.63	–	–	–
He corr (fmol)	12.484	13.229	5.472	8.728	9.462	12.441	3.099	2.993	3.383	8.113	1.604	81.008	0.010140	0.010049
1se	0.113	0.123	0.089	0.130	0.120	0.126	0.099	0.084	0.110	0.104	0.096	0.363	0.000056	0.000084
age (Ma)	14.04	10.11	12.90	10.37	10.09	10.17	9.30	9.06	16.34	15.64	9.18	11.28		11.38
1se	0.21	0.14	0.26	0.21	0.19	0.15	0.32	0.27	0.59	0.36	0.57	0.07	(a)	0.10
U (nmol/g)	66.02	138.51	33.89	52.26	94.01	26.67	84.36	23.33	86.29	34.22	55.25			
1se	0.77	1.20	0.40	0.67	1.22	0.27	0.99	0.24	1.30	0.65	0.78			
Th (nmol/g)	50.65	99.49	18.01	22.82	53.94	11.51	62.16	14.07	85.72	19.51	65.09			
1se	0.79	1.76	0.30	0.38	1.01	0.15	1.06	0.21	1.34	0.44	1.25			
He corr (nmol/g)	1.401	2.096	0.630	0.765	1.379	0.383	1.178	0.309	2.226	0.778	0.828			
1se	0.211	0.315	0.095	0.115	0.208	0.058	0.181	0.047	0.342	0.117	0.134			
P (nmol/g/Ma)	0.09966	0.20706	0.04879	0.07376	0.13650	0.03760	0.12657	0.03408	0.13604	0.04966	0.09014			
1se	0.00122	0.00206	0.00061	0.00098	0.00187	0.00039	0.00158	0.00037	0.00207	0.00096	0.00138		(b)	
												mean		
V = ln(U/He)	3.852618	4.191134	3.984828	4.223570	4.222197	4.244235	4.271090	4.323750	3.657474	3.784100	4.200060	4.086823		
1se	0.014744	0.012684	0.020112	0.019728	0.018197	0.014382	0.034098	0.029882	0.035898	0.022891	0.061588	0.008801		
W = ln(Th/He)	3.587669	3.860234	3.352618	3.395110	3.666715	3.403901	3.965709	3.818314	3.650881	3.222292	4.363991	3.662494		
1se	0.017989	0.019986	0.023031	0.022244	0.022711	0.016756	0.036317	0.031678	0.036152	0.025976	0.062956	0.009453		
cov(V,W)	0.000081	0.000086	0.000262	0.000223	0.000162	0.000103	0.001025	0.000786	0.001061	0.000164	0.003592	0.000062	(c)	

This table should be read from a to c and from left to right: (a) U, Th and He abundances and pooled age (11.28±0.14 Ma). [He*] is the α-ejection corrected He-abundance ([He*]≡[He]/F_t); (b) The U, Th and He concentrations, required for the calculation of a (U–Th)/He isochron. The isochron age is 12.0±4.2 Ma. (c) logratio transformed data (V,W) and the (dimensionless) geometric mean composition, resulting in the central age of 11.38±0.20 Ma.

Error-weighting can be done by trivial generalizations of Eqs. (13)–(15), which are implemented in the web-calculator. The geometric mean composition is given by the inverse logratio transformation (Aitchison, 1986; Weltje, 2002):

$$\overline{[U]} = \frac{e^{\overline{V}}}{e^{\overline{V}} + e^{\overline{W}} + 1}, \quad \overline{[Th]} = \frac{e^{\overline{W}}}{e^{\overline{V}} + e^{\overline{W}} + 1}, \quad \overline{[He]} = \frac{1}{e^{\overline{V}} + e^{\overline{W}} + 1}$$

(16)

With variances:

$$\begin{pmatrix} \hat{\sigma}_{\overline{U}}^2 \\ \hat{\sigma}_{\overline{Th}}^2 \\ \hat{\sigma}_{\overline{He}}^2 \end{pmatrix} = \begin{pmatrix} a^2 & b^2 & 2ab \\ b^2 & c^2 & 2bc \\ d^2 & e^2 & 2de \end{pmatrix} \begin{pmatrix} \hat{\sigma}_{\overline{V}}^2 \\ \hat{\sigma}_{\overline{W}}^2 \\ cov_{\overline{V},\overline{W}} \end{pmatrix}$$

(17)

where

$$a = \frac{e^{\overline{V}}(e^{\overline{W}} + 1)}{(e^{\overline{V}} + e^{\overline{W}} + 1)^2} \quad b = \frac{-e^{\overline{V}+\overline{W}}}{(e^{\overline{V}} + e^{\overline{W}} + 1)^2}$$

$$c = \frac{e^{\overline{W}}(e^{\overline{V}} + 1)}{(e^{\overline{V}} + e^{\overline{W}} + 1)^2} \quad d = \frac{-e^{\overline{V}}}{(e^{\overline{V}} + e^{\overline{W}} + 1)^2}$$

$$e = \frac{-e^{\overline{W}}}{(e^{\overline{V}} + e^{\overline{W}} + 1)^2}$$

The central age is then simply calculated by plugging $[U^-]$, $[Th^-]$ and $[He^-]$ and their uncertainties into Eqs. (2), (3) or (5).

As predicted (Fig. 5), the arithmetic mean age is older than the central age. There is less than 2% disagreement between the arithmetic mean age ($\sim$11.58 Ma) and the central age ($\sim$11.38 Ma), and 7% difference between the pooled age ($\sim$11.28 Ma) and the isochron age ($\sim$12.0 Ma).

5. Generalized equations for (U–Th–Sm)/He dating

For reasons given in the Introduction, [147]Sm is often neglected in helium thermochronometry. However, in rare

cases it does happen that apatite contains high abundances of Sm, affecting the helium age on the percent level. This section will explain how to add a fourth radioactive parent to the methods described above. The exact age equation (Eq. (2)) and the present-day helium production rate (Eq. (4)) can easily be generalized to include Sm:

$$[He] = \left(8 \frac{137.88}{138.88} (e^{\lambda_{238}t} - 1) + \frac{7}{138.88} (e^{\lambda_{235}t} - 1) \right)$$
$$\times [U] + 6(e^{\lambda_{232}t} - 1)[Th] + 0.1499(e^{\lambda_{147}t} - 1)[Sm]$$

(18)

and

$$P = \left(8 \frac{137.88}{138.88} \lambda_{238} + \frac{7}{138.88} \lambda_{235} \right)$$
$$\times [U] + 6\lambda_{232}[Th] + 0.1499\lambda_{147}[Sm]$$

(19)

With λ_{147} the decay constant of [147]Sm and all other parameters as in Eqs. (2) and (4). Using Eq. (19), calculating an isochron age for (U–Th–Sm)/He proceeds in exactly the same way as for the ordinary (U–Th)/He method, and the same is true for the pooled age (Fig. 6). Calculating (U–Th–Sm)/He central ages is also very similar, although the equations are a bit longer. In addition to V_i and W_i (Eq. (11)), we define a third logratio variable X_i ($1 \leq i \leq n$):

$$V_i = \ln\left(\frac{[U_i]}{[He_i]} \right), \quad W_i = \ln\left(\frac{[Th_i]}{[He_i]} \right), \quad X_i = \ln\left(\frac{[Sm_i]}{[He_i]} \right)$$

(20)

Because there are three instead of two logratio variables, the (U–Th–Sm)/He age equation cannot be visualized on a straightforward bivariate diagram, but forms a set of hypersurfaces in trivariate logratio-space (Fig. 7). Likewise, (U–Th–Sm)/He data do not form a ternary, but a tetrahedral system in
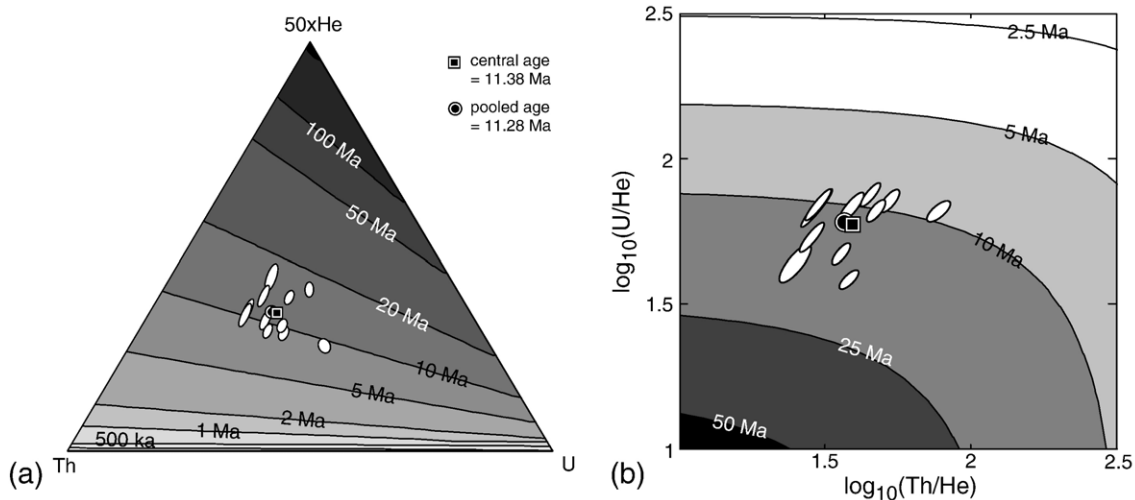

Fig. 6. (a) Ternary diagram of the Naxos data (Table 1). (b) The same data plotted in logratio-space. Error ellipses are 2σ.
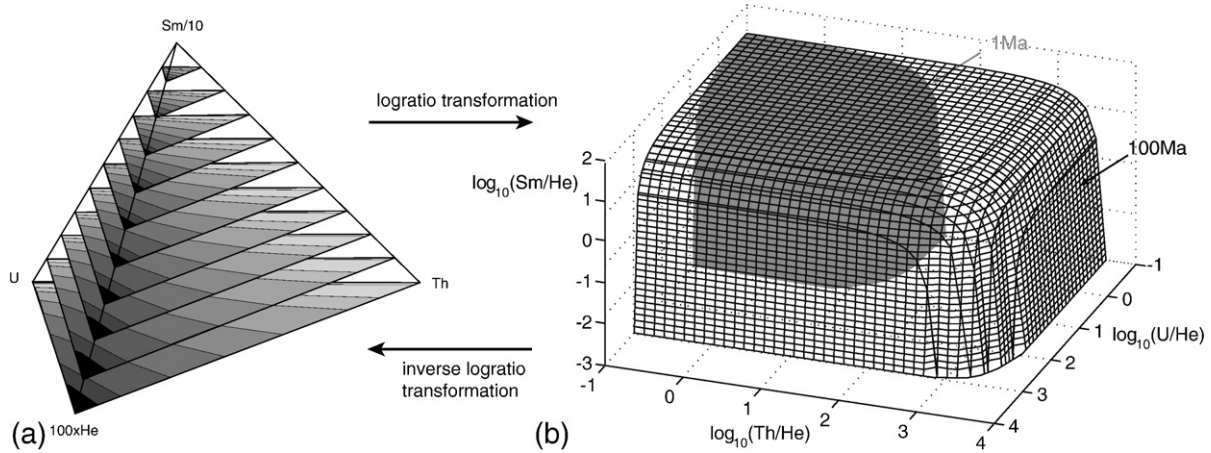
Fig. 7. The logratio transformation can easily be generalized to the case of 3 radioactive parents but this precludes a straightforward visualization on a two-dimensional diagram. (a) the (U–Th–Sm)/He age equation in compositional dataspace. (b) two hypersurfaces representing two ages in logratio-space.

compositional dataspace (Fig. 7). Generalizing the (co)variances of Eq. (12):

$$\hat{\sigma}^2_{V_i} = \left(\frac{\sigma U_i}{U_i}\right)^2 + \left(\frac{\sigma He_i}{He_i}\right)^2, \hat{\sigma}^2_{W_i} = \left(\frac{\sigma Th_i}{Th_i}\right)^2 + \left(\frac{\sigma He_i}{He_i}\right)^2,$$

$$\hat{\sigma}^2_{X_i} = \left(\frac{\sigma Sm_i}{Sm_i}\right)^2 + \left(\frac{\sigma He_i}{He_i}\right)^2$$

$$cov_{V_i,W_i} = cov_{V_i,X_i} = cov_{W_i,X_i} = \left(\frac{\sigma He_i}{He_i}\right)^2$$

(21)

Calculating the arithmetic logratio-means:

$$\bar{V} = \frac{1}{n}\sum_{i=1}^{n} V_i, \bar{W} = \frac{1}{n}\sum_{i=1}^{n} W_i, \bar{X} = \frac{1}{n}\sum_{i=1}^{n} X_i \qquad (22)$$

The (co-)variances of the logratio-means, propagating only the internal error:

$$\hat{\sigma}^2_{\bar{V}} = \frac{1}{n^2}\sum_{i=1}^{n} \hat{\sigma}^2_{V_i}, \hat{\sigma}^2_{\bar{W}} = \frac{1}{n^2}\sum_{i=1}^{n} \hat{\sigma}^2_{W_i}, \hat{\sigma}^2_{\bar{X}} = \frac{1}{n^2}\sum_{i=1}^{n} \hat{\sigma}^2_{X_i}$$

$$cov_{\bar{V},\bar{W}} = \frac{1}{n^2}\sum_{i=1}^{n}cov_{V_i,W_i}, cov_{\bar{V},\bar{X}} = \frac{1}{n^2}\sum_{i=1}^{n} cov_{V_i,X_i},$$

$$cov_{\bar{W},\bar{X}} = \frac{1}{n^2}\sum_{i=1}^{n}cov_{W_i,X_i} \qquad (23)$$

The (co-)variances of the logratio-means, propagating the external error:

$$\hat{\sigma}^2_{\bar{V}} = \frac{\sum_{i=1}^{n}(V_i - \bar{V})^2}{n(n-1)}, \hat{\sigma}^2_{\bar{W}} = \frac{\sum_{i=1}^{n}(W_i - \bar{W})^2}{n(n-1)}, \hat{\sigma}^2_{\bar{X}} = \frac{\sum_{i=1}^{n}(X_i - \bar{X})^2}{n(n-1)}$$

$$cov_{\bar{V},\bar{W}} = \frac{\sum_{i=1}^{n}(V_i - \bar{V})(W_i - \bar{W})}{n(n-1)}, cov_{\bar{V},\bar{X}} = \frac{\sum_{i=1}^{n}(V_i - \bar{V})(X_i - \bar{X})}{n(n-1)}$$

$$cov_{\bar{W},\bar{X}} = \frac{\sum_{i=1}^{n}(W_i - \bar{W})(X_i - \bar{X})}{n(n-1)} \qquad (24)$$

The inverse logratio transformation:

$$\overline{[U]} = \frac{e^{\bar{V}}}{e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1}, \quad \overline{[Th]} = \frac{e^{\bar{W}}}{e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1}$$

$$\overline{[Sm]} = \frac{e^{\bar{X}}}{e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1}, \quad \overline{[He]} = \frac{1}{e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1} \qquad (25)$$

Finally, calculating the standard error propagation of the geometric mean compositions:

$$\begin{pmatrix} \hat{\sigma}^2_{\bar{U}} \\ \hat{\sigma}^2_{\bar{Th}} \\ \hat{\sigma}^2_{\bar{Sm}} \\ \hat{\sigma}^2_{\bar{He}} \end{pmatrix} = \begin{pmatrix} a^2 & b^2 & c^2 & 2ab & 2ac & 2bc \\ b^2 & d^2 & e^2 & 2bd & 2be & 2de \\ c^2 & e^2 & f^2 & 2ce & 2cf & 2ef \\ g^2 & h^2 & i^2 & 2gh & 2gi & 2hi \end{pmatrix} \begin{pmatrix} \hat{\sigma}^2_{\bar{V}} \\ \hat{\sigma}^2_{\bar{W}} \\ \hat{\sigma}^2_{\bar{X}} \\ cov_{\bar{V},\bar{W}} \\ cov_{\bar{V},\bar{X}} \\ cov_{\bar{W},\bar{X}} \end{pmatrix}$$

(26)

with

$$a = \frac{e^{\bar{V}}\left(e^{\bar{W}} + e^{\bar{X}} + 1\right)}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}, \quad b = \frac{-e^{\bar{V}+\bar{W}}}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}$$

$$c = \frac{-e^{\bar{V}+\bar{X}}}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}, \quad d = \frac{e^{\bar{W}}\left(e^{\bar{V}} + e^{\bar{X}} + 1\right)}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}$$

$$e = \frac{-e^{\bar{W}+\bar{X}}}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}, \quad f = \frac{e^{\bar{X}}\left(e^{\bar{V}} + e^{\bar{W}} + 1\right)}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}$$

$$g = \frac{-e^{\bar{V}}}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}, \quad h = \frac{-e^{\bar{W}}}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}$$

$$i = \frac{-e^{\bar{X}}}{\left(e^{\bar{V}} + e^{\bar{W}} + e^{\bar{X}} + 1\right)^2}$$

An example of a well-behaved (U–Th–Sm)/He dataset from the Fish Lake Valley apatite standard (provided by Prof. Daniel Stockli, University of Kansas) is given in the web-calculator (http://pvermees.andropov.org/central). The arithmetic mean of 28 single-grain ages is 6.36±0.11 Ma, the pooled age 6.43±

0.21 Ma, the isochron ages 6.44±0.67 Ma (with an intercept of −0.005±0.056 fmol/μg, and the central age 6.41±0.14 Ma. Note that the central age is older and not younger than the arithmetic mean age. This indicates that random variations exceed the very small systematic difference between the arithmetic and geometric mean compositions. However, the central age probably still is more accurate than the arithmetic mean age because it is less sensitive to outliers.

6. Conclusions

This paper compared three ways to calculate an age from a single set of U, Th and He measurements and four ways to calculate the "average" of several aliquots of the same sample. U, Th and He form a ternary system, and the ternary diagram was introduced as an elegant way to make such a comparison. This reveals that the accuracy gained by the exact solution of the (U−Th)/He equation is easily lost if the average age of replicate measurements is calculated by the arithmetic mean. As a better alternative, the central age is calculated from the geometric mean composition of a dataset. In addition to the central age, the paper also introduced the pooled age and the isochron age as valuable alternatives to the arithmetic mean age in certain applications.

The pooled age is calculated by adding the U, Th, (Sm) and He contents of several single-and/or multi-grain aliquots of the same sample. Pooled ages are biased to high U−Th-grains which may be affected by radiation damage, but are the only sensible way to average multi-grain aliquots. The isochron age is given by the slope of a linear fit of a diagram that plots helium content against present-day helium production rate. In order to reduce the bias towards large grains, it is a good idea to transform the input data to units of concentration, which can be done by dividing the atomic abundances by the estimated volume or mass of the component grains. Doing so will translate the datapoints along a straight line through the origin of the isochron plot and improves its power for detecting "parentless helium". If there is no parentless helium, data must plot on a single line going through the origin. But if, instead, the data do not define a line, or this line does not go through the origin of the isochron diagram, parentless helium or a similar problem may be present. The isochron age is less well suited for ages older than 100 Ma because it uses the linearized age equation (Eq. (3)).

Although most (U−Th)/He geochronologists are probably already aware that some accuracy is lost by calculating the α-ejection correction by simply dividing the uncorrected (U−Th)/He age by the α-retention factor F_t, it bears repeating that instead, the measured helium concentration should be divided by F_t *before* the age calculation. The effects discussed in this paper are relatively minor, affecting the calculated ages by at most a few percent. Nevertheless, the added computational cost

of following the above recommendations pales in comparison with the cost of collecting, separating and analyzing samples. Therefore, there is no reason why not to gain the extra percent of accuracy. To facilitate the calculation of the central age, a web-based calculator is provided at http://pvermees.andropov.org/central. It implements the calculations of central ages with or without Sm, and offers several options for propagating internal or external uncertainties. The web-calculator also allows the calculation of error-weighted central ages, and includes two dataset for testing purposes: the inclusion-bearing (U−Th)/He data from Naxos which is also summarized in Table 1, and (U−Th−Sm)/He data from a Fish Lake Valley apatite lab standard.

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