# Error propagation for TIMS Pb/Pb geochronology

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The Pb-budget of meteorites consists of extraterrestrial and terrestrial components. To separate the two components, we spike the sample with a solution that contains synthetic $^{202}$Pb and $^{205}$Pb. The spike serves two purposes. First, the $^{205}$Pb in it is used as a tracer to compare the sample (which is a mixture of extraterrestrial and terrestrial Pb) with a blank solution (which contains only terrestrial Pb). Second, if the true $^{205}$Pb/$^{202}$Pb-ratio of the spike is known, then this can be used to correct for mass-dependent fractionation. The extraterrestrial $^{204}$Pb/$^{206}$Pb and $^{207}$Pb/$^{206}$Pb-ratios of the sample can then be estimated as

$$\begin{cases} [4/6]_e = \frac{4_s - 4_b}{6_s - 6_b} \\ [7/6]_e = \frac{7_s - 7_b}{6_s - 6_b} \end{cases} \tag{1}$$

respectively, where $x_s$ represents the amount (in pmol) of fractionation-corrected $^{20x}$Pb in the spike-sample-blank mixture, and $x_b$ is the corresponding amount in the spike-blank mixture:

$$x_* = M_*[x/5]_* F_*^{\beta(x)} \tag{2}$$

where $M_*$ is the amount (in pmol) of $^{205}$Pb added to the spike-sample-blank mixture (if $* = s$) or spike-blank mixture (if $* = b$); $[x/5]_*$ is the corresponding $^{20x}$Pb/$^{205}$Pb-ratio; and $F_*^{\beta(x)}$ is the kinetic fractionation factor of Young et al. (2002), with

$$F_* = \frac{[2/5]_t}{[2/5]_*} \text{ and} \tag{3}$$

$$\beta(x) = \frac{\ln(205) - \ln(m_x)}{\ln(205) - \ln(202)} \tag{4}$$

in which $m_x = 20x$ is the molar masses of $x$, and $[2/5]_t$ is the true atomic $^{202}$Pb/$^{205}$Pb-ratio of the spike.

Because isotopic ratios are strictly positive quantities whose uncertainties are best expressed in relative terms, it is useful to cast Equation 1 into a logarithmic form:

$$\begin{cases} l_{46} \equiv \ln[4/6]_e = l_4 - l_6 \\ l_{76} \equiv \ln[7/6]_e = l_7 - l_6 \end{cases} \tag{5}$$

where

$$l_4 = \ln(\exp[l_4(s)] - \exp[l_4(b)]) \tag{6}$$
$$l_6 = \ln(\exp[l_6(s)] - \exp[l_6(b)]) \tag{7}$$
$$l_7 = \ln(\exp[l_7(s)] - \exp[l_7(b)]) \tag{8}$$

with

$$l_x(*) = \ln M_* + \ln[x/5]_* + \beta(x)\left(\ln[2/5]_t - \ln[2/5]_*\right) \tag{9}$$

In order to solve Equation 5, we must first solve Equation 9 (for $x \in \{4,6,7\}$ and $* \in \{b,s\}$), and propagate its uncertainties. Let $\Sigma$ be the covariance matrix of the blank-corrected $l_*(x)$-measurements:

$$\Sigma = \begin{bmatrix} s[l_b(4)]^2 & s[l_b(4),l_s(4)] & s[l_b(4),l_b(6)] & s[l_b(4),l_s(6)] & s[l_b(4),l_b(7)] & s[l_b(4),l_s(7)] \\ s[l_s(4),l_b(4)]^2 & s[l_s(4)]^2 & s[l_b(4),l_b(6)] & s[l_b(4),l_s(6)] & s[l_b(4),l_b(7)] & s[l_b(4),l_s(7)] \\ s[l_b(6),l_b(4)]^2 & s[l_b(6),l_s(4)] & s[l_b(6)]^2 & s[l_b(6),l_s(6)] & s[l_b(6),l_b(7)] & s[l_b(6),l_s(7)] \\ s[l_s(6),l_b(4)]^2 & s[l_s(6),l_s(4)] & s[l_s(6),l_b(6)] & s[l_s(6)]^2 & s[l_s(6),l_b(7)] & s[l_s(6),l_s(7)] \\ s[l_b(7),l_b(4)]^2 & s[l_b(7),l_s(4)] & s[l_b(7),l_b(6)] & s[l_b(7),l_s(6)] & s[l_b(7)]^2 & s[l_b(7),l_s(7)] \\ s[l_s(7),l_b(4)]^2 & s[l_s(7),l_s(4)] & s[l_s(7),l_b(6)] & s[l_s(7),l_s(6)] & s[l_s(7),l_b(7)] & s[l_s(7)]^2 \end{bmatrix} \tag{10}$$

where $s[x]^2$, $s[y]^2$ and $s[x,y]$ are the (co) variances of $x$ and $y$; then conventional error propagation by first order Taylor approximation dictates that:

$$\Sigma = \begin{bmatrix} I_3 & 0_{3,5} & J_t \\ 0_{5,3} & J_s & J_t \end{bmatrix} \begin{bmatrix} \Sigma_b & 0_{5,3} & 0_{5,1} \\ 0_{3,5} & \Sigma_s & 0_{4,1} \\ 0_{1,5} & 0_{1,4} & s[5/2]_t^2 \end{bmatrix} \begin{bmatrix} I_3 & 0_{3,5} \\ 0_{5,3} & J_s^T \\ J_t^T & J_t^T \end{bmatrix} \tag{11}$$

where $I_n$ is the $n \times n$ identity matrix; $0_{n,m}$ is an $n \times m$ matrix of zeros; $J_s$ and $J_t$ are Jacobian matrices (with $J_s^T$ and $J_t^T$ their transpose):

$$J_s = \begin{bmatrix} \frac{1}{M_s} & \frac{-\beta(4)}{[2/5]_s} & \frac{1}{[4/5]_s} & 0 & 0 \\ \frac{1}{M_s} & \frac{-\beta(6)}{[2/5]_s} & 0 & \frac{1}{[6/5]_s} & 0 \\ \frac{1}{M_s} & \frac{-\beta(7)}{[2/5]_s} & 0 & 0 & \frac{1}{[7/5]_s} \end{bmatrix} ; \; J_t = \begin{bmatrix} \frac{\beta(4)}{[2/5]_t} \\ \frac{\beta(6)}{[2/5]_t} \\ \frac{\beta(7)}{[2/5]_t} \end{bmatrix} \tag{12}$$

and $\Sigma_s$ and $\Sigma_b$ are the covariance matrices of the sample and average blank, respectively. $\Sigma_b$ is estimated from repeat measurements of

$$l_b'(x) = \ln M_b + \ln[x/5]_b - \beta(x)\ln[2/5]_b \tag{13}$$

(for $x \in \{4,6,7\}$) whereas $\Sigma_s$ contains the analytical uncertainties of the raw measurements for the sample:

$$\Sigma_s = \begin{bmatrix} s[M_s]^2 & 0 & 0 & 0 & 0 \\ 0 & s[2/5]_s^2 & s([2/5]_s,[4/5]_s) & s([2/5]_s,[6/5]_s) & s([2/5]_s,[7/5]_s) \\ 0 & s([4/5]_s,[2/5]_s) & s[4/5]_s^2 & s([4/5]_s,[6/5]_s) & s([4/5]_s,[7/5]_s) \\ 0 & s([6/5]_s,[2/5]_s) & s([6/5]_s,[4/5]_s) & s[6/5]_s^2 & s([6/5]_s,[7/5]_s) \\ 0 & s([7/5]_s,[2/5]_s) & s([7/5]_s,[4/5]_s) & s([7/5]_s,[7/5]_s) & s[7/5]_s^2 \end{bmatrix} \tag{14}$$

Although it is possible to solve Equation 5 by plugging the $l_x(*)$ values from Equation 9 into Equations 6–7, this approach breaks down when the blank exceeds the signal. To rule out this possibility, it is better to estimate $l_{46}$ and $l_{76}$ using the method of maximum likelihood. Let $\Delta$ be a column vector (and $\Delta^T$ a row vector) of misfits:

$$\Delta = \begin{bmatrix} l_4(b) - c_{4b} \\ l_6(b) - c_{6b} \\ l_7(b) - c_{7b} \\ l_4(s) - \ln(\exp[c_{46} + c_6] + \exp[c_{4b}]) \\ l_6(s) - \ln(\exp[c_6] + \exp[c_{6b}]) \\ l_7(s) - \ln(\exp[c_{76} + c_6] + \exp[c_{7b}]) \end{bmatrix} \tag{15}$$

where $c_{4b}$, $c_{6b}$, $c_{7b}$, $c_6$, $c_{46}$, $c_{76}$ are the true (but unknown) values of $l_4(b)$, $l_6(b)$, $l_7(b)$, $l_6$, $l_{46}$ and $l_{76}(b)$, respectively. These parameters can be estimated by maximising the likelihood function ($\mathcal{L}$):

$$\mathcal{L} \propto -\frac{1}{2}\Delta^T \Sigma^{-1} \Delta \tag{16}$$

The uncertainties of $c_{4b}$, $c_{6b}$, $c_{7b}$, $c_6$, $c_{46}$, $c_{76}$ can be obtained by inverting the Hessian matrix of $\mathcal{L}$ with respect to the parameters.

# References

Young, E. D., Galy, A., and Nagahara, H. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochimica et Cosmochimica Acta*, 66(6):1095–1104, 2002.