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Derivation of isotope ratios, errors, and error correlations for U-Pb geochronology using ^{205}Pb-^{235}U-(^{233}U)-spiked isotope dilution thermal ionization mass spectrometric data

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[1] A comprehensive treatment of the derivation of U-Pb isotope ratios and their corresponding uncertainties from isotope dilution thermal ionization mass spectrometric measurements is presented. Standard parametric statistical methods of error propagation are utilized to convolve uncertainties associated with instrumental mass fractionation, tracer subtraction, blank Pb and U subtraction, and initial common Pb correction. Derivations include errors and error correlations for total sample U/Pb and Pb isotope ratios (including radiogenic and initial common Pb) for two- and three-dimensional isochron calculations, radiogenic U/Pb and Pb isotope ratios for concordia and radiogenic model age calculations, and the propagation of model age errors from radiogenic isotope ratios.

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1. Introduction

[2] U-Pb accessory mineral geochronology utilizing the isotope-dilution thermal ionization mass spectrometry (ID-TIMS) method has the demonstrated potential to provide radiometric age constraints for geological samples approaching, and potentially exceeding the 0.1% level of precision and accuracy. The analytical and instrumental methods of U-Pb ID-TIMS geochronology have reached their maturity over the past three decades, and have received intensive scrutiny regarding the appropriate methods of error propagation and assignment to measured U-Pb (and Pb-Pb) ratios and

their derivative ages [*Cumming*, 1969; *Ludwig*, 1980; *Mattinson*, 1987]. The influential paper of *Ludwig* [1980] described a method for the propagation of errors associated with U-Pb ID-TIMS geochronology. While the general nature of Ludwig's treatment has lent itself to widespread application over the past twenty-five years, advances in U-Pb analysis (e.g., reduction in analytical blank contributions, the widespread availability and use of high-purity mixed ^{205}Pb and double U "spikes" or "tracers") have made some of the assumptions of this treatment unnecessary or untenable, particularly for very high-precision geochronological studies. For example, although not treated by *Ludwig* [1980], errors associated with the use of a double U spike to correct instrumental isotopic fractionation should be accurately propagated into the estimate of molar U quantities. Similarly, in very low-Pb samples (e.g., <10 pg radiogenic Pb) the uncertainties associated with the subtraction of tracer Pb isotopes may become a significant source of error in derived isotope ratios. Additionally, the summary nature of *Ludwig* [1980] potentially obscures some of the underlying mathematics of the error propagation, particularly those in the isotope dilution calculations.

[3] We have revisited the problem of error propagation in U-Pb ID-TIMS mass spectrometry and geochronology, with a specific emphasis on the use of a mixed ^{205}Pb-^{235}U-^{233}U tracer, such as has been recently calibrated and distributed as part of the EARTHTIME Initiative for the sequencing of Earth history through the integration of high-precision geochronology and quantitative chronostratigraphy (http://www.earth-time.org). Our treatment is intended for both experts and novice users of U-Pb geochronological data, thus we have attempted to clearly capture all of the algebraic manipulation and derivative calculus used in the derivations. While recognizing that our statistical approach is not novel, we hope that by providing a comprehensive derivation, we may elucidate the general method of error propagation for students of geochronology, and inspire a similar degree of rigor in the propagation of errors for less mature U-Pb analytical techniques.

[4] The following sections detail the propagation of errors through the calculation of both radiogenic and sample (radiogenic + initial common) Pb and U/Pb isotope ratios, and radiogenic ^{206}Pb/^{238}U, ^{207}Pb/^{235}U, and ^{207}Pb/^{206}Pb model ages, including appropriate error correlations. The calculations utilize the error propagation approximation resulting from the Taylor series expansion of the function about its constituent variables (ignoring higher-order terms) [*Bevington and Robinson*, 1992], which in effect provides a linear extrapolation of the influences of arbitrarily small errors to the real errors of interest:

$$x = f(u, v, \ldots) \tag{1}$$

$$\sigma_x^2 = \sigma_u^2 \cdot \left(\frac{\partial x}{\partial u}\right)^2 + \sigma_v^2 \cdot \left(\frac{\partial x}{\partial v}\right)^2 + 2 \cdot \sigma_{uv}^2 \cdot \left(\frac{\partial x}{\partial u}\right) \cdot \left(\frac{\partial x}{\partial v}\right) + \ldots \tag{2}$$

where σ_x^2 is defined as the variance of x, σ_{uv}^2 is defined as the covariance between u and v, and $(\partial x/\partial u)$ is the first partial derivative of x with respect to u.

[5] In all of the following derivations, errors in the tracer Pb/U ratio (e.g., the moles of ^{205}Pb and ^{235}U in the tracer) are considered systematic and thus are ignored. Such errors are more appropriately evaluated for the data set as a whole by propagation in quadrature on the weighted mean or similar group statistics [*Schmitz et al.*, 2003]. On the other hand, errors in the tracer isotopic composition are propagated, as the effect of tracer subtraction on a reduced isotopic ratio is dependent upon the amount of tracer added and the amount of each isotope in the individual sample. The same is true for the amount and isotopic composition of Pb blank contributions and the initial common Pb isotopic composition. The amount of both species of common Pb subtracted from an analysis is sample dependent, and thus we consider that the errors for each should be propagated on a sample-by-sample basis. However, we do advocate that to develop a firm estimation of the sensitivity of a data set to the assumed initial common Pb composition, the constituent data be reduced with a range of geologically reasonable initial Pb isotope ratios, or better a full Monte Carlo simulation of initial Pb isotope ratios, and the variance in resulting radiogenic model ages incorporated into the final age interpretation [*Schmitz and Bowring*, 2001; *Schoene and Bowring*, 2006].

2. Sample U-Pb Ratios, Errors, and Error Correlations

[6] The following section details the propagation of errors through the calculation of ^{205}Pb-^{233}U-^{235}U-spiked sample U/Pb and Pb isotope ratios (where "sample" molar quantities and ratios comprise both

radiogenic and initial common Pb, but not tracer or blank Pb and U contributions), including errors and error correlations associated with Pb and U isotope fractionation corrections (including errors in U isotope fractionation estimation utilizing a double ^{233}U - ^{235}U tracer), and tracer and blank U and Pb subtractions. The resulting ratios, errors and error correlations may be used in the calculation of traditional ^{238}U/^{204}Pb-^{206}Pb/^{204}Pb, ^{235}U/^{204}Pb-^{207}Pb/^{204}Pb, and ^{207}Pb/^{204}Pb-^{206}Pb/^{204}Pb isochrons, as well as two and three-dimensional isochrons utilizing ^{238}U/^{206}Pb-^{207}Pb/^{206}Pb-^{204}Pb/^{206}Pb ratios [*Ludwig*, 1998].

[7] In the calculation of sample isotope quantities (e.g., ^{206}Pb sample, ^{207}Pb sample, ^{204}Pb initial, ^{238}U sample) and U/Pb isotope ratios, most uncertainties in the constituent variables are assumed to be uncorrelated. Exceptions are non-negligible error correlations (covariances) between measured isotope ratios in the expressions for ^{207}Pb sample and ^{204}Pb initial. Similarly, in the calculation of sample Pb isotope ratios, covariances between numerator and denominator must be calculated and applied.

[8] The abbreviations listed in Table 1 are used throughout the derivations.

2.1. Derivation of Molar Isotope Quantities and Errors

2.1.1. Sample ^{206}Pb

[9] First establishing the algebraic expression for sample ^{206}Pb,

$$Pb206s = [R65m \cdot Pb205t \cdot (1 + FPb)] - [R65t \cdot Pb205t] - [Pb206b] \quad (3)$$

the error propagation equation may be written as (assuming all errors are uncorrelated):

$$\sigma^2_{Pb206s} = \left[\left(\frac{\partial Pb206s}{\partial R65m}\right)\cdot\sigma_{R65m}\right]^2 + \left[\left(\frac{\partial Pb206s}{\partial R65t}\right)\cdot\sigma_{R65t}\right]^2 + \left[\left(\frac{\partial Pb206s}{\partial FPb}\right)\cdot\sigma_{FPb}\right]^2 + \left[\left(\frac{\partial Pb206s}{\partial Pb206b}\right)\cdot\sigma_{Pb206b}\right]^2 \quad (4)$$

[10] The partial derivatives are calculated as follows,

$$\left(\frac{\partial Pb206s}{\partial R65m}\right) = (1 + FPb)\cdot Pb205t \quad (5)$$

$$\left(\frac{\partial Pb206s}{\partial R65t}\right) = -Pb205t \quad (6)$$

$$\left(\frac{\partial Pb206s}{\partial FPb}\right) = R65m \cdot Pb205t \quad (7)$$

$$\left(\frac{\partial Pb206s}{\partial Pb206b}\right) = -1 \quad (8)$$

[11] These partial derivatives and variances can then be substituted into equation (4) to derive the uncertainty in sample ^{206}Pb.

2.1.2. Sample ^{207}Pb

[12] First establishing the algebraic expression for sample ^{207}Pb,

$$Pb207s = [R65m \cdot R76m \cdot (1 + 2 \cdot FPb) \cdot Pb205t] - (R65t \cdot R76t \cdot Pb205t) - (R76b \cdot Pb206b) \quad (9)$$

the error propagation equation may be written as (assuming all errors except $R65m$ and $R76m$, and $R65t$ and $R76t$ are uncorrelated):

$$\sigma^2_{Pb207s} = \left[\left(\frac{\partial Pb207s}{\partial R65m}\right)\cdot\sigma_{R65m}\right]^2 + \left[\left(\frac{\partial Pb207s}{\partial R76m}\right)\cdot\sigma_{R76m}\right]^2 + \left[\left(\frac{\partial Pb207s}{\partial R65t}\right)\cdot\sigma_{R65t}\right]^2 + \left[\left(\frac{\partial Pb207s}{\partial R76t}\right)\cdot\sigma_{R76t}\right]^2 + \left[\left(\frac{\partial Pb207s}{\partial FPb}\right)\cdot\sigma_{FPb}\right]^2 + \left[\left(\frac{\partial Pb207s}{\partial Pb206b}\right)\cdot\sigma_{Pb206b}\right]^2 + \left[\left(\frac{\partial Pb207s}{\partial R76b}\right)\cdot\sigma_{R76b}\right]^2 + 2\cdot\sigma^2_{R65m-R76m} \cdot \left(\frac{\partial Pb207s}{\partial R65m}\right)\cdot\left(\frac{\partial Pb207s}{\partial R76m}\right) + 2\cdot\sigma^2_{R65t-R76t}\cdot\left(\frac{\partial Pb207s}{\partial R65t}\right)\cdot\left(\frac{\partial Pb207s}{\partial R76t}\right) \quad (10)$$

[13] The partial derivatives are calculated as follows:

$$\left(\frac{\partial Pb207s}{\partial R65m}\right) = [R76m \cdot (1 + 2 \cdot FPb) \cdot Pb205t] \quad (11)$$

$$\left(\frac{\partial Pb207s}{\partial R76m}\right) = [R65m \cdot (1 + 2 \cdot FPb) \cdot Pb205t] \quad (12)$$

$$\left(\frac{\partial Pb207s}{\partial FPb}\right) = 2 \cdot R76m \cdot R65m \cdot Pb205t \quad (13)$$

Table 1. Abbreviations

Abbreviation	Description
	General
FPb	coefficient for linear Pb fractionation correction per unit mass difference
FU	coefficient for linear U fractionation correction per unit mass difference
$\lambda 235$	^{235}U decay constant
$\lambda 238$	^{238}U decay constant
*t*76	($^{207}Pb/^{206}Pb$) radiogenic model age
*t*75	($^{207}Pb/^{235}U$) radiogenic model age
*t*68	($^{206}Pb/^{238}U$) radiogenic model age
	Measured Ratios
Tracer quantities and ratios[a]	
*R*85*m*	($^{238}U/^{235}U$) measured
*R*35*m*	($^{233}U/^{235}U$) measured
*R*83*m*	($^{238}U/^{233}U$) measured
*R*65*m*	($^{206}Pb/^{205}Pb$) measured
*R*45*m*	($^{204}Pb/^{205}Pb$) measured
*R*75*m*	($^{207}Pb/^{205}Pb$) measured
*R*46*m*	($^{204}Pb/^{206}Pb$) measured
*R*76*m*	($^{207}Pb/^{206}Pb$) measured
Blank quantities and ratios	
*U*238*b*	moles (^{238}U) blank
*Pb*206*b*	moles (^{206}Pb) blank
*R*64*b*	($^{206}Pb/^{204}Pb$) blank
*R*76*b*	($^{207}Pb/^{206}Pb$) blank
*R*74*b*	($^{207}Pb/^{204}Pb$) blank
Initial Pb quantities and ratios[b]	
*Pb*206*c*	moles (^{206}Pb) initial
*Pb*204*c*	moles (^{204}Pb) initial
*R*64*c*	($^{206}Pb/^{204}Pb$) initial
*R*76*c*	($^{207}Pb/^{206}Pb$) initial
*R*74*c*	($^{207}Pb/^{204}Pb$) initial
Sample quantities and ratios	
*U*238*s*	moles (^{238}U) sample
*U*235*s*	moles (^{235}U) sample
*R*76*s*	($^{207}Pb/^{206}Pb$) sample (including radiogenic + initial Pb)
*R*46*s*	($^{204}Pb/^{206}Pb$) sample (including radiogenic + initial Pb)
*R*47*s*	($^{204}Pb/^{207}Pb$) sample (including radiogenic + initial Pb)
*R*86*s*	($^{238}U/^{206}Pb$) sample (including radiogenic + initial Pb)
*R*87*s*	($^{238}U/^{207}Pb$) sample (including radiogenic + initial Pb)
*R*57*s*	($^{235}U/^{207}Pb$) sample (including radiogenic + initial Pb)
*R*84*s*	($^{238}U/^{204}Pb$) sample (initial Pb)
*R*54*s*	($^{235}U/^{204}Pb$) sample (initial Pb)
*Pb*206*s*	moles (^{206}Pb) sample (including radiogenic + initial Pb)
*Pb*207*s*	moles (^{207}Pb) sample (including radiogenic + initial Pb)
Radiogenic Pb quantities and ratios	
*Pb*206*r*	moles (^{206}Pb) radiogenic
*Pb*207*r*	moles (^{207}Pb) radiogenic
*R*76*r*	($^{207}Pb/^{206}Pb$) radiogenic
*R*68*r*	($^{206}Pb/^{238}U$) radiogenic
*R*75*r*	($^{207}Pb/^{235}U$) radiogenic
*R*86*r*	($^{238}U/^{206}Pb$) radiogenic
*R*87*r*	($^{238}U/^{207}Pb$) radiogenic

[a] "Tracer" is defined as an artificially produced or enriched isotope which is added to a sample for the purposes of concentration determination through isotope dilution.

[b] "Initial" is defined as that Pb which was incorporated into the growing crystal at the time of formation.

$$\left(\frac{\partial Pb207s}{\partial R65t}\right) = -R76t \cdot Pb205t \tag{14}$$

$$\left(\frac{\partial Pb207s}{\partial R76t}\right) = -R65t \cdot Pb205t \tag{15}$$

$$\left(\frac{\partial Pb207s}{\partial Pb206b}\right) = -R76b \tag{16}$$

$$\left(\frac{\partial Pb207s}{\partial R76b}\right) = -Pb206b \tag{17}$$

[14] The covariance terms can be determined through the approximation for the error resulting from the product of two variables, $x = uv$, where for example $x = {}^{207}Pb/{}^{205}Pb$, $u = {}^{207}Pb/{}^{206}Pb$, and $v = {}^{206}Pb/{}^{205}Pb$:

$$\left(\frac{\sigma_x}{x}\right)^2 = \left(\frac{\sigma_u}{u}\right)^2 + \left(\frac{\sigma_v}{v}\right)^2 + 2 \cdot \frac{\sigma_{uv}^2}{u \cdot v} \tag{18}$$

[15] Solving for the covariance term:

$$\sigma_{uv}^2 = \frac{u \cdot v \cdot \left[\left(\frac{\sigma_x}{x}\right)^2 - \left(\frac{\sigma_u}{u}\right)^2 - \left(\frac{\sigma_v}{v}\right)^2\right]}{2} \tag{19}$$

[16] Thus in this case:

$$\sigma_{R76m-R65m}^2 = \frac{R76m \cdot R65m \cdot \left[\left(\frac{\sigma_{R75m}}{R75m}\right)^2 - \left(\frac{\sigma_{R76m}}{R76m}\right)^2 - \left(\frac{\sigma_{R65m}}{R65m}\right)^2\right]}{2} \tag{20}$$

$$\sigma_{R76t-R65t}^2 = \frac{R76t \cdot R65t \cdot \left[\left(\frac{\sigma_{R75t}}{R75t}\right)^2 - \left(\frac{\sigma_{R76t^2}}{R76t}\right) - \left(\frac{\sigma_{R65t}}{R65t}\right)^2\right]}{2} \tag{21}$$

[17] These partial derivatives, variances and covariances can then be substituted into equation (10) to derive the uncertainty in sample ^{207}Pb.

2.1.3. Sample (Initial) ^{204}Pb

[18] First establishing the algebraic expression for sample (initial) ^{204}Pb,

$$Pb204c = [R46m \cdot R65m \cdot (1 - FPb) \cdot Pb205t] - (R46t \cdot R65t \cdot Pb205t) - \left(\frac{Pb206b}{R64b}\right) \tag{22}$$

the error propagation equation may be written as (assuming all errors except $R46m$ and $R65m$, and $R46t$ and $R65t$ are uncorrelated):

$$\begin{aligned}\sigma_{Pb204c}^2 = &\left[\left(\frac{\partial Pb204c}{\partial R65m}\right) \cdot \sigma_{R65m}\right]^2 + \left[\left(\frac{\partial Pb204c}{\partial R46m}\right) \cdot \sigma_{R46m}\right]^2 \\ &+ \left[\left(\frac{\partial Pb204c}{\partial R65t}\right) \cdot \sigma_{R65t}\right]^2 + \left[\left(\frac{\partial Pb204c}{\partial R46t}\right) \cdot \sigma_{R46t}\right]^2 \\ &+ \left[\left(\frac{\partial Pb204c}{\partial FPb}\right) \cdot \sigma_{FPb}\right]^2 + \left[\left(\frac{\partial Pb204c}{\partial Pb206b}\right) \cdot \sigma_{Pb206b}\right]^2 \\ &+ \left[\left(\frac{\partial Pb204c}{\partial R64b}\right) \cdot \sigma_{R64b}\right]^2 + 2 \\ &\cdot \sigma_{R65m-R46m}^2 \cdot \left(\frac{\partial Pb204c}{\partial R65m}\right) \cdot \left(\frac{\partial Pb204c}{\partial R46m}\right) \\ &+ 2 \cdot \sigma_{R65t-R46t}^2 \cdot \left(\frac{\partial Pb204c}{\partial R65t}\right) \cdot \left(\frac{\partial Pb204c}{\partial R46t}\right)\end{aligned} \tag{23}$$

[19] The partial derivatives are calculated as follows,

$$\left(\frac{\partial Pb204c}{\partial R65m}\right) = [R46m \cdot (1 - FPb) \cdot Pb205t] \tag{24}$$

$$\left(\frac{\partial Pb204c}{\partial R46m}\right) = [R65m \cdot (1 - FPb) \cdot Pb205t] \tag{25}$$

$$\left(\frac{\partial Pb204c}{\partial FPb}\right) = -R46m \cdot R65m \cdot Pb205t \tag{26}$$

$$\left(\frac{\partial Pb204c}{\partial R65t}\right) = -R46t \cdot Pb205t \tag{27}$$

$$\left(\frac{\partial Pb204c}{\partial R46t}\right) = -R65t \cdot Pb205t \tag{28}$$

$$\left(\frac{\partial Pb204c}{\partial Pb206b}\right) = -\frac{1}{R64b} \tag{29}$$

$$\left(\frac{\partial Pb204c}{\partial R64b}\right) = \frac{Pb206b}{R64b^2} \tag{30}$$

and again the covariance terms can be calculated in the manner of equations (18)–(19):

$$\sigma_{R65m-R46m}^2 = \frac{R65m \cdot R46m \cdot \left[\left(\frac{\sigma_{R45m}}{R45m}\right)^2 - \left(\frac{\sigma_{R65m}}{R65m}\right)^2 - \left(\frac{\sigma_{R46m}}{R46m}\right)^2\right]}{2} \tag{31}$$

$$\sigma^2_{R65t-R46t} = \frac{R65t \cdot R46t \cdot \left[\left(\frac{\sigma_{R45t}}{R45t}\right)^2 - \left(\frac{\sigma_{R65t}}{R65t}\right)^2 - \left(\frac{\sigma_{R46t}}{R46t}\right)^2 \right]}{2} \quad (32)$$

[20] These partial derivatives, variances, and covariances then can be substituted into equation (23) to derive the uncertainty in sample (initial) ^{204}Pb.

2.1.4. Error in U Fractionation Factor (*FU*) for Double Spiked (^{233}U-^{235}U) Samples

[21] Because of the artificial nature of the ^{233}U tracer isotope, a unique algebraic expression for the linear uranium fractionation factor as the coefficient per unit mass difference can be derived from the relationships:

$$R85f = R85m \cdot (3 \cdot FU + 1) = \frac{U238s + U238t}{U235s + U235t} \quad (33)$$

$$R35f = R35m \cdot (1 - 2 \cdot FU) = \frac{U233t}{U235s + U235t} \quad (34)$$

where $R85f$ and $R35f$ represent the mass fractionation corrected ratios. Substituting the product ($U235s \cdot 137.88$) for $U238s$ (arising from the natural ^{235}U/^{238}U ratio) and manipulating equation (33):

$$U235s \cdot [R85m \cdot (3 \cdot FU + 1) - 137.88] = U235t \cdot [R85t - R85m \cdot (3 \cdot FU + 1)] \quad (35)$$

[22] Equation (34) can also be solved for $U235s$:

$$U235s = U233t \cdot \left[\frac{1}{R35m \cdot (1 - 2 \cdot FU)} - \frac{1}{R35t} \right] \quad (36)$$

[23] After substitution of equation (36) into (35), several cancellations result in the expression:

$$R35t \cdot [R85m \cdot (3 \cdot FU + 1) - 137.88] = (R85t - 137.88) \cdot [R35m \cdot (1 - 2 \cdot FU)] \quad (37)$$

[24] Expanding the products, gathering common terms and solving for FU yields:

$$FU = \left[\frac{R35t \cdot (137.88 - R85m) + R35m \cdot (R85t - 137.88)}{2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m} \right] \quad (38)$$

[25] The error propagation equation for FU may be written as (assuming all errors except $R85m$ and $R35m$, and $R85t$ and $R35t$ are uncorrelated):

$$\sigma^2_{FU} = \left[\left(\frac{\partial FU}{\partial R35t} \right) \cdot \sigma_{R35t} \right]^2 + \left[\left(\frac{\partial FU}{\partial R85m} \right) \cdot \sigma_{R85m} \right]^2 + \left[\left(\frac{\partial FU}{\partial R35m} \right) \cdot \sigma_{R35m} \right]^2 + \left[\left(\frac{\partial FU}{\partial R85t} \right) \cdot \sigma_{R85t} \right]^2 + 2 \cdot \sigma^2_{R85m \cdot R35m} \cdot \left(\frac{\partial FU}{\partial R85m} \right) \cdot \left(\frac{\partial FU}{\partial R35m} \right) + 2 \cdot \sigma^2_{R85t \cdot R35t} \cdot \left(\frac{\partial FU}{\partial R85t} \right) \cdot \left(\frac{\partial FU}{\partial R35t} \right) \quad (39)$$

[26] Through application of the chain and product rules, the partial derivatives are calculated as:

$$\left(\frac{\partial FU}{\partial R35t} \right) = \left(\frac{137.88 - R85m}{2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m} \right) - \left(\frac{3 \cdot R85m \cdot [R35t \cdot (R85m - 137.88) + R35m \cdot (137.88 - R85t)]}{[2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m]^2} \right) \quad (40)$$

$$\left(\frac{\partial FU}{\partial R85m} \right) = \left(\frac{-R35t}{2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m} \right) - \left(\frac{3 \cdot R35t \cdot [R35t \cdot (137.88 - R85m) + R35m \cdot (R85t - 137.88)]}{[2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m]^2} \right) \quad (41)$$

$$\left(\frac{\partial FU}{\partial R35m} \right) = \left(\frac{R85t - 137.88}{2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m} \right) - \left(\frac{2 \cdot (R85t - 137.88) \cdot [R35t \cdot (137.88 - R85m) + R35m \cdot (R85t - 137.88)]}{[2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m]^2} \right) \quad (42)$$

$$\left(\frac{\partial FU}{\partial R85t}\right) = \left(\frac{R35m}{2\cdot R35m\cdot(R85t-137.88)+3\cdot R35t\cdot R85m}\right) - \left(\frac{2\cdot R35m\cdot[R35t\cdot(137.88-R85m)+R35m\cdot(R85t-137.88)]}{[2\cdot R35m\cdot(R85t-137.88)+3\cdot R35t\cdot R85m]^2}\right) \quad (43)$$

[27] The covariance terms are determined through the approximation for the error resulting from the quotient of two variables, $x = u/v$:

$$\left(\frac{\sigma_x}{\mathrm{x}}\right)^2 = \left(\frac{\sigma_u}{\mathrm{u}}\right)^2 + \left(\frac{\sigma_v}{v}\right)^2 - 2\frac{\sigma_{uv}^2}{uv} \quad (44)$$

[28] Solving for the covariance term:

$$\sigma_{uv}^2 = \frac{u\cdot v\cdot\left\lfloor\left(\frac{\sigma_u}{\mathrm{u}}\right)^2+\left(\frac{\sigma_v}{v}\right)^2-\left(\frac{\sigma_x}{\mathrm{x}}\right)^2\right\rfloor}{2} \quad (45)$$

[29] Thus in this case:

$$\sigma_{R85m-R35m}^2 = \frac{R85m\cdot R35m\cdot\left\lfloor\left(\frac{\sigma_{R85m}}{R85m}\right)^2+\left(\frac{\sigma_{R35m}}{R35m}\right)^2-\left(\frac{\sigma_{R83m}}{R83m}\right)^2\right\rfloor}{2} \quad (46)$$

$$\sigma_{R85t-R35t}^2 = \frac{R85t\cdot R35t\cdot\left\lfloor\left(\frac{\sigma_{R85t}}{R85t}\right)^2+\left(\frac{\sigma_{R35t}}{R35t}\right)^2-\left(\frac{\sigma_{R83t}}{R83t}\right)^2\right\rfloor}{2} \quad (47)$$

[30] These partial derivatives, variances and covariances can then be substituted into equation (39) to derive the uncertainty in the uranium fractionation factor.

2.1.5. Sample ^{238}U

[31] First establishing the algebraic expression for sample ^{238}U (making the trivial assumption that blank ^{235}U is negligible; the term (1/137.88) arising from the natural ^{235}U/^{238}U ratio),

$$\begin{aligned} U238s &= [R85m\cdot(1+3\cdot FU)\cdot(U235s+U235t)] - (R85t\cdot U235t) - U238b \\ &= \left[R85m\cdot(1+3\cdot FU)\cdot\left(U238s\cdot\left(\frac{1}{137.88}\right)+U235t\right)\right] - (R85t\cdot U235t) - U238b \\ &= \left[U238s\cdot\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)\right] + [U235t\cdot R85m\cdot(1+3\cdot FU)] - (R85t\cdot U235t) - U238b \\ &= \frac{[U235t\cdot R85m\cdot(1+3\cdot FU)] - (R85t\cdot U235t) - U238b}{\left[1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)\right]} \end{aligned} \quad (48)$$

the error propagation equation may be written as:

$$\sigma_{U238s}^2 = \left[\left(\frac{\partial U238s}{\partial R85m}\right)\cdot\sigma_{R85m}\right]^2 + \left[\left(\frac{\partial U238s}{\partial R85t}\right)\cdot\sigma_{R85t}\right]^2 + \left[\left(\frac{\partial U238s}{\partial U238b}\right)\cdot\sigma_{U238b}\right]^2 + \left[\left(\frac{\partial U238s}{\partial FU}\right)\cdot\sigma_{FU}\right]^2 \quad (49)$$

[32] Note that to dramatically simplify our derivation, we are considering error correlations between the component terms of sample ^{238}U ($U238s$) and the uranium fractionation factor (FU) to be trivial, which is justified given the contrasting dominant error sources in each quantity and the fact that we have incorporated $R85m$-$R35m$ and $R85t$-$R35t$ covariances into the error on FU. The partial derivatives are calculated as follows:

$$\left(\frac{\partial U238s}{\partial R85m}\right) = \left\lfloor\frac{U235t\cdot(1+3\cdot FU)}{\left[1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)\right]}\right\rfloor + \left[\frac{U235t\cdot R85m\cdot(1+3\cdot FU)-(R85t\cdot U235t)-U238b}{\left[1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)\right]^2}\cdot\left(\frac{1+3\cdot FU}{137.88}\right)\right] \quad (50)$$

$$\left(\frac{\partial U238s}{\partial R85t}\right) = \left\lfloor\frac{-U235t}{1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)}\right\rfloor \quad (51)$$

$$\left(\frac{\partial U238s}{\partial U238b}\right) = \left\lfloor\frac{-1}{1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)}\right\rfloor \quad (52)$$

$$\left(\frac{\partial U238s}{\partial FU}\right) = \left\lfloor\frac{3\cdot U235t\cdot R85m}{1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)}\right\rfloor + \left[\frac{U235t\cdot R85m\cdot(1+3\cdot FU)-(R85t\cdot U235t)-U238b}{\left[1-\left(\frac{1}{137.88}\right)\cdot R85m\cdot(1+3\cdot FU)\right]^2}\cdot\left(\frac{3\cdot R85m}{137.88}\right)\right] \quad (53)$$

[33] These partial derivatives and variances can then be substituted into equation (49) to derive the uncertainty in sample ^{238}U.

2.1.6. Sample ^{235}U

[34] First establishing the simple algebraic expression for sample ^{235}U,

$$U235s = \left(\frac{1}{137.88}\right) \cdot U238s \tag{54}$$

the error propagation equation may be written as (assuming all errors are uncorrelated):

$$\sigma^2_{U235s} = \left[\left(\frac{\partial U235s}{\partial U238s}\right) \cdot \sigma_{U238s}\right]^2 \tag{55}$$

[35] The partial derivative is simply:

$$\left(\frac{\partial U235s}{\partial U238s}\right) = \left(\frac{1}{137.88}\right) \tag{56}$$

which can be substituted into equation (55) to derive the uncertainty in sample ^{238}U. Note the result that the relative error in sample ^{235}U ($U235s$) is equivalent to the relative error in sample ^{238}U ($U238s$).

2.2. Derivation of Sample Isotope Ratios and Errors

[36] The following derivations for sample isotope ratios and errors use the previously noted approximation for the error resulting from the quotient of two variables, $x = u/v$ (equation (45)). All constructed Pb isotope ratios are functions of one or more common terms, and as such covariance resulting from these common terms must be included in the error propagation. Analytical calculation of covariance utilizes the following relationship [*Bevington and Robinson*, 1992]:

$$\sigma^2_{uv} = \sigma^2_c \left(\frac{\partial u}{\partial c}\right)\left(\frac{\partial v}{\partial c}\right) \tag{57}$$

where u and v are functions of a common variable c. The total covariance is calculated as the sum of the shared individual covariances.

2.2.1. Sample ^{207}Pb/^{206}Pb

[37] We first recognize sample ^{207}Pb/^{206}Pb as the quotient of the previously derived terms, $Pb206s$ (equation (3)) and $Pb207s$ (equation (9)), and thus define the sample ^{207}Pb/^{206}Pb variance as:

$$\left(\frac{\sigma_{R76s}}{R76s}\right)^2 = \left(\frac{\sigma_{Pb207s}}{Pb207s}\right)^2 + \left(\frac{\sigma_{Pb206s}}{Pb206s}\right)^2 - \frac{2}{Pb207s \cdot Pb206s} \cdot \sigma^2_{Pb207s \cdot Pb206s} \tag{58}$$

[38] The variance terms were previously calculated for $Pb206s$ (equation (4)) and $Pb207s$ (equation (10)). Noting that $Pb206s$ and $Pb207s$ are functions of several common terms ($R65m$, $R65t$, FPb, $Pb206b$) the covariance between $Pb207s$ and $Pb206s$ is calculated as:

$$\begin{aligned}\sigma^2_{Pb207s \cdot Pb206s} = {} & \sigma^2_{R65m} \cdot \left(\frac{\partial Pb207s}{\partial R65m}\right) \cdot \left(\frac{\partial Pb206s}{\partial R65m}\right) \\ & + \sigma^2_{R65t} \cdot \left(\frac{\partial Pb207s}{\partial R65t}\right) \cdot \left(\frac{\partial Pb206s}{\partial R65t}\right) \\ & + \sigma^2_{FPb} \cdot \left(\frac{\partial Pb207s}{\partial FPb}\right) \cdot \left(\frac{\partial Pb206s}{\partial FPb}\right) \\ & + \sigma^2_{Pb206b} \cdot \left(\frac{\partial Pb207s}{\partial Pb206b}\right) \cdot \left(\frac{\partial Pb206s}{\partial Pb206b}\right)\end{aligned} \tag{59}$$

[39] Substituting the partial derivatives of $Pb206s$ (equations (5)–(8)) and $Pb207s$ (equations (11)–(17)) with respect to each common variable:

$$\begin{aligned}\sigma^2_{Pb207s \cdot Pb206s} = {} & \{R76m \cdot (1 + 2FPb) \cdot Pb205t\} \\ & \cdot \{(1 + FPb) \cdot Pb205t\} \cdot \sigma^2_{R65m} R65t^2 \\ & + \{2 \cdot R76m \cdot R65m \cdot Pb205t\} \\ & \cdot \{R65m \cdot Pb205t\} \cdot \sigma^2_{FPb} \\ & + \{-R76b\} \cdot \{-1\} \cdot \sigma^2_{Pb206b}\end{aligned} \tag{60}$$

[40] This covariance can be substituted into equation (58) to calculate the sample ^{207}Pb/^{206}Pb variance.

2.2.2. Sample ^{204}Pb/^{206}Pb

[41] We first recognize sample ^{204}Pb/^{206}Pb as the quotient of the previously derived terms, $Pb204c$ (equation (22)) and $Pb206s$ (equation (3)), and thus define the sample ^{204}Pb/^{206}Pb variance as:

$$\left(\frac{\sigma_{R46s}}{R46s}\right)^2 = \left(\frac{\sigma_{Pb204c}}{Pb204c}\right)^2 + \left(\frac{\sigma_{Pb206s}}{Pb206s}\right)^2 - \frac{2}{Pb204c \cdot Pb206s} \cdot \sigma^2_{Pb204c \cdot Pb206s} \tag{61}$$

[42] The variance terms were previously calculated for $Pb204c$ (equation (23)) and $Pb206s$ (equation (4)). Noting that $Pb204c$ and $Pb206s$ are functions of

several common terms ($R65m$, $R65t$, FPb, $Pb206b$), the covariance between $Pb204c$ and $Pb206s$ is calculated as:

$$\sigma^2_{Pb204c\cdot Pb206s} = \sigma^2_{R65m}\cdot\left(\frac{\partial Pb204c}{\partial R65m}\right)\cdot\left(\frac{\partial Pb206s}{\partial R65m}\right) + \sigma^2_{R65t}\cdot\left(\frac{\partial Pb204c}{\partial R65t}\right)\cdot\left(\frac{\partial Pb206s}{\partial R65t}\right) + \sigma^2_{FPb}\cdot\left(\frac{\partial Pb204c}{\partial FPb}\right)\cdot\left(\frac{\partial Pb206s}{\partial FPb}\right) + \sigma^2_{Pb206b}\cdot\left(\frac{\partial Pb204c}{\partial Pb206b}\right)\cdot\left(\frac{\partial Pb206s}{\partial Pb206b}\right) \quad (62)$$

[43] Substituting the partial derivatives of $Pb206s$ (equations (5)–(8)) and $Pb204c$ (equation (24)–(30)) with respect to each common variable:

$$\sigma^2_{Pb204c\cdot Pb206s} = \{R46m\cdot(1-FPb)\cdot Pb205t\}\cdot\{(1+FPb)\cdot Pb205t\}\cdot\sigma^2_{R65m} + \{-R46t\cdot Pb205t\}\cdot\{-Pb205t\}\cdot\sigma^2_{R65t} + \{-R46m\cdot R65m\cdot Pb205t\}\cdot\{R65m\cdot Pb205t\}\cdot\sigma^2_{FPb} + \left\{\frac{-1}{R64b}\right\}\cdot\{-1\}\cdot\sigma^2_{Pb206b} \quad (63)$$

[44] This covariance can be substituted into equation (61) to calculate the $^{204}Pb/^{206}Pb$ variance. Note that the relative error in sample $^{204}Pb/^{206}Pb$ is equivalent to the relative error in sample $^{206}Pb/^{204}Pb$.

2.2.3. Sample $^{204}Pb/^{207}Pb$

[45] We first recognize sample $^{204}Pb/^{207}Pb$ as the quotient of the previously derived terms, $Pb204c$ (equation (22)) and $Pb207s$ (equation (9)), and thus define the sample $^{204}Pb/^{207}Pb$ variance as:

$$\left(\frac{\sigma_{R47s}}{R47s}\right)^2 = \left(\frac{\sigma_{Pb204c}}{Pb204c}\right)^2 + \left(\frac{\sigma_{Pb207s}}{Pb207s}\right)^2 - \frac{2}{Pb204c\cdot Pb207s}\cdot\sigma^2_{Pb204c\cdot Pb207s} \quad (64)$$

[46] The variance terms were previously calculated for $Pb204c$ (equation (23)) and $Pb207s$ (equation (10)). Note that $Pb204c$ and $Pb207s$ are functions of the common terms: $R65m$, $R65t$, F, $Pb206b$. The covariance between $Pb204c$ and $Pb207s$ is calculated as:

$$\sigma^2_{Pb204c\cdot Pb207s} = \sigma^2_{R65m}\cdot\left(\frac{\partial Pb204c}{\partial R65m}\right)\cdot\left(\frac{\partial Pb207s}{\partial R65m}\right) + \sigma^2_{R65t}\cdot\left(\frac{\partial Pb204c}{\partial R65t}\right)\cdot\left(\frac{\partial Pb207s}{\partial R65t}\right) + \sigma^2_{FPb}\cdot\left(\frac{\partial Pb204c}{\partial FPb}\right)\cdot\left(\frac{\partial Pb207s}{\partial FPb}\right) + \sigma^2_{Pb206b}\cdot\left(\frac{\partial Pb204c}{\partial Pb206b}\right)\cdot\left(\frac{\partial Pb207s}{\partial Pb206b}\right) \quad (65)$$

[47] Substituting the partial derivatives of $Pb207s$ (equations (11)–(17)) and $Pb204c$ (equations (24)–(30)) with respect to each common variable:

$$\sigma^2_{Pb204c\cdot Pb207s} = \{R46m\cdot(1-FPb)\cdot Pb205t\}\cdot\{R76m\cdot(1+2\cdot FPb)\cdot Pb205t\}\cdot\sigma^2_{R65m} + \{-R46t\cdot Pb205t\}\cdot\{-R76t\cdot Pb205t\}\cdot\sigma^2_{R65t} + \{-R46m\cdot R65m\cdot Pb205t\}\cdot\{2\cdot R76m\cdot R65m\cdot Pb205t\}\cdot\sigma^2_{FPb} + \left\{-\frac{1}{R64b}\right\}\cdot\{-R76b\}\cdot\sigma^2_{Pb206b} \quad (66)$$

[48] This covariance can be substituted into equation (64) to calculate the $^{204}Pb/^{207}Pb$ variance. Note that the relative error in sample $^{204}Pb/^{207}Pb$ is equivalent to the relative error in sample $^{207}Pb/^{204}Pb$.

2.2.4. Sample $^{238}U/^{206}Pb$, $^{238}U/^{207}Pb$, $^{238}U/^{204}Pb$, $^{235}U/^{207}Pb$, $^{235}U/^{204}Pb$

[49] For the U/Pb ratios, errors in numerator and denominator are considered essentially uncorrelated, eliminating the covariance terms. The resulting elementary expression for the propagated error for the quotient of two uncorrelated parameters ($x = u/v$) is:

$$\frac{\sigma_{RXYs}}{RXYs} = \sqrt{\left(\frac{\sigma_{U23Xs}}{U23Xs}\right)^2 + \left(\frac{\sigma_{Pb20Ys}}{Pb20Ys}\right)^2} \quad (67)$$

where $U23Xs$, $Pb20Ys$, and $RXYs$ are shorthand for the necessary isotope quantities and ratios.

2.3. Derivation of Sample Isotope Ratio Error Correlations

[50] The correlation coefficient (ρ or rho) between two isotope ratios is defined as the quotient of the covariance and the product of the standard deviations for each ratio:

$$\rho_{uv} = \frac{\sigma^2_{uv}}{\sigma_u\sigma_v} \quad (68)$$

[51] To solve for the correlation coefficient analytically requires an estimate of the ratio covariance, for which we take advantage of the previously noted error equation for the quotient of two vari-

ables, $x = u/v$ (equations (44)–(45)). Substituting equation (45) into equation (68):

$$\rho_{uv} = \frac{u\cdot v\left[\frac{\left(\frac{\sigma_u}{u}\right)^2+\left(\frac{\sigma_v}{v}\right)^2-\left(\frac{\sigma_x}{x}\right)^2}{2}\right]}{\sigma_u\cdot\sigma_v} = \frac{u\cdot v\cdot\left[\left(\frac{\sigma_u}{u}\right)^2+\left(\frac{\sigma_v}{v}\right)^2-\left(\frac{\sigma_x}{x}\right)^2\right]}{2\cdot\sigma_u\cdot\sigma_v} = \frac{\left(\frac{\sigma_u}{u}\right)^2+\left(\frac{\sigma_v}{v}\right)^2-\left(\frac{\sigma_x}{x}\right)^2}{2\cdot\left(\frac{\sigma_u}{u}\right)\cdot\left(\frac{\sigma_v}{v}\right)} \quad (69)$$

[52] Using a simplified notation for the relative errors (or coefficients of variance):

$$\%\sigma_u = \frac{\boldsymbol{\sigma}_u}{u}\ ;\ \%\sigma_v = \frac{\sigma_v}{v}\ ;\ \%\sigma_x = \frac{\boldsymbol{\sigma}_x}{x} \quad (70)$$

(note that this definition is functionally acceptable as the factor of 100 percentage multiplier cancels in the next expression) and substituting yields:

$$\rho_{uv} = \frac{\%\sigma_u^2+\%\sigma_v^2-\%\sigma_x^2}{2\cdot\%\sigma_u\cdot\%\sigma_v} \quad (71)$$

2.3.1. Rho $^{238}U/^{204}Pb$-$^{206}Pb/^{204}Pb$, Rho $^{235}U/^{204}Pb$-$^{207}Pb/^{204}Pb$, Rho $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$, and Rho $^{238}U/^{206}Pb$-$^{204}Pb/^{206}Pb$

[53] We can now define x, u, and v, and make the appropriate substitutions to define the equations for each correlation coefficient. Defining $U23Xs$, $Pb20Ys$, $Pb20Zs$, and $RXYs$, $RXZs$, and $RYZs$ as shorthand for the necessary isotope quantities and ratios:

$$x = RXYs = \frac{U23Xs}{Pb20Ys} \quad (72)$$

$$u = RXZs = \frac{U23Xs}{Pb20Zs} \quad (73)$$

$$v = RXZs = \frac{Pb20Ys}{Pb20Zs} \quad (74)$$

$$\rho_{RXZs-RYZs} = \frac{\%\sigma_{RXZs}^2+\%\sigma_{RYZs}^2-\%\sigma_{RXYs}^2}{2\cdot\%\sigma_{RXZs}\cdot\%\sigma_{RYZs}} \quad (75)$$

[54] In our specific cases:

$$\rho_{R84s-R64s} = \frac{\%\sigma_{R84s}^2+\%\sigma_{R64s}^2-\%\sigma_{R86s}^2}{2\cdot\%\sigma_{R84s}\cdot\%\sigma_{R64s}} \quad (76)$$

$$\rho_{R54s-R74s} = \frac{\%\sigma_{R54s}^2+\%\sigma_{R74s}^2-\%\sigma_{R57s}^2}{2\cdot\%\sigma_{R54s}\cdot\%\sigma_{R74s}} \quad (77)$$

$$\rho_{R86s-R76s} = \frac{\%\sigma_{R86s}^2+\%\sigma_{R76s}^2-\%\sigma_{R87s}^2}{2\cdot\%\sigma_{R86s}\cdot\%\sigma_{R76s}} \quad (78)$$

$$\rho_{R86s-R46s} = \frac{\%\sigma_{R86s}^2+\%\sigma_{R46s}^2-\%\sigma_{R84s}^2}{2\cdot\%\sigma_{R86s}\cdot\%\sigma_{R46s}} \quad (79)$$

2.3.2. Rho $^{207}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$-$^{204}Pb/^{206}Pb$

[55] Similarly defining $Pb20Xs$, $Pb20Ys$, $Pb20Zs$, and $RXYs$, $RXZs$, and $RYZs$ as shorthand for the necessary isotope quantities and ratios:

$$x = RXYs = \frac{Pb20Xs}{Pb20Ys} = \frac{u}{v} \quad (80)$$

$$u = RXZs = \frac{Pb20Xs}{Pb20Zs} \quad (81)$$

$$v = RYZs = \frac{Pb20Ys}{Pb20Zs} \quad (82)$$

$$\rho_{RXZs-RYZs} = \frac{\%\sigma_{RXZs}^2+\%\sigma_{RYZs}^2-\%\sigma_{RXYs}^2}{2\cdot\%\sigma_{RXZs}\cdot\%\sigma_{RYZs}} \quad (83)$$

[56] In our specific cases:

$$\rho_{R74s-R64s} = \frac{\%\sigma_{R74s}^2+\%\sigma_{R64s}^2-\%\sigma_{R76s}^2}{2\cdot\%\sigma_{R74s}\cdot\%\sigma_{R64s}} \quad (84)$$

$$\rho_{R76s-R46s} = \frac{\%\sigma_{R76s}^2+\%\sigma_{R46s}^2-\%\sigma_{R74s}^2}{2\cdot\%\sigma_{R76s}\cdot\%\sigma_{R46s}} \quad (85)$$

3. Radiogenic U-Pb Ratios, Errors, and Error Correlations

[57] The following section details the propagation of errors through the calculation of radiogenic $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$, and $^{207}Pb/^{206}Pb$ ratios, including errors and error correlations associated with Pb and U isotope fractionation corrections (including errors in U isotope fractionation estimation utilizing a double ^{233}U - ^{235}U tracer), tracer and blank U and Pb subtractions, and initial common Pb corrections. The resulting ratios, errors and error correlations may be used in the calcula-

tion and depiction of traditional Wetherill and Tera-Wasserburg type concordia diagrams, and radiogenic U-Pb and Pb-Pb model age calculations.

3.1. Derivation of Molar Isotope Quantities and Errors

3.1.1. Radiogenic $^{206}Pb^*$

[58] First establishing the algebraic expression for radiogenic ^{206}Pb,

$$\begin{aligned} Pb206r = {} & [R65m \cdot Pb205t \cdot (1 + FPb)] \\ & - [R65t \cdot Pb205t] - [Pb206b] - R64c \\ & \cdot \left\{ [R46m \cdot R65m \cdot Pb205t \cdot R64c \cdot (1 - FPb)]. \right. \\ & \left. - (R45t \cdot Pb205t) - \left(\frac{Pb206b}{R64b} \right) \right\} \end{aligned} \tag{86}$$

the error propagation equation may be written as (assuming all errors except $R65m$ and $R46m$, and $R65t$ and $R45t$ are uncorrelated):

$$\begin{aligned} \sigma^2_{Pb206r} = {} & \left[\left(\frac{\partial Pb206r}{\partial R65m} \right) \cdot \sigma_{R65m} \right]^2 + \left[\left(\frac{\partial Pb206r}{\partial R46m} \right) \cdot \sigma_{R46m} \right]^2 \\ & + \left[\left(\frac{\partial Pb206r}{\partial R65t} \right) \cdot \sigma_{R65t} \right]^2 + \left[\left(\frac{\partial Pb206r}{\partial R45t} \right) \cdot \sigma_{R45t} \right]^2 \\ & + \left[\left(\frac{\partial Pb206r}{\partial FPb} \right) \cdot \sigma_{FPb} \right]^2 + \left[\left(\frac{\partial Pb206r}{\partial Pb206b} \right) \cdot \sigma_{Pb206b} \right]^2 \\ & + \left[\left(\frac{\partial Pb206r}{\partial R64b} \right) \cdot \sigma_{R64b} \right]^2 + \left[\left(\frac{\partial Pb206r}{\partial R64c} \right) \cdot \sigma_{R64c} \right]^2 \\ & + 2 \cdot \sigma^2_{R65m-R46m} \cdot \left(\frac{\partial Pb206r}{\partial R65m} \right) \cdot \left(\frac{\partial Pb206r}{\partial R46m} \right) \\ & + 2 \cdot \sigma^2_{R45t-R65t} \cdot \left(\frac{\partial Pb206r}{\partial R45t} \right) \cdot \left(\frac{\partial Pb206r}{\partial R65t} \right) \end{aligned} \tag{87}$$

[59] The partial derivatives are then calculated as follows:

$$\left(\frac{\partial Pb206r}{\partial R65m} \right) = [(1 + FPb) - R64c \cdot R46m \cdot (1 - FPb)] \cdot Pb205t \tag{88}$$

$$\left(\frac{\partial Pb206r}{\partial R46m} \right) = -R64c \cdot R65m \cdot (1 - FPb) \cdot Pb205t \tag{89}$$

$$\left(\frac{\partial Pb206r}{\partial R65t} \right) = -Pb205t \tag{90}$$

$$\left(\frac{\partial Pb206r}{\partial R45t} \right) = R64c \cdot Pb205t \tag{91}$$

$$\left(\frac{\partial Pb206r}{\partial FPb} \right) = (1 + R64c \cdot R46m) \cdot R65m \cdot Pb205t \tag{92}$$

$$\left(\frac{\partial Pb206r}{\partial Pb206b} \right) = \frac{R64c}{R64b} - 1 \tag{93}$$

$$\left(\frac{\partial Pb206r}{\partial R64b} \right) = \frac{-R64c \cdot Pb206b}{R64b^2} \tag{94}$$

$$\begin{aligned} \left(\frac{\partial Pb206r}{\partial R64c} \right) = {} & [-R46m \cdot R65m \cdot Pb205t \cdot (1 - FPb)] \\ & + (R45t \cdot Pb205t) + \left(\frac{Pb206b}{R64b} \right) \end{aligned} \tag{95}$$

[60] The covariance between $R65m$ and $R46m$ has been derived in equation (31). The covariance between $R65t$ and $R45t$ is calculated by the method of equations (44)–(45):

$$\sigma^2_{R45t-R65t} = \frac{R45t \cdot R65t \cdot \left[\left(\frac{\sigma_{R45t}}{R45t} \right)^2 + \left(\frac{\sigma_{R65t}}{R65t} \right)^2 - \left(\frac{\sigma_{R46t}}{R46t} \right)^2 \right]}{2} \tag{96}$$

[61] These partial derivatives, variances, and covariances then can be substituted into equation (87) to derive the uncertainty in radiogenic ^{206}Pb.

3.1.2. Radiogenic $^{207}Pb^*$

[62] First establishing the algebraic expression for radiogenic ^{207}Pb,

$$\begin{aligned} Pb207r = {} & [R65m \cdot R76m \cdot Pb205t \cdot (1 + 2 \cdot FPb)] \\ & - [R65t \cdot R76t \cdot Pb205t] - [R76b \cdot Pb206b] \\ & - R64c \cdot R76c \cdot \{ [R46m \cdot R65m \cdot Pb205t \\ & \cdot (1 - FPb)] - [R45t \cdot Pb205t] - \left[\left(\frac{Pb206b}{R64b} \right) \right] \} \end{aligned} \tag{97}$$

the error propagation equation may be written as (assuming all errors except $R65m$, $R46m$ and $R76m$, and $R65t$, $R45t$ and $R76t$ are uncorrelated):

$$\sigma^2_{Pb207r} = \left[\left(\frac{\partial Pb207r}{\partial R65m}\right)\cdot\sigma_{R65m}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R76m}\right)\cdot\sigma_{R76m}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R46m}\right)\cdot\sigma_{R46m}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R65t}\right)\cdot\sigma_{R65t}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R76t}\right)\cdot\sigma_{R76t}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R45t}\right)\cdot\sigma_{R45t}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial FPb}\right)\cdot\sigma_{FPb}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial Pb206b}\right)\cdot\sigma_{Pb206b}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R76b}\right)\cdot\sigma_{R76b}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R64b}\right)\cdot\sigma_{R64b}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R76c}\right)\cdot\sigma_{R76c}\right]^2 + \left[\left(\frac{\partial Pb207r}{\partial R64c}\right)\cdot\sigma_{R64c}\right]^2 + 2\cdot\sigma^2_{R65m-R76m}\cdot\left(\frac{\partial Pb207r}{\partial R65m}\right)\cdot\left(\frac{\partial Pb207r}{\partial R76m}\right) + 2\cdot\sigma^2_{R65m-R46m}\cdot\left(\frac{\partial Pb207r}{\partial R65m}\right)\cdot\left(\frac{\partial Pb207r}{\partial R46m}\right) + 2\cdot\sigma^2_{R65t-R76t}\cdot\left(\frac{\partial Pb207r}{\partial R65t}\right)\cdot\left(\frac{\partial Pb207r}{\partial R76t}\right) + 2\cdot\sigma^2_{R45t-R65t}\cdot\left(\frac{\partial Pb207r}{\partial R45t}\right)\cdot\left(\frac{\partial Pb207r}{\partial R65t}\right) \quad (98)$$

[63] The partial derivatives are then calculated as follows:

$$\left(\frac{\partial Pb207r}{\partial R65m}\right) = [R76m\cdot(1+2\cdot FPb) - R64c\cdot R76c\cdot R46m\cdot(1-FPb)]\cdot Pb205t = [R76m\cdot(1+2\cdot FPb) - R74c\cdot R46m\cdot(1-FPb)]\cdot Pb205t \quad (99)$$

$$\left(\frac{\partial Pb207r}{\partial R76m}\right) = R65m\cdot(1+2\cdot FPb)\cdot Pb205t \quad (100)$$

$$\left(\frac{\partial Pb207r}{\partial R46m}\right) = -R64c\cdot R76c\cdot R65m\cdot(1-FPb)\cdot Pb205t = -R74c\cdot R65m\cdot(1-FPb)\cdot Pb205t \quad (101)$$

$$\left(\frac{\partial Pb207r}{\partial FPb}\right) = (2\cdot R76m + R64c\cdot R76c\cdot R46m)\cdot R65m\cdot Pb205t = (2\cdot R76m + R74c\cdot R46m)\cdot R65m\cdot Pb205t \quad (102)$$

$$\left(\frac{\partial Pb207r}{\partial R65t}\right) = -R76t\cdot Pb205t \quad (103)$$

$$\left(\frac{\partial Pb207r}{\partial R76t}\right) = -R65t\cdot Pb205t \quad (104)$$

$$\left(\frac{\partial Pb207r}{\partial R45t}\right) = R64c\cdot R76c\cdot Pb205t = R74c\cdot Pb205t \quad (105)$$

$$\left(\frac{\partial Pb207r}{\partial Pb206b}\right) = -R76b + \frac{R64c\cdot R76c}{R64b} = \frac{R64c\cdot R76c}{R64b} - \frac{R64b\cdot R76b}{R64b} = \frac{R74c - R74b}{R64b} \quad (106)$$

$$\left(\frac{\partial Pb207r}{\partial R64b}\right) = \frac{-R64c\cdot R76c\cdot Pb206b}{R64b^2} = \frac{-R74c\cdot Pb206b}{R64b^2} \quad (107)$$

$$\left(\frac{\partial Pb207r}{\partial R76b}\right) = -Pb206b \quad (108)$$

$$\left(\frac{\partial Pb207r}{\partial R64c}\right) = [-R46m\cdot R65m\cdot Pb205t\cdot R76c\cdot(1-FPb)] + (R45t\cdot Pb205t\cdot R76c) + \left(\frac{Pb206b}{R64b}\cdot R76c\right) \quad (109)$$

$$\left(\frac{\partial Pb207r}{\partial R76c}\right) = [-R46m\cdot R65m\cdot Pb205t\cdot R64c\cdot(1-FPb)] + (R45t\cdot Pb205t\cdot R64c) + \left(\frac{Pb206b}{R64b}\cdot R64c\right) \quad (110)$$

[64] The covariance terms have been derived in equations (20), (21), (31) and (96). These partial derivatives, variances, and covariances then can be substituted into equation (98) to derive the uncertainty in radiogenic ^{207}Pb.

3.2. Derivation of Radiogenic Isotope Ratios and Errors

[65] As in section 2.2, the following derivations for radiogenic isotope ratios and errors use the approximation for the error resulting from the quotient of two variables (equation (45)). Radiogenic Pb/U ratios utilize the molar sample ^{238}U and ^{235}U equations and errors derived in sections 2.1.5 and 2.1.6. Covariance between numerator and denominator of the ^{207}Pb*/^{206}Pb* ratio is derived according to the method described in section 2.2.

3.2.1. Radiogenic $^{207}Pb^*/^{206}Pb^*$

[66] We first recognize $^{207}Pb^*/^{206}Pb^*$ as a quotient of the previously derived terms, *Pb206r* (equation (86)) and *Pb207r* (equation (97)), and thus define the $^{207}Pb^*/^{206}Pb^*$ variance as:

$$\left(\frac{\sigma_{R76r}}{R76r}\right)^2 = \left(\frac{\sigma_{Pb207r}}{Pb207r}\right)^2 + \left(\frac{\sigma_{Pb206r}}{Pb206r}\right)^2 - \frac{2}{Pb207r \cdot Pb206r} \cdot \sigma^2_{Pb207r \cdot Pb206r} \quad (111)$$

[67] We have previously derived the variances for radiogenic ^{206}Pb (equation (87)) and ^{207}Pb (equation (98)). Note that *Pb*207*r* and *Pb*206*r* are functions of numerous common terms: *R*65*m*, *R*46*m*, *R*65*t*, *R*45*t*, *FPb*, *R*64*b*, *Pb*206*b*, *R*64*c*. The covariance between *Pb*207*r* and *Pb*206*r* is thus calculated as:

$$\begin{aligned}(\sigma^2_{Pb207r-Pb206r}) = {} & \sigma^2_{R65m} \cdot \left(\frac{\partial Pb207r}{\partial R65m}\right) \cdot \left(\frac{\partial Pb206r}{\partial R65m}\right) \\ & + \sigma^2_{R46m} \cdot \left(\frac{\partial Pb207r}{\partial R46m}\right) \cdot \left(\frac{\partial Pb206r}{\partial R46m}\right) \\ & + \sigma^2_{R65t} \cdot \left(\frac{\partial Pb207r}{\partial R65t}\right) \cdot \left(\frac{\partial Pb206r}{\partial R65t}\right) \\ & + \sigma^2_{R45t} \cdot \left(\frac{\partial Pb207r}{\partial R45t}\right) \cdot \left(\frac{\partial Pb206r}{\partial R45t}\right) \\ & + \sigma^2_{FPb} \cdot \left(\frac{\partial Pb207r}{\partial FPb}\right) \cdot \left(\frac{\partial Pb206r}{\partial FPb}\right) \\ & + \sigma^2_{Pb206b} \cdot \left(\frac{\partial Pb207r}{\partial Pb206b}\right) \cdot \left(\frac{\partial Pb206r}{\partial Pb206b}\right) \\ & + \sigma^2_{R64b} \cdot \left(\frac{\partial Pb207r}{\partial R64b}\right) \cdot \left(\frac{\partial Pb206r}{\partial R64b}\right) \\ & + \sigma^2_{R64c} \cdot \left(\frac{\partial Pb207r}{\partial R64c}\right) \cdot \left(\frac{\partial Pb206r}{\partial R64c}\right) \quad (112)\end{aligned}$$

[68] The reader is referred to the derivations of *Pb*206*r* (section 3.1.1) and *Pb*207*r* (section 3.1.2) for the partial derivatives to substitute into equation (112).

3.2.2. Radiogenic $^{206}Pb^*/^{238}U$, $^{207}Pb^*/^{235}U$, $^{207}Pb^*/^{238}U$

[69] For the Pb*/U ratios (e.g., $^{206}Pb^*/^{238}U$, $^{207}Pb^*/^{235}U$, $^{207}Pb^*/^{238}U$), errors in numerator and denominator are considered essentially uncorrelated, eliminating the covariance terms.

$$x = \frac{u}{v} = \frac{Pb20Xr}{U23Ys} = RXYr \quad (113)$$

$$\frac{\sigma_{RXYr}}{RXYr} = \sqrt{\left(\frac{\sigma_{Pb20Xr}}{Pb20Xr}\right)^2 + \left(\frac{\sigma_{U23Ys}}{U23Ys}\right)^2} \quad (114)$$

where *Pb*20*Xr*, *U*23*Yr*, and *RXYr* are shorthand for the necessary isotope quantities and ratios. Note that the relative error in $^{206}Pb^*/^{238}U$ is equivalent to the relative error in $^{238}U/^{206}Pb^*$ for the purposes of representation in the Tera-Wasserburg concordia diagram. Similarly, the relative error in $^{207}Pb^*/^{238}U$ is equivalent to the relative error in $^{238}U/^{207}Pb^*$ for the purposes of calculating error correlations for the Tera-Wasserburg concordia diagram.

3.3. Derivation of Radiogenic Isotope Ratio Error Correlations

[70] The correlation coefficient (ρ or rho) between two radiogenic isotope ratios is calculated according to the derivation of section 2.3. The following error correlations are applicable to the Wetherill and Tera-Wasserburg concordia diagrams.

3.3.1. Rho $^{207}Pb^*/^{235}U$-$^{206}Pb^*/^{238}U$

$$x = R76r = \frac{Pb207r}{Pb206r} \quad (115)$$

$$u = R75r = \frac{Pb207r}{U235s} \quad (116)$$

$$v = R68r = \frac{Pb206r}{U238s} \quad (117)$$

$$\rho_{R75r-R68r} = \frac{\%\sigma^2_{R75r} + \%\sigma^2_{R68r} - \%\sigma^2_{R76r}}{2 \cdot \%\sigma_{R75r} \cdot \%\sigma_{R68r}} \quad (118)$$

3.3.2. Rho $^{238}U/^{206}Pb^*$ - $^{207}Pb^*/^{206}Pb^*$

$$x = R87r = \frac{U238s}{Pb207r} \quad (119)$$

$$u = R86r = \frac{U238s}{Pb206r} \quad (120)$$

$$v = R76r = \frac{Pb207r}{Pb206r} \quad (121)$$

$$\rho_{R86r-R76r} = \frac{\%\sigma^2_{R86r} + \%\sigma^2_{R76r} - \%\sigma^2_{R87r}}{2 \cdot \%\sigma_{R86r} \cdot \%\sigma_{R76r}} \quad (122)$$

4. Radiogenic U-Pb and Pb-Pb Ages

4.1. Errors for $^{206}Pb^*/^{238}U$ and $^{207}Pb^*/^{235}U$ Ages

[71] Recalling the solution to the decay equation, and corresponding age equation for the ^{238}U-$^{206}Pb^*$ system:

$$R68r = e^{\lambda 238 \cdot t68} - 1 \tag{123}$$

$$t68 = \left(\frac{1}{\lambda 238}\right) \cdot \ln(R68r + 1) \tag{124}$$

the error propagation equation may be written as (assuming $\lambda 238$ is a constant):

$$\sigma_{t68}^2 = \sigma_{R68r}^2 \cdot \left(\frac{\partial t68}{\partial R68r}\right)^2 \tag{125}$$

[72] Evaluating the partial derivative of $t68$ with respect to $R68r$,

$$\left(\frac{\partial t68}{\partial R68r}\right) = \left(\frac{1}{\lambda 238}\right) \cdot \left(\frac{1}{R68r + 1}\right) \tag{126}$$

and substituting the derivative results in the $^{206}Pb^*/^{238}U$ age error:

$$\sigma_{t68} = \left(\frac{1}{\lambda 238}\right) \cdot \left(\frac{\sigma_{R68r}}{R68r + 1}\right) \tag{127}$$

[73] By analogous derivation, the $^{207}Pb^*/^{235}U$ age error is:

$$\sigma_{t75} = \left(\frac{1}{\lambda 235}\right) \cdot \left(\frac{\sigma_{R75r}}{R75r + 1}\right) \tag{128}$$

4.2. Error for $^{207}Pb^*/^{206}Pb^*$ Age

[74] Recalling the solution to the decay equation for the $^{207}Pb^*$-$^{206}Pb^*$ system,

$$R76r = \left(\frac{1}{137.88}\right) \cdot \left(\frac{e^{\lambda 235 \cdot t76} - 1}{e^{\lambda 238 \cdot t76} - 1}\right) = \left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda 235 \cdot t76} - 1\right) \cdot \left(e^{\lambda 238 \cdot t76} - 1\right)^{-1} \tag{129}$$

the error propagation equation may be written as (assuming $\lambda 235$ and $\lambda 238$ are constants),

$$\sigma_{R76r}^2 = \left[\left(\frac{\partial R76r}{\partial t76}\right) \cdot \sigma_{t76}\right]^2 \tag{130}$$

which may be solved analytically for σ_{t76}:

$$\sigma_{t76} = \frac{\sigma_{R76r}}{\left(\frac{\partial R76r}{\partial t76}\right)} \tag{131}$$

[75] In order to evaluate the partial derivative of $R76r$ with respect to $t76$, we apply the product rule:

$$\left(\frac{\partial R76r}{\partial t76}\right) = \left[\left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda 235 \cdot t76} - 1\right)\right] \cdot \frac{\partial}{\partial t76}\left[\left(e^{\lambda 238 \cdot t76} - 1\right)^{-1}\right] + \left[\left(e^{\lambda 238 \cdot t76} - 1\right)^{-1}\right] \cdot \frac{\partial}{\partial t76}\left[\left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda 235 \cdot t76} - 1\right)\right] \tag{132}$$

[76] In order to evaluate the two constituent derivatives, we then apply the chain rule:

$$\frac{\partial}{\partial t76}\left[\left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda 235 \cdot t76} - 1\right)\right] = \left(\frac{1}{137.88}\right) \cdot \lambda 235 \cdot \left(e^{\lambda 235 \cdot t76}\right) \tag{133}$$

$$\frac{\partial}{\partial t76}\left[\left(e^{\lambda 238 \cdot t76} - 1\right)^{-1}\right] = (-1) \cdot \left(e^{\lambda 238 \cdot t76} - 1\right)^{-2} \cdot \lambda 238 \cdot \left(e^{\lambda 238 \cdot t76}\right) \tag{134}$$

[77] Making the appropriate substitutions:

$$\sigma_{t76} = \frac{\sigma_{R76r}}{\left[\frac{\left(\frac{1}{137.88}\right) \cdot \lambda 235 \cdot \left(e^{\lambda 235 \cdot t76}\right)}{e^{\lambda 238 \cdot t76} - 1}\right] - \left[\frac{\left(\frac{1}{137.88}\right) \cdot \lambda 238 \cdot \left(e^{\lambda 238 \cdot t76}\right) \cdot \left(e^{\lambda 235 \cdot t76} - 1\right)}{\left(e^{\lambda 238 \cdot t76} - 1\right)^2}\right]} \tag{135}$$

[78] We note that this expression is equivalent to equation (3) of *Ludwig* [2000], without decay constant errors.

5. Discussion

[79] An accompanying spreadsheet formulation of these derivations (auxiliary material[1] Table S1) illustrates a number of analytical examples, including data for zircon and titanite from the Oligocene Fish Canyon Tuff (FCT) [*Schmitz and Bowring*, 2001], zircons from the Mesoproterozoic Duluth Complex Anorthosite Series (AS3) [*Schmitz et al.*, 2003] and zircons from a Permo-Triassic tuff (SO3; J. Crowley, unpublished data, 2006). The following discussion traces the contributions of various analytical uncertainties to the propagated error in the radiogenic $^{206}Pb^*/^{238}U$ ratio, in order to establish the importance of each measurement or correction to high-precision geochronology, as well as potentially guide future improvements in analytical protocols and precisions. We leave it to the reader to apply a similar analysis to $^{207}Pb^*/^{235}U$ and $^{207}Pb^*/^{206}Pb^*$ ratio errors.

[80] While tracer subtraction has generally not been previously incorporated into error propagation schemes, our analysis indicates that it can be a nontrivial source of error for samples over-spiked (e.g., $^{206}Pb/^{205}Pb < 1$) with a relatively impure tracer [*Parrish and Krogh*, 1987], if the relatively high $^{206}Pb/^{205}Pb$ of the tracer is not precisely measured (e.g., to 0.01% or better). The magnitude of the contribution of tracer ^{206}Pb subtraction to the $^{206}Pb^*/^{238}U$ error is illustrated in Figure 1 for three scenarios using two tracers. The first two scenarios involve use of the aforementioned relatively impure ^{205}Pb-rich spike ("GSC"), with two different propagated errors in tracer $^{206}Pb/^{205}Pb$. Error contributions of >10% are evident for overspiked samples assuming a tracer $^{206}Pb/^{205}Pb$ error of 0.1%; fortunately the error contribution decreases as the square of the assumed tracer $^{206}Pb/^{205}Pb$ error (Figure 1). The third scenario involves relatively imprecise knowledge of the tracer $^{206}Pb/^{205}Pb$ ratio for a more pure ^{205}Pb spike ("ET"), such as that used in the recently prepared EARTHTIME mixed Pb-U tracer solution. Figure 1 clearly illustrates how the use of the pure spike makes error contributions to the $^{206}Pb^*/^{238}U$ ratio error from spike subtraction trivial.

[81] Measurement errors in both Pb and U isotope ratios contribute a major component to the total $^{206}Pb^*/^{238}U$ error for all zircon analyses, as illustrated in Figures 2, 3, and 4b. The errors on measured $^{206}Pb/^{205}Pb$, $^{238}U/^{235}U$, and $^{233}U/^{235}U$ (the last through the U fractionation correction, *FU*) are generally the largest subequal contributors, while error contribution from the measured $^{204}Pb/^{206}Pb$ is proportionately smaller. Of the four measured ratios, only the error in $^{204}Pb/^{206}Pb$ is uncorrelated with its percentage contribution to the $^{206}Pb^*/^{238}U$ error. Measurement errors for the other three ratios are strongly positively correlated with their contributions to the $^{206}Pb^*/^{238}U$ error (Figure 3). This fact emphasizes the importance of very high precision isotope ratio measurements for precise geochronology, either through static Faraday measurements (U and large Pb samples) or peak jumping on a linear, large dynamic range ion-counting system, ideally accommodating count rates to the megahertz (Mcps) range. In addition to the requisite precision, robust linearity over this range is clearly critical to the measurement accuracy of the very large $^{206}Pb/^{204}Pb$ ratios (and very small ^{204}Pb ion signals) of radiogenic samples.

[82] Fractionation correction error is a major contributor to the $^{206}Pb^*/^{238}U$ error (Figures 2 and 4c), either manifested as a combination of measurement and tracer ratio errors for double-spiked U analyses, or as the reproducibility of an empirical fractionation correction factor estimated from standard Pb analyses. The latter is usually a more imprecise quantity and thus larger contributor to the total $^{206}Pb^*/^{238}U$ error. This is particularly true with the advent of U isotope analysis as the double oxide species using a silica gel emitter. The lower temperatures and more stable ion currents of oxide analyses result in a more reproducible mass fractionation; this fact is illustrated in Figure 2 by the contrast in FU versus FPb error contributions between the SO3 zircon analyses (UO_2^+) and FCT and AS3 zircon analyses (U^+). In the future, application of a double ^{202}Pb-^{205}Pb spike for internal fractionation correction should also significant decrease the *FPb* error contribution. We note that the algorithms from this paper can be used with double Pb spikes as well, if the variance of *FPb* is calculated internally using analogous methods to those used for *FU*.

[83] Finally, we can assess the contributions of errors associated with blank and initial common Pb subtraction (Figures 2 and 4a). In fact, due to the nature of the partial derivatives of radiogenic

[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gc/2006gc001492. Other auxiliary material files are in the HTML.

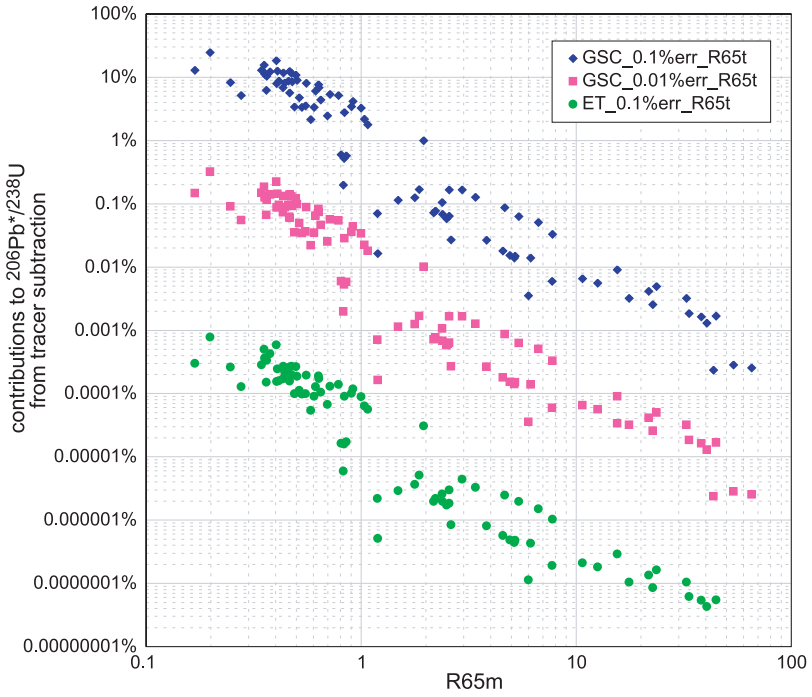

Figure 1. Contribution to radiogenic $^{206}Pb^*/^{238}U$ error from tracer subtraction (e.g., tracer ^{206}Pb) as a function of measured $^{206}Pb/^{205}Pb$ for three scenarios and two tracer compositions. "GSC" represents a relatively high $^{206}Pb/^{205}Pb$ tracer [*Parrish and Krogh*, 1987]; "ET" represents a lower $^{206}Pb/^{205}Pb$ tracer used in the EARTHTIME mixed spike. Each data point represents an individual zircon or sphene analysis (see auxiliary material spreadsheet file Table S1).

^{206}Pb with respect to Pb blank amount and blank and initial Pb isotope composition, error contributions from these three variables are relatively minor in the zircon analyses summarized in Figures 2 and 4. Of the three quantities, Pb blank amount predominates over a wide range of $^{206}Pb/^{204}Pb$, yet for the assumed blank amount in the range of 1–2 picograms ±25% (1σ) (the main group of analyses in Figure 4a) the contribution to $^{206}Pb^*/^{238}U$ error from blank amount uncertainty (being negatively correlated with $^{206}Pb/^{204}Pb$) only exceeds 10% at $^{206}Pb/^{204}Pb < 1000$. The smaller group of analyses in Figure 4a with substantially lower contributions to $^{206}Pb^*/^{238}U$ error from blank amount uncertainty are the SO3 zircons, which have significantly lower total common Pb and assumed blank amount uncertainty (average common Pb is ~0.3 pg, and all common Pb is assumed to be blank), thus illustrating how modern low-blank analysis can substantially mitigate errors associated with common Pb correction. Exploring this limit further, if procedural Pb blanks are reduced below 0.5 pg, then the analysis of only 5 pg of $^{206}Pb^*$ is required to essentially obviate errors associated with common Pb correction. Figure 5 illustrates the combination of relevant factors including U content, age and mass of zircon which yields the necessary 5 pg of $^{206}Pb^*$.

[84] It is worth noting that blank and initial common Pb composition uncertainties usually have contributions to $^{206}Pb^*/^{238}U$ error nearly two orders of magnitude less than that contributed from Pb blank amount. However, an interesting crossover in error contributions occurs at $^{206}Pb/^{204}Pb$ ratios of approximately 100–200, whereby error contributions from uncertainty in initial common Pb composition begin to predominate over not only the other common Pb variables, but all sources of error. This phenomenon is illustrated in Figures 2 and 4a by Fish Canyon sphene analyses.

[85] Figures 4b and 4c illustrate how substantial dilution of the error contributions from most measurement errors (with the exception of *R*46*m*) and fractionation correction uncertainties only takes place at relatively low $^{206}Pb/^{204}Pb$ ratios (<100). The obvious exception is the error contribution from *R*46*m*, which is inversely proportional to $^{206}Pb/^{204}Pb$ (Figure 4b) as would be expected by the increasingly important role this measured ratio

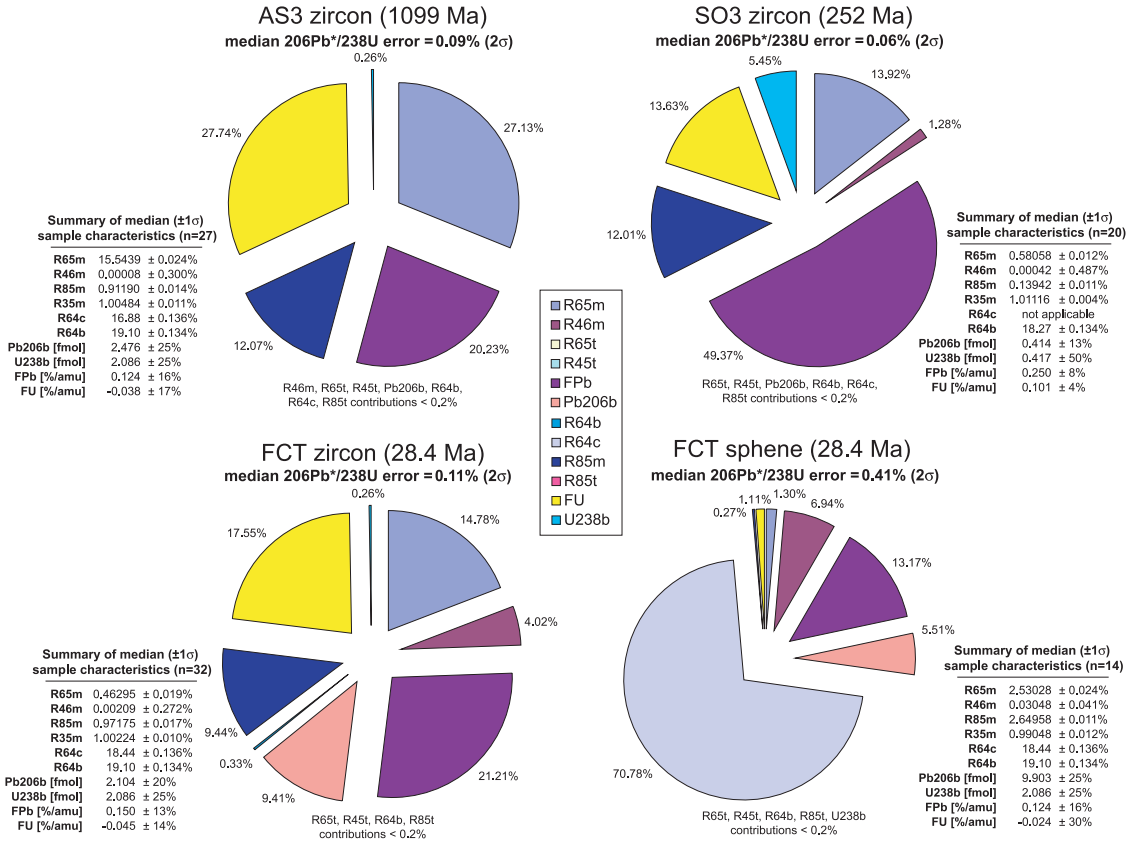

Figure 2. Percentage contributions of all sources of analytical uncertainty to the radiogenic $^{206}Pb^*/^{238}U$ error for four large, high-quality data sets. Percentages as well as listed values and uncertainties for analytical parameters represent the median (measured or assumed) values for each data set; all analyses may be found in the auxiliary material spreadsheet file Table S1. The median radiogenic $^{206}Pb^*/^{238}U$ error of each data set is listed above each chart. Assigned tracer composition uncertainties follow those of the "GSC_0.01%" scenario of Figure 1, resulting in their negligible error contributions.

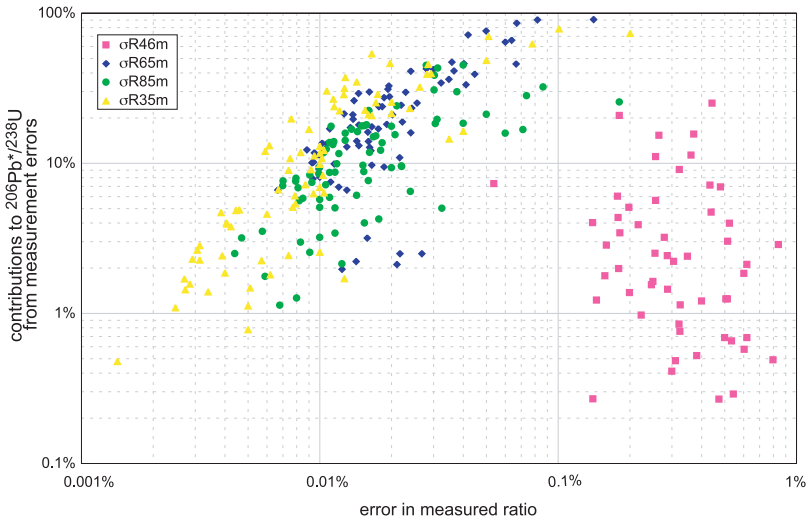

Figure 3. Contributions to radiogenic $^{206}Pb^*/^{238}U$ error from isotope ratio measurement uncertainties as a function of measured error for each ratio. Each data point represents an individual zircon or sphene analysis (see the auxiliary material spreadsheet file Table S1).

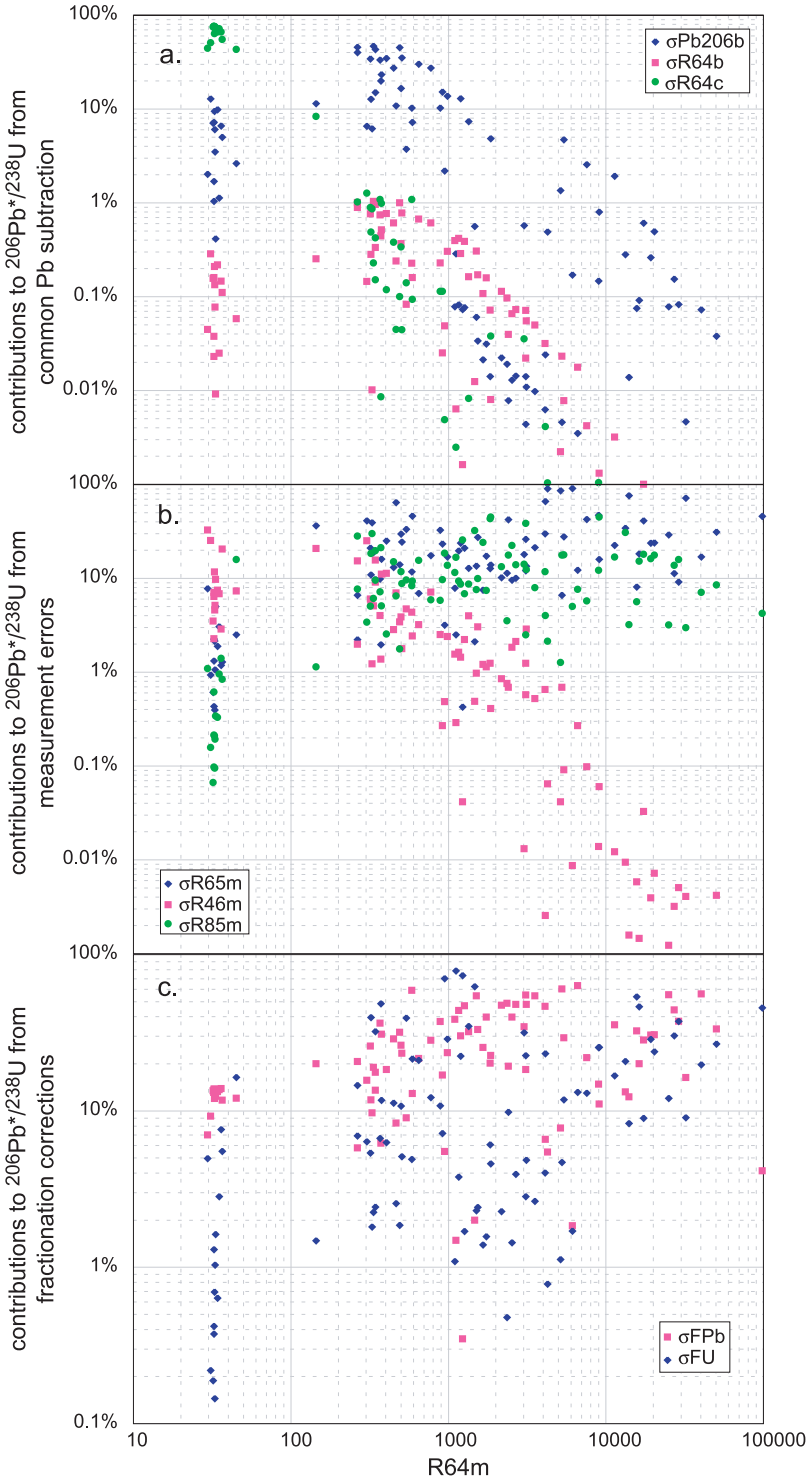

Figure 4. Contributions to radiogenic $^{206}Pb^*/^{238}U$ error from uncertainties in (a) common Pb subtraction variables, (b) isotope ratio measurements, and (c) fractionation corrections, as a function of measured $^{206}Pb/^{204}Pb$, a proxy for the radiogenic/common Pb ratio. Each data point represents an individual zircon or sphene analysis (see the auxiliary material spreadsheet file Table S1).

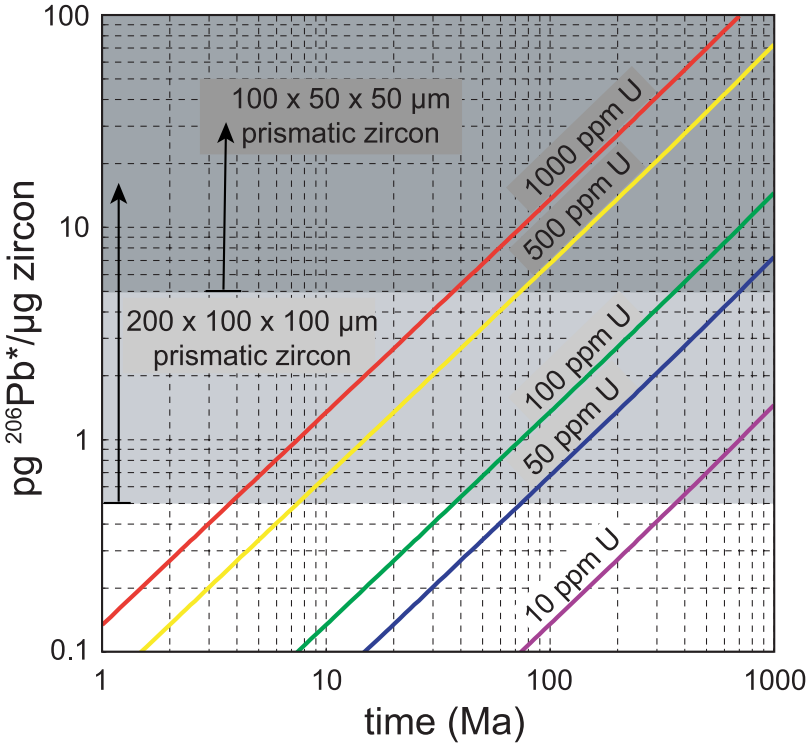

Figure 5. Graph of accumulated radiogenic ^{206}Pb* per microgram of zircon versus age, illustrating the combination of U content, zircon mass, and time necessary to produce 5 pg of radiogenic ^{206}Pb*, which is a minimum amount to obviate errors associated with common Pb correction for a 0.5 pg procedural Pb blank. A single zircon grain 200 μm in long dimension with an aspect ratio of 2:1 weighs approximately 10 μg; thus all concentrations above 0.5 pg/μg zircon will produce >5 pg of radiogenic ^{206}Pb* at ages older than the intersection of this concentration and the appropriate U concentration line (e.g., 7 Ma for a 500 ppm U zircon). A single zircon grain 100 μm in long dimension with an aspect ratio of 2:1 weighs approximately 1 μg; thus all concentrations above 5 pg/μg zircon will produce >5 pg of radiogenic ^{206}Pb* at ages older than the intersection of this concentration and the appropriate U concentration line (e.g., 70 Ma for a 500 ppm U zircon).

plays for blank correction in low sample/blank analyses [*Mattinson*, 1987].

[86] In summary, this analysis of error contribution to ^{206}Pb*/^{238}U ratio (and ultimately age) uncertainty not only quantitatively illustrates the necessary sample characteristics and mass spectrometric methods required for U-Pb geochronology at the level of 0.1% age resolution, but also serves as a tool to illuminate the way toward improvements in that resolution through refinements in Pb fractionation correction, better mass spectrometry, and cleaner sample preparation.

Acknowledgments

[87] This contribution was catalyzed by discussions with Felix Oberli on error propagation, and the ongoing efforts of participants in the EARTHTIME project. We thank James Crowley for the use of his unpublished data. Reviews and editorial comments by Kenneth Ludwig, James Mattinson, and Vincent Salters greatly improved the manuscript.

References

Bevington, P. R., and D. K. Robinson (1992), *Data Reduction and Error Analysis for the Physical Sciences*, 2nd ed., 328 pp., McGraw-Hill, New York.

Cumming, G. L. (1969), A recalculation of the age of the solar system, *Can. J. Earth Sci.*, *4*, 719–735.

Ludwig, K. R. (1980), Calculation of uncertainties of U-Pb isotope data, *Earth Planet. Sci. Lett.*, *46*, 212–220.

Ludwig, K. R. (1998), On the treatment of concordant uranium-lead ages, *Geochim. Cosmochim. Acta*, *62*, 665–676.

Ludwig, K. R. (2000), Decay constant errors in U-Pb concordia-intercept ages, *Chem. Geol.*, *166*, 315–318.

Mattinson, J. M. (1987), U-Pb ages of zircons: A basic examination of error propagation, *Chem. Geol.*, *66*, 151–162.

Parrish, R. R., and T. E. Krogh (1987), Synthesis and purification of 205Pb for U-Pb geochronology, *Chem. Geol.*, *66*, 103–110.

Schmitz, M. D., and S. A. Bowring (2001), U-Pb zircon and titanite systematics of the Fish Canyon Tuff: An assessment of high-precision U-Pb geochronology and its application to young volcanic rocks, *Geochim. Cosmochim. Acta*, *65*, 2571–2587.

Schmitz, M. D., et al. (2003), Evaluation of the Duluth Complex Anorthositic Series (AS3) zircons as a geochronological standard: New high-precision IDTIMS analyses, *Geochim. Cosmochim. Acta*, *67*, 3665–3672.

Schoene, B., and S. A. Bowring (2006), U-Pb systematics of the McClure Mountain syenite: Thermochronological constraints on the age of the $^{40}Ar/^{39}Ar$ standard MMhb, *Contrib. Mineral. Petrol.*, *151*, 615–630.