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. Introduction

U-Pb accessory mineral geochronology utilizing the isotope-dilution thermal ionization mass spectrometry (ID-TIMS) method has 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.

[1] 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.

[2] 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:

\[
x = f(u, v, \ldots)
\]

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

where \(\sigma_x^2\) is defined as the variance of \(x\), \(\sigma_u^2\) is defined as the covariance between \(u\) and \(v\), and \((\partial x/\partial u)\) is the first partial derivative of \(x\) with respect to \(u\).

[3] In all of the following derivations, errors in the tracer Pb/U ratio (e.g., the moles of \(^{206}\)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

[4] The following section details the propagation of errors through the calculation of \(^{206}\)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 $^{207}$U/$^{206}$Pb, $^{206}$Pb/$^{204}$Pb, $^{207}$U/$^{206}$Pb, and $^{207}$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,

\[
Pb_{206s} = \left[ R65m \cdot Pb_{205s} \cdot (1 + FPb) \right] - \left[ R65t \cdot Pb_{205t} \right] - \left[ Pb_{206b} \right] \tag{3}
\]

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

\[
\sigma_{Pb_{206s}}^2 = \left[ \left( \frac{\partial Pb_{206s}}{\partial R65m} \right)^2 \cdot \sigma_{R65m}^2 \right] + \left[ \left( \frac{\partial Pb_{206s}}{\partial Pb_{205s}} \right)^2 \cdot \sigma_{Pb_{205s}}^2 \right] + \left[ \left( \frac{\partial Pb_{206s}}{\partial FPb} \right)^2 \cdot \sigma_{FPb}^2 \right] + \left[ \left( \frac{\partial Pb_{206s}}{\partial Pb_{206b}} \right)^2 \cdot \sigma_{Pb_{206b}}^2 \right] + 2 \cdot \sigma_{R65m-R76m} \cdot \left( \frac{\partial Pb_{207s}}{\partial R65m} \right) \cdot \left( \frac{\partial Pb_{207s}}{\partial R76m} \right) \tag{4}
\]

[10] The partial derivatives are calculated as follows,

\[
\left( \frac{\partial Pb_{206s}}{\partial R65m} \right) = (1 + FPb) \cdot Pb_{205s} \tag{5}
\]

\[
\left( \frac{\partial Pb_{206s}}{\partial Pb_{205s}} \right) = \left( \frac{\partial Pb_{207s}}{\partial R65m} \right) = \left( \frac{\partial Pb_{207s}}{\partial R76m} \right) = -\frac{R65m}{R65t} \cdot Pb_{205t} \tag{6}
\]

\[
\left( \frac{\partial Pb_{206s}}{\partial FPb} \right) = R65m \cdot Pb_{205t} \tag{7}
\]

\[
\left( \frac{\partial Pb_{206s}}{\partial Pb_{206b}} \right) = -1 \tag{8}
\]

[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,

\[
Pb_{207s} = \left[ R65m \cdot R76m \cdot (1 + 2 \cdot FPb) \right] \cdot Pb_{205t} - \left( R65t \cdot R76t \cdot Pb_{205t} \right) - \left( R76b \cdot Pb_{206b} \right) \tag{9}
\]

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

\[
\sigma_{Pb_{207s}}^2 = \left[ \left( \frac{\partial Pb_{207s}}{\partial R65m} \right)^2 \cdot \sigma_{R65m}^2 \right] + \left[ \left( \frac{\partial Pb_{207s}}{\partial R76m} \right)^2 \cdot \sigma_{R76m}^2 \right] + \left[ \left( \frac{\partial Pb_{207s}}{\partial Pb_{205t}} \right)^2 \cdot \sigma_{Pb_{205t}}^2 \right] + \left[ \left( \frac{\partial Pb_{207s}}{\partial FPb} \right)^2 \cdot \sigma_{FPb}^2 \right] + \left[ \left( \frac{\partial Pb_{207s}}{\partial Pb_{206b}} \right)^2 \cdot \sigma_{Pb_{206b}}^2 \right] + 2 \cdot \sigma_{R65m-R76m} \cdot \left( \frac{\partial Pb_{207s}}{\partial R65m} \right) \cdot \left( \frac{\partial Pb_{207s}}{\partial R76m} \right) + 2 \cdot \sigma_{R65m-R76m} \cdot \left( \frac{\partial Pb_{207s}}{\partial Pb_{205t}} \right) \cdot \left( \frac{\partial Pb_{207s}}{\partial Pb_{206b}} \right) \tag{10}
\]

[13] The partial derivatives are calculated as follows:

\[
\left( \frac{\partial Pb_{207s}}{\partial R65m} \right) = \left( \frac{\partial Pb_{207s}}{\partial R76m} \right) = \left( \frac{\partial Pb_{207s}}{\partial Pb_{205t}} \right) = \left( \frac{\partial Pb_{207s}}{\partial Pb_{206b}} \right) = R65m \cdot (1 + 2 \cdot FPb) \cdot Pb_{205t} \tag{11}
\]

\[
\left( \frac{\partial Pb_{207s}}{\partial FPb} \right) = R76m \cdot (1 + 2 \cdot FPb) \cdot Pb_{205t} \tag{12}
\]

\[
\left( \frac{\partial Pb_{207s}}{\partial Pb_{206b}} \right) = 2 \cdot R76m \cdot R65m \cdot Pb_{205t} \tag{13}
\]
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td><em>FPb</em></td>
<td>coefficient for linear Pb fractionation correction per unit mass difference</td>
</tr>
<tr>
<td><em>FU</em></td>
<td>coefficient for linear U fractionation correction per unit mass difference</td>
</tr>
<tr>
<td><em>λ₂³⁵</em></td>
<td>²³⁵U decay constant</td>
</tr>
<tr>
<td><em>λ₂³⁸</em></td>
<td>²³⁸U decay constant</td>
</tr>
<tr>
<td><em>t₇₆</em></td>
<td>(²⁰⁷Pb/²⁰⁶Pb) radiogenic model age</td>
</tr>
<tr>
<td><em>t₇₅</em></td>
<td>(²⁰⁷Pb/²³⁵U) radiogenic model age</td>
</tr>
<tr>
<td><em>t₆₈</em></td>
<td>(²⁰⁶Pb/²³⁸U) radiogenic model age</td>
</tr>
</tbody>
</table>

**Measured Ratios**

<table>
<thead>
<tr>
<th>Tracer quantities and ratios&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td><em>R₈₅m</em></td>
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<td><em>R₃₅m</em></td>
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<tbody>
<tr>
<td><em>U₂³⁸b</em></td>
</tr>
<tr>
<td><em>P₆₂⁰⁶b</em></td>
</tr>
<tr>
<td><em>R₆₄b</em></td>
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<tr>
<td><em>R₇₆b</em></td>
</tr>
<tr>
<td><em>R₇₄b</em></td>
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</tbody>
</table>

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<tr>
<th>Initial Pb quantities and ratios&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td><em>P₆₂⁰⁶c</em></td>
</tr>
<tr>
<td><em>P₆₂⁰₄c</em></td>
</tr>
<tr>
<td><em>R₆₄c</em></td>
</tr>
<tr>
<td><em>R₇₆c</em></td>
</tr>
<tr>
<td><em>R₇₄c</em></td>
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<table>
<thead>
<tr>
<th>Sample quantities and ratios</th>
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</tr>
<tr>
<td><em>U₂³⁵s</em></td>
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<tr>
<td><em>R₇₆s</em></td>
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</tr>
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</tr>
<tr>
<td><em>R₇₄s</em></td>
</tr>
<tr>
<td><em>R₅₄s</em></td>
</tr>
<tr>
<td><em>P₆₂⁰⁶s</em></td>
</tr>
<tr>
<td><em>P₆₂⁰₇s</em></td>
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</table>

<table>
<thead>
<tr>
<th>Radiogenic Pb quantities and ratios</th>
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</tr>
<tr>
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</tr>
<tr>
<td><em>R₇₆r</em></td>
</tr>
<tr>
<td><em>R₆₈r</em></td>
</tr>
<tr>
<td><em>R₇₅r</em></td>
</tr>
<tr>
<td><em>R₆₄r</em></td>
</tr>
<tr>
<td><em>R₇₄r</em></td>
</tr>
</tbody>
</table>

<sup>a</sup>“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.

<sup>b</sup>“Initial” is defined as that Pb which was incorporated into the growing crystal at the time of formation.
\[
\left( \frac{\partial \text{Ph207s}}{\partial R65t} \right) = -R76t \cdot \text{Ph205t} \tag{14}
\]
\[
\left( \frac{\partial \text{Ph207s}}{\partial \text{R76t}} \right) = -R65t \cdot \text{Ph205t} \tag{15}
\]
\[
\left( \frac{\partial \text{Ph207s}}{\partial \text{Ph206b}} \right) = -R76b \tag{16}
\]
\[
\left( \frac{\partial \text{Ph207s}}{\partial \text{R76b}} \right) = -\text{Ph206b} \tag{17}
\]

[14] The covariance terms can be determined through the approximation for the error resulting from the product of two variables, \( x = u \cdot v \), where for example \( x = \text{76Pb} / \text{205Pb} \), \( u = \text{77Pb} / \text{206Pb} \), and \( v = \text{206Pb} / \text{205Pb} \):

\[
\left( \frac{\sigma}{x} \right)^2 = \left( \frac{\sigma}{u} \right)^2 + \left( \frac{\sigma}{v} \right)^2 + 2 \cdot \frac{\sigma}{u} \cdot \frac{\sigma}{v} \tag{18}
\]

[15] Solving for the covariance term:

\[
\sigma_{uv}^2 = \frac{\left( \sigma_x^2 - \left( \frac{\sigma}{u} \right)^2 \right.}{2} \tag{19}
\]

[16] Thus in this case:

\[
\sigma_{R76m-R65m}^2 = \\
\frac{R76m \cdot R65m}{2} \cdot \left( \frac{\sigma_{75m}^2}{R75m} - \left( \frac{\sigma}{76m} \right)^2 \right) - \left( \frac{\sigma_{76m}^2}{R76m} \right)^2 \tag{20}
\]

\[
\sigma_{R76t-R65t}^2 = \\
\frac{R76t \cdot R65t}{2} \cdot \left( \frac{\sigma_{75t}^2}{R75t} - \left( \frac{\sigma}{76t} \right)^2 \right) - \left( \frac{\sigma_{76t}^2}{R76t} \right)^2 \tag{21}
\]

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

### 2.1.3. Sample (Initial) \( \text{204Pb} \)

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

\[
\text{Ph204c} = \left[ R46m \cdot R65m \cdot (1 - FPb) \cdot \text{Ph205t} \right] \\
\left( R46t \cdot R65t \cdot \text{Ph205t} \right) - \left( \frac{\text{Ph206b}}{R64b} \right) \tag{22}
\]

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

\[
\sigma_{R65m-R46m}^2 = \\
\frac{R65m \cdot R46m}{2} \cdot \left( \frac{\sigma_{75m}^2}{R75m} - \left( \frac{\sigma}{76m} \right)^2 \right) - \left( \frac{\sigma_{76m}^2}{R76m} \right)^2 \tag{31}
\]
\[
\sigma_{R5t-R46t}^2 = \frac{\left(\frac{\partial \phi}{\partial R5t}\right)^2 + \left(\frac{\partial \phi}{\partial R46t}\right)^2}{2}
\]

[20] These partial derivatives, variances, and covariances then can be substituted into equation (23) to derive the uncertainty in sample (initial) \(^{206}\)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:

\[
R5sf = R5sm \cdot (3 \cdot FU + 1) = U238s + U238t
\]

\[
R5sf = R5sm \cdot (1 - 2 \cdot FU) = \frac{U233t}{U235s + U235t}
\]

where \(R5sf\) and \(R5sf\) 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):

\[
U235s \cdot [R5sm \cdot (3 \cdot FU + 1) - 137.88] = U235s \cdot [R5sm \cdot (3 \cdot FU + 1)]
\]

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

\[
U235s = U233t \cdot \frac{1}{R5sm \cdot (1 - 2 \cdot FU)} - \frac{1}{R5st}
\]

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

\[
R5sf \cdot [R5sm \cdot (3 \cdot FU + 1) - 137.88] = (R85t - 137.88) \cdot [R5sm \cdot (1 - 2 \cdot FU)]
\]

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

\[
FU = \frac{[R5st \cdot (137.88 - R85m) + R5sm \cdot (R85t - 137.88)]}{2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m}
\]

[25] The error propagation equation for \(FU\) may be written as (assuming all errors except \(R85m\) and \(R5sm\), and \(R85t\) and \(R5st\) are uncorrelated):

\[
\sigma_{FU}^2 = \left(\frac{\partial FU}{\partial R5sm}\right)^2 \cdot \sigma_{R5sm}^2 + \left(\frac{\partial FU}{\partial R85m}\right)^2 \cdot \sigma_{R85m}^2 + 2 \cdot \sigma_{R5sm, R85m} \cdot \frac{\partial FU}{\partial R85m} \cdot \frac{\partial FU}{\partial R5sm} + 2 \cdot \sigma_{R5s, R85t} \cdot \frac{\partial FU}{\partial R85t} \cdot \frac{\partial FU}{\partial R5st}
\]

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

\[
\frac{\partial FU}{\partial R5sm} = \frac{R85t - 137.88}{2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m} - \frac{2 \cdot (R85t - 137.88) \cdot [R5st \cdot (137.88 - R85m) + R5sm \cdot (R85t - 137.88)]}{[2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m]^2}
\]

\[
\frac{\partial FU}{\partial R85m} = \frac{-3 \cdot R85t}{2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m} - \frac{3 \cdot R85t \cdot (137.88 - R85m) + 3 \cdot R5st \cdot (R85t - 137.88)}{[2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m]^2}
\]

\[
\frac{\partial FU}{\partial R5st} = \frac{-3 \cdot R85t}{2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m} - \frac{3 \cdot R85t \cdot (137.88 - R85m) + 3 \cdot R5st \cdot (R85t - 137.88)}{[2 \cdot R5sm \cdot (R85t - 137.88) + 3 \cdot R5st \cdot R85m]^2}
\]
\[
\left( \frac{\partial F_U}{\partial R85t} \right)_{R85m} = \left( \frac{R35m}{2 \cdot R35m \cdot (R85t - 137.88) + 3 \cdot R35t \cdot R85m} \right) \]

The error propagation equation may be written as:

\[
\sigma^2_{U/238s} = \left[ \left( \frac{\partial U/238s}{\partial R85m} \right) \cdot \sigma_{R85m} \right]^2 + \left[ \left( \frac{\partial U/238s}{\partial R85t} \right) \cdot \sigma_{R85t} \right]^2 + \left[ \left( \frac{\partial U/238s}{\partial F_U} \right) \cdot \sigma_{F_U} \right]^2
\]

[32] Note that to dramatically simplify our derivation, we are considering error correlations between the component terms of sample 238U (U/238s) and the uranium fractionation factor (F_U) 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 F_U. The partial derivatives are calculated as follows:

\[
\left( \frac{\partial U/238s}{\partial R85m} \right)_{R85t} = \left[ U235t \cdot (1 + 3 \cdot F_U) \right] \frac{1 - \left( \frac{1}{137.88} \right) \cdot R85m \cdot (1 + 3 \cdot F_U)}{1 - \left( \frac{1}{137.88} \right) \cdot U235t \cdot R85m \cdot (1 + 3 \cdot F_U)}
\]

\[
\left( \frac{\partial U/238s}{\partial R85t} \right)_{R85m} = \left[ -U235t \right] \frac{1 - \left( \frac{1}{137.88} \right) \cdot R85m \cdot (1 + 3 \cdot F_U)}{1 - \left( \frac{1}{137.88} \right) \cdot U235t \cdot R85m \cdot (1 + 3 \cdot F_U)}
\]

\[
\left( \frac{\partial U/238s}{\partial F_U} \right)_{R85m} = \left[ -1 \right] \frac{3 \cdot U235t \cdot R85m}{1 - \left( \frac{1}{137.88} \right) \cdot R85m \cdot (1 + 3 \cdot F_U)}
\]

2.1.5. Sample 238U

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

\[
U/238s = \left[ R85m \cdot (1 + 3 \cdot F_U) \cdot (U/235s + U/235t) \right] - (R85t \cdot U/235t) - U/238b
\]

\[
= \left[ R85m \cdot (1 + 3 \cdot F_U) \cdot U/238s \cdot \left( \frac{1}{137.88} \right) + U/235t \right] - (R85t \cdot U/235t) - U/238b
\]

\[
= \left[ U/238s \cdot \left( \frac{1}{137.88} \right) \cdot R85m \cdot (1 + 3 \cdot F_U) \right] + [U/235t \cdot R85m \cdot (1 + 3 \cdot F_U)] - (R85t \cdot U/235t) - U/238b
\]

\[
= \left[ U/235t \cdot R85m \cdot (1 + 3 \cdot F_U) - (R85t \cdot U/235t) - U/238b \right] \left[ 1 - \left( \frac{1}{137.88} \right) \cdot R85m \cdot (1 + 3 \cdot F_U) \right]
\]

[33] These partial derivatives and variances can then be substituted into equation (49) to derive the uncertainty in sample 238U.
2.1.6. Sample $^{235}\text{U}$

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

$$U_{235s} = \frac{1}{137.88} \cdot U_{238s}$$  \hspace{1cm} (54)

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

$$\sigma^2_{U_{235s}} = \left[ \frac{\partial U_{235s}}{\partial U_{238s}} \right]^2 \cdot \sigma^2_{U_{238s}}$$  \hspace{1cm} (55)

[35] The partial derivative is simply:

$$\left( \frac{\partial U_{235s}}{\partial U_{238s}} \right) = \frac{1}{137.88}$$  \hspace{1cm} (56)

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

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]:

$$\sigma^2_{uv} = \sigma^2_{u} \cdot \frac{\partial v}{\partial c} \cdot \frac{\partial u}{\partial c}$$  \hspace{1cm} (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 $^{207}\text{Pb}/^{206}\text{Pb}$

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

$$\frac{\sigma_{\text{Pb}207s}/\text{Pb}206s}{\sigma_{\text{Pb}206s}} = \left( \frac{\sigma_{\text{Pb}207s}/\text{Pb}206s}{\sigma_{\text{Pb}206s}} \right)^2 + \left( \frac{\sigma_{\text{Pb}206s}/\text{Pb}206s}{\sigma_{\text{Pb}206s}} \right)^2 - \frac{2}{\text{Pb}206s \cdot \text{Pb}206s} - \frac{2}{\sigma_{\text{Pb}207s}/\text{Pb}206s}$$  \hspace{1cm} (58)

[38] The variance terms were previously calculated for $\text{Pb}206s$ (equation (4)) and $\text{Pb}207s$ (equation (10)). Noting that $\text{Pb}206s$ and $\text{Pb}207s$ are functions of several common terms ($\text{R65m}, \text{R65}, \text{FPb}, \text{Pb206b}$) the covariance between $\text{Pb}207s$ and $\text{Pb}206s$ is calculated as:

$$\sigma^2_{\text{Pb}207s}/\text{Pb}206s = \sigma^2_{\text{R65m}} + \sigma^2_{\text{R65}} + \sigma^2_{\text{FPb}} + \sigma^2_{\text{Pb206b}}$$  \hspace{1cm} (59)

[39] Substituting the partial derivatives of $\text{Pb}206s$ (equations (5)–(8)) and $\text{Pb}207s$ (equations (11)–(17)) with respect to each common variable:

$$\sigma^2_{\text{Pb}207s}/\text{Pb}206s = \{ \text{R65m} \cdot (1 + 2\text{FPb}) \cdot \text{Pb}205r \} \cdot \{ \text{R65m} \cdot (1 + 2\text{FPb}) \cdot \text{Pb}205r \} \cdot \sigma^2_{\text{R65m}} \cdot \sigma^2_{\text{R65}} \cdot \sigma^2_{\text{FPb}}$$  \hspace{1cm} (60)

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

2.2.2. Sample $^{204}\text{Pb}/^{206}\text{Pb}$

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

$$\frac{\sigma_{\text{Pb}204c}/\text{Pb}206s}{\sigma_{\text{Pb}206s}} = \left( \frac{\sigma_{\text{Pb}204c}/\text{Pb}206s}{\sigma_{\text{Pb}206s}} \right)^2 + \left( \frac{\sigma_{\text{Pb}206s}/\text{Pb}206s}{\sigma_{\text{Pb}206s}} \right)^2 - \frac{2}{\text{Pb}206s \cdot \text{Pb}206s} - \frac{2}{\sigma_{\text{Pb}204c}/\text{Pb}206s}$$  \hspace{1cm} (61)

[42] The variance terms were previously calculated for $\text{Pb}204c$ (equation (23)) and $\text{Pb}206s$ (equation (4)). Noting that $\text{Pb}204c$ and $\text{Pb}206s$ are functions of
several common terms \((R65m, R65t, FPb, Ph206b)\), the covariance between \(Pb206s\) and \(Pb206s\) is calculated as:

\[
\sigma_{Pb204c-Pb206s}^2 = \sigma_{R65m}^2 \left( \frac{\partial Pb204c}{\partial R65m} \right)^2 + \frac{\partial Pb206s}{\partial R65m} \right)^2 + \frac{\partial Pb204c}{\partial Fp} \right)^2 + \frac{\partial Pb206s}{\partial Fp} \right)^2 + \frac{\partial Pb204c}{\partial Pb206b} \right)^2 + \frac{\partial Pb206s}{\partial Pb206b} \right)^2 \]  \(204\) Pb/\(207\) Pb

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:

\[
\sigma_{Pb204c-Pb207s}^2 = \sigma_{R65m}^2 \left( \frac{\partial Pb204c}{\partial R65m} \right)^2 + \frac{\partial Pb207s}{\partial R65m} \right)^2 + \frac{\partial Pb204c}{\partial Fp} \right)^2 + \frac{\partial Pb207s}{\partial Fp} \right)^2 + \frac{\partial Pb204c}{\partial Pb206b} \right)^2 + \frac{\partial Pb207s}{\partial Pb206b} \right)^2 \]  \(204\) Pb/\(207\) Pb

This covariance can be substituted into equation (61) 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 \(206\) Pb/\(204\) Pb.

2.2.3. Sample \(204\) Pb/\(207\) Pb

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:

\[
\sigma_{R47s}^2 \left( \frac{\partial Pb204c}{\partial R47s} \right)^2 + \frac{\partial Pb207s}{\partial R47s} \right)^2 = \frac{2}{Pb204c \cdot Pb207s} \]

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

\[
\rho_{uv} = \frac{\sigma_{uv}}{\sigma_u \sigma_v} \]

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):

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

(69)

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

\[
\%\sigma_u = \frac{\sigma_u}{u} ; \%\sigma_v = \frac{\sigma_v}{v} ; \%\sigma_x = \frac{\sigma_x}{x}
\]

(70)

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

\[
\rho_{uv} = \frac{\%\sigma_u^2 + \%\sigma_v^2 - \%\sigma_x^2}{2 \cdot \%\sigma_u \cdot \%\sigma_v}
\]

(71)

**2.3.1. Rho** \(^{238}\text{U}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}, \text{Rho} ^{235}\text{U}/^{204}\text{Pb} - ^{207}\text{Pb}/^{204}\text{Pb}, \text{Rho} ^{238}\text{U}/^{206}\text{Pb} - ^{207}\text{Pb}/^{206}\text{Pb}, \text{and Rho} ^{238}\text{U}/^{206}\text{Pb} - ^{207}\text{Pb}/^{206}\text{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:

\[
x = RXYs = \frac{U23Xs}{Pb20Ys}
\]

(72)

\[
u = RXZs = \frac{U23Xs}{Pb20Zs}
\]

(73)

\[
v = RYZs = \frac{Pb20Ys}{Pb20Zs}
\]

(74)

\[
\rho_{RXZs - RYZs} = \frac{\%\sigma_{RXZs}^2 + \%\sigma_{RYZs}^2 - \%\sigma_{RXYs}^2}{2 \cdot \%\sigma_{RXZs} \cdot \%\sigma_{RYZs}}
\]

(75)

[56] In our specific cases:

\[
\rho_{84s - 64s} = \frac{\%\sigma_{84s}^2 + \%\sigma_{64s}^2 - \%\sigma_{86s}^2}{2 \cdot \%\sigma_{84s} \cdot \%\sigma_{64s}}
\]

(76)

**2.3.2. Rho** \(^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb} and \(^{207}\text{Pb}/^{206}\text{Pb} - ^{204}\text{Pb}/^{206}\text{Pb}

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

\[
x = RXYs = \frac{Pb20Xs}{Pb20Ys} - \frac{u}{v}
\]

(80)

\[
u = RXZs = \frac{Pb20Xs}{Pb20Zs}
\]

(81)

\[
v = RYZs = \frac{Pb20Ys}{Pb20Zs}
\]

(82)

\[
\rho_{RXZs - RYZs} = \frac{\%\sigma_{RXZs}^2 + \%\sigma_{RYZs}^2 - \%\sigma_{RXYs}^2}{2 \cdot \%\sigma_{RXZs} \cdot \%\sigma_{RYZs}}
\]

(83)

[56] In our specific cases:

\[
\rho_{84s - 64s} = \frac{\%\sigma_{84s}^2 + \%\sigma_{64s}^2 - \%\sigma_{86s}^2}{2 \cdot \%\sigma_{84s} \cdot \%\sigma_{64s}}
\]

(84)

\[
\rho_{76s - 64s} = \frac{\%\sigma_{76s}^2 + \%\sigma_{64s}^2 - \%\sigma_{74s}^2}{2 \cdot \%\sigma_{76s} \cdot \%\sigma_{64s}}
\]

(85)

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

[57] The following section details the propagation of errors through the calculation of radiogenic \(^{206}\text{Pb}/^{238}\text{U} , ^{207}\text{Pb}/^{235}\text{U}, \) and \(^{207}\text{Pb}/^{206}\text{Pb} \) ratios, including errors and error correlations associated with Pb and U isotope fractionation corrections (including errors in U isotope fractionation estimation utilizing a double \(^{231}\text{U} - ^{235}\text{U} \) 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 Terawasserburg 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

First establishing the algebraic expression for radiogenic $^{206}$Pb,

\[
Ph_{206r} = [R65m \cdot Ph_{205t} \cdot (1 + FPb)] - [R65t \cdot Ph_{205t}] - [Ph_{206b}] - R64c \\
- \left\{ [R46m \cdot R65m \cdot Ph_{205t} \cdot R64c \cdot (1 - FPb)], \\
- (R45t \cdot Ph_{205t}) - \left( \frac{Ph_{206b}}{R64b} \right) \right\} 
\]

(86)

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

\[
\sigma_{Ph_{206r}}^2 = \left[ \frac{\partial Ph_{206r}}{\partial R65m} \cdot \sigma_{R65m} \right]^2 + \left[ \frac{\partial Ph_{206r}}{\partial R46m} \cdot \sigma_{R46m} \right]^2 \\
+ \left[ \frac{\partial Ph_{206r}}{\partial R65t} \cdot \sigma_{R65t} \right]^2 + \left[ \frac{\partial Ph_{206r}}{\partial R45t} \cdot \sigma_{R45t} \right]^2 \\
+ \left[ \frac{\partial Ph_{206r}}{\partial FPb} \cdot \sigma_{FPb} \right]^2 + \left[ \frac{\partial Ph_{206r}}{\partial Ph_{206b}} \cdot \sigma_{Ph_{206b}} \right]^2 \\
+ \left[ \frac{\partial Ph_{206r}}{\partial R64c} \cdot \sigma_{R64c} \right]^2 + \left[ \frac{\partial Ph_{206r}}{\partial R64b} \cdot \sigma_{R64b} \right]^2 \\
+ 2 \cdot \sigma_{R65m-R46m} (\partial Ph_{206r}/\partial R65m) \cdot (\partial Ph_{206r}/\partial R46m) \\
+ 2 \cdot \sigma_{R45t-R65t} (\partial Ph_{206r}/\partial R45t) \cdot (\partial Ph_{206r}/\partial R65t) 
\]

(87)

The partial derivatives are then calculated as follows:

\[
\frac{\partial Ph_{206r}}{\partial R65m} = [(1 + FPb) - R64c \cdot R46m \cdot (1 - FPb)] \cdot Ph_{205t} 
\]

(88)

\[
\frac{\partial Ph_{206r}}{\partial R46m} = -R64c \cdot R65m \cdot (1 - FPb) \cdot Ph_{205t} 
\]

(89)

[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):

\[
\sigma_{R45t-R65t}^2 = \frac{\left( \frac{\partial R45t}{\partial R65t} \right)^2 + \left( \frac{\partial R45t}{\partial R65m} \right)^2 + \left( \frac{\partial R45t}{\partial R45m} \right)^2}{2} 
\]

(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

First establishing the algebraic expression for radiogenic $^{207}$Pb,

\[
Ph_{207r} = [R65m \cdot R76m \cdot Ph_{205t} \cdot (1 + 2 \cdot FPb)] \\
- [R65t \cdot R76t \cdot Ph_{205t}] - [R76b \cdot Ph_{206b}] \\
- R64c \cdot R76c \cdot \{ [R46m \cdot R65m \cdot Ph_{205t}] \\
\cdot (1 - FPb) - [R45t \cdot Ph_{205t} \cdot \left( \frac{Ph_{206b}}{R64b} \right) \} 
\]

(97)

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

\[
\frac{\partial \text{Ph}_{207t}}{\partial \text{R65m}} = R76m \cdot (1 + 2 \cdot \text{FPh}) - R64c \cdot R76c \cdot R46m
\]

\[
\frac{\partial \text{Ph}_{207t}}{\partial \text{R76m}} = R65m \cdot (1 + 2 \cdot \text{FPh}) - R64c \cdot R76c \cdot R46m
\]

\[
\frac{\partial \text{Ph}_{207t}}{\partial \text{R46m}} = -R64c \cdot R76c \cdot R65m \cdot (1 - \text{FPh}) \cdot Ph_{205t}
\]

\[
\frac{\partial \text{Ph}_{207t}}{\partial \text{FPb}} = 2 \cdot R76m + R64c \cdot R76c \cdot R46m \cdot R65m \cdot Ph_{205t}
\]

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 $^{207}\text{Pb}$.

### 3.2. Derivation of Radiogenic Isotope Ratios and Errors

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 $^{238}\text{U}$ and $^{235}\text{U}$ equations and errors derived in sections 2.1.5 and 2.1.6. Covariance between numerator and denominator of the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio is derived according to the method described in section 2.2.
3.2.1. Radiogenic $^{207}\text{Pb}^*/^{206}\text{Pb}^*$

We first recognize $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ as a quotient of the previously derived terms, $\text{Pb}206r$ (equation (86)) and $\text{Pb}207r$ (equation (97)), and thus define the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ variance as:

$$
\frac{\left( \sigma^{207}\text{Pb}^*/^{206}\text{Pb}^* \right)}{\text{R76r}} = \frac{\left( \sigma\text{Pb207r} \right)^2}{\text{Pb207r} \cdot \text{Pb206r}} + \frac{\left( \sigma\text{Pb206r} \right)^2}{\text{Pb206r}} - \frac{\left( \sigma\text{Pb207r} \cdot \text{Pb206r} \right)^2}{\text{Pb207r} \cdot \text{Pb206r}}.
$$

(111)

We have previously derived the variances for radiogenic $^{206}\text{Pb}$ (equation (87)) and $^{207}\text{Pb}$ (equation (98)). Note that $\text{Pb}207r$ and $\text{Pb}206r$ are functions of numerous common terms: $R65m$, $R46m$, $R65t$, $R45t$, $FPb$, $R64b$, $\text{Pb}206b$, $R64c$. The covariance between $\text{Pb}207r$ and $\text{Pb}206r$ is thus calculated as:

$$
\left( \sigma\text{Pb207r} \cdot \text{Pb206r} \right)^2 = \sigma_{R65m}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial R65m} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial R65m} \right) + \sigma_{R46m}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial R46m} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial R46m} \right) + \sigma_{R65t}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial R65t} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial R65t} \right) + \sigma_{R45t}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial R45t} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial R45t} \right) + \sigma_{FPb}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial FPb} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial FPb} \right) + \sigma_{R64b}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial R64b} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial R64b} \right) + \sigma_{R64c}^2 \cdot \left( \frac{\partial \text{Pb207r}}{\partial R64c} \right) \cdot \left( \frac{\partial \text{Pb206r}}{\partial R64c} \right).
$$

(112)

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

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

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

$$
x = \frac{\text{Pb}20Xr}{U23Yr} = \text{RXYr}
$$

(113)

$$
\frac{\sigma_{\text{RXYr}}}{\text{RXYr}} = \sqrt{\left( \frac{\sigma_{\text{Pb20Xr}}}{\text{Pb20Xr}} \right)^2 + \left( \frac{\sigma_{\text{U23Yr}}}{\text{U23Yr}} \right)^2}
$$

(114)

where $\text{Pb}20Xr$, $U23Yr$, and $\text{RXYr}$ are shorthand for the necessary isotope quantities and ratios. Note that the relative error in $^{206}\text{Pb}^*/^{238}\text{U}$ is equivalent to the relative error in $^{238}\text{U}/^{206}\text{Pb}^*$ for the purposes of representation in the Tera-Wasserburg concordia diagram. Similarly, the relative error in $^{207}\text{Pb}^*/^{238}\text{U}$ is equivalent to the relative error in $^{238}\text{U}/^{207}\text{Pb}^*$ for the purposes of calculating error correlations for the Tera-Wasserburg concordia diagram.

3.3. Derivation of Radiogenic Isotope Ratio Error Correlations

[69] The correlation coefficient ($\rho$ or $\rho c$) 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 $^{207}\text{Pb}^*/^{235}\text{U}$-$^{206}\text{Pb}^*/^{238}\text{U}$

$$
x = \frac{\text{R76r}}{\text{R75r}} = \frac{\text{Pb}207r}{\text{U235s}}
$$

(115)

$$
u = \frac{\text{R68r}}{\text{U238s}} = \frac{\text{Pb}206r}{\text{U238s}}
$$

(116)

$$
\rho_{\text{R75r} - \text{R68r}} = \frac{\% \sigma_{\text{R75r}} + \% \sigma_{\text{R68r}} - \% \sigma_{\text{R76r}}}{2 \cdot \% \sigma_{\text{R75r}} \cdot \% \sigma_{\text{R68r}}}
$$

(118)

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

$$
x = \frac{\text{R87r}}{\text{R86r}} = \frac{\text{U238s}}{\text{Pb}206r}
$$

(119)

$$
\rho_{\text{R86r} - \text{R87r}} = \frac{\% \sigma_{\text{R86r}} + \% \sigma_{\text{R87r}} - \% \sigma_{\text{R87r}}}{2 \cdot \% \sigma_{\text{R86r}} \cdot \% \sigma_{\text{R87r}}}
$$

(122)
4. Radiogenic U-Pb and Pb-Pb Ages

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

Recalling the solution to the decay equation, and corresponding age equation for the $^{238}\text{U}^{206}\text{Pb}^*$ system:

$$R68r = e^{\lambda238 \cdot r68} - 1$$  \hspace{1cm} (123)

$$r68 = \left(\frac{1}{\lambda238}\right) \cdot \ln(R68r + 1)$$  \hspace{1cm} (124)

The error propagation equation may be written as (assuming $\lambda238$ is a constant):

$$\sigma^2_{r68} = \sigma_{R68r}^2 \cdot \left(\frac{\partial r68}{\partial R68r}\right)^2$$  \hspace{1cm} (125)

Evaluating the partial derivative of $r68$ with respect to $R68r$,

$$\left(\frac{\partial r68}{\partial R68r}\right) = \left(\frac{1}{\lambda238}\right) \cdot \left(\frac{1}{R68r + 1}\right)$$  \hspace{1cm} (126)

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

$$\sigma_{r68} = \frac{1}{\lambda238} \cdot \left(\frac{\sigma_{R68r}}{R68r + 1}\right)$$  \hspace{1cm} (127)

By analogous derivation, the $^{207}\text{Pb}^*/^{235}\text{U}$ age error is:

$$\sigma_{r75} = \frac{1}{\lambda235} \cdot \left(\frac{\sigma_{R75r}}{R75r + 1}\right)$$  \hspace{1cm} (128)

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

Recalling the solution to the decay equation for the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ system,

$$R76r = \left(\frac{1}{137.88}\right) \cdot \left(\frac{e^{\lambda235 \cdot r76} - 1}{e^{\lambda235 \cdot r76} - 1}\right)$$

$$= \left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda235 \cdot r76} - 1\right) \cdot \left(e^{\lambda238 \cdot r76} - 1\right)^{-1}$$  \hspace{1cm} (129)

Evaluating the partial derivative of $R76r$ with respect to $r76$, we apply the product rule:

$$\left(\frac{\partial R76r}{\partial r76}\right) = \left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda235 \cdot r76} - 1\right)$$

$$= \left(\frac{1}{137.88}\right) \cdot \lambda235 \cdot \left(e^{\lambda235 \cdot r76} - 1\right)$$  \hspace{1cm} (130)

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

$$\frac{\partial}{\partial r76} \left[\left(e^{\lambda238 \cdot r76} - 1\right)^{-1}\right] = (-1) \cdot \left(e^{\lambda238 \cdot r76} - 1\right)^{-2} \cdot \lambda238 \cdot \left(e^{\lambda238 \cdot r76} - 1\right)$$  \hspace{1cm} (131)

Making the appropriate substitutions:

$$\sigma_{r76} = \frac{\sigma_{R76r}}{\partial R76r/\partial r76}$$  \hspace{1cm} (132)

$$\sigma_{r76} = \left[\left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda235 \cdot r76} - 1\right)\right]$$

$$= \left(\frac{1}{137.88}\right) \cdot \lambda235 \cdot \left(e^{\lambda235 \cdot r76} - 1\right)$$  \hspace{1cm} (133)

$$\sigma_{r76} = \left[\left(e^{\lambda238 \cdot r76} - 1\right)^{-1}\right]$$

$$= (-1) \cdot \left(e^{\lambda238 \cdot r76} - 1\right)^{-2} \cdot \lambda238 \cdot \left(e^{\lambda238 \cdot r76} - 1\right)$$  \hspace{1cm} (134)

$$\sigma_{R76r} = \left[\left(\frac{1}{137.88}\right) \cdot \left(e^{\lambda235 \cdot r76} - 1\right)\right]$$

$$= \left(\frac{1}{137.88}\right) \cdot \lambda235 \cdot \left(e^{\lambda235 \cdot r76} - 1\right)$$  \hspace{1cm} (135)
We note that this expression is equivalent to equation (3) of Ludwig [2000], without decay constant errors.

5. Discussion

An accompanying spreadsheet formulation of these derivations (auxiliary material 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 $^{206}\text{Pb}/^{238}\text{U}$ 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 $^{207}\text{Pb}/^{235}\text{U}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratio errors.

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., $^{206}\text{Pb}/^{205}\text{Pb} < 1$) with a relatively impure tracer [Parrish and Krogh, 1987], if the relatively high $^{206}\text{Pb}/^{205}\text{Pb}$ of the tracer is not precisely measured (e.g., to 0.01% or better). The magnitude of the contribution of tracer $^{206}\text{Pb}$ subtraction to the $^{206}\text{Pb}/^{238}\text{U}$ error is illustrated in Figure 1 for three scenarios using two tracers. The first two scenarios involve use of the aforementioned relatively impure $^{205}\text{Pb}$-rich spike (“GSC”), with two different propagated errors in tracer $^{206}\text{Pb}/^{205}\text{Pb}$. Error contributions of $>10\%$ are evident for overspiked samples assuming a tracer $^{206}\text{Pb}/^{205}\text{Pb}$ error of 0.1%; fortunately the error contribution decreases as the square of the assumed tracer $^{206}\text{Pb}/^{205}\text{Pb}$ error (Figure 1). The third scenario involves relatively imprecise knowledge of the tracer $^{206}\text{Pb}/^{205}\text{Pb}$ ratio for a more pure $^{203}\text{Pb}$ 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 $^{206}\text{Pb}/^{238}\text{U}$ ratio error from spike subtraction trivial.

Measurement errors in both Pb and U isotope ratios contribute a major component to the total $^{206}\text{Pb}/^{238}\text{U}$ error for all zircon analyses, as illustrated in Figures 2, 3, and 4b. The errors on measured $^{206}\text{Pb}/^{205}\text{Pb}$, $^{238}\text{U}/^{235}\text{U}$, and $^{233}\text{U}/^{235}\text{U}$ (the last through the U fractionation correction, $F_U$) are generally the largest subequal contributors, while error contribution from the measured $^{204}\text{Pb}/^{206}\text{Pb}$ is proportionately smaller. Of the four measured ratios, only the error in $^{204}\text{Pb}/^{206}\text{Pb}$ is uncorrelated with its percentage contribution to the $^{206}\text{Pb}/^{238}\text{U}$ error. Measurement errors for the other three ratios are strongly positively correlated with their contributions to the $^{206}\text{Pb}/^{235}\text{U}$ 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 $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (and very small $^{204}\text{Pb}$ ion signals) of radiogenic samples.

Fractionation correction error is a major contributor to the $^{206}\text{Pb}/^{238}\text{U}$ 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 $^{206}\text{Pb}/^{238}\text{U}$ 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 $F_U$ versus $F_{Pb}$ error contributions between the SO3 zircon analyses (UO$_2$) and FCT and AS3 zircon analyses (U$^+$). In the future, application of a double $^{202}\text{Pb}/^{205}\text{Pb}$ spike for internal fractionation correction should also significantly decrease the $F_{Pb}$ error contribution. We note that the algorithms from this paper can be used with double Pb spikes as well, if the variance of $F_{Pb}$ is calculated internally using analogous methods to those used for $F_U$.

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
206Pb 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 206Pb/204Pb, 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 206Pb*/238U error from blank amount uncertainty (being negatively correlated with 206Pb/204Pb) only exceeds 10% at 206Pb/204Pb < 1000. The smaller group of analyses in Figure 4a with substantially lower contributions to 206Pb*/238U 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 206Pb* 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 206Pb*.

[84] It is worth noting that blank and initial common Pb composition uncertainties usually have contributions to 206Pb*/238U error nearly two orders of magnitude less than that contributed from Pb blank amount. However, an interesting crossover in error contributions occurs at 206Pb/204Pb 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 R46m) and fractionation correction uncertainties only takes place at relatively low 206Pb/204Pb ratios (<100). The obvious exception is the error contribution from R46m, which is inversely proportional to 206Pb/204Pb (Figure 4b) as would be expected by the increasingly important role this measured ratio

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**Figure 1.** Contribution to radiogenic 206Pb*/238U error from tracer subtraction (e.g., tracer 206Pb) as a function of measured 206Pb/205Pb for three scenarios and two tracer compositions. “GSC” represents a relatively high 206Pb/205 Pb tracer [Parrish and Krogh, 1987]; “ET” represents a lower 206Pb/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).
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 $^{206}\text{Pb}/^{238}\text{U}$ error from uncertainties in (a) common Pb subtraction variables, (b) isotope ratio measurements, and (c) fractionation corrections, as a function of measured $^{206}\text{Pb}/^{204}\text{Pb}$, 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).
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.

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References


