1 Supplementary Data: Analytical Solutions to the Error Analysis Problem

To determine the factors controlling methodological precision in the mixed spike method we need to solve:

\[ \text{relerr}_{(F+1)}^2 = \text{relerr}_m^2 \left( \frac{m^2}{(F+1)^2} \right) \left( \frac{\partial(F+1)}{\partial m} \right)^2. \] (1)

Let's break Equation 1 into reasonable pieces. We start by expanding the boxed term \((F+1)^2\), substituting \(F = (m-x)/(o-m)\), a shorthand form of Equation 9 or 10 from the main text. Here \(m\), \(x\), and \(o\) refer to the isotope ratios of the mixed solid, the enriched culture solution, and the natural abundance initial solid, respectively.

\[
(F + 1)^2 = \left[ \left( \frac{m-x}{o-m} \right) + 1 \right]^2 = \left[ \frac{m-x}{o-m} \right] \left[ \frac{m-x}{o-m} + 1 \right] \\
= \left( \frac{m-x}{o-m} \right)^2 + 2 \left( \frac{m-x}{o-m} \right) + 1 \\
= m^2 - 2mx + x^2 \frac{(o-m)^2}{(o-m)^2} + 2m - 2x + 1 \\
= m^2 - 2mx + x^2 \frac{(o-m)^2}{(o-m)^2} + (2m - 2x) \frac{(o-m)^2}{(o-m)^2} + (o-m)^2 \\
= m^2 - 2mx + x^2 \frac{(o-m)^2}{(o-m)^2} + 2mo - 2m^2 - 2ox + 2mx + o^2 - 2mo + m^2 \\
= m^2 - 2mx + x^2 + 2mo - 2m^2 - 2ox + 2mx + o^2 - 2mo + m^2 \\
= \frac{m^2 - 2mx + x^2 + 2mo - 2m^2 - 2ox + 2mx + o^2 - 2mo + m^2}{(o-m)^2} \\
= \frac{x^2 - 2ox + o^2}{(o-m)^2} \\
= \frac{(x-o)^2}{(o-m)^2} \frac{(o-x)^2}{(o-m)^2} \left( \frac{\partial(F+1)}{\partial m} \right)^2 \] (2)

Substituting this result, \((F + 1)^2 = (o-x)^2/(o-m)^2\), into Equation 1, we are one step closer to a solution:

\[ \text{relerr}_{(F+1)}^2 = \text{relerr}_m^2 \left( \frac{m^2}{(o-x)^2} \right) \left( \frac{\partial(F+1)}{\partial m} \right)^2. \] (3)

We now differentiate the last term in Equation 3, \(\partial(F+1)/\partial m\), after substituting \(F = (m-x)/(o-m)\):
\[
\frac{\partial (F + 1)}{\partial m} = \frac{\partial}{\partial m} \left[ \frac{(m - x)}{(o - m)} + 1 \right]
\]
\[
= \frac{\partial}{\partial m} \frac{(m - x)}{(o - m)}
\]
\[
= \frac{1}{(o - m)} \frac{\partial}{\partial m} \left( m - x + (m - x) \frac{\partial}{\partial m} (o - m)^{-1} \right)
\]
\[
= \frac{1}{(o - m)} \frac{m - x}{(o - m)^2} + \frac{o - m}{(o - m)^2} \frac{m - x}{(o - m)^2} = \frac{o - x}{(o - m)^2}
\]
\[
= \frac{o - x}{(o - m)^2} = \frac{o - x}{(o - m)^2} \tag{4}
\]

We can now substitute this result, \(\frac{\partial^2 (F + 1)}{\partial m^2} = \frac{(o - x)^2}{(m - o)^4} \), into Equation 3 and simplify:

\[
\text{relerr}_{(F+1)}^2 = \text{relerr}_m^2 m^2 \frac{(m - o)^2}{(o - x)^2} \frac{(o - x)^2}{(m - o)^4}
\]
\[
= \text{relerr}_m^2 \frac{m^2}{(o - x)^2} \frac{(o - x)^2}{(m - o)^2} \frac{(o - x)^2}{(m - o)^2} = \text{relerr}_m^2 \frac{m^2}{(m - o)^2} \tag{5}
\]

Equation 5 represents a simple analytical expression that puts the relative uncertainty in \((F + 1)\) due to instrumental error in terms of two measurable isotope ratios. This is the same expression as Equation 15 in the main text.

We are still not finished, however, even after all the algebra up to this point. Equation 5 would be more useful if it were put in terms of general experimental parameters instead of \(o\) and \(m\), since the ratios \(o\) and \(m\) can differ between isotope systems and between different growth experiments in non-intuitive ways. To improve the applicability of Equation 5 we choose two master parameters which can be used to describe a mixed spike experiment: the isotope enrichment of the growth solution \((S = x/o)\) and the mole fraction of new growth,

\[
\chi_x = [F + 1]^{-1} = \left[ \frac{(m - x)}{(o - m)} + 1 \right]^{-1} \tag{6}
\]

This definition for the mole fraction of new growth comes from Equation 6 in the main text.
Let's start the transformation to new parameters by taking the square root of Equation 5, putting it in simpler form:

\[ |\text{rel err}_{(F+1)}| = |\text{rel err}_m| \frac{m}{m-o}. \]  

(7)

We can use the positive root because \( m, o \), and the magnitude of the error terms are all real positive numbers. Furthermore, \( m \) is always greater than \( o \) when materials are grown from enriched solutions.

We will now embark on an extended algebraic adventure to express \( m/(m-o) \) in terms of \( S \) and \( \chi_x \), transforming Equation 7 into a more useful form. Simplifying \( m/(m-o) \),

\[ \frac{m}{m-o} = \frac{m/o}{m/o-1} = \frac{m/o - 1 + 1}{m/o - 1} = \frac{m/o - 1}{m/o - 1} + \frac{1}{m/o - 1} = 1 + \frac{1}{m/o - 1}. \]  

(8)

After substituting this result into Equation 7, we have modified the relative error expression,

\[ |\text{rel err}_{(F+1)}| = |\text{rel err}_m| \left[ 1 + \frac{1}{m/o - 1} \right]. \]  

(9)

Thus, our algebraic target involves putting \( S \) and \( \chi_x \) in terms of some expression that can be used to replace \( m/o \). Using what we know about \( S \) and \( \chi_x \), we now proceed towards this goal. The definition of isotope enrichment, \( S = x/o \), can
be used to replace $x$ in the definition of $\chi_x$, (Equation 6).

\[
x = S o ,
\]

and

\[
\chi_x = \left[ \frac{m - x}{o - m} + 1 \right]^{-1}
= \left[ \frac{m - S o}{o - m} + 1 \right]^{-1}
= \left[ \frac{m - S o + o - m}{o - m} \right]^{-1}
= \left[ \frac{m - S o + o - m}{o - m} \right]^{-1}
= \left[ \frac{o - S o}{o - m} \right]^{-1}
= \frac{o - S o}{o - m}
= \frac{1 - m / o}{1 - S} .
\] (10)

Continuing, we take Equation 10 and solve for $S$ and $\chi_x$ in terms of $m/o$,

\[
\chi_x = \frac{1 - m / o}{1 - S}
\chi_x (1 - S) = 1 - m / o
(S - 1) \chi_x = m / o - 1
\] (11)

Comparing Equation 11 with the simplified error expression derived in Equation 9 shows that a simple substitution is all that is necessary to finish our transformation. We substitute $(S - 1)\chi_x$ for the dominator $m/o - 1$ in Equation 9 and we finally have an analytical expression describing the main source of methodological uncertainty in a mixed spike experiment as a function of general experimental parameters,

\[
|\text{rel err}_{(F+1)}| = |\text{rel err}_m| \left[ 1 + \frac{1}{(S - 1)\chi_x} \right] .
\] (12)

This expression is the same as Equation 16 in the main text.