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:

$$rel\ err_{(F+1)}{}^2 = rel\ err_m{}^2 \frac{m^2}{\boxed{(F+1)^2}} \left(\frac{\partial(F+1)}{\partial m}\right)^2 . \tag{1}$$

Lets 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.

$$\begin{aligned}
(F+1)^2 &= \left[\left(\frac{m-x}{o-m}\right)+1\right]^2 = \left[\left(\frac{m-x}{o-m}\right)+1\right]\left[\left(\frac{m-x}{o-m}\right)+1\right] \\
&= \left(\frac{m-x}{o-m}\right)^2 + 2\left(\frac{m-x}{o-m}\right) + 1 \\
&= \frac{m^2-2mx+x^2}{(o-m)^2} + \frac{2m-2x}{(o-m)} + 1 \\
&= \frac{m^2-2mx+x^2}{(o-m)^2} + \frac{(2m-2x)(o-m)}{(o-m)^2} + \frac{(o-m)^2}{(o-m)^2} \\
&= \frac{m^2-2mx+x^2}{(o-m)^2} + \frac{2mo-2m^2-2ox+2mx}{(o-m)^2} + \frac{o^2-2mo+m^2}{(o-m)^2} \\
&= \frac{m^2-2mx+x^2+2mo-2m^2-2ox+2mx+o^2-2mo+m^2}{(o-m)^2} \\
&= \frac{\cancel{m^2}\cancel{-2mx}+x^2+\cancel{2mo}\cancel{-2m^2}-2ox+\cancel{2mx}+o^2\cancel{-2mo}+\cancel{m^2}}{(o-m)^2} \\
&= \frac{x^2-2ox+o^2}{(o-m)^2} \\
&= \frac{(x-o)^2}{(o-m)^2} = \frac{(o-x)^2}{(m-o)^2}
\end{aligned} \tag{2}$$

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

$$rel\ err_{(F+1)}{}^2 = rel\ err_m{}^2\ m^2 \frac{(m-o)^2}{(o-x)^2} \left(\frac{\partial(F+1)}{\partial m}\right)^2 . \tag{3}$$

We now differentiate the last term in Equation 3, $\partial(F+1)/\partial m$, after substituting $F = (m-x)/(o-m)$:

$$
\begin{aligned}
\frac{\partial(F+1)}{\partial m} &= \frac{\partial}{\partial m}\left[\left(\frac{m-x}{o-m}\right)+1\right] \\
&= \frac{\partial}{\partial m}\left(\frac{m-x}{o-m}\right) \\
&= \frac{1}{(o-m)}\frac{\partial}{\partial m}(m-x) + (m-x)\frac{\partial}{\partial m}(o-m)^{-1} \\
&= \frac{1}{(o-m)} + \frac{m-x}{(o-m)^2} \\
&= \frac{o-m}{(o-m)^2} + \frac{m-x}{(o-m)^2} \\
&= \frac{o\cancel{-m}+\cancel{m}-x}{(o-m)^2} \\
&= \frac{o-x}{(o-m)^2} = \frac{o-x}{(m-o)^2}
\end{aligned} \tag{4}
$$

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

$$
\begin{aligned}
rel\ err_{(F+1)}{}^2 &= rel\ err_m{}^2\ m^2 \frac{(m-o)^2}{(o-x)^2}\frac{(o-x)^2}{(m-o)^4} \\
&= rel\ err_m{}^2\ m^2 \frac{\cancel{(m-o)^2}}{\cancel{(o-x)^2}}\frac{\cancel{(o-x)^2}}{\cancel{(m-o)^2}\,(m-o)^2} \\
&= rel\ err_m{}^2\ \frac{m^2}{(m-o)^2}
\end{aligned} \tag{5}
$$

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.

Lets start the transformation to new parameters by taking the square root of Equation 5, putting it in simpler form:

$$\left|rel\ err_{(F+1)}\right| = |rel\ err_m|\ \frac{m}{m-o}\ . \tag{7}$$

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 χ_x, transforming Equation 7 into a more useful form. Simplifying $m/(m-o)$,

$$\begin{aligned}\frac{m}{m-o} &= \frac{m/o}{m/o-1} \\ &= \frac{m/o-1+1}{m/o-1} \\ &= \frac{m/o-1}{m/o-1} + \frac{1}{m/o-1} \\ &= 1 + \frac{1}{m/o-1}\ . \end{aligned} \tag{8}$$

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

$$\left|rel\ err_{(F+1)}\right| = |rel\ err_m|\ \left[1 + \frac{1}{m/o-1}\right]\ . \tag{9}$$

Thus, our algebraic target involves putting S and χ_x in terms of some expression that can be used to replace m/o. Using what we know about S and χ_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 χ_x, (Equation 6).

$$
\begin{aligned}
x &= So \;, \\
&\text{and} \\
\chi_x &= \left[\frac{m-x}{o-m}+1\right]^{-1} \\
&= \left[\frac{m-So}{o-m}+1\right]^{-1} \\
&= \left[\frac{m-So}{o-m}+\frac{o-m}{o-m}\right]^{-1} \\
&= \left[\frac{m-So+o-m}{o-m}\right]^{-1} \\
&= \left[\frac{\cancel{m}-So+o\cancel{-m}}{o-m}\right]^{-1} \\
&= \left[\frac{o-So}{o-m}\right]^{-1} = \frac{o-m}{o-So} = \frac{1-m/o}{1-S} \;. \qquad (10)
\end{aligned}
$$

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

$$
\begin{aligned}
\chi_x &= \frac{1-m/o}{1-S} \\
\chi_x\,(1-S) &= 1-m/o \\
(S-1)\,\chi_x &= m/o-1 \qquad (11)
\end{aligned}
$$

Comparing Equation 11 with the simplified error expression derivied in Equation 9 shows that a simple substation 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,

$$
\left|rel\ err_{(F+1)}\right| = |rel\ err_m| \left[1+\frac{1}{(S-1)\chi_x}\right] \;. \qquad (12)
$$

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