Appendix:

Error analysis: $\dfrac{^{87}\text{Sr}}{^{86}\text{Sr}}$ Ratio

The final ratio sought is the molecular amounts of ^{87}Sr and ^{86}Sr. This should, to a first approximation, be equal to the ratios of the corrected intensities read out by the instrument, denoted as:

$$R = \frac{I_{87Sr}}{I_{86Sr}} \qquad (3)$$

However, the intensity measured at m/z = 87 (I_{87}) may have contributions of both Sr, thus:

$$R = \frac{I_{87} - I_{87Rb}}{I_{86Sr}} \qquad (4)$$

Since the contribution from ^{87}Rb cannot be observed directly, the magnitude of its intensity is calculated based on the interference-free Rb isotope at m/z 85. The ratio of Rb isotopes $\dfrac{^{87}\text{Rb}}{^{85}\text{Rb}}$ (denoted as R_{Rb}) can then be used to provide an expression for R based on measured quantities from the mass spectrum.

$$R = \frac{I_{87} - R_{Rb}I_{85Rb}}{I_{86Sr}} \qquad (5)$$

If it is assumed that the primary contribution to error can be determined by Poisson statistics, viz.,

$$\sigma_x^2 = I_x \qquad (6)$$

Then an error function can be derived for the final ratio:

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$$\sigma_R{}^2 = \left(\frac{1}{I_{86Sr}}\right)^2 I_{87} + \left(\frac{-I_{85Rb}}{I_{86Sr}}\right)^2 \sigma_{R_{Rb}}{}^2 + \left(\frac{-R_{Rb}}{I_{86Sr}}\right)^2 I_{85Rb}$$

$$+ \left(\frac{-(I_{87} + R_{Rb}I_{85Rb})}{I_{86Sr}{}^2}\right)^2 I_{86Sr} \tag{7}$$

This can be converted to a *relative standard deviation* and simplified (also found in the discussion section as eq. 2).

$$\frac{\sigma_R}{R} = \frac{\sqrt{I_{87} + I_{85Rb}{}^2 \sigma_{R_{Rb}}{}^2 + R_{Rb}^2 I_{85Rb} + \dfrac{\left(I_{87} - R_{Rb}I_{85Rb}\right)^2}{I_{86Sr}}}}{I_{86Sr} R} \tag{8}$$

Mass Bias Correction

It is also necessary to analyze the error in the ratio of Rb isotopes used, R_{Rb}. The value used is based on a corrected version of the natural abundance, termed $R_{Rb,true}$. The dependency of the ratio of true to experimental isotope ratios is not analytically known, but a number of relationships have been employed. In this work, an exponential mass bias law was used, with a correction factor termed ε. The mass bias correction factor is determined by the equation:

$$\frac{R_{true}}{R_{exptl}} = e^{\Delta m \varepsilon} \tag{9}$$

This equation is generalized for any isotope ratio, where R_{true} is the true ratio value but R_{exptl} is the value observed in the experiment. Δm is the mass difference between the two masses used in the ratio. It can be rearranged to a more useful form:

$$\varepsilon = \frac{1}{\Delta m} \ln\left(\frac{R_{true}}{R_{exptl}}\right) \tag{10}$$

In this study, determining the value for ε relies on the ratio of ^{88}Sr and ^{86}Sr (to calculate an R_{exptl}), which are limited by Poisson statistics. The mass difference does not contribute any significant error, nor does the true ratio of the ratio (which has been well characterized and does not vary).[15] Thus,

$$\sigma_\varepsilon = \left(\frac{\partial \varepsilon}{\partial R_{exptl}} \right) \sigma_{R_{exptl}} = \left(\frac{1}{R_{exptl} \Delta m} \right) \sigma_{R_{exptl}} \tag{11}$$

Since R_{ex} is just the ratio of the signals at mass 88 and 86 and is assumed to be count limited, the error in that ratio is:

$$\sigma R_{exptl} = R_{exptl} \sqrt{\frac{1}{I_{86}} + \frac{1}{I_{88}}} \tag{12}$$

When this set into equation 14, the error in the mass bias factor is found to be

$$\sigma_\varepsilon = \frac{1}{\Delta m} \sqrt{\frac{1}{I_{86}} + \frac{1}{I_{88}}} \tag{13}$$

This mass bias factor must then be applied to determine what the observed value of the R_{Rb} ratio will be used. This uses a rearranged version of eq. 9 or 10 to solve for the $R_{Rb,exptl}$. The error treatment is similar, and shows that the error in the ratio will be:

$$\sigma_{R_{Rb,exptl}}^2 = \left(\frac{\partial R_{Rb,exptl}}{\partial \varepsilon} \right)^2 \sigma_\varepsilon^2 = \frac{R_{Rb,true}^2 \cdot \Delta m^2}{e^{2\Delta m \varepsilon}} \sigma_\varepsilon^2$$

$$= \frac{R_{Rb,true}^2}{e^{2\Delta m \varepsilon}} \cdot \left(\frac{1}{I_{86}} + \frac{1}{I_{88}} \right) \tag{14}$$