Fractionation is a primarily mass-dependent phenomenon that affects the distribution of isotopes of individual elements during processes in which there is mass transfer. There are rare instances of mass-independent fractionation, but, for our purposes, the simplest explanation of the cause of mass-dependent fractionation is that, for isotopes of a single element, the lighter-mass isotopes have lower binding energy than the heavier isotopes. As a consequence, in any process that involves the breaking of chemical bonds, regardless of bond type, the bonds of the lighter isotopes are preferentially broken, and the lighter isotope is preferentially represented in the product of the process.

During thermal ionization mass spectrometry, the fundamental processes are the evaporation of atoms from the filament in response to heating, the ionization of the evaporated atoms, and the acceleration of the resulting ions into the mass analyzer of the mass spectrometer. It is during the evaporation step, primarily, that lighter isotopes are preferentially removed from the filament, so that the isotopic ratios that are measured during the course of an analysis will tend to show a systematic shift with time. This shift will produce increasing ratios as a function of time when the light isotope is used as the denominator. The extent of fractionation depends on absolute mass, on the mass difference between the isotopes, and on the temperature. The greatest natural fractionations in processes that occur near the earth’s surface approach 1%, and are observed for isotopes of hydrogen.

In the case of lead, the absolute mass is large and the mass difference is 4 mass units or less; in natural terrestrial processes, there is little or no observable fractionation. In the mass spectrometer, however, the filament is at high temperature (roughly 1200° - 1400°C) and is in a vacuum – measurable fractionation occurs, so that all data have to be corrected for this systematic bias. We have measured the fractionation of lead in our mass spectrometers by analyzing multiple samples of a standard whose isotopic composition has been accurately determined.

The fractionation of isotopes during any process of evaporation is described by the Rayleigh equation:

\[ \frac{R}{R_0} = f^{(\alpha - 1)} \]

where \( R \) is the isotopic ratio of material remaining in the reservoir (i.e., the filament) at any instant, \( R_0 \) is the initial isotopic ratio of the whole sample, \( f \) is the mass fraction of the sample remaining in the reservoir, and \( \alpha \) is the isotopic fractionation factor, defined as the isotopic ratio in the product / isotopic ratio of material remaining in the reservoir. In practice, for small values of \( \alpha \), this can be approximated by a linear equation:

\[ R_{\text{true}} = R_{\text{meas}} \times (\delta M \alpha/100) + 1 \]
where $\delta M$ is the mass difference in amu for the isotope pair, and the factor of 100 is included because $\alpha$ is usually expressed as %/amu. If we solve for $\alpha$ (assuming a mass difference of 1), this can be written as

$$\alpha = ((R_{\text{true}} - R_{\text{meas}}) / R_{\text{meas}}) \times 100.$$  

Values of $\alpha$ can be positive or negative, depending on a number of factors. For the mass spectrometer configuration with which your Pb samples were measured, the value of $\alpha = 0.12 \pm 0.03$%/amu.

1. For the following data, calculate the “true” isotopic compositions by making the necessary fractionation corrections.

2. Assuming that the typical uncertainty of a measured ratio is 0.05%, what is the greatest source of uncertainty in analyses of the isotopic composition of lead?

**Measured Values:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>206/204</th>
<th>207/204</th>
<th>208/204</th>
<th>207/206</th>
<th>208/206</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS-981</td>
<td>16.9113</td>
<td>15.4580</td>
<td>36.5940</td>
<td>0.914096</td>
<td>2.16396</td>
</tr>
<tr>
<td>12.119 #2</td>
<td>18.4321</td>
<td>15.5574</td>
<td>37.9817</td>
<td>0.844187</td>
<td>2.06109</td>
</tr>
<tr>
<td>12.119 #8</td>
<td>17.2215</td>
<td>15.4436</td>
<td>36.8678</td>
<td>0.896904</td>
<td>2.14097</td>
</tr>
</tbody>
</table>

In the case of Sr, the natural abundances of $^{86}\text{Sr}$ and $^{88}\text{Sr}$ are practically invariant, and, by convention, $^{86}\text{Sr}/^{88}\text{Sr}$ is defined to be 0.1194. Attached is a data file showing Sr isotopic compositions during a single mass spectrometer run of the Sr isotopic standard, NBS-987 (or NIST 987). For these data:

3. Calculate the value of $\alpha$ per amu, assuming that $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, for each measurement.

4. Calculate a linearly fractionation-corrected value for $^{87}\text{Sr}/^{86}\text{Sr}$ (this ratio is variable in nature) for each measurement.

5. Plot the raw data in coordinates of $^{86}\text{Sr}/^{88}\text{Sr}$ (abscissa) vs. $^{87}\text{Sr}/^{86}\text{Sr}$, and the corrected data in coordinates of $^{86}\text{Sr}/^{88}\text{Sr}$ (raw) vs. $^{87}\text{Sr}/^{86}\text{Sr}$ (corrected). These plots should show the effect of fractionation during analysis quite dramatically.

6. Based on these measurements, what is the best estimate of the actual value of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST-987?

7. What is the uncertainty of this measurement?

**Due Date: March 31, 2011**