$BaPO_2^+$ and Tl^+ isobaric interference corrections for Pb analyses

Part I. Background, Inputs

Typically, U and Pb are analyzed by TIMS after a chemical purification step (anion exchange chemistry) that separates the U and Pb from other species. This permits the analyst to assume everything of mass 202 and 204 to 208 on the mass spectrometer consists of pure Pb, and ratios of the signals at these masses represent Pb isotope ratios. If, however, the polyatomic ion $BaPO_2^+$ or the ion Tl^+ is present, it may evaporate and ionize at the same time as Pb and contribute some component of the signal at these masses. These isobaric (same mass/charge ratio) interferences must be subtracted from the measured isotope ratios to calculate accurate Pb isotope ratios.

The correction is performed by measuring masses that are known to contain other isotopes of these species. Specifically, about 70% of $BaPO_2^+$ is mass 201, with smaller contributions to masses 193 to 205. Tl^+ has only two masses, 203 (~30%) and 205 (~70%). Thus, the isotopic composition (IC) of Tl^+ is known, and the IC of $BaPO_2^+$ can be calculated from the relative abundances of its constituent elements (see next). The isotope ratios of the interferences along with the measured ratios can then be "known" variables in a system of equations that solves to the unknown pure Pb isotope ratios.

Calculating the $BaPO_2^+$ isotopic composition

Barium has seven stable isotopes, whose relative abundances are presented below, taken from IUPAC accepted values (de Laeter et al. 2003). No isotopic variations have been reported for a range of terrestrial and meteoritic samples (Eugster et al. 159, de Laeter and Date 422)

Ba

mass	**130**	**132**	**134**	**135**	**136**	**137**	**138**
abundance	0.106%	0.101%	2.417%	6.592%	7.854%	11.232%	71.698%

Phosphorous has only one stable isotope, $^{31}\mathbf{P}$.

Oxygen has three stable isotopes, whose relative abundances vary slightly in nature due to low-temperature fractionation. The average values, accepted by IUPAC (de Laeter et al. 2003), are

O

mass	**16**	**17**	**18**
abundance	99.757%	0.038%	0.205%

The total mass of each $BaPO_2^+$ polyatomic ion is the sum of the four constituent element masses. The relative abundance of any given mass is the sum of the relative abundances of each species which add to that mass.

For example, the minimum mass of $BaPO_2^+$—193—results from the combination $^{130}Ba^{31}P^{16}O^{16}O$; its relative abundance among all $BaPO_2^+$ species is $(0.106\%)(100\%)(99.757\%)(99.757\%) = 0.1055\%$.

The maximum mass—205—is $^{138}Ba^{31}P^{18}O^{18}O$; its relative abundance is $(71.698\%)(100\%)(0.205\%)(0.205\%) = 3.01 \times 10^{-4}\%$.

Each total mass between 193 and 205 may be created by combinations of the other isotopes. For instance, mass 194 can be produced from either $^{130}Ba^{31}P^{16}O^{17}O$ or $^{130}Ba^{31}P^{17}O^{16}O$. The total abundance is the sum of the two species abundances: $(0.106\%)(100\%)(99.757\%)(0.038\%) + (0.106\%)(100\%)(0.038\%)(99.757\%) = 8.04 \times 10^{-5}\%$.

There are $7 \times 3 \times 3 = 63$ possible combinations, each of which sum to between 193 and 205 mass units. Instead of having the user calculate and sum all 63 possibilities, we should implement a short code inside of Tripoli to do the work. The inputs, which will become the model, are simply the relative abundances of each of the isotopes, as presented above. EARTHTIME can certify values for these. Thus, the “BaPO2 Component Isotopes” model will look like:

$BaPO_2$ Component Isotopes

variable name	*value*
pct130Ba_BaPO2	0.106
pct132Ba_BaPO2	0.101
pct134Ba_BaPO2	2.417
pct135Ba_BaPO2	6.592
pct136Ba_BaPO2	7.854
pct137Ba_BaPO2	11.232
pct138Ba_BaPO2	71.698
pct16O_BaPO2	99.757
pct17O_BaPO2	0.038
pct18O_BaPO2	0.205

There will be no uncertainties associated with this model. The measurement error should be large enough as to dwarf the contribution of the error in the isotope ratios.

To calculate the $BaPO_2^+$ IC, first determine the mass and abundance of the 63 combinations one at a time. Make the user-input Ba and O abundances into two vectors, and use three nested *for* loops:

```
mass_Ba = {130, 132, 134, 135, 136, 137, 138}
mass_O = {16, 17, 18}
abundance_Ba = {0.00106, 0.00101, 0.02417, 0.06592, 0.07854, 0.11232, 0.71698}
abundance_O = {.99757, 0.00038, 0.00205}
```

```
n = 0
for i = 1 to 7
    for j = 1 to 3
        for k = 1 to 3
            n = n + 1
            mass_BaPO2(n) = mass_Ba(i) + mass_O(j) + mass_O(k) + 31
            abundance_BaPO2(n) = abundance_Ba(i) * abundance_O(j) * abundance_O(k)
        end for (k)
    end for (j)
end for (i)
```

This creates two vectors of length 63, one containing all the masses and the other all the relative abundances. Next, add up the abundances for each of the $BaPO_2^+$ masses. My (sloppy ad hoc) code looks like this:

```
n = 0;
for m = 193 to 205
    n = n + 1;
        for o = 1:63
        if mass_BaPO2(o) == m
            isotopicComposition_BaPO2(n) = isotopicComposition_BaPO2(n)+ abundance_BaPO2(o)
        end if
    end for (o)
end for (m)
```

The vector isotopicComposition_BaPO2 has 13 elements, containing the relative abundances of the masses 193 to 205 in $BaPO_2^+$. The result should be:

$BaPO_2$ Isotopic Composition: Relative abundances

isotopic mass	*abundance*
193	0.00105485
194	0.00000080
195	0.00100943
196	0.00000077
197	0.02405681
198	0.06561834

199	0.07830760
200	0.11210400
201	0.71390631
202	0.00100339
203	0.00293308
204	0.00000159
205	0.00000301

Retain a large number of digits for each of these abundances for the next step.

Finally, the interference correction algorithm uses as inputs the abundance ratios of 201 through 204 $BaPO_2^+$ to 205. This is the quotient of the relative abundances above.

$BaPO_2$ Isotopic Composition: Isotope Ratios

variable name	*value*
r201_205BaPO2	236933
r202_205BaPO2	333.008
r203_205BaPO2	973.441
r204_205BaPO2	0.52739

The Tl^+ Isotopic Composition

Thallium has two stable isotopes, ^{203}Tl and ^{205}Tl. The following are the most recently published relative abundances, which the user should be able to input as the "Tl IC" model.

Tl Isotopic Composition: Relative abundances

mass	**203**	**205**
abundance	29.52%	70.48 %

Tripoli can then internally calculate the ratio of ^{203}Tl to ^{205}Tl, which is used by the interference correction algorithm.

Tl Isotopic Composition: Isotope Ratios

variable name	*value*
r203_205Tl	0.41884

Part II. Interference Correction Algorithm

Tripoli should have a button, much like the Fractionation Correction button, for $BaPO_2^+$ and Tl^+ correction. The button can be automatically highlighted/activated if Tripoli detects 201/205 and 203/205 amongst the measured ratios. If a 202/205 ratio is also detected, then perform the correction according to "Correction for $BaPO_2$, Tl, and fractionation with a mixed ^{202}Pb-^{205}Pb tracer." If no 202/205 ratio is detected, then perform the correction according to "Correction for $BaPO_2$, Tl interferences with a ^{205}Pb tracer."

Algorithm for $BaPO_2$, Tl, and fractionation correction with a mixed ^{202}Pb-^{205}Pb tracer

If 201/205, 202/205, and 203/205 ratios are detected, then a r202_205t value is needed for the correction algorithm. If the user has selected an active tracer with 202/205 ≠ 0, then use this tracer. If not, prompt the user to select one.

The BaPO2, Tl, and fractionation corrections can all be performed on each ratio using the measured 201/205, 202/205, and 203/205 values. If all three species are present, then they make contributions to the following masses:

Contributions to masses 201 through 208 from each species

201	**202**	**203**	**204**	**205**	**206**	**207**	**208**
$BaPO_2$	Pb	Tl	Pb	Pb	Pb	Pb	Pb
	$BaPO_2$	$BaPO_2$	$BaPO_2$	Tl			
				$BaPO_2$			

To determine the Pb isotope ratios, the measured ratios must be corrected for these interfering species and a linear mass fractionation term. Thus, the measured 201/205, 202/205, and 203/205 measured ratios can be expressed as

$$\left(\frac{201}{205}\right)_m = \frac{201BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 4\alpha)$$

$$\left(\frac{202}{205}\right)_m = \frac{202BaPO_2 + 202Pb}{205Pb + 205Tl + 205BaPO_2} / (1 - 3\alpha)$$

$$\left(\frac{203}{205}\right)_m = \frac{203Tl + 203BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 2\alpha)$$

where R_m is a measured ratio, XBa, XTl, and XPb are the $BaPO_2$, Tl, and Pb contributions to mass X, and α is the fractionation correction coefficient. Since all species contribute to mass 205, we can express each signal as a ratio of its 205 contribution. For instance, *201BaPO$_2$* becomes *r201_205BaPO$_2$* × *205Ba.* It is assumed that all the 202Pb and 205Pb derives from the tracer, so that the 202Pb/205Pb ratio is that of the tracer. The ratios of $BaPO_2$ and Tl to their 205 masses were derived and named in Part I. The ratios expressed in terms of 205 masses become:

$$\left(\frac{201}{205}\right)_m = \frac{r201\_205BaPO_2 \cdot 205BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 4\alpha)$$

$$\left(\frac{202}{205}\right)_m = \frac{r202\_205BaPO_2 \cdot 205BaPO_2 + r202\_205t \cdot 205Pb}{205Pb + 205Tl + 205BaPO_2} / (1 - 3\alpha)$$

$$\left(\frac{203}{205}\right)_m = \frac{r203\_205Tl \cdot 205Tl + r203\_205BaPO_2 \cdot 205BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 2\alpha)$$

Finally, we're not interested in the absolute magnitude of the $BaPO_2$ and Tl corrections, but their size relative to the true Pb isotope ratios. We can therefore divide the numerator and the denominator of the three right-hand side fractions by 205Pb, essentially normalizing each species' contribution. Dividing the top and bottom of the fractions by the same variable is equivalent to multiplying by one and does not change their value. The terms that were previously '205Pb' are now 1. The equations become

$$\left(\frac{201}{205}\right)_m = \frac{r201\_205BaPO_2 \cdot (205BaPO_2/205Pb)}{1 + (205Tl/205Pb) + (205BaPO_2/205Pb)} / (1 - 4\alpha)$$

$$\left(\frac{202}{205}\right)_m = \frac{r202\_205BaPO_2 \cdot (205BaPO_2/205Pb) + r202\_205t}{1 + (205Tl/205Pb) + (205BaPO_2/205Pb)} / (1 - 3\alpha)$$

$$\left(\frac{203}{205}\right)_m = \frac{r203\_205Tl \cdot (205Tl/205Pb) + r203\_205BaPO_2 \cdot (205BaPO_2/205Pb)}{1 + (205Tl/205Pb) + (205BaPO_2/205Pb)} / (1 - 2\alpha)$$

There are now three equations, and three unknowns: $205BaPO_2/205Pb$, (r205BaPO2_205Pb), $205Tl/205Pb$ (r205Tl_205Pb), and α (alphaPb). This system can be solved using the 201/205, 202/205, and 203/205 measured ratios for each cycle to implement a cycle-wise correction. Once determined, these corrections can be applied all the other measured ratios (see next). The analytical solutions to this system are

$$\begin{aligned}
&\boldsymbol{r205BaPO_2_205Pb} \\
&= (r201_205m\ (4\, r202_205t \cdot r203_205Tl - 2\, r202_205t \cdot r203_205m - r202_205m \\
&\cdot r203_205Tl))/(2\, r201_205m \cdot r202_205BaPO_2 \cdot r203_205m - r201_205m \cdot r202_205m \\
&\cdot r203_205BaPO_2 - r201_205BaPO_2 \cdot r202_205m \cdot r203_205m - 4\, r201_205m \cdot r202_205BaPO_2 \\
&\cdot r203_205Tl + 3\, r201_205BaPO_2 \cdot r202_205m \cdot r203_205Tl + r201_205m \cdot r202_205m \\
&\cdot r203_205Tl)
\end{aligned}$$

$$\boldsymbol{r205Tl\_205Pb} = -(r201\_205m \cdot r202\_205m \cdot r203\_205BaPO_2 - 4\, r201\_205m \cdot r202\_205t \cdot r203\_205BaPO_2 - 2\, r201\_205m \cdot r202\_205BaPO_2 \cdot r203\_205m + r201\_205BaPO_2 \cdot r202\_205m \cdot r203\_205m + 2\, r201\_205BaPO_2 \cdot r202\_205t \cdot r203\_205m + 2\, r201\_205m \cdot r202\_205t \cdot r203\_205m)/(r201\_205m \cdot r202\_205m \cdot r203\_205BaPO_2 - 2\, r201\_205m \cdot r202\_205BaPO_2 \cdot r203\_205m + r201\_205BaPO_2 \cdot r202\_205m \cdot r203\_205m + 4\, r201\_205m \cdot r202\_205BaPO_2 \cdot r203\_205Tl - 3\, r201\_205BaPO_2 \cdot r202\_205m \cdot r203\_205Tl - r201\_205m \cdot r202\_205m \cdot r203\_205Tl)$$

$$\boldsymbol{alphaPb} = (r201\_205m \cdot r202\_205t \cdot r203\_205BaPO_2 - r201\_205BaPO_2 \cdot r202\_205t \cdot r203\_205m + r201\_205m \cdot r202\_205BaPO_2\, r203\_205Tl - r201\_205BaPO_2 \cdot r202\_205m \cdot r203\_205Tl + r201\_205BaPO_2 \cdot r202\_205t \cdot r203\_205Tl - r201\_205m \cdot r202\_205t \cdot r203\_205Tl)/(4\, r201\_205m \cdot r202\_205t \cdot r203\_205BaPO_2 - 2\, r201\_205BaPO_2 \cdot r202\_205t \cdot r203\_205m + 4\, r201\_205m \cdot r202\_205BaPO_2 \cdot r203\_205Tl - 3\, r201\_205BaPO_2 \cdot r202\_205m \cdot r203\_205Tl - 4\, r201\_205m \cdot r202\_205t \cdot r203\_205Tl)$$

Calculating the fully corrected ratios

These values can now be used to correct the four Pb isotope ratios to 205Pb that U-Pb_Redux uses for data reduction. Following the table of contributions to each mass from the interfering species, the four measured ratios can be expressed as

$$r204\_205m = \frac{204Pb + 204BaPO_2}{205Pb + 205Tl + 205BaPO_2}/(1-\alpha) \qquad r207\_205m = \frac{207Pb}{205Pb + 205Tl + 205BaPO_2}/(1+2\alpha)$$

$$r206\_205m = \frac{206Pb}{205Pb + 205Tl + 205BaPO_2}/(1+\alpha) \qquad r208\_205m = \frac{208Pb}{205Pb + 205Tl + 205BaPO_2}/(1+3\alpha)$$

The 204BaPO2 contribution can again be re-cast as the 204BaPO2/205BaPO2 ratio times the 205BaPO2 contribution:

$$r204\_205m = \frac{204Pb + r204\_205BaPO2 \cdot 205BaPO_2}{205Pb + 205Tl + 205BaPO_2}/(1-\alpha)$$

Finally, the numerators and denominators of the fractions on the right hand side can be divided through by 205Pb. This normalization yields the both the true Pb isotope ratios and the ratios of the BaPO2 and Tl interferences to 205Pb that we derived above. Each of the full equations

$$r204\_205m = \frac{204Pb/205Pb + r204\_205BaPO2 \cdot (205BaPO_2/205Pb)}{1 + 205Tl/205Pb + 205BaPO_2/205Pb} / (1 - \alpha)$$

$$r206\_205m = \frac{206Pb/205Pb}{1 + 205Tl/205Pb + 205BaPO_2/205Pb} / (1 + \alpha)$$

$$r207\_205m = \frac{207Pb/205Pb}{1 + 205Tl/205Pb + 205BaPO_2/205Pb} / (1 + 2\alpha)$$

$$r208\_205m = \frac{208Pb/205Pb}{1 + 205Tl/205Pb + 205BaPO_2/205Pb} / (1 + 3\alpha)$$

can then be solved for true Pb isotope ratios:

$$\boldsymbol{r204\_205fc} = r204\_205m\ (1 - alphaPb)\ (1 + r205Tl\_205Pb + r205BaPO_2\_205Pb)$$
$$- r204\_205BaPO2 \cdot r205BaPO_2\_205Pb$$

$$\boldsymbol{r206\_205fc} = r206\_205m\ (1 + alphaPb)\ (1 + r205Tl\_205Pb + r205BaPO_2\_205Pb)$$

$$\boldsymbol{r207\_205fc} = r207\_205m\ (1 + 2\ alphaPb)\ (1 + r205Tl\_205Pb + r205BaPO_2\_205Pb)$$

$$\boldsymbol{r208\_205fc} = r208\_205m\ (1 + 3\ alphaPb)\ (1 + r205Tl\_205Pb + r205BaPO_2\_205Pb)$$

Where r204_205fc is the fully corrected $^{204}Pb/^{205}Pb$ ratio, etc. The other five ratios that Redux uses to determine the correlation coefficients can be determined by dividing these ratios.

$$\boldsymbol{r206\_204fc} = r206\_205fc/r204\_205fc$$

$$\boldsymbol{r206\_207fc} = r206\_205fc/r207\_205fc$$

$$\boldsymbol{r206\_208fc} = r206\_205fc/r208\_205fc$$

$$\boldsymbol{r207\_204fc} = r207\_205fc/r204\_205fc$$

$$\boldsymbol{r208\_204fc} = r208\_205fc/r204\_205fc$$

These ratios should be flagged as “fractionation corrected” by Tripoli, then exported to Redux.

Algorithm for $BaPO_2$, Tl, and fractionation correction when no 202/205 ratio is detected

With no 202/205 ratio, the user must first input a value for alphaPb. This can be prompted for the same way that U sample components are now. To be more informative, this prompt can also contain information about the BaPO2 and Tl isotopic composition.

With no 202, we're interested in masses 201, 203, 204, 205, 206, 207, and 208:

Contributions to masses 201 through 208 from each species

201	203	204	205	206	207	208
$BaPO_2$	Tl	Pb	Pb	Pb	Pb	Pb
	$BaPO_2$	$BaPO_2$	Tl			
			$BaPO_2$			

To determine the Pb isotope ratios, the measured ratios must be corrected for these interfering species and the input linear mass fractionation term. Thus, the measured 201/205 and 203/205 measured ratios can be expressed as

$$\left(\frac{201}{205}\right)_m = \frac{201BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 4\alpha)$$

$$\left(\frac{203}{205}\right)_m = \frac{203Tl + 203BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 2\alpha)$$

where R_m is a measured ratio, XBa, XTl, and XPb are the $BaPO_2$, Tl, and Pb contributions to mass X, and α is the fractionation correction coefficient. Since all species contribute to mass 205, we can express each signal as a ratio of its 205 contribution. For instance, *$201BaPO_2$* becomes *$r201\_205BaPO_2$* × *205Ba.* The ratios of $BaPO_2$ and Tl to their 205 masses were derived and named in Part I. The ratios expressed in terms of 205 masses become:

$$\left(\frac{201}{205}\right)_m = \frac{r201\_205BaPO_2 \cdot 205BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 4\alpha)$$

$$\left(\frac{203}{205}\right)_m = \frac{r203\_205Tl \cdot 205Tl + r203\_205BaPO_2 \cdot 205BaPO_2}{205Pb + 205Tl + 205BaPO_2} / (1 - 2\alpha)$$

Finally, we're not interested in the absolute magnitude of the $BaPO_2$ and Tl corrections, but their size relative to the true Pb isotope ratios. We can therefore divide the numerator and the denominator of the three right-hand side fractions by 205Pb, essentially normalizing each species' contribution. Dividing the top and bottom of the fractions by the same variable is equivalent to multiplying by one and does not change their value. The terms that were previously '205Pb' are now 1. The equations become

$$\left(\frac{201}{205}\right)_m = \frac{r201\_205BaPO_2 \cdot (205BaPO_2/205Pb)}{1 + (205Tl/205Pb) + (205BaPO_2/205Pb)} / (1 - 4\alpha)$$

$$\left(\frac{203}{205}\right)_m = \frac{r203\_205Tl \cdot (205Tl/205Pb) + r203\_205BaPO_2 \cdot (205BaPO_2/205Pb)}{1 + (205Tl/205Pb) + (205BaPO_2/205Pb)} / (1 - 2\alpha)$$

There are now two equations, and two unknowns: $205BaPO_2/205Pb$, (r205BaPO2_205Pb) and $205Tl/205Pb$ (r205Tl_205Pb). α (alphaPb) has already been input by the user. This system can be solved for each cycle's pair of 201/205 and 203/205 measured ratios to implement a cycle-wise correction. Once determined, the correction can be applied to the other measured ratios (see next). The analytical solutions to this system are

$$\begin{aligned}
&\boldsymbol{r205BaPO_2_205Pb} \\
&= -(r201_205m \cdot r203_205Tl \cdot (-1 + 4 \cdot alphaPb))/(r201_205m \cdot r203_205Ba \\
&- r201_205Ba \cdot r203_205m + r201_205Ba \cdot r203_205Tl - r201_205m \cdot r203_205Tl \\
&- 4 \cdot r201_205m \cdot r203_205Ba \cdot alphaPb
\end{aligned}$$

$$\begin{aligned}
&\boldsymbol{r205Tl_205Pb} = -(r201_205m \cdot r203_205Ba - r201_205Ba \cdot r203_205m \\
&- 4 \cdot r201_205m \cdot r203_205Ba \cdot alphaPb + 2 \cdot r201_205Ba \cdot r203_205m \cdot alphaPb)/ \\
&(r201_205m \cdot r203_205Ba - r201_205Ba \cdot r203_205m \\
&+ r201_205Ba \cdot r203_205Tl - r201_205m \cdot r203_205Tl - 4 \cdot r201_205m \cdot r203_205Ba \cdot alphaPb \\
&+ 2 \cdot r201_205Ba \cdot r203_205m \cdot alphaPb + 4 \cdot r201_205m \cdot r203_205Tl \cdot alphaPb)
\end{aligned}$$

Calculating the fully corrected ratios

The fully corrected ratios are calculated in exactly the same way as those for the mixed 202-205 tracer.