

Converting Al and Be isotope ratio measurements to nuclide concentrations in quartz

Greg Balco
Cosmogenic Nuclide Lab, University of Washington

May 8, 2006

1 Introduction

This document describes how to reduce a Be or Al isotope ratio measurement, provided by an accelerator-mass-spectrometer measurement, to a ^{10}Be or ^{26}Al concentration in quartz, which is the quantity needed to calculate an exposure age or an erosion rate. This process also incorporates the ^{10}Be process blank and its uncertainty into the final estimate of the nuclide concentration in the sample.

The information needed to do this is as follows. For a ^{10}Be measurement, one needs: 1) the measured $^{10}\text{Be}/^9\text{Be}$ isotope ratio and its 1-standard-error uncertainty; 2) the mass of Be added as carrier in the chemical processing and its uncertainty; 3) the mass of the quartz sample itself; and 4) the typical number of atoms of ^{10}Be in a laboratory process blank, and its uncertainty.

To determine this last item, the ‘typical’ number of ^{10}Be atoms in the process blank, one also needs the measured isotope ratios and the carrier concentrations used for one or more process blanks that were run together with samples. Basically, the procedure is to first calculate the number of ^{10}Be atoms in your process blanks, then use this information to decide on the correct blank value to use in computing the ^{10}Be concentrations in the samples. The discussion below goes in the opposite order – beginning with the situation for samples and then going on to a discussion of blanks – for better clarity in the explanation.

For an ^{26}Al measurement, one needs the corresponding information for Al, except that Al carrier is not commonly used for ^{26}Al measurements. The total amount of natural Al measured in the sample is used instead.

2 Converting the $^{10}\text{Be}/^9\text{Be}$ ratio to the ^{10}Be concentration in quartz

The accelerator mass spectrometer actually measures the ratio $R_{10/9}$ of atoms of ^{10}Be to atoms of ^9Be in the target sample. The atoms of both isotopes that actually get to the accelerator can come from a variety of sources: they can be in the actual quartz sample itself, they can be in the ^9Be carrier that is added during chemical processing, or they can be unwanted atoms that arrive sometime during the chemical processing. Thus, the ratio $R_{10/9}$ is made up as follows:

$$R_{10/9} = \frac{n_{10,S} + n_{10,C} + n_{10,P}}{n_{9,S} + n_{9,C} + n_{9,P}} \quad (1)$$

Where $n_{10,S}$ is the number of atoms of ^{10}Be in the sample; $n_{10,C}$ is the number of atoms of ^{10}Be in the Be carrier (which is supposed to be pure ^9Be , but in reality always contains some amount of ^{10}Be); $n_{10,P}$ is the number of atoms of ^{10}Be added accidentally during processing; and $n_{9,S}$, $n_{9,C}$ and $n_{9,P}$ are the numbers of atoms of ^9Be that come from the same three sources.

Note: some AMS labs, Lawrence Livermore in particular, provide two isotope ratios in their results: an uncorrected ratio, and a ‘blank-corrected’ ratio which takes into account one of the process blanks that the user submitted with their sample. The object of this document is to describe how to do the blank correction, so $R_{10/9}$ here refers to the isotope ratio that has *not* already had the process blank subtracted from it. AMS labs handle this differently in their results, so you should check to determine which value you have.

The quantity we actually want to know is the number of atoms per gram of quartz in the sample, which isn’t in this equation yet. Call it N_{10} , the capital N denoting a concentration in atoms $\cdot \text{g}^{-1}$ rather than a number of atoms. $n_{10,s}$, the total number of atoms in the sample, is $N_{10}M_q$, where M_q is the mass of the quartz sample (g). This makes Equation 1:

$$R_{10/9} = \frac{N_{10}M_q + n_{10,C} + n_{10,P}}{n_{9,S} + n_{9,C} + n_{9,P}} \quad (2)$$

We can simplify this equation in two ways.

First, Be is a rare element in the environment, so (in nearly all cases), the amount of ^9Be that is in the original sample and occurs from contamination in the lab is very much less than the relatively large amount of ^9Be that we add in the form of carrier. Basically, $n_{9,S} \ll n_{9,C}$ and $n_{9,P} \ll n_{9,C}$, so $n_{9,S} + n_{9,C} + n_{9,P} \simeq n_{9,C}$.

Second, the standard practice in nearly all laboratories is to use the same amount of ^9Be carrier for all samples and all process blanks, that is, blanks that are subjected to the entire chemical extraction process in parallel with the samples. Thus, the number of atoms of ^{10}Be added with the carrier $n_{10,C}$ will be the same for all samples and process blanks. Also, we have to assume that the number of atoms of ^{10}Be added accidentally during processing $n_{10,P}$ will always be the same for all samples, at least within a particular batch of samples processed together. Thus, the quantity $n_{10,C} + n_{10,P}$ will always be the same for samples and process blanks, so we can simply call $n_{10,C} + n_{10,P} = n_{10,B}$, that is, the number of atoms of ^{10}Be in a process blank. Section 4 below describes how to decide on a value for $n_{10,B}$.

With these two simplifications we have:

$$R_{10/9} = \frac{N_{10}M_q + n_{10,B}}{n_{9,C}} \quad (3)$$

The number of atoms of ^9Be in the carrier $n_{9,C}$ is calculated from the mass of Be added as carrier:

$$n_{9,C} = \frac{M_C N_A}{A_{Be}} \quad (4)$$

where M_C is the mass of Be added as carrier (g), N_A is Avogadro’s number (6.022×10^{23} atoms $\cdot \text{mol}^{-1}$), and A_{Be} is the molar weight of Be (9.012 g $\cdot \text{mol}^{-1}$). For example, most labs add $250 \mu\text{g}$ of ^9Be as carrier, which contains $250 \times 10^{-6} * 6.022 \times 10^{23} / 9.012 = 1.671 \times 10^{19}$ atoms of ^9Be .

This gives:

$$R_{10/9} = \frac{N_{10}M_q + n_{10,B}}{\frac{M_C N_A}{A_{Be}}} = \frac{A_{Be} (N_{10}M_q + n_{10,B})}{M_C N_A} \quad (5)$$

which we can solve to get the formula for the quantity we actually want, N_{10} :

$$N_{10} = \frac{1}{M_q} \left(\frac{R_{10/9} M_C N_A}{A_{Be}} - n_{10,B} \right) \quad (6)$$

3 Uncertainty in ^{10}Be concentration

The uncertainty in the ^{10}Be concentration in the quartz sample must take into account three sources of uncertainty: the uncertainty in the isotope ratio measurement (which we will call $\sigma R_{10/9}$), the uncertainty in the number of atoms in the process blanks ($\sigma n_{10,B}$), and the uncertainty in the mass of Be added as carrier (σM_C). The isotope ratio uncertainty $\sigma R_{10/9}$ is supplied by the AMS lab. The blank uncertainty $\sigma n_{10,B}$ is discussed below. The uncertainty in the Be carrier mass comes from the fact that the Be carrier is added in solution, and the Be concentration in the solution has some uncertainty. The uncertainty in the Be concentration in typical commercial Be solutions is about 1%, so the uncertainty in the Be carrier mass is typically $\sigma M_C = 0.01 M_C$.

Using standard error-propagation methods, the formula for the uncertainty in the ^{10}Be concentration in quartz, that is, σN_{10} , is:

$$\sigma N_{10} = \sqrt{\left(\frac{\partial N_{10}}{\partial R_{10/9}} \sigma R_{10/9} \right)^2 + \left(\frac{\partial N_{10}}{\partial n_{10,b}} \sigma n_{10,b} \right)^2 + \left(\frac{\partial N_{10}}{\partial M_C} \sigma M_C \right)^2} \quad (7)$$

where:

$$\frac{\partial N_{10}}{\partial R_{10/9}} = \frac{M_C N_A}{M_q A_{Be}} \quad (8)$$

$$\frac{\partial N_{10}}{\partial n_{10,B}} = \frac{-1}{M_q} \quad (9)$$

$$\frac{\partial N_{10}}{\partial M_C} = \frac{R_{10/9} N_A}{M_q A_{Be}} \quad (10)$$

4 Estimating the number of ^{10}Be atoms in the blank

The process blank protocol used in most chemical processing laboratories consists of processing one blank in parallel with each batch of 8-10 samples. As no sample is added to the process blank, the number of ^{10}Be atoms eventually found in it must come either from the ^9Be carrier or from contamination during processing. By analogy with the discussion above, the number of ^{10}Be atoms in a particular process blank is:

$$n_{10,B}^* = \frac{R_{10/9} M_C N_A}{A_{Be}} \quad (11)$$

Now $R_{10/9}$ is the $^{10}\text{Be}/^9\text{Be}$ ratio measured in the process blank and M_C is the mass of Be carrier used in the process blank. The other symbols are as used above. The superscripted star is intended to indicate that this is the number of ^{10}Be atoms in a particular blank, and not necessarily the summary value that should be used above in calculating the nuclide concentration in a particular sample (although it might be – see discussion below). The analytical uncertainty in the number of ^{10}Be atoms in the particular process blank is:

$$\sigma n_{10,B}^* = \sqrt{\left(\frac{\partial n_{10,B}^*}{\partial R_{10/9}} \sigma R_{10/9}\right)^2 + \left(\frac{\partial n_{10,B}^*}{\partial M_C} \sigma M_C\right)^2} \quad (12)$$

where:

$$\frac{\partial n_{10,B}^*}{\partial R_{10/9}} = \frac{M_C N_A}{A_{Be}} \quad (13)$$

$$\frac{\partial n_{10,B}^*}{\partial M_C} = \frac{R_{10/9} N_A}{A_{Be}} \quad (14)$$

Again, $\sigma R_{10/9}$ is the uncertainty in the measured $^{10}\text{Be}/^9\text{Be}$ ratio of the process blank, and σM_C is the uncertainty in the mass of Be carrier added to the process blank.

Having now calculated the number of atoms of ^{10}Be in a *particular* process blank n_{10}^* , there are two ways to think about what blank value to use in determining the nuclide concentration in a sample, depending on what you believe about the source of the ^{10}Be contamination in the laboratory.

One common way to think about this is to assume that all the samples in a particular batch are equally contaminated by unwanted ^{10}Be atoms during processing. This would be true if these unwanted ^{10}Be atoms came from sources that were common to all the samples in a batch. The simplest way to accomplish this would be if acids or other reagents were the source of the spurious ^{10}Be . In fact, the way we have set up this procedure, we know this to be true in part, because some (if not most) of the unwanted ^{10}Be atoms come from the Be carrier, which is common to all the samples in the batch as well as the process blank that was processed along with them. This approach suggests that, when determining the nuclide concentration in a particular sample, the ^{10}Be blank that should be taken into account is precisely the amount that was measured in the process blank run together with that sample. In this case, the values of $n_{10,B}$ and $\sigma n_{10,B}$ that should be used in Equations 6 and 7 are the values of $n_{10,B}^*$ and $\sigma n_{10,B}^*$ calculated for the particular process blank that was run together in the same batch as your sample.

The second way to think about this is to assume that the number of atoms of unwanted ^{10}Be in each sample is different. This would be the case if contamination came from soil particles, or other dust particles enriched in atmospherically produced ^{10}Be that found their way into the lab; or if it came from cross-contamination between samples sometime during the chemical processing. If this were true, and we took the number of ^{10}Be atoms and their measurement uncertainty for a single blank as representative of the unwanted ^{10}Be atoms in all samples, we would risk using a blank uncertainty $\sigma n_{10,B}$ that was too small. The measurement uncertainty for a particular process blank would not take into account the fact that there might be a different number of unwanted ^{10}Be atoms in the other samples in the batch. In this situation, it would be better to look at a series of process blanks run over a long period of time (as long as they were run using the same Be carrier solution). Then we would use the average and standard deviation of the long-term series of process blanks, instead of the value of any one blank, as the representative blank value and uncertainty to be applied to all of the samples run during this time.

Here's an example. Figure 1 shows a series of process blanks run over a 6-month period. All the process blanks contained the same amount of the same Be carrier, but the difference between blanks was much greater than the measurement precision of each individual blank. Eventually this problem was traced to unwanted ^{10}Be atoms in the Al metal used to make the accelerator cathodes used to hold the Be samples for analysis, and it turned out that the

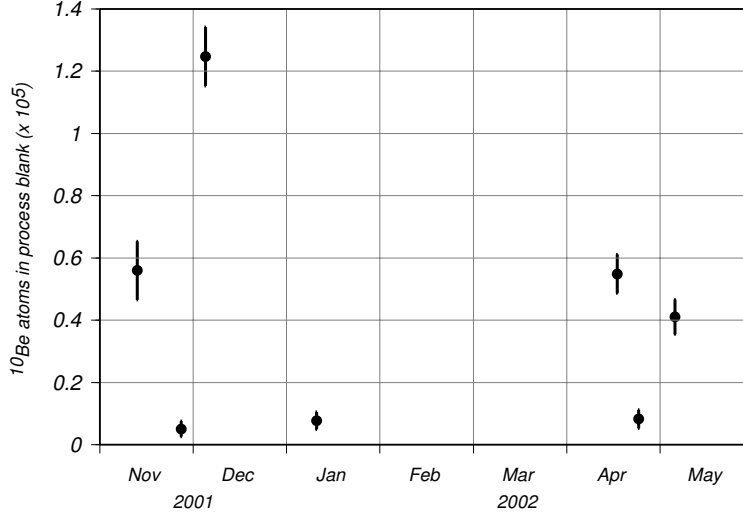


Figure 1: Example of ^{10}Be process blank measurements over a 6-month period

number of spurious ^{10}Be atoms that turned up in the measurement was extremely variable between cathodes. This indicated that the number of unwanted ^{10}Be atoms would be different for each sample, and that if we used the blank value and uncertainty measured for only the particular blank that was run in the same batch as a particular sample, we would underestimate the uncertainty in the sample nuclide concentration. Thus, for all the samples run during this period, it seemed best to use an $n_{10,B}$ and $\sigma n_{10,B}$ derived from the average and standard deviation of all these blanks ($n_{10,B} = 45000$ and $\sigma n_{10,B} = 46000$), instead of the measured value for any particular one of the blanks.

5 Modifications for ^{26}Al

This procedure is essentially the same for ^{26}Al . The only major difference in the chemical processing is that the quartz sample typically contains a relatively large amount of total Al, so it is not necessary to add Al carrier. Thus, the total number of atoms of stable ^{27}Al in the sample, here denoted $n_{27,S}$, replaces the number of atoms of the stable nuclide added as carrier. This quantity is:

$$n_{27,S} = \frac{M_{Al,S} N_A}{A_{Al}} \quad (15)$$

where A_{Al} is the molar weight of Al ($26.982 \text{ g} \cdot \text{mol}^{-1}$) and $M_{Al,S}$ is the mass of Al in the sample (g). The mass of Al in the sample is usually determined by ICP-OES or AA analysis of an aliquot taken immediately after the sample has been dissolved. The ^{26}Al concentration in quartz, N_{26} , is then:

$$N_{26} = \frac{1}{M_q} \left(\frac{R_{26/27} M_{Al,S} N_A}{A_{Al}} - n_{26,B} \right) \quad (16)$$

where $R_{26/27}$ is the measured $^{26}\text{Al}/^{27}\text{Al}$ ratio. The uncertainty σN_{26} is:

$$\sigma N_{26} = \sqrt{\left(\frac{\partial N_{26}}{\partial R_{26/27}} \sigma R_{26/27}\right)^2 + \left(\frac{\partial N_{26}}{\partial n_{26,B}} \sigma n_{26,B}\right)^2 + \left(\frac{\partial N_{26}}{\partial M_{Al,S}} \sigma M_{Al,S}\right)^2} \quad (17)$$

where:

$$\frac{\partial N_{26}}{\partial R_{26/27}} = \frac{M_{Al,S} N_A}{M_q A_{Al}} \quad (18)$$

$$\frac{\partial N_{26}}{\partial n_{26,B}} = \frac{-1}{M_q} \quad (19)$$

$$\frac{\partial N_{26}}{\partial M_{Al,S}} = \frac{R_{26/27} N_A}{M_q A_{Al}} \quad (20)$$

One determines the process blank for ^{26}Al measurements in the same way as for ^{10}Be , as described above. ^{26}Al is a much less common nuclide in the environment, so generally ^{26}Al blanks are less important than ^{10}Be blanks.

6 Traps for the unwary

There are several situations in which the procedure described above will give the wrong results, because they violate the assumptions we've made in simplifying Equation 1:

1. *Unexpected ^9Be in sample.* We assume that the amount of ^9Be in the sample is much less than the amount added as carrier, so $n_{9,S}$ can be ignored. Sometimes this isn't true, and the quartz sample contains some Be. This is rare, and almost invariably occurs when the quartz is from a beryl-bearing granite or pegmatite, so there are small amounts of beryl left in the supposedly pure quartz sample. Beryl is not as soluble in HF as quartz, but some of it will dissolve and contribute Be in addition to the Be added as carrier. The only way to detect this is to measure Be as well as Al concentration in the HF solution after sample dissolution, and compare the amount of Be that is actually in the solution to the amount added as carrier.
2. *Use of different carriers, or different amounts of carrier.* We assume that the number of atoms of ^{10}Be contributed by the carrier is always the same, so we can simplify by making $n_{10,C} + n_{10,P} = n_{10,B}$. This is the same as assuming that the same carrier solution, and the same amount of carrier solution, is used for all samples and process blanks. If this isn't true, $n_{10,C}$ and $n_{10,B}$ must be kept separate and estimated individually.
3. *Al carrier addition after [Al] measurement.* Sometimes there's not enough Al in the quartz sample to extract the minimum amount needed for the AMS measurement, so it's necessary to add some amount of ^{27}Al carrier. If this is added at the time of dissolution, before the aliquot is taken out for [Al] measurement, there is no effect on the procedure described above. The amount of Al you measure in the aliquot is the sum of the Al that was actually in the sample and the Al added as carrier, but you can treat these two sources the same and simply use the total amount of Al as your value for $M_{Al,S}$. If the Al carrier is added after the [Al] measurement has been made, however, it makes the data reduction much more complicated, and the entire procedure described above must be revised.