Determining Mo, Sb, Sn and W in basalt reference materials by ICP-MS and using the methods of isotope dilution and standard addition.

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Abstract

The combination of isotope dilution and standard addition by ICP-MS is used to determine the Mo, Sb, Sn and W compositions of basalt reference materials. There are few concentration data published for these four elements and the existing values display a significant variability. The two methods of quantitation we used are agreed to give high precision results, which is necessary since the analyzed reference basalts are used for calibrating unknown rock samples in trace element ICP-MS analyses. We describe the way the samples and the isotope dilution spikes are prepared and explain the methods used to reduce the data and correct for all the interferences and measurement bias. We were able to obtain concentration values with less than 5\% \(1\sigma\) standard deviation for most of the analyzed standards, improving our knowledge of the standard compositions and allowing the improvement of the calibration curves used in routine trace element analyses. However, there is a slight bias between the values obtained by standard addition and isotope dilution for the four elements. Even though we couldn’t do further analyses to determine the cause of this bias we have tried to list up all the problematic elements in this study and the improvements that can be made.

Keywords: Inductively coupled plasma methods; Trace elements analysis; Isotope dilution; Standard addition.
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1 Introduction

The study of igneous rocks trace elements geochemistry can provide a better understanding of the processes responsible for the magma differentiation, bring information about the chemical composition of the source and it also allows a time-integrated view of these evolutions thanks to the radiogenic isotopes. Since each element has unique chemical properties there is a unique geochemical information contained in the variation of their concentration in rocks.

The trace elements analysis of rock samples by ICP-MS (inductively coupled plasma mass spectrometry) can be performed assuming that there is a linear relation between the concentration of a given element in solution and the intensity (counts per second) measured by the instrument. Knowing the composition of standard rock samples allows us to build a calibration curve (intensity versus concentration) on which we can fit the unknown rock samples to determine their composition. These igneous rock samples of known composition are called geochemical reference materials and are provided by institutions like the United States Geological Survey (USGS) or the Geological Survey of Japan (GSJ). The following chart introduces the reference materials under study:

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Provenance</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-1</td>
<td>Andesite, Guano Valley</td>
<td>USGS</td>
</tr>
<tr>
<td>AGV-2</td>
<td>Andesite, Guano Valley</td>
<td>USGS</td>
</tr>
<tr>
<td>BCR-2</td>
<td>Basalt, Columbia River</td>
<td>USGS</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>Basalt, Hawaiian Volcanic Observatory</td>
<td>USGS</td>
</tr>
<tr>
<td>CHEPR</td>
<td>Basalt, East Pacific Ridge</td>
<td>In house</td>
</tr>
<tr>
<td>DNC-1</td>
<td>Dolerite, North Carolina</td>
<td>USGS</td>
</tr>
<tr>
<td>JB-2</td>
<td>Basalt, Japan (Oshima volcano)</td>
<td>GSJ</td>
</tr>
<tr>
<td>JB-3</td>
<td>Basalt, Japan (Fuji volcano)</td>
<td>GSJ</td>
</tr>
<tr>
<td>MAR</td>
<td>Basalt</td>
<td>In house</td>
</tr>
<tr>
<td>VE 32</td>
<td>Basalt</td>
<td>In house</td>
</tr>
</tbody>
</table>

Figure 1. Reference basalts whose composition in Mo, Sb, Sn and W are determined in this study.

Even though certificates of analysis are provided with these standards, the composition for some elements is not always available or is too poorly constrained to be used to build a calibration curve. We report below some results obtained for Sn by ICP-MS on basalts prior to this study. The ICP-MS outputs are drift corrected and normalized and the standard compositions are coming from the USGS, GSJ and the internet database GeoReM. The GeoReM database compiles the published concentrations values obtained using different analytical methods.
Figure 2. Calibration curves obtained with five different standard samples. Left panel: concentration values coming from the GeoReM database. The regression is made through the values used by the Lamont-Doherty Earth Observatory of Columbia University and the deviation to other values in the database is used to obtain the error bar. Right panel: concentration values certified by the USGS and the GSJ.

We can see that the Sn concentrations in the reference basalts are not determined precisely enough, the result being an intercept too far from zero, a correlation with a correlation coefficient less than 0.99 (left panel) and a slope significantly changing between the two calibrations. Similar graphs are obtained when we look at the elements Mo, Sb and W. Thus, our goal is to use isotope dilution and standard addition methods to acquire new concentration values for the ten standards listed in figure 1.

In a first part we shall describe the elements under study and the isotopes of interest. We will then introduce the theory behind the analytical methods used, before describing the way we prepared the samples. Finally, we shall give some guidelines about the ICP-MS measurements and the data reduction so as to present and discuss our results in the last section.

2 Elements of interest

The elements studied here are Mo, Sb, Sn and W. Different stable isotopes of these elements exist in the nature. Isotopes have the same number of protons (the same atomic number) but different numbers of neutrons. The isotope of each element has a given natural abundance, showed in the following figure:

Figure 3. Elemental abundance chart showing the isotopes of interest in this study (purple cells).

As we can see in this chart, the isotopes of two different elements can have the same mass; for example $^{94}$Mo and $^{94}$Zr. This will result in an isobaric interference: the intensity measured by the ICP-MS at mass 94 is the contribution of both isotopes. We can easily correct this interference, but as Zr and Hf (this latter interfering with W) are abundant elements in the rock samples we are not going to use the isotopes having isobaric interferences in this study. Exceptions are made ($^{123}$Te interfering with $^{123}$Sb, $^{98}$Ru interfering with $^{98}$Mo) since the interfering isotopes have either a low abundance or a low concentration in the rock samples.

For W, there is also a significant effect of oxide interference. For example $^{166}$Er$^{16}$O diatomic molecules that can form in the ICP-MS have the same mass as $^{182}$W, resulting in a bias in the
measurement. Since Er is an element quite abundant in the rock samples under study, we will have to correct for these oxide interferences.

Figure 3 shows the isotopes that we are eventually going to use in our measurements. They appear in the purple cells.

3 Analytical methods

Trace element measurement can be achieved by using three main analytical methods: standard addition, isotope dilution and external calibration. In this study we have focused on isotope dilution and standard addition, which are agreed to be the most accurate methods, especially for the contents. In the following parts we are going to present the theoretical background of these two methods.

3.1 Isotope dilution

The isotope dilution method is based on altering the natural abundance of two isotopes of an element by adding a known quantity of a solution enriched in one or several isotopes (spike) to the rock samples. Then, after measuring the non-natural ratios of the mixture, we can calculate the concentration of the element of interest in the rock sample using a simple mass-balance equation based on the amount of spike, its isotopic compositions, the amount of rock dissolved and the natural isotopic compositions of the sample. This method requires that the element have at least two stable isotopes (i.e. a stable natural ratio). The following figure shows the composition of the spikes provided by Oak Ridge that we are using:

![Figure 4. Compositions of the spikes used. The isotopes in orange are the isotopes used for the isotope dilution calculation, according to the explanation given in the previous paragraph.](image)

Let us clarify the principle of the method of isotope dilution by looking at the equations that we use and taking the element Mo as an example.

3.1.1 Equations of isotope dilution

As was said previously, at least two stable isotopes are necessary to perform isotope dilution measurements. The spike is enriched in a particular isotope (\(^{95}\)Mo in this case), used to normalize the counts of the other isotopes. Let us develop the equations by using the ratio \(^{97}\)Mo/\(^{95}\)Mo.
The isotope ratio measured on an ICP-MS quadrupole is \( \frac{^{97}Mo}{^{95}Mo} \).

The natural isotopic ratio in the sample \( \frac{^{97}Mo}{^{95}Mo} \) is given by the chart of natural abundances.

The isotopic ratio in the spike \( \frac{^{97}Mo}{^{95}Mo} \) is certified by the seller.

When we add a known quantity of spike to the sample, the resulting ratio of the mixture is

\[
\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{mix}} = \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sa}} + \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}} \]

In this formula we have separated the contribution of the spike and the sample by introducing the mixing ratio \( \alpha_{\text{sa}} = \frac{N_{^{95}Mo}^{\text{sa}}}{N_{^{95}Mo}^{\text{sa}} + N_{^{95}Mo}^{\text{sp}}} \), where \( N_{^{95}Mo}^{\text{sa}} \) is the number of moles of \(^{95}Mo\) in the sample.

We have \( \alpha_{\text{sa}} + \alpha_{\text{sp}} = 1 \) and therefore

\[
\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{mix}} = \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sa}} \alpha_{\text{sa}} + \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}} (1 - \alpha_{\text{sa}})
\]

\[
\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{mix}} = \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sa}} + \left[ \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sa}} - \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}} \right] \alpha_{\text{sa}}
\]

\[
\alpha_{\text{sa}} = \frac{\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{mix}} - \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}}}{\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sa}} - \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}}}
\]

Then we have

\[
\frac{\alpha_{\text{sa}}}{\alpha_{\text{sp}}} = \frac{N_{^{95}Mo}^{\text{sa}}}{N_{^{95}Mo}^{\text{sa}}} = \frac{\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{mix}} - \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}}}{\left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sa}} - \left( \frac{^{97}Mo}{^{95}Mo} \right)_{\text{sp}}} = R.
\]

If we use the explicit form of \( \frac{N_{^{95}Mo}^{\text{sa}}}{N_{^{95}Mo}^{\text{sa}}} \) we find that

\[
R = \frac{\text{Mass}_{^{95}Mo} \cdot \text{Concentration}_{^{95}Mo}^{\text{sa}} \cdot \text{Abundance}_{^{95}Mo}^{\text{sa}}}{\text{Mass}_{^{95}Mo} \cdot \text{Concentration}_{^{95}Mo}^{\text{sp}} \cdot \text{Abundance}_{^{95}Mo}^{\text{sp}}}
\]

In this last equation, the only unknown is \( \text{Concentration}_{^{95}Mo}^{\text{sa}} \) since \( R \) is measured by ICP-MS. This formula allows us to determine the concentration of the element of interest in the sample.

### 3.2 Standard addition

While we added a spike with a modified isotopic composition in isotope dilution, standard addition requires the use of a single element standard solution with a natural isotopic composition (the same composition as the rock sample). We want to add a known quantity of single element standard solution to the standard basalt sample solution in order to build a calibration curve. We
analyzed 4 different aliquots: a first one with only the standard basalt solution, and 3 with an increasing quantity of Mo, Sb, Sn and W. We did not want to add either too much or insufficient single element solution; thus, adding 2, 3 and 4 times the amount of element originally present in the basalt sample solution happened to be a good compromise. Thanks to the values already published or reported by the USGS or JGS, we were able to estimate the amount of single element to add to 5 mL of basalt sample solution.

![Standard addition calibration curve](image)

**Figure 5.** Example of standard addition calibration curve showing the ICP-MS counts versus the concentration of the element of interest added to the sample solution.

When we build this calibration curve, we plot (a plot = une intrigue ou un complot) the concentration of the element that we added in the tube. Hence, the intercept with the vertical axe gives (after correcting for the dilution effect) the concentration of the element in the sample tube.

4 Preparing the solutions

ICP-MS measurements are performed on solutions. The samples need first to be dissolved and then diluted in an acidic solution in which the elements of interest are stable and weak enough not to damage the ICP-MS during the measurements. We add to this sample solution either a spike solution or a standard solution, depending upon the method used. In the following section, we describe how to obtain the spike solutions and the dissolved rock sample solutions.

**4.1 Spike preparation and calibration**

4.1.1 Spike dissolution

The Mo, Sb, Sn and W spikes were originally a 1 mg powder or piece of wire. Sb and W were dissolved in 1.5 mL of aqua regia (HCl + HNO₃) and Mo and Sn in 0.5 mL of HF and 1 mL of 8N HNO₃. The dissolution was made during 12 hours at 90°C, with several sonication steps during the last 6 hours. Then the 1.5 mL spike solutions were diluted in 98.5 mL of 1% nitric acid, giving 10 ppm solutions (1 mg to 100 g). We prepared 100 g of 10 ppb spike solutions for each element by diluting 100 mg of 10 ppm solution in 99.9 g of 1% nitric acid. These 10 ppb spike solutions were then calibrated.
### 4.1.2 Spike calibration

The calibration of the spikes is made by reverse isotope dilution using a standard solution whose concentration is known accurately or certified by the seller (High Purity Standards) instead of an unknown sample.

The equation obtained in section 3.1: 

\[
R = \frac{\text{Mass}_{\text{sa}} \cdot \text{Concentration}_{\text{sp}}^{\text{Mo}} \cdot \text{Abundance}_{\text{sp}}^{\text{Mo}}}{\text{Mass}_{\text{sp}} \cdot \text{Concentration}_{\text{sp}}^{\text{Mo}} \cdot \text{Abundance}_{\text{sp}}^{\text{Mo}}},
\]

where \( R \) is measured by ICP-MS, allows us to determine the \( \text{Concentration}_{\text{sp}}^{\text{Mo}} \), which is the only unknown in this equation since we know \( \text{Concentration}_{\text{sa}}^{\text{Mo}} \). The standard solutions used for the spike calibration were made with single element solutions of Mo, Sb, Sn and W, with a natural isotopic ratio and a concentration of 1000 ppm ± 3 ppm.

The ICP-MS measurement of the isotope ratio of the mix between the spike solutions and the single element standard solutions are made by running the following sequence of tubes:

1. Blank 1
2. Standard solution
3. Standard solution + spikes 1
4. Standard solution
5. Standard solution + spikes 2
6. Standard solution
7. Standard solution + spikes 3
8. Standard solution
9. Blank 2

The blanks are used for the blank correction and the standard solutions in positions 2, 4, 6 and 8 for the mass fractionation correction (see section 5.2).

We carried out an additional measurement on the spikes. By running the spike solutions through the ICP-MS, we were able to determine their isotopic ratio and thus the abundance of the elements isotopes in the spikes. We found abundances similar to those certified by the spike provider, what means that we really know the composition of the spikes and thus our isotope dilution measurements are possible.

### 4.2 Preparation of the samples

We describe in this section the way standard basalt powders are dissolved in order to be run though the ICP-MS and mixed with the spikes.

#### 4.2.1 Dissolution process

The following chemistry steps are realized using the Picotrace dissolution system, within a class-10 hood in a clean room. Within each sample batch, we always prepared blanks, corresponding to a full chemistry done in a beaker without sample. We try to run at least 2 blanks in every rack (one rack containing 16 beakers).

1. **Weighing out the samples**: we weigh 50 mg of sample powder with a \( 10^{-1} \) mg precision balance.
2. **First dissolution:** we add 1.5 mL of double-distilled 8N HNO3 and 0.5 mL of HF to the sample powder in every beaker and then put the sealed and pressurized beakers on the hot plate at 180°C during 13 hours.

3. **Evaporation:** after the beakers have cooled, we take off the lid making sure that we do not lose any droplet and then place the evaporation lid onto the beakers. We connect the evaporation lid to a neutralizing solution in which the evaporation products are collected and let it stand for 12 hours at 80°C.

4. **Second dissolution:** after the samples in the beakers have been dried, we add 2 mL of 8N HNO3 in each beaker and then put the beaker rack on the hot plate at 180°C during 13 hours.

5. **Dilution:** we put the dissolved samples in individual 100 mL clean bottles with 2 mL of 8N HNO3 and fill in with 18 mega-ohm water to reach a weight of 100 g.

The sample preparation described above leads to a 2000 times (2k) dilution: 50 mg of sample in 100 g. It is possible to weigh 100 mg of sample powder first and then double all the acid amounts in order to have a 1k dilution. We used both dilutions in this study, which gave reproducible and consistent results though we noticed a small sensitivity drop after running 1k-diluted samples. This is probably due to the fact that 1k samples make the ICP-MS cones dirtier since they are more concentrated than 2k samples.

4.2.2 **Mixing the spikes and the sample for isotope dilution**

To analyze a standard sample by isotope dilution, we run through the ICP-MS four different sample solutions:
- an unspiked sample solution used to get the natural isotope ratio;
- three sample solutions spiked with different amounts of spike in order to have good statistical measurements.

Mixing the spikes and the sample can be done during the fourth step of the dissolution process described above, allowing to reach a good isotopic equilibrium because of the long heating time. This method forces us to prepare 4 different sample solutions per standard basalt analysis, which is highly time-consuming. However, we were able to get consistent and reproducible results by preparing only 100 mL of unspiked sample solution and mixing it with the spikes the night before we carried out the ICP-MS analyses. This method only requires the preparation (dissolution and dilution processes) of one unspiked sample solution and allows us to prepare more samples in the rack of 16 beakers.

As was said previously, the quantity of interest in isotope dilution is $R_{mix} = \left( \frac{^{97}Mo}{^{95}Mo} \right)_{mix}$. We do not want this ratio to be too close to the isotope ratio of the spike (overspiking) or too close to the natural ratio of the sample (underspiking). The calculation of the error magnification factor reveals that this value reaches its minimum when $R_{mix} = \sqrt{R_{sp} R_{su}}$ were $R_{sp}$ and $R_{su}$ are the isotope ratios of respectively the spike and the sample [1]. This optimal ratio has a value quite far from unity: its order of magnitude is $10^{-2}$.
Actually, additional problems must be considered. The quadrupole ICP-MS works in a mode called “counting mode” (see section 5.1), which means that the measurement is made by sweeping the mass spectrum very fast. As the detector needs a finite time period to handle each ion signal pulse at a given mass, a dead time effect often appears: at higher count rates, the observed count rate $I$ (Hz) deviates from the true rate of arrival at the detector $I_0$ (Hz) according to the relation: $\frac{1}{I} = \frac{1}{I_0} - \tau$ where $\tau$ (s) is the detector dead time [3]. Unless we use a multicolonlector ICP-MS or we do complicated measurements and corrections, we can minimize dead time issues by using a mixing ratio close to 1. The best precision measurements in this study were obtained by using a mixing ratio close to 1.

4.2.3 Mixing equations

At this step we dispose of one 1k or 2k-diluted standard basalt solution per sample and four solutions of isotope spike (Mo, Sb, Sn and W, with a concentration around 10 ppb). Thanks to the concentration values in the standard basalts published prior to this study [2], we can roughly calculate the amount of spike to add to the sample to get $R_{mix}$ close to one. Let us develop an example with the element W and the ratio $^{183}W/^{182}W$. We have:

\[
\begin{align*}
^{182}W_{mix} &= x^{182}W_{sp} + (1-x)^{182}W_{sa} \\
^{182}W_{sp} &= \text{Abundance}^{182}W_{sp} \\
^{182}W_{sa} &= \text{Abundance}^{182}W_{sa} \\
^{183}W_{mix} &= x^{183}W_{sp} + (1-x)^{183}W_{sa} \\
^{183}W_{sp} &= \text{Abundance}^{183}W_{sp} \\
^{183}W_{sa} &= \text{Abundance}^{183}W_{sa}
\end{align*}
\]

where $x = \frac{\text{weight}_{sp}}{\text{weight}_{sp} + \text{weight}_{sa}}$ is the weight mixing ratio and where the abundances are given figure 3 for the sample (natural ratio) and figure 4 for the spike. $W_{sa}$ is known thanks the published or certified values and $W_{sp}$ is determined during the spike calibration. We calculate in an Excel worksheet $R_{mix} = ^{183}W_{mix}/^{182}W_{mix}$ and determine the value of weight$_{sp}$ leading to a mixing ratio close to one. It is worth underlining that this is a rough calculation used just to have an approximated idea of the spike amount to use. In the case of 1k-diluted samples the following figure shows the weight of standard solution used and the three weights of spikes added for each of the standard basalts analyzed.

<table>
<thead>
<tr>
<th>Name</th>
<th>weight (mg)</th>
<th>Mo</th>
<th>Sb</th>
<th>Sn</th>
<th>W</th>
<th>Spike concentration range</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-1</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb Mo, Sb, Sn, and 0.2 ppb W</td>
</tr>
<tr>
<td>AGV-2</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>BCR-2</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>5000</td>
<td>30, 40, 50</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>CHEP1</td>
<td>5000</td>
<td>30, 40, 50</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>DNC-1</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>JB-2</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>JB-3</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>MAR</td>
<td>5000</td>
<td>30, 40, 50</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
<tr>
<td>VE 32</td>
<td>5000</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>50, 80, 90</td>
<td>10 ppb</td>
</tr>
</tbody>
</table>

Figure 6. Quantity of spike and standard solution to mix for the isotope dilution measurement. Four tubes are prepared: 1 without spike and 3 with the 3 spike weights indicated here.
5 The ICP-MS measurements

In this section we introduce some basics concerning the ICP-MS instrumentation, the way to run the samples and the data reduction.

5.1 ICP-MS basics

A quadrupole ICP-MS is composed of the following elements:
- a sample introduction system: peristaltic pump, nebulizer and spray chamber, getting the sample solutions in the instrument;
- a 6000°C plasma torch ionizing the atoms in the samples;
- an interface, link between the plasma torch and the vacuum mass spectrometer;
- two lenses focusing the ions;
- a quadrupole sorting the ions by their mass-to-charge ratio m/z;
- a detector counting the ions passing through the detector;
- a computer interface controlling the instrument and collecting the data.

The quadrupole, composed of 4 rods, works by changing its voltage and radio frequency very fast to allow only the ions with a given m/z ratio to pass between the rods and get out of the detector to hit the detector. All this instrumentation has a complex parameterization and the ICP-MS must be tuned before we can use it. The tuning step consists in analyzing a tuning solution containing elements covering the entire mass spectrum. By adjusting the different setting of the instrument (ions focusing, lens position…) we can vary the intensity measured by the ICP-MS for a given element. The aim of this step is to find the instrument parameters resulting in the highest sensitivity in the measurement of the elements having a mass close to that of Mo, Sb, Sn and W.

The measurement is made by the instrument by sweeping the mass spectrum very fast and many times in order to count the ions hitting the detector. For this study, we chose to repeat this operation 5 times, which means that the instrument measured the intensities (cps) over the mass spectrum of the analyzed isotopes 5 times for a given sample and then took the average value of these five repeats. The raw data given by the ICP-MS is this average value and have a \( 1\sigma \) standard deviation lower than 1%. To improve our measurements all the tubes were analyzed in our runs twice, which provides an idea of the reproducibility of the measurement.

Between two different tubes analyses, a 1% HNO\(_3\) washing solution is run in order to rinse the spray chamber and the tubing. In some runs we could notice that after analyzing concentrated sample solutions, the blanks were abnormally high, revealing a memory effect. Thus, we increased the washing time from 50 to 100 seconds.

5.2 Running the samples

We present in this subsection the list of the samples as they were run in our different isotope dilution, standard addition and reverse isotope dilution analysis. This sample list was established regarding to the corrections to apply (see next section). For each run, all the tubes were analyzed to times in order to obtain a good statistical measurement.
**5.3 Data reduction**

Isotope dilution is based on ratios measurement whereas we use the ICP-MS counts (cps) in standard addition. For both methods, we have to apply corrections to the raw data given by the instrument.

5.3.1 Blank correction

The blank correction allows us to estimate the contamination occurring during the sample preparation and the background noise of the ICP-MS. During the dissolution of the samples we prepared blank solutions corresponding to a complete chemistry done in a beaker without sample. The blank solutions were used when performing isotope dilution or standard addition measurements. For the spike calibration we used 1% HNO₃ solutions as blanks. As shown in the sample list (section 5.2), a blank is periodically analyzed. The blank values are around a few hundred cps, compared to hundreds of thousands cps for the other tubes. The impact of the instrument background on the measurements is therefore negligible.

For example, if we assume that there is a linear evolution of the blank values between tubes 1 and 8, characterized by a \( \text{slope} = (\text{blank}_2 - \text{blank}_1)/(8-1) \) and an initial value \( \text{blank}_1 \), we can interpolate what would have been the raw counts for a given tube and subtract it to the measured signal using the following formula:

\[
\text{value}_{\text{corrected}} = \text{value}_{\text{uncorrected}} - (\Delta_{\text{tube-blank}} \cdot \text{slope} + \text{blank}_1)
\]

where \( \Delta_{\text{tube-blank}} \) is the difference of the tube numbers between the tube where the correction is made and the tube where the blank is. This is illustrated in the following figure:
5.3.2 Drift correction

At times it took us up to 12 hours to carry out ICP-MS runs. During a run, various parameters such as temperature and nebulizer efficiency are variable, causing a change in sensitivity in the instrument—a sensitivity drop called instrument drift. For isotope dilution and reverse isotope dilution (spikes calibration), as we use an isotope ratio, the effect of the drift is negligible because it affects in the same way both the numerator and the denominator of the ratio (figure 8). Therefore, we do not correct the instrument drift when measuring the ratios for the isotope dilution. This drift effect on the counts and the ratios is illustrated in the following figure:

For standard addition, we use the counts to build the calibration curve and the drift correction is mandatory. The correction is made by normalizing the blank corrected values to an internal standard: 30 mg of a 1 ppm solution of In, Tb and Lu is added in every tube. As the drift is mass dependent, we use $^{115}$In to correct Mo, Sb and Sn values, $^{159}$Tb to correct Er values (used for the oxides correction) and $^{175}$Lu to correct W values. The normalization is made using this formula:
\[ \text{value}_{\text{corrected}} = \text{value}_{\text{uncorrected}} \times \left( \frac{IS_{\text{average}}}{IS_{\text{tube}}} \right) \]

where \( IS_{\text{average}} \) is the average value of the internal standard blank corrected counts in all the sample tubes analyzed in the run (i.e. the value used for the normalization) and \( IS_{\text{tube}} \) is the blank corrected counts in the tube where the correction is made. The formula and the effect on the measurement are shown in the following figures:

Figure 9. Part of the Excel worksheet showing the calculation used in the drift correction.

Figure 10. Plot of the \(^{167}\)Er counts before and after normalization to the internal standard.

5.3.3 Oxides interferences correction

As explained in section 2, there are interferences with Er oxides when we measure the W isotopes: \(^{166}\)Er\(^{16}\)O with \(^{182}\)W, \(^{166}\)Er\(^{16}\)O with \(^{183}\)W, \(^{168}\)Er\(^{16}\)O with \(^{184}\)W and \(^{170}\)Er\(^{16}\)O with \(^{186}\)W. A tube containing 5 ppb of Er solution was run periodically during the analysis and two Er isotopes analyzed by the instrument: \(^{166}\)Er and \(^{167}\)Er. In the tube containing only 5 ppb of Er the ICP-MS measures several thousands of counts for W, what means that Er oxides are forming. The oxide formation factor can be evaluated by calculating in the 5 ppb Er tubes the ratio \( \frac{W}{^{166}\text{Er}} = \frac{^{166}\text{Er} \cdot ^{16}\text{O}}{^{166}\text{Er}} \). During the experiments, this factor was always between 0.3 and 0.4%.

As the oxide formation is matrix-dependant the right way to correct the interference would be to add Er in all the tubes in order to do a very precise correction, but since the oxide formation factor is very low, an easier correction can be applied.
For all the 5 ppb Er tubes, calculate the oxide factors $^{182}\text{W} / ^{166}\text{Er}$, $^{183}\text{W} / ^{166}\text{Er}$, $^{184}\text{W} / ^{166}\text{Er}$ and $^{186}\text{W} / ^{166}\text{Er}$ (this is an arbitrary choice since we can use another Er oxide). Then for each W isotope we take the average value of the oxide factors in the 5 ppb Er tubes. The correction is then made in all the sample tubes using the formula:

\[
\begin{align*}
^{182}\text{W}_{\text{true}} &= ^{182}\text{W}_{\text{measured}} - ^{166}\text{Er} \cdot \text{oxyde}^{182}_{\text{g}} \\
^{183}\text{W}_{\text{true}} &= ^{183}\text{W}_{\text{measured}} - ^{166}\text{Er} \cdot \text{oxyde}^{183}_{\text{g}}
\end{align*}
\]

5.3.4 Mass fractionation correction

Even after applying the previous corrections to the counts, our ICP-MS shows that the measured ratios deviate from their true values because of a mass fractionation effect. This effect can occur during extraction, transmission or detection and affects the measured ion intensities as a function of the mass. Causes such as space-charge effects and high speed ion motion issues are commonly accepted and there are mainly two ways to correct for this effect [4], [5]:

- bracketing the samples with a standard solution of known isotopic composition;
- adding an additional element close in mass to that of the analyte of interest to perform an inter-element normalization.

This latter method is often used for the study of radiogenic isotopes and requires the use of a mathematical model for the mass discrimination. The first approach was used in this study.

In this method the analyzed tubes are bracketed either with an unspiked solution in the case of isotope dilution or with a single element standard solution in the case of spike calibration (reverse isotope dilution). Bracketing with unspiked solutions and single element standard solutions allows us to avoid matrix-effect issues since these solutions are bracketing solutions that have the same matrix. The two bracketing solutions have natural isotope ratios. For these solutions, the ratios calculated with to the blank-, drift- and oxide corrected counts are different from the natural values. Dividing the natural ratio by the measured ratio gives a mass discrimination factor. Assuming that the drift in mass discrimination between the bracketing solutions approximates a linear interpolation [4], we can calculate the mass discrimination factor in every tube between the two bracketing solutions. Then we simply multiply the uncorrected isotope ratio by the mass discrimination factor to get the mass fractionation-corrected ratio. The following figure illustrates this calculation. In this example the natural $^{121}\text{Sb} / ^{123}\text{Sb}$ ratio is 1.206 and the measured ratio ranging from 1.276 to 1.273.

![Figure 11](image)

**Figure 11.** Procedure used to correct for the mass discrimination using two bracketing solutions with a natural isotopic ratio.
6 Results and discussions

6.1 Spikes calibration

Based on the theoretical concentration of our 10 ppm spike stock solution, we prepared two 40 ppb and one 10 ppb solutions, with all the dilutions based on weight. The measurements were made in two days, with two different runs, which represents 120 concentration values for Mo, 96 for Sn, 24 for Sb and 72 for W. The concentrations measured thanks to the three solutions presented less than 1% 2 σ RSD. We here present the composition of the 10 ppb spike solutions used for the isotope dilution measurements:

<table>
<thead>
<tr>
<th></th>
<th>W</th>
<th>Sb</th>
<th>Mo</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (ppb)</td>
<td>9.559058</td>
<td>9.717691</td>
<td>13.78942</td>
<td>15.29239</td>
</tr>
<tr>
<td>2 σ % RSD</td>
<td>0.06913</td>
<td>0.09378</td>
<td>0.08681</td>
<td>0.124691</td>
</tr>
</tbody>
</table>

Figure 12. Concentration of the spike solutions used for our isotope dilution measurements.

The concentrations are slightly different from the theoretical 10 ppb value calculated assuming that 1 mg of sample has been dissolved and diluted in 100 g of 1% HNO₃. This means that the original metal spikes were not exactly weighing 1 mg, and this is precisely the reason why we have to calibrate the spikes after their creation. The result obtained by reverse isotope dilution is quite satisfying and thanks to the dilution corrections we can find out the concentration of the original spike stock solution that the laboratory may use for other analyses.

6.2 Isotope dilution results

In this subsection we report the results obtained with 3 isotope dilution runs on samples coming from 3 independent dissolutions:

<table>
<thead>
<tr>
<th></th>
<th>AGV-1</th>
<th>AGV-2</th>
<th>BCR-2</th>
<th>BHVO-2</th>
<th>CHEPR</th>
<th>DNC-1</th>
<th>JB-2</th>
<th>JB-3</th>
<th>MAR</th>
<th>VE 32</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>0.577572</td>
<td>0.545459</td>
<td>0.507809</td>
<td>0.230778</td>
<td>NA</td>
<td>0.048861</td>
<td>0.416412</td>
<td>1.57215</td>
<td>NA</td>
<td>0.079969</td>
</tr>
<tr>
<td></td>
<td>0.021686</td>
<td>0.035939</td>
<td>0.030256</td>
<td>0.012806</td>
<td>NA</td>
<td>0.005129</td>
<td>0.016944</td>
<td>0.06564</td>
<td>NA</td>
<td>0.023489</td>
</tr>
<tr>
<td>2 σ</td>
<td>3.75%</td>
<td>6.49%</td>
<td>5.96%</td>
<td>5.56%</td>
<td>NA</td>
<td>10.94%</td>
<td>3.85%</td>
<td>4.22%</td>
<td>NA</td>
<td>29.37%</td>
</tr>
<tr>
<td>% RSD</td>
<td>0.477044</td>
<td>0.069698</td>
<td>0.029317</td>
<td>0.018293</td>
<td>0.004733</td>
<td>0.079918</td>
<td>0.066831</td>
<td>0.017466</td>
<td>0.02506</td>
<td>0.061033</td>
</tr>
<tr>
<td>Sb</td>
<td>10.61%</td>
<td>13.15%</td>
<td>13.22%</td>
<td>13.66%</td>
<td>9.68%</td>
<td>9.28%</td>
<td>43.48%</td>
<td>13.16%</td>
<td>44.20%</td>
<td>58.63%</td>
</tr>
<tr>
<td>Sn</td>
<td>4.32922</td>
<td>1.93592</td>
<td>2.0891</td>
<td>1.694787</td>
<td>1.4681</td>
<td>1.200437</td>
<td>0.603022</td>
<td>0.969801</td>
<td>0.747365</td>
<td>1.117532</td>
</tr>
<tr>
<td></td>
<td>0.411235</td>
<td>0.08379</td>
<td>0.148668</td>
<td>0.075125</td>
<td>0.099486</td>
<td>0.056788</td>
<td>0.058861</td>
<td>0.026423</td>
<td>0.049144</td>
<td>0.033011</td>
</tr>
<tr>
<td>9.50%</td>
<td>1.44%</td>
<td>7.12%</td>
<td>4.43%</td>
<td>6.78%</td>
<td>6.73%</td>
<td>9.75%</td>
<td>2.72%</td>
<td>6.58%</td>
<td>2.95%</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>2.031587</td>
<td>1.90789</td>
<td>NA</td>
<td>4.067648</td>
<td>0.65455</td>
<td>0.139734</td>
<td>0.899583</td>
<td>1.100423</td>
<td>0.220685</td>
<td>0.502242</td>
</tr>
<tr>
<td></td>
<td>0.184933</td>
<td>0.162238</td>
<td>NA</td>
<td>0.631598</td>
<td>0.054777</td>
<td>0.028106</td>
<td>0.154218</td>
<td>0.042902</td>
<td>0.02023</td>
<td>0.041456</td>
</tr>
<tr>
<td>9.11%</td>
<td>8.19%</td>
<td>15.53%</td>
<td>9.34%</td>
<td>20.11%</td>
<td>15.91%</td>
<td>3.93%</td>
<td>9.17%</td>
<td>8.26%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 13. Concentration values obtained by isotope dilution. The concentration is given in ppm and is an average value of all the measurements (3 runs and 2 repeats per run).

Some values are not available because the samples have been contaminated during crushing and now have contents not comparable to natural abundances. CHEPR and MAR powders were obtained by crushing the rock samples in a beaker made out of W.
6.3 Standard addition results

The results presented here were obtained with 2 standard addition runs on samples coming from two independent dissolutions (the same samples that were analyzed by isotope dilution). Let us take a look at some calibration curves:

Figure 14. Standard addition calibration curves for Sn in two different samples.

On these calibration curves we can see 2 points per tube, corresponding to the 2 repeats during the run. The point intercepting with the vertical axis corresponds to the sample concentration with a dilution correction factor. The $R^2$ coefficient is very good. With such a calibration curve, we are able to determine one concentration value per isotope measured (referring to section 2 for the isotopes of interest). The average and 2σ values are obtained using the measurements made with all the available isotopes in all the runs. Here are the results:

<table>
<thead>
<tr>
<th></th>
<th>AGV-1</th>
<th>AGV-2</th>
<th>BCR-2</th>
<th>BHVO-2</th>
<th>CHEPR</th>
<th>DNC-1</th>
<th>JB-2</th>
<th>JB-3</th>
<th>MAR</th>
<th>VE 32</th>
<th>Average 2σ</th>
<th>Average 2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>0.50448</td>
<td>0.498396</td>
<td>0.456955</td>
<td>0.190652</td>
<td>NA</td>
<td>0.050273</td>
<td>0.300424</td>
<td>1.273415</td>
<td>NA</td>
<td>0.053416</td>
<td>0.024422</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.014604</td>
<td>0.057596</td>
<td>0.033942</td>
<td>0.011979</td>
<td>NA</td>
<td>0.004237</td>
<td>0.039237</td>
<td>0.290228</td>
<td>NA</td>
<td>0.004234</td>
<td>0.07393</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>4.079947</td>
<td>0.428195</td>
<td>0.322138</td>
<td>0.129603</td>
<td>0.02378</td>
<td>0.690354</td>
<td>0.214753</td>
<td>0.083482</td>
<td>0.027033</td>
<td>0.024422</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.092629</td>
<td>0.465244</td>
<td>0.043702</td>
<td>0.0102</td>
<td>0.006573</td>
<td>0.02066</td>
<td>0.014887</td>
<td>0.0045</td>
<td>0.00353</td>
<td>0.00477</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>2.27%</td>
<td>10.30%</td>
<td>13.57%</td>
<td>7.87%</td>
<td>27.64%</td>
<td>2.99%</td>
<td>6.93%</td>
<td>5.39%</td>
<td>13.06%</td>
<td>19.56%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.03713</td>
<td>1.707419</td>
<td>2.042584</td>
<td>1.422826</td>
<td>1.357024</td>
<td>1.02623</td>
<td>0.551831</td>
<td>0.741388</td>
<td>0.632252</td>
<td>0.945871</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.13682</td>
<td>0.107527</td>
<td>0.158003</td>
<td>0.040257</td>
<td>0.112615</td>
<td>0.079492</td>
<td>0.039798</td>
<td>0.021847</td>
<td>0.012577</td>
<td>0.023304</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>3.36%</td>
<td>6.30%</td>
<td>7.78%</td>
<td>2.83%</td>
<td>8.30%</td>
<td>7.21%</td>
<td>7.21%</td>
<td>2.95%</td>
<td>1.99%</td>
<td>2.46%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.899194</td>
<td>1.620754</td>
<td>NA</td>
<td>3.60066</td>
<td>0.547816</td>
<td>0.1434</td>
<td>0.934137</td>
<td>0.66553</td>
<td>0.194184</td>
<td>0.45844</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.151862</td>
<td>0.136839</td>
<td>NA</td>
<td>0.789708</td>
<td>0.057036</td>
<td>0.038041</td>
<td>0.123117</td>
<td>0.03754</td>
<td>0.027462</td>
<td>0.048126</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.01%</td>
<td>7.52%</td>
<td>NA</td>
<td>21.67%</td>
<td>8.80%</td>
<td>26.53%</td>
<td>13.18%</td>
<td>4.32%</td>
<td>14.16%</td>
<td>10.50%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 15. Concentration values obtained by standard addition.

Some values are slightly different from those obtained by isotope dilution. In the following section we compare both methods.

6.4 Comparison of the two analytical methods

The following graph represents the results obtained by isotope dilution versus those obtained by standard addition with a logarithmic scale:
Figure 16. Plot of the concentration values obtained by the two methods of quantitation (logarithmic scale). A bias is noticeable, isotope dilution values are a bit higher than standard addition values.

We used the same single element standard solution to perform the standard addition and to calibrate the spikes. Thus, should there be a problem with the certified concentration of the standard solution, this would affect both methods of quantitation the same way, which is obviously not the case. For Mo, the bias is very low and both methods yield the same results within the error bars. This means that there may be a problem with the calibration of the spikes.

The last run we did was a reverse calibration of the single element standard solutions. We mixed 5 g of 10 ppb standard solution with 30 mg of 10 ppb spikes and recalculated the composition of the standard solutions. As the spikes were calibrated assuming that the concentration of the single element standard solutions was 1000 ppm ± 3 ppm, the measurement is supposed to lead to the same concentration value. The values we found were from 2 up to 10% higher. This can be explained by the evaporation of the standard solutions between the spikes calibration and this measurement, resulting in an apparently higher concentration of the solutions. As we performed the standard addition measurements after the isotope dilution, this evaporation effect is likely to affect the standard addition values. If the single element standard solutions have evaporated, the true amount of element added to the sample tubes is higher than what we calculated and thus the slope of our calibration is lower than what is should be. This effect is illustrated on the following figure.
Figure 17. Calibration curve obtained if we use higher single element standard solutions concentrations. The new calibration (brown line) leads to a concentration higher than the previous calibration (blue line). Both calibrations are going through the sample point.

This effect is likely to explain why we obtained standard addition concentration values always slightly lower than the isotope dilution values (figure 16).

People at the laboratory are now trying to redo the standard addition measurements using two new solutions: a new single element standard solution and a homemade solution prepared by dissolving ultra high purity metals. These new measurements will probably say if there is an evaporation issue and bring new concentration values supposedly matching the isotope dilution values.

The four next figures show the calibrations obtained using the ICP-MS corrected output data collected within the last 4 years at Harvard on the standard we analyzed and our new data set. In all the figures, the top panel shows the calibration obtained with the concentration values used prior to this study and found in press; the middle panels shows the calibration using the concentration values obtained by isotope dilution and the bottom panels shows the calibration using the concentration values obtained by standard addition. For the isotope dilution and standard addition values, we made enhanced the calibrations: we used a solver to recalculate, within the error bars, the concentration values leading to the best possible calibration ($R^2$ close to 1 and intercept close to 0). Even with the enhanced calibrations, we notice a difference in the slopes for isotope dilution and standard addition.
Figure 18. Calibration curves for the element Mo obtained using the previous concentration values and the new concentration values obtained by standard addition and isotope dilution.
Figure 19. Calibration curves for the element Sb obtained using the previous concentration values and the new concentration values obtained by standard addition and isotope dilution.
Figure 20. Calibration curves for the element Sn obtained using the previous concentration values and the new concentration values obtained by standard addition and isotope dilution.
Figure 21. Calibration curves for the element W obtained using the previous concentration values and the new concentration values obtained by standard addition and isotope dilution.
7 Conclusion

The use of standard addition and isotope dilution ICP-MS allowed us to obtain new concentration values of Mo, Sb, Sn and W in 10 geochemical reference basalts. Several runs were made before we could obtain conclusive and reproducible results because we had to find the right amounts of spike and single element solution to add to the samples. For most of the samples we were able to reach a precision below 5% RSD (1σ). Some concentration values are not known with less than a 10% precision especially when the sample contains less than 0.1 ppm and when there is a slight bias remaining between the results obtained by both methods. The use of the new concentration values with drift corrected ICP-MS data obtained before this study in the laboratory is providing good calibration curves and for the 4 elements under study it is possible to enhance these calibrations to get the correlation close to 1 and the intercept close to 0. Compared to the calibration curves shown in figure 2, the new concentration values are providing much better results.

To go further in this study and solve the problems encountered, it would be interesting to prepare new single element standard solutions by dissolving high purity Mo, Sb, Sn and W metals, and then redo the standard addition calibrations. For the ratio measurements in isotope and reverse isotope dilution, the detector dead time should be evaluated by one of the existing methods [3] in order to bring the appropriate correction.

Acknowledgements

I am deeply grateful to all those who made my scientific and human experience at Harvard just wonderful.

My endless thanks go to Stéphane who accepted me as his student, built up this project for me, answered all my questions, constantly advised and supervised me. He was so obliging all the time and among many other things showed me around Boston and lent me his bike.

I want to thank Zhongxing who spent so much time sharing his knowledge about instrumentation and chemistry, and constantly provided me with precious advice and help.

I am grateful to Charlie who gave me a warm welcome at the Hofmann lab and made Martha’s Vineyard a great experience.

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I wish too to thank Rady for her availability and help in making this trip possible.

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References


