

### ANALYTICAL METHODOLOGY

#### THE MASS SPECTROMETER

In most cases, isotopic abundances are measured by mass spectrometry. The exceptions are, as we have seen, short-lived radioactive isotopes, the abundances of which are determined by measuring their decay rate, and in fission track dating, where the abundance of  $^{238}\text{U}$  is measured, in effect, by inducing fission. (Another exception is spectroscopic measurement of isotope ratios in stars. Frequencies of electromagnetic emissions of the lightest elements are sufficiently dependent on nuclear mass that emissions from different isotopes can be resolved. We will discuss this when we consider stable isotopes.) A mass spectrometer is simply a device that can separate atoms or molecules according to their mass. There are a number of different kinds of mass spectrometers operating on different principles. Undoubtedly the vast majority of mass spectrometers are used by chemists for qualitative or quantitative analysis of organic compounds. We will focus exclusively, however, on mass spectrometers used for isotope ratio determination. Most isotope ratio mass spectrometers are of a similar design, the magnetic-sector, or Nier mass spectrometer\*, a schematic of which is shown in Figure 15.1. It consists of three essential parts: an ion source, a mass analyzer and a detector. There are, however, several variations on the design of the Nier mass spectrometer. Some of these modifications relate to the specific task of the instrument; others are evolutionary improvements. We will first consider the Nier mass spectrometer, and then briefly consider a few other kinds of mass spectrometers.

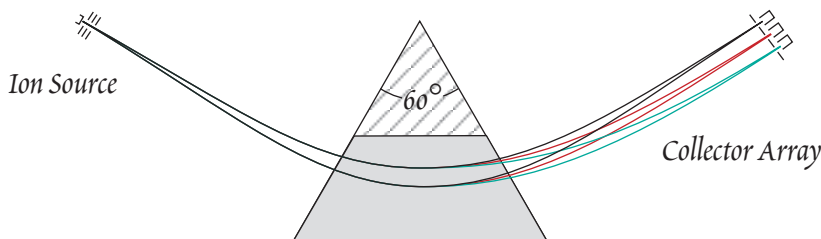


Figure 6.1. The magnetic sector or Nier mass spectrometer. This instrument uses a  $60^\circ$  magnetic sector, but  $90^\circ$  magnetic sectors are also sometimes used.

#### The Ion source

As its name implies, the job of the ion source is to provide a stream of energetic ions to the mass analyzer. Ions are most often produced by either *thermal ionization*, for solid-source mass spectrometers, or *electron bombardment*, for gas-source mass spectrometers.

In thermal ionization, a solution containing the element(s) of interest is dried or electroplated onto a ribbon of high-temperature metal, generally Re (rhenium), Ta (tantalum), or W (tungsten), welded to two supports. The ribbon is typically 0.010" thick, 0.030" wide and 0.3" long. In the simplest situation, the ribbon is placed in the instrument and heated by passing an electric current of several amperes through it. At temperatures between about  $1100^\circ\text{C}$  and  $1800^\circ\text{C}$  the sample evaporates in the low pressure environment of the mass spectrometer. Depending on the element and its first ionization

\* It was developed by Alfred Nier of the University of Minnesota in the 1930's. Nier used his instrument to determine the isotopic abundances of many of the elements. In the course of doing so, however, he observed variations in the ratios of isotopes of a number of stable isotopes as well as Pb isotopes and hence was partly responsible for the fields of stable and radiogenic isotope geochemistry. He also was the first to use a mass spectrometer for geochronology, providing the first radiometric age of the solar system. In the 1980's he was still designing mass spectrometers, this time miniature ones which could fly on spacecraft on interplanetary voyages. These instruments provided measurements of the isotopic composition of atmospheric gases of Venus and Mars. Nier died in 1994.

# Geol. 655 Isotope Geochemistry

## Lecture 15

Spring 1998

potential (i.e., the energy required to remove one electron from the atom), some or all the atoms will also ionize. The efficiency with which the sample ionizes determines the amount of sample needed. The alkali metals ionize quite easily; the ionization efficiency for Cs, for example, approaches 100%. For some other elements, it is as low as 0.1% or lower. On top of this, modern mass spectrometers have transmission efficiencies of only 50%, which is to say only 50% of the ions produced reach the detector.

In some cases, the rare earth elements for example, there is a tendency for the element to evaporate as a molecule, most typically an oxide, rather than as a metal atom. This problem can be overcome by using two or three filaments. In this case the sample is loaded on one or two filaments, from which it is evaporated at relatively low temperatures. The neutral atoms or molecules are then decomposed and ionized by another filament kept at much higher temperature (~1900-2000°C). In general, a double or triple filament technique will have a somewhat lower ionization efficiency than a single filament technique. Except where one wishes to measure very small samples, this disadvantage is offset by the simpler mass spectra of the metal as opposed to the oxide (recall that O has three isotopes) and problems of isobaric interferences with measurement of the oxide. In some cases, for example U and Th, carbon is loaded along with the sample as a reducing agent so that the metal rather than the oxide will be evaporated.

For some elements, molecular species are intentionally created because one or another of their properties makes isotopic analysis easier or more accurate. For example, Os isotopic composition is now determined by analyzing the mass spectra of  $\text{OsO}_4^-$ , because Os does not evaporate at temperatures achievable by thermal ionization. B isotope ratios are typically measured by measuring the mass spectra of sodium or cesium metaborate, because errors resulting from mass fractionation are much smaller for these heavy molecules than for B.

Ionization efficiency can sometimes be increased by using a suitable substrate with a high work function. The greater energy required to evaporate the atom results in a higher likelihood of its also being ionized. Tantalum oxide, for example, is a good substrate for analysis of Sr. Ionization efficiency can also be increased by altering the chemical form of the element of interest so that its evaporation temperature is increased (ionization is more likely at higher temperatures). For example, when a silica gel suspension is loaded along with Pb, the evaporation temperature of Pb is increased by several hundred degrees, and the ionization efficiency improved by orders of magnitude.

Finally, the sample may be loaded in a particular chemical form in order to (1) form a positive rather than negative ion (or visa versa) and (2) provide a molecule of high mass to minimize mass fractionation, as for boron, or to promote or inhibit the formation of oxides.

Electron bombardment is somewhat more straightforward. The gas is slowly leaked into the mass spectrometer through a small orifice. A beam of electrons, typically produced by a hot filament (normally Re), is shot across the gas stream. Electron-molecule collisions will knock one of the outer electrons out of its orbit, ionizing the molecule or atom. Carbon and oxygen are analyzed as  $\text{CO}_2^-$ ; other species are analyzed as single atom ions.

Most solid source mass spectrometers constructed of the last 10 years or more employ a turret source in which a number of samples (typically 6-20) can be loaded. The turret is rotated so that each sample comes into position for analysis. Gas source mass spectrometers often employ automated gas inlet systems, which allow for automated analysis of many samples.

Several other methods for producing ions are used in special circumstances. Some of these may see wider use in the future. The first is *ion sputtering*. This method is somewhat like electron bombardment, except positive ions, typically O, rather than electrons are fired at the sample and it is used for solids not gases. This is the standard method of ion production in an ion probe, which is a variety of mass spectrometer. A recently developed method of ion production is *resonance ionization*. In this technique, a laser, tuned to a frequency appropriate for ionization of the element of interest, is fired at the sample. Continuous emission lasers of sufficient power are not currently available, so pulsed lasers are used. Finally, an *inductively coupled plasma* (ICP) is also used as an ion source. This operates by passing a carrier gas, generally Ar, through an induction coil, which heats the gas to ~8000°K, a temperature at the gas is completely ionized. The sample is aspirated, generally as a so-

# Geol. 655 Isotope Geochemistry

## Lecture 15

Spring 1998

lution, into the plasma and is also ionized. The ions flow through an orifice into mass spectrometer. Generally, this is a quadrupole mass spectrometer, but magnetic sector mass spectrometers can also be used. The ICP-MS of the quadrupole type is designed primarily for elemental analysis, but has been used, at least experimentally, for Os isotopic analysis and reconnaissance isotopic analysis of Pb. ICP-MS employing a magnetic sector mass spectrometer can produce isotope ratio data of comparable quality to thermal ionization instruments, but these instruments are relatively recent developments are not widely used.

After the ions are produced, they are accelerated by an electrostatic potential, typically in the range of 5-20 kV for magnetic sector mass spectrometers (in thermal ionization mass spectrometers, the filament with the sample are at this potential). The ions move through a series of slits between charged plates. The charge on the plates also serves to collimate the ions into a beam. Generally the potential on the plates can be varied somewhat; in varying the potential on the plates, one attempts to maximize the beam intensity by 'steering' as many ions as possible through the slits. Thus the source produces a narrow beam of nearly monenergetic ions.

### The Mass Analyzer

The function of the mass analyzer is really two-fold. The main purpose is to separate the ions according to their mass (strictly speaking, according to their mass/charge ratio). But as is apparent in Figure 15.1, the mass analyzer also acts as a lens, focusing the ion beam on the detector.

A charged particle moving in a magnetic field experiences a force

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B} \quad 15.1$$

where  $\mathbf{B}$  is the magnetic field strength,  $\mathbf{v}$  is the particle velocity, and  $q$  is its charge (bold is used to denote vector quantities). Note that force is applied perpendicular to the direction of motion (hence it is more properly termed a torque), and it is also perpendicular to the magnetic field vector. Since the force is always directed perpendicular to the direction of motion, the particle begins to move in a circular path. The motion is thus much like swinging a ball at the end of a string, and we can use equation for a centripetal force:

$$F = m \frac{v^2}{r} \quad 15.2$$

This can be equated with the magnetic force:

$$m \frac{v^2}{r} = qv \times B \quad 15.3$$

The velocity of the particle can be determined from its energy, which is the accelerating potential,  $V$ , times the charge:

$$Vq = \frac{1}{2} mv^2 \quad 15.4$$

Solving 15.4 for  $v^2$ , and substituting in equation 15.3 yields (in non-vector form):

$$2 \frac{V}{r} = \sqrt{\frac{2Vq}{m}} B \quad 15.5$$

Solving 15.5 for the mass/charge ratio:

$$\frac{m}{q} = \frac{B^2 r^2}{2V} \quad 15.6$$

relates the mass/charge ratio, the accelerating potential, the magnetic field, and the radius of curvature of the instrument. If  $B$  is in gauss,  $r$  in cm, and  $V$  in volts, this equation becomes:

$$\frac{m}{q} = 4.825 \times 10^{-5} \frac{B^2 r^2}{V} \quad 15.6a$$

with  $m$  in daltons and  $e$  in units of electronic charge. For a given set of conditions, a heavier particle will move along a longer radius than a lighter one. In other words, the lighter isotopes experience greater deflections in the mass analyzer.

The radius of the Cornell mass spectrometer is 27 cm; it typically operates at 8 kV. Masses are selected for analysis by varying the magnetic field (note that in principle we could also vary the accelerating potential; however doing so has a second order effect on beam intensity, which is undesirable), generally in the range of a few thousand gauss.

Mass spectrometers built in the last 15 years or so employ a design 'trick' that has the effect of extending their effective radius, which results in higher resolution (better separation between the masses at the collector). It was shown in the 1950's that if the ions entered the magnetic field at an angle of  $26.5^\circ$  rather than at  $90^\circ$ , the effective radius of the mass analyzer doubles. Thus our instrument has an effective radius of 54 cm. An additional advantage of this 'extended geometry' is that the ion beam is focused in the 'z' direction (up-down) in addition to the x-y direction. This is an important effect because it allows all the ion beam to enter the detector, which in turn allows the use of multiple detectors. In addition, current commercial mass spectrometers have further modifications to the magnet pole faces to produce a linear focal plane, which is helpful in the multiple collectors currently in use.

Collisions of ions with ambient gas result in velocity and energy changes and cause the beam to broaden. To minimize this, the mass spectrometer is evacuated to  $10^{-6}$  to  $10^{-9}$  torr (mm Hg  $\sim 10^{-3}$  atm). Where very high resolution is required, an energy filter is employed. This is simply an electrostatic field. The electric field force is not proportional to velocity, as is the magnetic field. Instead, ions are deflected according to their energy. The radius of curvature is given by:

$$R = \frac{2V}{V_2} \quad 6.7$$

where  $V_2$  is the electrostatic potential of the energy filter and  $V$  is the energy of the ions (equal to the accelerating potential). Ion sputtering produces ions of a variety of energy, hence an energy filter is generally required with this method of ion production. ICP sources also produce ions that are less monochromatic than thermal ionization or electron bombardment, so energy filters are also used with high precision ICP mass spectrometers. Instruments employing both mass and energy filters are sometimes called double focusing instruments. An example is shown in Figure 15.2.

### The Collector

In general, ions are 'collected', or detected, at the focal plane of the mass spectrometer in one of two ways. The most common method, particularly for solid source mass spectrometers, is with a 'Faraday cup', which is shown schematically in Figure 15.3. As the name implies, this is a metal cup, generally a few millimeters wide and several centimeters deep (the depth is necessary to prevent ions and electrons from escaping). After passing through a narrow slit, ions strike

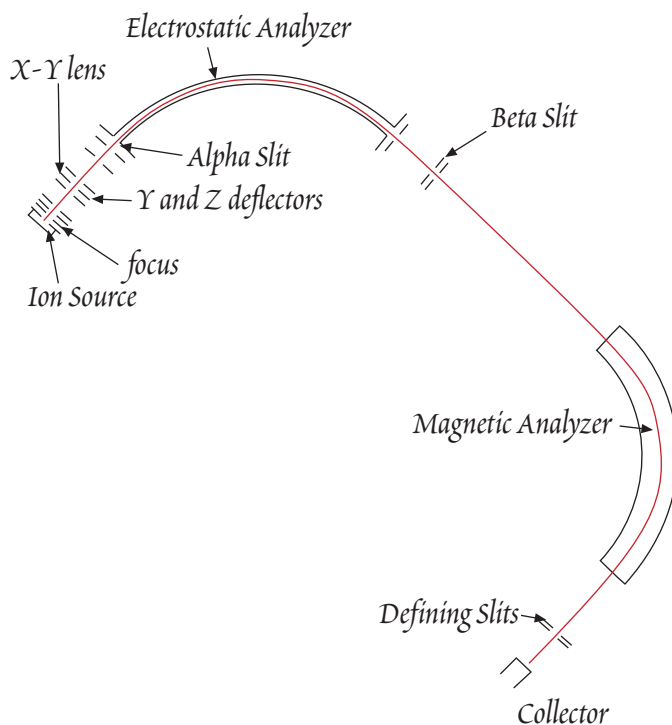


Figure 15.2. A double focusing or Nier-Johnson mass spectrometer with both magnetic and electrostatic sectors. After Majer (1977).

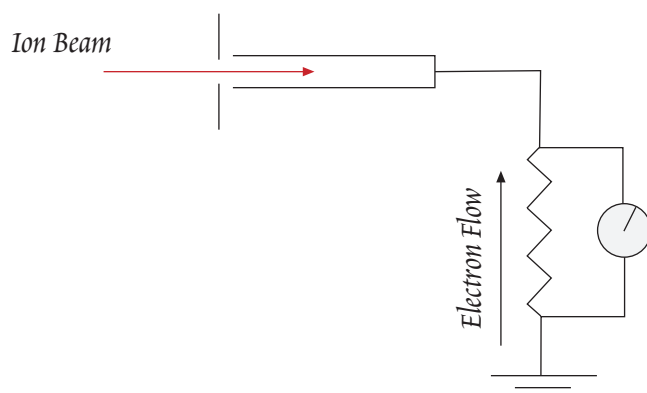


Figure 15.3. Schematic drawing of a Faraday cup configured for positive ions. Electron flow would reverse for negative ions.

the Faraday cup and are neutralized by electrons flowing to the cup from ground. The ion current into the cup is determined by measuring the voltage developed across a resistor as electrons flow to the cup to neutralize the ion current. The voltage is amplified, converted to a digital signal, and sent to a computer that controls data acquisition. (In the old days, the voltage would be sent to a chart recorder. Isotope ratios were measured by measuring the displacement of the pen trace with a ruler.) In most mass spectrometers, the resistor has a value of  $10^{11}$  ohms. Since  $V = I\Omega$ , an ion current of  $10^{-11}$  A will produce a voltage of 1 V. Typical ion currents are on the order of  $10^{-15}$

to  $10^{-10}$  A. In the design of the collector, care must be exercised that ions or free electrons produced when the ion strikes the cup cannot escape from the cup. A surface coating of carbon of the cup with carbon provides a "soft landing" and aids in minimizing the generation of ions from the surface. One must also insure that stray ions or electrons cannot enter the cup. This is done by placing wires or plates with small negative or positive potentials in appropriate locations in front of the collector assembly, which serve to collect stray ions.

Most modern mass spectrometers now employ a number of Faraday cups arrayed along the focal plane so that several isotopes can be collected simultaneously. The spacing of the Faraday cups varies from element to element. In the Cornell instrument, the positioning of cups is done using stepping motors under computer control. For accurate isotopic analysis, and "accurate" means a few tens of ppms, all the ions of each isotope being measured must be completely collected. In addition, each Faraday cup is connected to its own dedicated amplifier and digital voltmeter. The gain and background characteristics of these amplifiers vary, and this must somehow be corrected for in the analysis. This is done in one of two possible ways. The first is to measure the ion current of one isotope in each of the cups in use. This allows for a normalization of the gain factors. This method will be explained in detail below. The other method is to electronically calibrate each amplifier by passing a known current through each. The resulting calibration is used by the computer to correct the observed intensities. In addition, the amplifier gains are temperature sensitive. For this reason, the amplifiers are housed in an insulated container whose temperature is controlled to within  $0.01^\circ\text{C}$ .

The second method of detection is the use of a multiplier, either an electron multiplier or photomultiplier. In an electron multiplier, illustrated in Figure 15.4, ions strike a charged dynode. The collision produce a number of free electrons, which then move down a potential gradient. Each one of the electrons strikes a second electrode, again producing a number of free electrons. This process continues through a series of 10 or so electrodes to produce a cascade or shower of electrons. The net effect is an amplification of the signal of typically 100. The Cornell instrument employs a slightly different

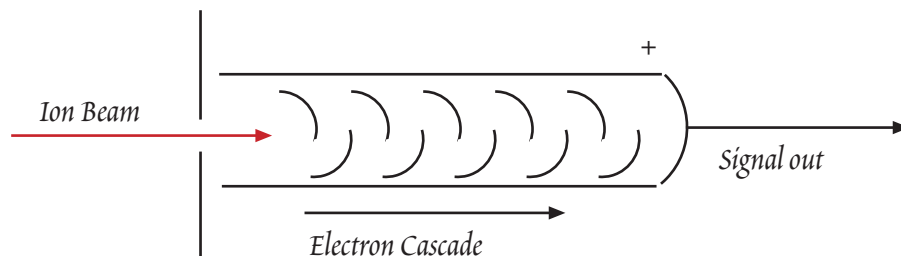


Figure 15.4. Schematic of an electron multiplier.

method of signal multiplication: a Daly detector (named for its inventor), illustrated in Figure 15.5.

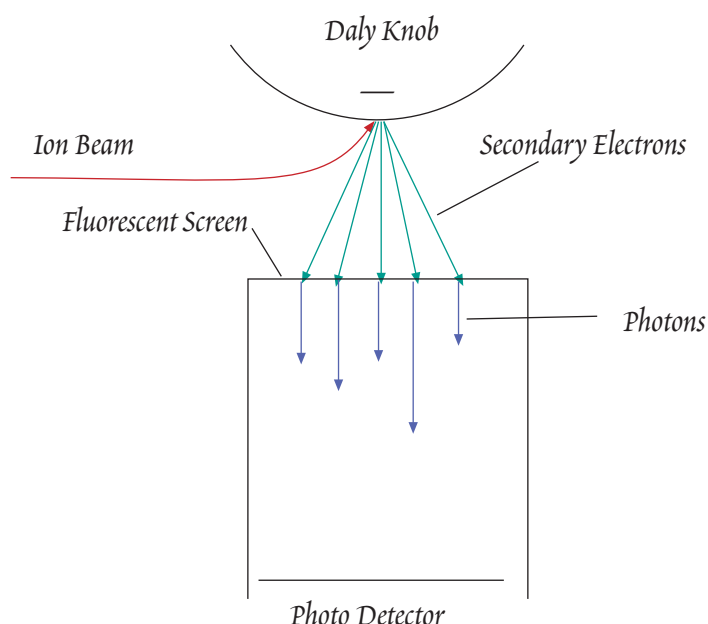


Figure 15.5. Schematic of the Daly Detector.

been greatly enhanced by the advent of accelerator mass spectrometers, providing both more precise results from old applications (e.g.,  $^{14}\text{C}$  dating) and new applications (identifying subducted sediment with  $^{10}\text{Be}$ ). Mass spectrometry is a much more efficient method of detecting atoms than counting their

Ions strike a charged electrode, producing electrons as in the electron multiplier. However, these electrons then strike a fluorescent screen producing light, which is later converted to electrical signal. The net effect is also an amplification of a factor of 100.

Multipliers are used for weak signals because of their very low signal-to-noise ratio. Typically, a multiplier is useful for signals of  $10^{-13}$  A or less. However, at higher beam intensities, the greater accuracy of the Faraday cup outweighs the signal-to-noise advantage of the multiplier.

### ACCELERATOR MASS SPECTROMETRY

Traditionally, cosmogenic nuclides have been measured by counting their decays. In the past decade or so, the utility of these cosmogenic nuclides in geochemistry and geochronology has

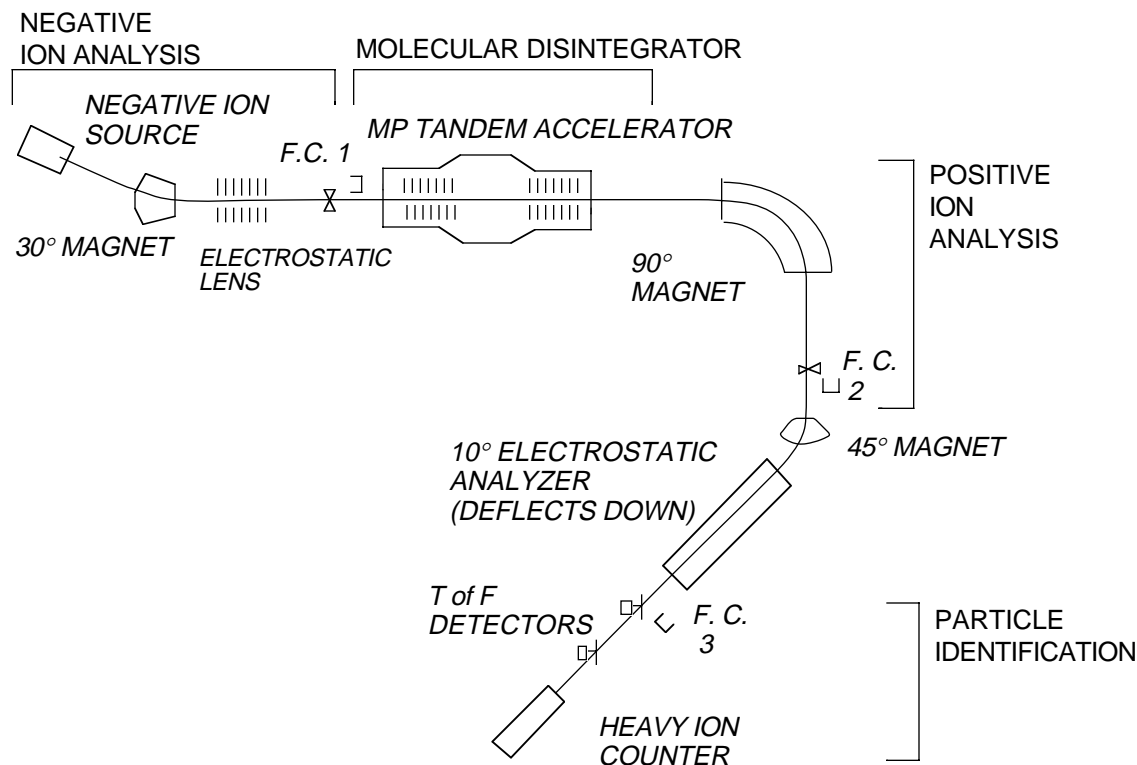


Figure 15.6. The accelerator mass spectrometer at the University of Rochester. F.C. 1, 2, & 3 are faraday cups, T of F detectors are time of flight detectors. After Litherland (1980).

# Geol. 655 Isotope Geochemistry

## Lecture 15

Spring 1998

decays in most instances. For example, the  $^{14}\text{C}/^{12}\text{C}$  ratio in the atmosphere is  $10^{-12}$ . One gram of this carbon produces about 15 beta decays per minute. But this gram contains about  $10^{10}$  atoms of  $^{14}\text{C}$ . Even at an efficiency of ion production and detection of only 1%, 70 $\mu\text{g}$  of carbon can produce an ion beam that will result in detection of 36,000 atoms  $^{14}\text{C}$  per hour. It would take 65 years for the same amount of carbon to produce 36,000 beta decays. However, there are some severe limitations with conventional mass spectrometry in measuring very small isotope ratios (down to  $10^{-15}$ ). Two problems must be overcome: limitations of resolution, and isobaric interferences. Conventional mass spectrometers have resolutions of only about a ppm at  $\Delta m$  of 1 amu, and a fraction of an amu at  $\Delta m$  of 2, so only about 1 in  $10^6$  atoms detected at the  $^{14}\text{C}$  position would actually be  $^{12}\text{C}$ . Both this and the isobaric interference problem can be improved in conventional mass spectrometry, but only at the expense of efficiency.

The techniques involved in accelerator mass spectrometry vary with the element of interest, but most applications share some common features that we will briefly consider. Figure 15.6 is an illustration of the University of Rochester accelerator mass spectrometer. We will consider its application in  $^{14}\text{C}$  analysis as an example. A beam of  $\text{C}^-$  is produced by sputtering a graphite target with  $\text{Cs}^+$  ions. There are several advantages in producing, in the initial stage, negative ions, the most important of which in this case is the instability of the negative ion of the principal atomic isobar,  $^{14}\text{N}$ . The ions are accelerated to 20keV (an energy somewhat higher than most conventional mass spectrometers) and separated with the first magnet, so that only ions with  $m/q$  of 14 enter the accelerator. The Faraday cup FC 1 (before accelerator) is used to monitor the intensity of the  $^{12}\text{C}$  beam. In the accelerator, the ions are accelerated to about 8 MeV, and then electrons removed (through high-energy collisions with Ar gas) to produce  $\text{C}^{4+}$  ions. The reason for producing multiply charged ions is that there are no known stable molecular ions with charge greater than +2. Thus the production of multiply charged ions effectively separates  $^{14}\text{C}$  ions from molecular isobaric ions such as  $^{12}\text{CH}_2$ . The now positively charged ions are separated from residual ions through two more magnetic sectors, and an electrostatic one (which selects for ion energy  $E/q$ ). The final detector distinguishes  $^{14}\text{C}$  from residual  $^{14}\text{N}$ ,  $^{12}\text{C}$ , and  $^{13}\text{C}$  by the rate at which they lose energy through interaction with a gas (range, effectively).

### ANALYTICAL STRATEGIES

Isotopic variations in nature are very often quite small. For example, variations in Nd (neodymium) isotope ratios are measured in parts in 10,000. There are exceptions, of course. He isotope ratios, as well as Ar isotope ratios, can vary by orders of magnitude, as can Pb in exceptional circumstances (minerals rich in uranium). These small variations necessitate great efforts in precise measurements (in the Cornell laboratory, for example, we can reproduce measurements of our Nd isotope standard to about 30 ppm,  $2\sigma$ ). In this section we will briefly discuss some of the methods employed in isotope geochemistry to reduce analytical error. We will exclude, for the moment, the problem of contamination. We will also exclude, for the most part, a discussion of instrument and electronics design, though these are obviously important.

One technique used universally to reduce analytical errors is to make a *large number of measurements*. Thus a value for the  $^3\text{He}/^4\text{He}$  ratio reported in a paper will actually be the mean of perhaps 100 individual ratios measured during a 'run' or analysis. Any short-term drift or noise in the instrument and its electronics, as well as in the ion beam intensity, will tend to average out. The use of *multiple collectors* and simultaneous measurement of several isotopes essentially eliminates errors resulting from fluctuations in ion beam intensity. This, however, introduces other errors related to the relative gains of the amplifiers. A final way to minimize errors is to *measure a large signal*. It can be shown that the uncertainty in measuring  $x$  number of counts is  $\sqrt{x}$ . Thus the uncertainty in measuring 100 atoms is 10%, but the uncertainty in measuring 1,000,000 atoms is only 0.1%. These 'counting statistics' are the ultimate limit in analytical precision, but they come into play only for very small sample sizes.

In mass spectrometry of gaseous elements such as H, O, N, S, and C (the latter does not, of course, always occur as a gas; however, it is always converted to  $\text{CO}_2$  for analysis), the instruments are designed to switch quickly between samples and standards. In other words, a number of ratios of a sample will be measured, then the inlet valve will be switched to allow a standard gas into the machine

and a number of ratios of the standard will be measured. This process can be repeated several times during an analysis. The measurement of standards thus calibrates the instrument and any drift in instrument response can be corrected for. However, this is not practical for solid source instruments because switching between sample and standard cannot be done quickly. It is also impractical for noble gas analysis because of the small quantities involved, and the difficulty of completely purging a standard gas from the instrument.

### Mass Fractionation

One of the most important sources of error in solid source mass spectrometry results from the tendency of the lighter isotopes of an element to evaporate more readily than the heavier isotopes (we will discuss the reasons for this later in the course when we deal with stable isotope fractionations). This means that the ion beam will be richer in light isotopes than the sample remaining on the filament. As the analysis proceeds, the solid will become increasingly depleted in light isotopes and the ratio of a light isotope to a heavy one will continually decrease. This effect can produce variations up to a percent or so per mass unit (though it is generally much less). This would be fatal for Nd, for example, where natural isotopic variations are much less than a percent, if there were no way to correct for this effect. Fortunately, a correction can be made. The trick is to measure the ratio of two isotopes that are not radiogenic; that is a ratio that should not vary in nature. For Sr, for example, we measure the ratio of  $^{86}\text{Sr}/^{88}\text{Sr}$ . By convention, we assume that the value of this ratio is equal to 0.11940. Any deviation from the value is assumed to result from mass fractionation in the mass spectrometer. The simplest assumption about mass fractionation is that it is linearly dependent on the difference in mass of the isotopes we are measuring. In other words, the fractionation between  $^{87}\text{Sr}$  and  $^{86}\text{Sr}$  should be exactly half that between  $^{88}\text{Sr}$  and  $^{86}\text{Sr}$ . So if we know how much the  $^{86}\text{Sr}/^{88}\text{Sr}$  has fractionated from the 'true' ratio, we can calculate the amount of fractionation between  $^{87}\text{Sr}$  and  $^{86}\text{Sr}$ . Formally, we can write the *linear mass fractionation law* as:

$$\alpha(u,v) = \left[ \frac{R_{uv}^N}{R_{uv}^M} - 1 \right] / \Delta m_{uv} \quad 15.8$$

where  $\alpha$  is the fractionation factor between two isotopes  $u$  and  $v$ ,  $\Delta m$  is the mass difference between  $u$  and  $v$  (e.g., 2 for 86 and 88),  $R^N$  is the 'true' or 'normal' isotope ratio (e.g., 0.11940 for 86/88), and  $R^M$  is the measured ratio. The correction to the ratio of two other isotopes (e.g.,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) is then calculated as:

$$R_{ij}^C = R_{ij}^M (1 + \alpha(i,j) \Delta m_{ij}) \quad 15.9$$

where  $R^C$  is the corrected ratio and  $R^M$  is the measured ratio of  $i$  to  $j$  and

$$\alpha(i,j) = \frac{\alpha(u,v)}{1 - \alpha(u,v) \Delta m_{vj}} \quad 15.10$$

If we choose isotopes  $v$  and  $j$  to be the same (e.g., to both be  $^{86}\text{Sr}$ ), then  $\Delta m_{vj} = 0$  and  $\alpha(i,j) = \alpha(u,v)$ . A convention that is unfortunate in terms of the above equations, however, is that we speak of the 86/88 ratio, when we should speak of the 88/86 ratio (= 8.37521). Using the 88/86 ratio, the 'normalization' equation for Sr becomes:

$$\left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)^C = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)^M \left[ 1 + \left( \frac{8.37521}{(^{87}\text{Sr}/^{86}\text{Sr})^M} \right) / 2 \right] \quad 15.11$$

A more accurate description of mass fractionation is the *power law*. The fractionation factor is:

$$\alpha = \left[ \frac{R_{uv}^N}{R_{uv}^M} \right]^{1/\Delta m_{uv}} - 1 \quad 15.12$$



# Geol. 655 Isotope Geochemistry

## Lecture 15

Spring 1998

The corrected ratio is computed as:  $R_{i,j}^C = R_{i,j}^M [1 + \alpha] \Delta m_{i,j}$  15.13

or:  $R_{i,j}^C = R_{i,j}^M \left[ 1 + \alpha \Delta m_{i,j} + \frac{1}{2} \Delta m_{i,j} (\Delta m_{i,j} - 1) \alpha^2 + \dots \right]$  15.14

Since  $\alpha$  is a small number, higher order terms may be dropped.

Finally, it is claimed that the power law correction is not accurate and that the actual fractionation is described by an *exponential law*, from which the fractionation factor may be computed as:

and the correction is:  $\alpha = \frac{\ln[R_{uv}^N/R_{uv}^M]}{m_j \ln(m_u/m_v)}$  15.15

$$R_{i,j}^C = R_{i,j}^M \left( \frac{m_i}{m_j} \right)^{\alpha m_j} = R_{i,j}^M \left[ 1 + \alpha \Delta m_{i,j} - \alpha \frac{m_{i,j}^2}{2m_j} + \alpha^2 \frac{m_{i,j}^2}{2} + \dots \right] \quad 15.16$$

The exponential law appears to provide the most accurate correction for mass fractionation. However, all of the above laws are empirical rather than theoretical. The processes of evaporation and ionization are complex, and there is as yet no definitive theoretical treatment of mass fractionation during this process.

### Simultaneous Correction of Mass Fractionation and Gain Bias in Multiple Collection

We can now return to the question of correcting for the differing gains of amplifiers when more than one collector is used. I mentioned we could calibrate the gains electronically, or that we could measure one isotope in each cup and use this intensity as a calibration. A simplistic approach to the latter method would put us at the mercy of fluctuations in the ion beam intensity, whereas eliminating fluctuations in ion beam intensity is, however, one principal advantage of multiple collection (the other advantage is speed). An alternative approach would be to measure ratios of intensities. If we could measure the intensities of two isotopes whose ratio is known, we could use these intensities to correct for gain differences. An example of a known ratio would be  $^{86}\text{Sr}/^{88}\text{Sr}$ . The only difficulty is that this ratio will vary due to mass fractionation. Fortunately, there is a way to simultaneously correct for both mass fractionation and gain differences. Taking a simple case of measuring three strontium isotopes in two collectors, we proceed by first measuring  $^{87}\text{Sr}$  in cup 1 and  $^{86}\text{Sr}$  in cup 2. By changing the magnetic field, we then measure  $^{88}\text{Sr}$  in cup 1 and  $^{87}\text{Sr}$  in cup 2. The corrected  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is then given by:

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{true}} = \sqrt{\frac{{}^{87'}\text{Sr}}{{}^{86'}\text{Sr}} \times \frac{{}^{87''}\text{Sr}}{{}^{88''}\text{Sr}} \times 8.37521} \quad 15.17$$

where ' indicates an intensity measured in cup 1, '' an intensity in cup 2, and 8.37521 is the 'true'  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio. I will leave it as an exercise for you to demonstrate that this equation does in fact correct for both fractionation and gain differences. The sole disadvantage is its reliance on the linear mass fractionation law, which is the least accurate.

### REFERENCES AND SUGGESTIONS FOR FURTHER READING

- Dickin, A. 1995. *Radiogenic Isotope Geochemistry*. Cambridge: Cambridge University Press.
- Elmore, D. and F. M. Phillips. 1987. Accelerator mass spectrometry measurements of long-lived radioisotopes. *Science*. 236: 543-550.
- Litherland, A. E. 1980. Ultrasensitive mass spectrometry with accelerators. *Ann. Rev. Nucl. Part. Sci.* 30: 437-473.
- Majer, J. R. 1977. *The mass spectrometer*. London: Wykeham Publications.
- Wasserburg, G. J., S. B. Jacobsen, D. J. DePaolo, M. T. McCulloch and T. Wen. 1981. Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochim. Cosmochim. Acta*. 45: 2311-2324.

# Geol. 655 Isotope Geochemistry

## Lecture 15

Spring 1998

Wunderlich, R. K., I. D. Hutcheon, G. J. Wasserburg and G. A. Blake. 1992. Laser-induced isotopic selectivity in the resonance ionization of Os. *Intern. J. Mass Spec. Ion Proc.* 115: 123-155.