Analytical Methods

Huge diversity of techniques, analytes, methods.

- radiation damage methods
- elemental
- isotopic
- extractive/purification
- in situ
- mass spectrometry

Will only review some important common ones.
Whole rock

some isochron techniques

$^{40}\text{Ar}^{39}\text{Ar}$ dating

Mineral separation

crushing: mechanical or HV

magnetic: Frantz, etc.

density: heavy liquids

methylene iodide (3.32 g/cm$^3$)

acetylene tetrabromide (2.97 g/cm$^3$)

bromoform (2.89 g/cm$^3$)

Clerici (thallium malonate formate) (4.25 g/cm$^3$)

Sodium polytungstate (3.10 g/cm$^3$)

lithium polytungstate (2.82 g/cm$^3$)

dissolution

± elemental extraction

e.g., TIMS

ICP-MS

gas release

e.g., noble gas dating

In situ

e.g., LA-ICP-MS, SIMS
Acid dissolution

HNO₃, HF, HClO₄, HCl

PTFE, PFA

Blanks: pg, fg, fmol, etc.

Clean labs: class 100, 1000, etc.; particles > 0.5 µm/ft³ of air: typical indoor air: Class 1,000,000
Isotope Dilution

### Known quantities:
- sample mass
- isotopic composition

### Measured quantities:
- isotope ratio

\[
N_W = S_W \left( \frac{W_N}{W_S} \right) \left[ \frac{\text{Ab}_S^A - R_m \text{Ab}_N^B}{R_m \text{Ab}_N^B - \text{Ab}_S^A} \right]
\]

- \(N_W\) = mass of normal element in mixture
- \(S_W\) = mass of spike element in mixture
- \(W_N\) = atomic mass of normal element
- \(W_S\) = atomic mass of spike element
- \(\text{Ab}_S^A\) = fractional abundance of isotope A in spike, etc.
- \(R_m\) = measured ratio of isotopes A/B in mixture

### Some features:
1. High precision & accuracy measurements of low concentrations
2. Small amounts can be measured
3. Accuracy depends on measurements of spike, calibration
4. Interferences "cancel out"
5. Multiple elements can be spiked/measured
6. Accuracy depends on mass spec fractionation (see double/triple spiking)
7. Spike-sample mixing must be complete
8. Long-term spike conc change potential
9. Spike/sample ratio should be optimized to prevent error magnification
Ion exchange chromatography

mass interferences: $^{87}\text{Rb} - ^{87}\text{Sr}; ^{187}\text{Re} - ^{187}\text{Os}$

commonly used to prep for TIMS, ICP-MS

relies on difference in partition/distribution coefficients

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*Fig. 3.3.* Elution curves for a cation ion exchange column designed to separate Hf, Rb, Sr, and Lu from major elements in the sample. In this case, the sample is loaded in a solution of 1\text{n} HCl and 0.1\text{n} HF. The HF causes high-field-strength elements such as Ti and Hf to form fluoride anions that do not stick to the resin. These elements are washed off the column with the addition of 10 mL of this acid mixture. At that point, the acid is changed to 2.5\text{n} HCl. Most of the major elements (dashed lines), with the exception of Ca, elute quickly in this acid. Rb and Sr are reasonably well isolated in this step. Once Sr is eluted, the acid strength is increased to 4\text{n} in order to wash out the REE, including Lu, Sm, and Nd.
Chemical dating techniques
SEM total-Pb dating (e.g., monazite)
(U-Th)/He (sometimes)

Others not needing mass spectrometry
FT/ESR/OSL/TL
"counting" (decay) techniques

Mass Spectrometry

• 1899 Wilhelm Wien: ions accelerated in electric field are bent by magnetic field, deflection is a function of mass/charge or ion and magnetic field

• 1918, 1919: Dempster, Aston record ion beams of ions with different masses on photographic plates

• Dempster discovers $^{235}$U
• Aston gets Nobel Prize for discovering 212 naturally occurring isotopes and "whole number rule"
Mass spectrometry

1. ionization of sample
2. acceleration and focusing of ions into collimated beam by electric fields
3. separation of ions according to m/z
4. detector to quantify magnitude of ion beam at each m/z
5. vacuum to allow unimpeded transit of ions from source to detector

Fig. 3.4. Left: Dempster's first mass spectrometer. Ions are generated in section “G” and accelerated by an electric field through the source slit (S₁) after which they enter into a magnetic field (region A) that causes them to curve through a 180° arc and separates the ions according to their charge to mass ratio. Either the accelerating voltage or magnetic field strength can be adjusted so that an ion beam of only a single mass passes through the detector slit (S₂) to hit the detector plate (E). (Source: Dempster [1918]. Reproduced with permission of American Physical Society.) Right: schematic path of an accelerated ion with velocity \( v \), mass \( m \), and charge \( z \), through an orthogonal magnetic field \( B \). Single-detector mass spectrometers vary \( B \) and \( v \) to direct and measure incoming intensities of ions of different \( m/z \) in the detector. Multidetector systems measure multiple \( m/z \) ions with a single set of \( B \) and \( v \).
Ionization

1880s: arc

electron bombardment: spiraling electrons hit sample gas: noble gases, CO₂, O₂

thermal ionization: heat salt to high Ts (>1800 °C) 0.1-50% ionization of Cr, Rb, Sr, Sm, Nd, Re, Os, W, Pb, U
  - does not work well for elements with high ionization potentials (e.g., Hf)
    - NdO⁺
    - adding Ba(OH)₂ increases OsO₃⁻ ions (up to 5%) (requires changing polarity of MS)
  - causes mass fractionation...
Ionization

ICP: 5,000 - 10,000 °C Ar plasma
- sample introduced as aerosol mixed with carrier gas
- effectively ionizes even elements with high ionization potential (Th, Hf)
- often combined with in situ laser-ablation
- range of ionized molecules produced: doubly-charged, oxides, nitrides, argides, hydrides
Ionization

**Ion-impact ionization**
- AMS: accelerated Cs\(^+\) ions impact chemically purified sample deposited on a surface, produces negatively charged ions that are extracted into MS
- SIMS (or ion-probe): usually Cs\(^+\) or O\(^-\) ions impact sample with ~10 kV to break bonds and sputter material
  - can focus beam to nm scales
  - often used for U/Pb, nano-SIMS
  - only about 0.0001-0.1% of material is ionized, and can have wide range of energy, charge, molecular ionization, large mass-dependent fractionation

![Schematic example of the sputtering and ionization process involved in the SIMS ion source. A beam of energetic (~10 kV) negative ions of oxygen is focused on the sample surface. The impact of the primary ions breaks chemical bonds on the sample surface liberating a mixture of molecules, neutral ions, and positive ions of the sample. The ions are extracted by an electric field to be introduced into the mass analyzer.](image-url)
Ionization

Laser-resonance ionization

- selectively tuned wavelength of laser radiation can excite specific electron (energy) of particular element; if a 2nd ionization occurs before decay back to ground state, atom becomes ionized
- limitation is need to get target into elemental form
- currently mainly used for pre-solar grains
- may become more important in future?

Figure 3.8: Selective ionization of Re or Os using laser light of different wavelength. The mass scans on the left of the figure show the ion spectrum emitted by a mixed sample of Re and Os when the laser light is varied from 297.70 nm (ionizing Re) to 297.15 nm (ionizing Os). The schematic electronic transitions involved are shown on the right.
Extraction and focusing of ions

ion source
• accelerates ions towards mass analyzer
• metal plates with different charges shape and focus the beam by altering the electric field in the ions path
• ions emerging from source will have more uniform energy and accelerating voltage

For ions traveling perpendicular to electric field lines:

\[ \frac{1}{2}mv^2 = qV \]

\( m = \text{mass}, \ v = \text{velocity}, \ q = \text{charge}, \ V = \text{voltage} \)

Radius of curvature of ion traveling in direction not-parallel to electric field lines:

\[ r = \frac{mv^2}{qV} \]
Mass fractionation can be as much as 10% per mass unit correction methods:

- frequently/rapidly switch between sample and standard of known isotopic composition (often used in noble gases)
- compare/correct mass fractionation measured on another element (often used in ICP-MS)
- double-spiking (e.g., $^{233}\text{U}/^{236}\text{U}$ or $^{202}\text{Pb}/^{205}\text{Pb}$)
- exponential, linear, power corrections, exp:

$$R_{ij} = (R_{ij})_m \times \left( \frac{M_i}{M_j} \right)^{FF}$$

$$FF = \ln \left( \frac{(R_{kj})_m}{(R_{kj})_f} \right) / \ln \left( \frac{M_k}{M_j} \right)$$

**Figure 3.10:** Isotope ratio variation during the measurement of Sr by thermal ionization. Panel a shows a histogram of the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios while panel b shows the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to be perfectly anti-correlated with the measured $^{86}\text{Sr}/^{88}\text{Sr}$ ratio. Using the deviation of the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio from an assumed constant ratio equal to 0.1194 allows for the correction of the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the instrument-induced mass fractionation. Panel c shows that this fractionation correction reduces the total range in $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.8% to 0.03%.
Mass analyzer

**Magnetic sector**

In addition to separating ions by mass, sectors also refocus ions of same m/z traveling in dispersed paths.

\[ r = \sqrt{\frac{2mv}{qB^2}} \]

**Figure 3.11:** Flight paths through a 90° sector magnet. The ions leave the ion source with a certain angular dispersion represented by the three solid black lines. In the magnet, represented by the prism, the beams are curved by the magnetic field that separates the ions by their mass to charge ratio with the dotted line representing the lighter, and the dashed the heavier of the two isotopes. The magnet also corrects for the dispersion of the beam leaving the ion source so that each isotope beam is refocused at a point along the line connecting the source slit and the detector slit that passes through the center of the circle defined by the radius (R) of the magnet.

**Quadrupole**

Combined RF alternating field and DC voltage on rods causes oscillating paths of ions, with radius proportional to m/z. Frequencies and DC are varied so that only ions of specific m/z get through.

Simple and cheap, but low mass resolution

**Figure 3.12:** Schematic illustration of the means of mass separation in a quadrupole mass analyzer. In this image, the red trajectory maps the path of an ion whose mass to charge ratio is resonant with the frequency of the voltage applied to the quadrupole. The blue path is for an ion of different mass to charge that is forced into increasing oscillations until it touches one of the quadrupole rods and is neutralized.
Mass resolution

\[
\text{resolution} = \frac{\delta M \times \left[\frac{m_2 + m_1}{2}\right]}{\Delta M \times (m_2 - m_1)}
\]

where \(m_1\) and \(m_2\) are masses of adjacent peaks, \(\delta M\) is the distance between the midpoint of the peaks for these two masses, and \(\Delta M\) is the width of the peak at either 10% or 50% of its full height.

![Diagram of mass resolution](image)

**Fig. 3.12.** Mass scan of two adjacent isotopes of masses \(m_1\) and \(m_2\) at two different resolutions. The width of the source slit is constant between (a) and (b), but the collector slit is twice as wide in (b) as in (a), allowing each ion beam to fully enter the detector over a wider range of apparent mass. Because only the slit widths were changed between these scans, the separation between the peaks (\(\delta M\)) remains the same, so the resolution is reduced in scan (b). (Source: Carlson [2013]. Reproduced with permission of Elsevier.)

Turner et al., 1998
Mass resolution

In magnetic sector MSs, resolution depends primarily on widths of image slit \( S \), at the end of the ion source), detector slit \( D \), at entrance to detector), and radius \( r \) of magnet.

So resolution \( = \frac{r}{S + D} \).

Can increase resolution by making slits narrower, but then you get fewer ions.

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**Figure 3.14:** Illustration of the dependence of peak shape on source and detector slit width. In each panel, the magnetic field is being slowly changed so that the ion beam is scanned across the detector slit producing the signal at the detector denoted by the bold black line. The boxes show the width of the ion beam in three examples for different source slit widths, but the same detector slit width. The slope of the side of the peak reflects the width of the incoming beam. The flat top is created when the incoming beam is thinner than the detector slit so that over a range in magnetic field, the whole beam passes through the detector slit into the detector. In C, the beam width is the same as the detector width, so as soon as all of the beam enters the detector, the beam encounters the opposite edge of the detector slit causing the signal size to go down as the beam continues its scan out of the detector slit.
Mass resolution and resolving power

mass resolution = this divided by this

resolving power = this divided by this
Abundance sensitivity

Combining sector and ESA

Figure 3.16: Schematic illustration of a double-focusing mass spectrometer combining electrostatic and magnetic sectors. This instrument is a secondary ion mass spectrometer (SIMS or ion probe) that sputters the solid sample using a primary ion beam (yellow) to create ions from the sample (brown) that are then accelerated into an electrostatic analyzer to allow selection of a small energy window of the sputtered sample ions. The ions that meet the energy window of the electrostatic analyzer pass through a slit into a magnetic sector that performs the mass separation of the beam into its constituent isotopes, refocusing the isotope beam at the detector slit. Figure from (Williams, 1998).
Detectors

Faraday Cups: "buckets" made of steel or graphite, connected to electrical ground through $10^{10}$-$10^{13}$ $\Omega$ resistor. Every positive ion entering the cup is electrically neutralized by an electron traveling from ground through the resistor. **Voltage (signal) = current (strength of ion beam) x resistance (amplifier).**

![Faraday cup diagram](image)

**Fig. 3.17.** A typical Faraday cup design and schematic signal quantification electronics. The gray rectangle shows the side view of the cup. The ion beam enters the hollow cup through a small, electrically grounded, slit placed in front of the Faraday. The Faraday cup is connected to ground only through a high-ohmage resistor so that the ion current flowing into the Faraday creates a current across the resistor that can be converted to a voltage proportional to the ion current size. Most Faraday cups will have one or more plates with a thin slit near the entrance to the cup to which a voltage is applied in order to repel secondary electrons back into the Faraday cup when they are ejected from the cup material by the energetic impact of the incoming ions. (Source: Carlson [2013]. Reproduced with permission of Elsevier.)

**Issues:**
- Johnson noise (thermally induced electron movements)
- Instability (to T, P, humidity) of high-ohmage resistors (so sometime placed in low vac/T-controlled)
- Secondary electrons generated near front of cup
Detectors

Ion multipliers

1. Discrete dynode electron multipliers (DDEM)
2. Continuous dynode electron multipliers (CDEM)
3. Daly detector

Issues:
• much better signal amplification
• amplification is probabilistic
• slight mass dependence
• max out, burn out
• max precision $\sim 10^3-10^4$, compared with $10^6$ for Faradays
• decay time on Daly, dead-time on EMs
Detectors

Ion multipliers

Analog vs. pulse counting modes

**analog** is like Faraday detection, all arriving electrons are summed to derive average signal size

**pulse counting** just counts events, and is used at low ion currents
decreases mass dependency
can eliminate "noise" of the multiplier

at larger signals, need to worry about dead time

\[
CPS_{\text{Real}} \approx \frac{CPS_{\text{Meas}}}{(1 - CPS_{\text{Meas}} \times \tau)}
\]

\(\tau = \text{dead time, generally tens of ns}\)

if count rates are \(~\text{few million cps}\), need to switch to Faraday cups

*Fig. 3.19.* Example of pulse counting applied to the signal supplied by an electron multiplier. Ion arrivals create bursts of electrons in the multiplier that can be of varying size. Pulse counting ignores the magnitude of the pulse and simply counts each pulse as a single ion. One can set a discrimination level (dashed line) below which the pulse is not counted. The width of the peak shows the recovery time of the electron multiplier after each ion arrival, which is the "dead time" of the electron multiplier.
Vacuum Systems

A: Rotary vein mechanical ("rough") pump where the spring-loaded rod inside the rotating cylinder seals a volume between the rotating cylinder and the pump wall. As this volume expands, it draws in gas (right side) from the vacuum system, compresses it, and expels it from the pump (left side).

B: Cutaway view of interior of a turbomolecular pump, showing turbine blades near top (input), and exhaust port to backing pump near base. Cross section of the turbine blades inside a turbo pump. The ports at the bottom of the picture connect with a mechanical backing pump that removes the gases compressed by the spinning turbine blades.

C: Schematic of the working components of an ion pump, showing magnets on exterior of pump case, titanium cathodes, and side view of a cylindrical anode.

Typical pressures in UHV lines: $\sim 10^{-4} - 10^{-7}$ Pa ($10^{-6} - 10^{-9}$ Torr or mbar)

- Polished SS components, Cu gaskets, baking at 20-300 °C, getters
- Rough/mech pump: $\sim 1 - 0.01$ Pa
- Turbomolecular pump: $\sim 10^{-4} - 10^{-7}$ Pa
- Ion pump: $< 10^{-4} - 10^{-9}$ Pa

Other types: sorption pumps, diffusion pumps, cryopumps
Fig. 4.1. The conventional understanding of accuracy and precision. Measured data, plotted as 250 points, have a true mean at the origin of each plot, and the mean of the measured data is plotted with an “x”. Circles centered on the true value are drawn for reference. If the data sets are unbiased as in (a) and (c), the mean of a data set with lower precision is likely to be farther from the true value than the mean of a more precise data set. Because the accuracy depends on the difference between the measured and true values, in the language of the VIM this means a less precise data set is likely to be less accurate. (See insert for color representation of the figure.)
• “error” is diff between measured value and true value

• “uncertainty” is measurement of dispersion of values attributed to quantity being measured...involves a confidence interval which is often 1 or 2 $\sigma$, which implies Gaussian distribution of measurements...

• Measurement’s error can come from random or systematic components.

• Uncertainty refers to precision alone.
For a single variable, for instance a reported date, the normal distribution takes the shape of the familiar “bell curve” (Fig. 4.3). The formula for the curve is written \( f(x|\mu, \sigma) \), where the probability density is a function \( f \) of the variable of interest \( x \), if you know (the vertical bar symbolizes “given”) both the mean \( \mu \) of the distribution and its standard deviation \( \sigma \) (equation 4.1).

\[
f(x|\mu, \sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2}
\]

(4.1)

The actual values returned by the probability density function \( f \) are less important than the area under the curve it creates (Fig. 4.3). The area under the entire curve is unity, and the probability that \( \mu \) lies between two prospective values \( x_1 \) and \( x_2 \) is simply the area under the curve between those two values. For instance, 68.3\% of the area underneath the normal distribution lies within the interval \( \pm 1\sigma \) of the mean, and 95.4\% within \( \pm 2\sigma \) of the mean. If a reported uncertainty is normally distributed, then there should be a \( \sim 68.3\% \) chance that the true value lies within \( \pm 1\sigma \) of the mean, and \( \sim 95.4\% \) within \( \pm 2\sigma \) of the mean.
Fig. 4.4. Anatomy of an uncertainty ellipse. One thousand bivariate normally distributed random numbers are plotted, along with the $2\sigma$ ellipse that illustrates the bivariate analog of their mean and standard deviation. On the $x$-axis and $y$-axis, the probability distributions for the $x$ and $y$ variables are plotted. They are univariate normal distributions, and known as marginal distributions. Note that the horizontal and vertical tangents of the ellipse correspond to the $2\sigma$ uncertainty envelopes for the $x$ and $y$ variables. The ellipse encloses a smaller number of points than the 95% confidence intervals, including only 86% of the simulated data. Therefore, a $2\sigma$ uncertainty ellipse is not a 95% uncertainty envelope. (See insert for color representation of the figure.)

$$f(x | \mu, \Sigma) = \frac{1}{\sqrt{|2\pi \Sigma|}} e^{-\frac{1}{2}(x-\mu)^T \Sigma^{-1} (x-\mu)}$$
pretend this is actually a whole bunch of individual measurements of x that compose something looking like a sort of smooth distribution.

The natural measure of central tendency for approximately normally distributed data is the *arithmetic mean* \( \bar{x} \), and the natural measure of the scatter between the data points is the *sample standard deviation* \( s \), the square root of the *sample variance* \( s^2 \).

\[
\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \\
\sigma^2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2 \\
s = \sqrt{\sigma^2}
\] (4.3)

Equations (4.3) are probably the most commonly used equations for interpreting data, so they deserve some explanation and analysis. The equations describe \( n \) successive measurements of a variable \( x \), the focus of our study. Here, \( x \) could stand for anything that can be measured quantitatively: the diameter of a mineral, the mass of a sample, or an isotope ratio. The \( i \) in each of the summations is an index: for instance, the first measurement \((i = 1)\) is \( x_1 \), the second \((i = 2)\) is \( x_2 \), through the last measurement \((i = n)\), which is \( x_n \). The statistics \( \bar{x} \), \( s \), and \( \sigma^2 \) can be calculated for data with any type of statistical distribution, but the \( \pm 1\sigma \) and \( \pm 2\sigma \) intervals are only 68% and 95% confidence intervals for the normal distribution. Box 4.1 explains the difference between \( \mu \) versus \( \bar{x} \) and \( \sigma \) versus \( s \). Both the variance and the standard deviation describe the data point-to-data point variability of the data—increasing the sample size, \( n \), does not change their expected value. The reason there is an \((n - 1)\) in the denominator of the sample variance is explored in detail in Section 4.3.5.
4.3.2 Average values: the standard error of the mean

When the iid assumptions for calculating a mean, variance, and standard deviation have been met, then it is possible to ask how well the mean is known. The more measurements \( n \) of a variable that are made, the more information is available and the better the mean of that variable is known. Intuitively, this means we should have a more precise estimate of the mean and its uncertainty. This is not reflected in the variance or standard deviation of the data set, whose expected values do not change with increasing \( n \). Instead, the variance and standard deviation in equations (4.3) can be used to calculate the variance of the mean, \( s^2_{\bar{x}} \), and the standard deviation of the mean, \( s_{\bar{x}} \).

\[
\begin{align*}
\frac{s^2_{\bar{x}}}{n} &= \frac{1}{n(n-1)} \sum_{i=1}^{n} (x_i - \bar{x})^2 = \frac{\sigma^2}{n} \\
\frac{s_{\bar{x}}}{n} &= \sqrt{\frac{s^2_{\bar{x}}}{n}} = \sqrt{\frac{\sigma^2}{n}} = \frac{s}{\sqrt{n}}
\end{align*}
\]

(4.4)

The standard deviation of the mean is also called the standard error of the mean, or simply the standard error, and these three terms are often used synonymously in statistics, geochronology, and thermochronology literature (see Box 4.2). The standard error is used to calculate and report the uncertainty in many replicate measurements of the same mean value, \( \bar{x} \), and for normally distributed data, the uncertainty in the mean is normally distributed. After \( n \) measurements, the true value of the mean would be expected to be within the interval \( \bar{x} \pm s_{\bar{x}} \) about 68% of the time and about 95% of the time for the interval \( \bar{x} \pm 2s_{\bar{x}} \).
a simple representation of weighted mean, using uncertainty of individual measurements as weights

weighted mean, and uncertainty of the weighted mean

Our analysis of two measurements can be generalized to cover any number of measurements. Suppose we have \( N \) separate measurements of a quantity \( x \),

\[
x_1 \pm \sigma_1, \quad x_2 \pm \sigma_2, \ldots, \quad x_N \pm \sigma_N,
\]

with their corresponding uncertainties \( \sigma_1, \sigma_2, \ldots, \sigma_N \). Arguing much as before, we find that the best estimate based on these measurements is the weighted average

\[
x_{\text{wav}} = \frac{\sum w_i x_i}{\sum w_i}, \tag{7.10}
\]

where the sums are over all \( N \) measurements, \( i = 1, \ldots, N \), and the weight \( w_i \) of each measurement is the reciprocal square of the corresponding uncertainty,

\[
w_i = \frac{1}{\sigma_i^2}, \tag{7.11}
\]

for \( i = 1, 2, \ldots, N \).

Because the weight \( w_i = 1/\sigma_i^2 \) associated with each measurement involves the square of the corresponding uncertainty \( \sigma_i \), any measurement that is much less precise than the others contributes very much less to the final answer (7.10). For example, if one measurement is four times less precise than the rest, its weight is 16 times less than the other weights, and for many purposes this measurement could simply be ignored.

Because the weighted average \( x_{\text{wav}} \) is a function of the original measured values \( x_1, x_2, \ldots, x_N \), the uncertainty in \( x_{\text{wav}} \) can be calculated using error propagation. As you can easily check (Problem 7.8), the uncertainty in \( x_{\text{wav}} \) is

\[
\sigma_{x_{\text{wav}}} = \frac{1}{\sqrt{\sum w_i}}. \tag{7.12}
\]

This rather ugly result is perhaps a little easier to remember if we rewrite (7.11) as

\[
\sigma_i = \frac{1}{\sqrt{w_i}}. \tag{7.13}
\]

Paraphrasing Equation (7.13), we can say that the uncertainty in each measurement is the reciprocal square root of its weight. Returning to Equation (7.12), we can paraphrase it similarly to say that the uncertainty in the grand answer \( x_{\text{wav}} \) is the reciprocal square root of the sum of all the individual weights; in other words, the total weight of the final answer is the sum of the individual weights \( w_i \).
General Formula for Error Propagation: If \( q = q(x, \ldots, z) \) is any function of \( x, \ldots, z \), then

\[
\delta q = \sqrt{\left( \frac{\partial q}{\partial x} \delta x \right)^2 + \cdots + \left( \frac{\partial q}{\partial z} \delta z \right)^2}
\]

(provided all errors are independent and random)

and

\[
\delta q \leq \left| \frac{\partial q}{\partial x} \right| \delta x + \cdots + \left| \frac{\partial q}{\partial z} \right| \delta z
\]

(always).

Figure 3.2. Because any side of a triangle is less than the sum of the other two sides, the inequality \( \sqrt{a^2 + b^2} < a + b \) is always true.
WR Sm/Nd isochron: ~2.6 Ga
WR Rb/Sr isochron: ~1.7 Ga
mineral Rb/Sr isochron: ~1.4 Ga