

4.2e Terminology

The dates derived from equation 4.9 or 4.11 are expressed in units of kiloyears (ka), megayears (Ma), and gigayears (Ga):

$$1 \text{ ka} = 10^3 \text{ y} \quad 1 \text{ Ma} = 10^6 \text{ y} \quad 1 \text{ Ga} = 10^9 \text{ y}$$

These units specify dates in the past and should not be followed by the word *ago*. In addition, they do not represent intervals of time. For example, the preferred expression is "The age of this rock is 100 Ma, which means that it has existed for 100 million years (My)."

In addition, the word *date* is not synonymous with the word *age* because a suite of rocks can have a spectrum of dates that record events in their geological history as revealed by different isotopic chronometers. In some cases, none of the isotopic dates corresponds to the age of the rocks, depending on how that term is defined by the investigator. Instead, different isotopic chronometers can provide information concerning magma sources or protoliths, the date of crystallization of the minerals, dates of subsequent isotopic re-equilibration during episodes of metamorphism, cooling of the rocks after initial crystallization or after their last episode of metamorphism, as well as evidence for hydrothermal alteration and/or chemical weathering. Therefore, isotopic methods of dating can provide much more information about a body of cogenetic rocks than merely their age.

4.3 FITTING OF ISOCHRONS

The dating of rocks or minerals begins with the selection of a suite of samples that, on the basis of prior geological evaluation, are likely to satisfy the assumption that all specimens chosen for analysis formed at the same time, had the same initial abundance of the radiogenic daughters, and are likely to have remained closed systems. Samples that show evidence of chemical weathering or of other forms of postdepositional alteration must be excluded at the outset. After the values of D and N of the samples have been determined and have been plotted on the isochron diagram, the problem arises of fitting the "best" straight line to the data points. The fit of

the data points to a straight line is never "perfect" because of errors arising from the analyses of the samples. These analytical errors give rise to corresponding uncertainties in the date and initial value of D that can be derived from the analytical data.

The term *analytical error* generally means the deviation of a measured value from its true value. Such errors may be random or systematic. Random errors have a "normal," or Gaussian, distribution about the arithmetic mean of the measurements that approaches the true value as the number of measurements increases. Systematic errors, on the other hand, are consistent differences between the true value and a set of measurements such that their arithmetic mean is displaced from the true value. Therefore, random errors determine the precision of a set of measurements while systematic errors limit their accuracy. Systematic errors in the measurements of D and N lead to similar systematic errors in the value of D_0 and in the date derived from an isochron. Such errors must obviously be eliminated as nearly as possible to assure the accuracy of the results. The important considerations in fitting isochrons are

1. how to use the analytical errors of the coordinates in determining the best slope and intercept, and
2. how to decide whether a particular point fits the isochron within the analytical errors.

If it can be shown that a point does not fit the isochron within random analytical errors, then either the coordinates of that data point have systematic analytical error or the sample does not satisfy the prerequisite assumptions of dating by the isochron method. It may have a different age or a different value of D_0 compared with other samples in the suite or it may not have remained a closed system.

The simplest method of fitting an isochron to data points is to draw the best straight line by eye on a piece of graph paper. If the scale is sufficiently large, the slope and intercept can be determined from the graph with enough accuracy to serve at least as a good first approximation. This method is useful for obtaining preliminary estimates of the slope and intercept but should be replaced by a more objective approach in any serious evaluation of isochrons.

should be X^2

4.3a Unweighted Regression

A somewhat better method is the *least-squares* regression procedure, which consists of minimizing the deviations of either the x - or the y -coordinate from the best line in the slope–intercept form. The equations for calculating the best slope m and intercept b of a straight line are

$$m = \frac{\sum XY - (\sum X)(\sum Y)/n}{\sum Y^2 - (\sum X)^2/n} \quad (4.12)$$

$$b = \frac{(\sum X)(\sum XY) - \sum Y(\sum X^2)}{(\sum X)^2 - n(\sum X^2)} \quad (4.13)$$

where y represents the N -coordinate in equation 4.8, x is the D -coordinate in the same equation, and n is the number of data points. Some electronic calculators have built-in linear regression functions that can be executed with a few key strokes. The simple least-squares regression is based on the assumption that the deviations of the data points from the best straight line are due only to errors in the y -coordinates and that the x -coordinates are free of error. This is clearly not a good assumption for fitting isochrons because in geochronometry both the x - and y -coordinates have analytical errors.

The preferred method of calculating the slope and intercept of the isochron must take into account the known analytical errors of the coordinates of the data points on the isochron diagram. This is accomplished by the use of weighting factors that are calculated from the reciprocals of the analytical errors of each coordinate. The problem of fitting isochrons and of determining the best slope and intercept from analytical data has been treated elsewhere:

York, 1966, *Can. J. Phys.*, 46:1845–1847. McIntyre et al., 1966, *J. Geophys. Res.*, 71:5459–5468. York, 1967, *Earth Planet. Sci. Lett.*, 2:479–482. York, 1969, *Earth Planet. Sci. Lett.*, 5:320–324. Williamson, 1969, *Can. J. Phys.*, 46:1845–1847. Brooks et al., 1972, *Rev. Geophys. Space Phys.*, 10:551–577. Cameron et al., 1981, *Geochim. Cosmochim. Acta*, 45:1087–1097, and Powell et al., 2002, *Chem. Geol.*, 185:191–204

and additional references cited therein. Serious students of geochronometry may wish to acquire a copy of the *Geochronological Toolkit* prepared by Ludwig (2000).

4.3b Weighted Regression

The formulation of the weighted regression equation by York (1966, 1969) is based on minimizing a parameter S that is the weighted residual sum of squares of data points relative to a straight line $y = mx + b$ (Harmer and Eglinton, 1990). The value of this parameter is

$$S = \sum [(Y_i - mX_i - b)^2 Z_i] \quad (4.14)$$

where Y_i, X_i = measured values of the X and Y parameters of each data point

m = slope of the best-fit straight line

b = intercept on the Y -axis of the best-fit straight line

Z_i = weighting term for each sample in the regression

The parameter Z_i is defined by the equation

$$Z_i = \frac{W_X, W_Y}{m^2 W_Y + W_X - 2m r_i (W_X, W_Y)^{1/2}} \quad (4.15)$$

where W_X, W_Y = weighting factors for X - and Y -coordinates of any data point i

r_i = correlation between analytical errors of X and Y for any sample i

The weighting factors for the X - and Y -coordinates are expressed as

$$W_x \text{ or } y = \frac{1}{\sigma_x^2 \text{ or } y} \quad (4.16)$$

where σ^2 is the variance of the analytical errors of X and Y . Therefore Z_i can be expressed in terms of the analytical errors:

$$Z_i = \frac{1}{m^2 \sigma_{X_i}^2 + \sigma_{Y_i}^2 - 2mr_i \sigma_{X_i} \sigma_{Y_i}} \quad (4.17)$$

The regression line must pass through the weighted center of gravity of the measurements whose coordinates X_m and Y_m are

$$X_m = \frac{\sum(Z_i X_i)}{\sum Z_i} \quad (4.18)$$

$$Y_m = \frac{\sum(Z_i Y_i)}{\sum(Z_i)} \quad (4.19)$$

The slope of the weighted regression line obtained by minimizing the parameter S takes the form

$$m = \frac{\sum[Z_i^2 V_i (U_i/W_{Y_i} + m V_i/W_{X_i} - r_i V_i/\alpha_i)]}{\sum[Z_i^2 U_i (U_i/W_{Y_i} + m V_i/W_{X_i} - m r_i V_i/\alpha_i)]} \quad (4.20)$$

where

$$\alpha_i = (W_{X_i} W_{Y_i})^{1/2} \quad (4.21)$$

$$U_i = X_i - X_m \quad (4.22)$$

$$V_i = Y_i - Y_m \quad (4.23)$$

and all summations in equations 4.18–4.20 include all of the samples used in the regression (n).

Equation 4.20 must be solved by iteration, which means that the equation is first solved by substituting an estimated value of m into the right side of equation 4.20 and the results are used to refine m until the differences between successively calculated values are reduced to the desired level of precision.

The intercept b of the regression line is calculated from the equation

$$Y_m = mX_m + b \quad (4.24)$$

by substituting the best value of m obtained above and using the coordinates of the weighted center of gravity. Therefore,

$$b = Y_m - mX_m \quad (4.25)$$

The variances σ^2 of the slope and intercept of the weighted regression line are calculated from

$$(\sigma_m)^2 = \frac{1}{\sum(Z_i U_i^2)} \quad (4.26)$$

$$(\sigma_b)^2 = (\sigma_m)^2 \frac{\sum(Z_i X_i^2)}{\sum Z_i} \quad (4.27)$$

Note that Harmer and Eglington (1990) pointed out that equation 4.27 was incorrectly printed in the original formulation of York (1969, p. 323).

This presentation of the equations required to carry out a weighted regression of analytical data illustrates the fact that these calculations are laborious and therefore require the use of appropriate computer software. All of the currently active research groups engaged in geochronometry by the abundances of stable radiogenic isotopes use computer programs that, in many cases, are based on the equations of York (1966, 1969). Some of the computer codes being used were originally provided by D. York (University of Toronto), G. A. McIntyre (CSIRO, Canberra), I. Wendt (Bundesanstalt für Bodenforschung, Hannover), and C. Brooks (Carnegie Institution of Washington). The dates obtained from a given data set by these weighted regression codes may differ slightly in some cases because of differences in computational strategies and undocumented magnitudes of the analytical errors. Harmer and Eglington (1990) recommended that the calculation of dates by weighted-regression procedures should be standardized to permit accurate comparisons of dates reported by different laboratories. Computer codes that could be adopted for this purpose have been published by Eglington and Harmer (1989) and Ludwig (2000).

4.3c Goodness of Fit

The goodness of fit of a data set to a straight line is indicated by the *mean sum of weighted deviations* (MSWD), defined as

$$\text{MSWD} = \frac{S}{n-2} \quad (4.28)$$

where S is defined by equation 4.14, $n-2$ is the number of degrees of freedom of S , and n is the number of samples being regressed (Harmer and Eglington, 1990). The numerical value of MSWD calculated from equation 4.28 depends on both the number of samples being regressed (n) and the magnitudes of the analytical errors that determine the weighting factors used to calculate Z_i .

When the regression is based on a very large number of samples ($n = \infty$) and the analytical

errors are based on a large number of replicates, the value of the MSWD should be equal to or less than 1. In that case, the scatter of the data points above and below the best-fit line is consistent with the analytical errors of X and Y and the line is an isochron.

In cases where the number of samples and the number of replicates are both small, the limiting value of the MSWD required for the line to qualify as an isochron increases. Brooks et al. (1972) constructed a table that gives the expected values of MSWD at the 95 percent confidence limit for different values of the number of samples (n_s) and the number of replicates (n_r). For example, the table predicts that a well-defined isochron based on five samples and five replicates has an MSWD equal to 5.41 at the 95 percent confidence limit. In cases where the MSWD calculated from such a data set ($n_s = 5$, $n_r = 5$) is greater than 5.41, the scatter of the data points is greater than expected. In such cases, the deviations of the data points from

the best-fit line are caused not only by analytical errors but also by geological errors. In other words, the samples that were analyzed do not satisfy the assumptions of dating. In this case, the best-fit line is not an isochron and the date derived from it is not a reliable age determination. Instead, such lines are called "errorchrons" and dates derived from them are suspect.

The graph in Figure 4.3 demonstrates the relation between the limiting value of the MSWD and the number of samples n_s for different numbers of duplicates n_r . If the analytical errors are well known from a large number of duplicates (e.g., $n_r = 120$), then the limiting value of the MSWD for 10 samples is 2.02 at the 95 percent confidence limit. However, if only 10 duplicates were analyzed, the limiting MSWD is 3.07. The dependence of the limiting value of the MSWD on the number of replicates n_r requires that the magnitudes of analytical errors should be determined for each data set by replicating the

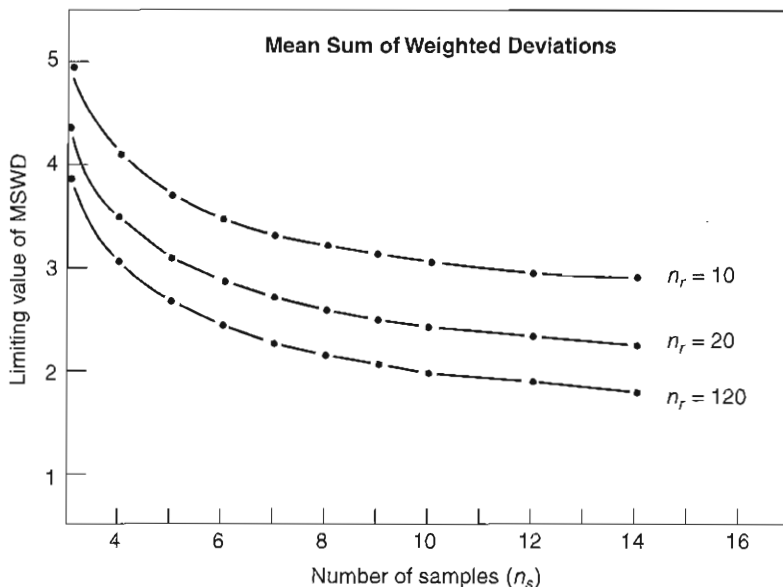


FIGURE 4.3 Dependence of the MSWD of isochrons defined by samples whose analytical errors account for the scatter of data points about the best-fit straight line at the 95 percent confidence limit. In cases where the MSWD calculated from equation 4.28 exceeds the limiting value of the MSWD for the same number of samples (n_s) and duplicates (n_r), the line is not an isochron but is called an errorchron and the date derived from it is questionable. Based on calculations by Brooks et al. (1972) and Harmer and Eglinton (1990).

analyses many times. This requirement is difficult to satisfy because of the excessive amount of analytical labor. Therefore, geochronometry laboratories assign analytical errors based on past experience and determine limiting values of MSWD for arbitrarily selected values of n , (e.g., 20, 40, 60).

In summary, the evaluation of the goodness of fit of a given data set to a best-fit line relies on the comparison between the MSWD calculated from equation 4.28 and a statistically predicted value of the MSWD whose magnitude depends on the number of samples and the number of replicates. This procedure becomes flawed when the magnitudes of the analytical errors associated with each sample are not determined by replication but are assigned on the basis of past experience.

4.4 MASS SPECTROMETRY AND ISOTOPE DILUTION

The development of isotopic methods of dating rocks and minerals was made possible by the invention of mass spectrometers in the early part of the twentieth century. The first instrument was built by J. J. Thomson at the Cavendish Laboratory of the University of Cambridge and was used to demonstrate that neon has two isotopes of differing masses ($^{20}_{10}\text{Ne}$ and $^{22}_{10}\text{Ne}$). Thomson's "positive-ray apparatus" used photographic emulsions to detect the neon isotopes and therefore was a mass spectrograph. Modern versions of this instrument use electronic methods of measuring the intensities of the ion beams and are called mass spectrometers.

Thomson's work was followed up by F. W. Aston in England and by A. J. Dempster at the University of Chicago. Aston (1919) and Dempster (1918) designed mass spectrographs they used in subsequent years to discover the naturally occurring isotopes of most of the elements in the periodic table and to measure their masses and their abundances. The design of mass spectrographs was further improved in the 1930s by K. T. Bainbridge, J. Mattauch, and R. Herzog. At the end of that decade, the work of discovering the naturally occurring isotopes of the elements and of measuring their masses and abundances was virtually complete. Since then, mass spectrometers have been employed in a wide range of research

problems in physics, chemistry, and biology. In addition, mass spectrometers based on a design by Nier (1940) made possible the measurement and interpretation of variations in the isotopic compositions of certain elements in natural materials and thus permitted the spectacular growth of isotope geology. The design of modern mass spectrometers has been treated by Duckworth (1958), McDowell (1963), Milne (1971), and others.

4.4a Principles of Mass Spectrometry

A mass spectrometer is an instrument designed to separate charged atoms and molecules on the basis of their masses based on their motions in magnetic fields. Most of the mass spectrometers currently in use in isotope geology have evolved from the work of Dempster and Bainbridge and follow the design of Nier (1940), whose mass spectrometers achieved a high level of accuracy and reliability of operation.

The modern Nier-type mass spectrometer consists of three essential parts: (1) a source of a monoenergetic beam of ions, (2) a magnetic analyzer, and (3) an ion collector, identified in Figure 4.4. All three parts of the mass spectrometer are evacuated to pressures of the order of 10^{-6} – 10^{-9} mm Hg. Both gaseous and solid samples can be analyzed, depending on the design of the ion source. For a mass analysis of a gaseous sample, such as Ar or CO_2 , the sample gas is allowed to leak into the source through a small orifice while the system is being pumped (dynamic analysis) or a small amount of gas is admitted into the mass spectrometer with the pump valves closed (static analysis). The molecules are then ionized by bombardment with electrons. The resulting positively charged ions are accelerated by a high-voltage electric field and are collimated into a beam by means of suitably spaced slit plates. For the mass analysis of solid samples, a salt of the element is deposited on a filament that is then mounted in the source. The filament (composed of Ta, Re, or W) is heated electrically to a temperature sufficient to volatilize the element to be analyzed. The high temperature of the evaporating filament or of an adjacent incandescent filament causes ionization of the atoms in the vapor. The resulting ions are then accelerated and collimated into a beam as before.