

## Chapter 2

# Geochronometric Models

### 2.1 Isochron Model

At closure of a parent–daughter system some (initial) quantity of daughter substance is frequently observed. The age definition becomes impossible. To make a detour around this difficulty, an isochron model is applied.

#### 2.1.1 Isochron Plane

Consider the isochron model for the Rb–Sr method that implies:

$$^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb}(e^{\lambda \cdot t} - 1)$$

The expression represents extensive values (i.e. concentrations). To get intensive values (i.e. ratios), divide the equation term by term into the quantity of the stable isotope  $^{86}\text{Sr}$ :

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}}(e^{\lambda \cdot t} - 1)$$

Obtain:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} - \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 - \frac{^{87}\text{Rb}}{^{86}\text{Sr}}(e^{\lambda \cdot t} - 1) = 0 \quad (2.1)$$

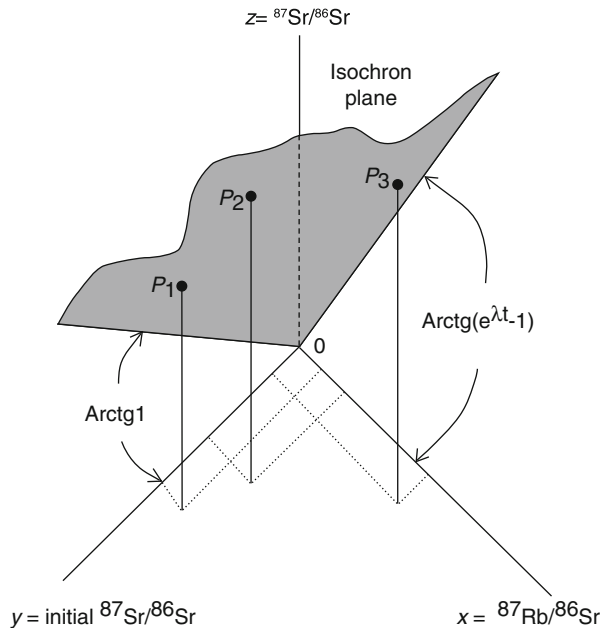
The modern  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios are accessible to measurements. The other two members of Eq. (2.1) remain unknown. Therefore, as a function of two variables, the age of a probe may be presented in a three-dimensional space:

$$z = F(x, y) \quad \text{or} \quad \Phi(x, y, z) = 0$$

Assume that measured ratios in three probes differ on initial strontium isotope ratios, but have an identical age, i.e. that they belong to a single isochron. Three data points  $P_1$ ,  $P_2$ , and  $P_3$  (Fig. 2.1) will define an isochron plane in space:

$$Cz - By - Ax = 0 \quad (2.2)$$

**Fig. 2.1** All data points of coeval probes lie on the isochron plane. Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of individual probes may differ



where

$$C = 1; \quad z = \frac{^{87}\text{Sr}}{^{86}\text{Sr}}; \quad B = 1; \quad y = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0; \quad A = (e^{\lambda \cdot t} - 1); \quad x = \frac{^{87}\text{Rb}}{^{86}\text{Sr}}$$

The track of the isochron plane on a coordinate plane  $yOz$  corresponds to  $^{87}\text{Sr}/^{86}\text{Sr} = \text{initial } ^{87}\text{Sr}/^{86}\text{Sr}$ , i.e. a straight line, which goes through the beginning of the coordinates with a slope equal to 1. Respectively, the track of the isochron plane on a coordinate plane  $xOz$  corresponds to  $^{87}\text{Sr}/^{86}\text{Sr} = (^{87}\text{Rb}/^{86}\text{Sr})(e^{\lambda \cdot t} - 1)$ , i.e. a straight line, which goes through the beginning of the coordinates with a slope  $\text{arctg}(e^{\lambda \cdot t} - 1)$ . Hence, *any data points of coeval probes always belong to a single isochron plane.*

Is it possible to determine an isochron plane by measurements of  $z = ^{87}\text{Sr}/^{86}\text{Sr}$  and  $x = ^{87}\text{Rb}/^{86}\text{Sr}$  for points  $x_1 z_1; x_2 z_2; x_3 z_3$ ?

Substitute the measured coordinates in Eq. (2.2):

$$\begin{aligned} z_1 - y_1 - Ax_1 &= 0 \\ z_2 - y_2 - Ax_2 &= 0 \\ z_3 - y_3 - Ax_3 &= 0 \end{aligned} \tag{2.3}$$

The point (0, 0, 0) (i.e. the origin of coordinates) lies in the isochron plane. The system of three equations (2.3) contains four unknowns:  $y_1$ ,  $y_2$ ,  $y_3$ , and  $A$ . While adding equations, we always get one more unknown. This approach to an isochron plane measurement cannot yield positive results. For solution, an additional ratio is required.

Take into account that the value of  $y_i$  cannot be less than the value of any other primary object in the Solar system. Such a value of  $0.698\,990 \pm 0.000\,047$  was referred to as BABI (Basaltic Achondrite Best Initial) by Papanastassiou and Wasserburg (1969). The initial  $A_{\max} = (z_0 - 0.699)/x_0$ , therefore, the least value among the obtained initial  $A_{\max}$  will define the largest possible age.

Further, note that the differences  $y_i$  are maintained at any  $y$ :

$$\frac{z_0 - 0.699}{x_0} = \frac{z_k - y_k}{x_k}$$

or

$$\frac{z_0}{x_0} - \frac{z_k}{x_k} = \frac{0.699}{x_0} - \frac{y_k}{x_k}$$

Thus, at any chosen  $A$ , one can estimate whether a difference in initial strontium ratio is available, i.e. whether the assumption about sin-genetic relations of samples is valid.

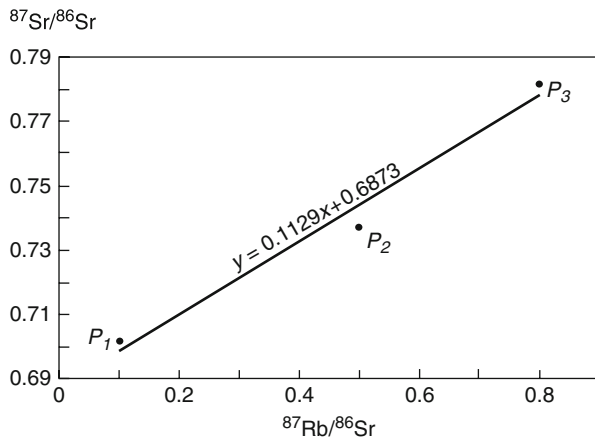
Further, we explain the specified features of the isochron model by a numerical example. Take a set of probes having the common age of 1 Ga  $A = e^{1.42 \cdot 10^{-10} \times 1 \cdot 10^9} - 1 = 1.4301 \cdot 10^{-2}$  and the following precisely calculated data:

	$x$	$y$	$z$	$A$
1	0.1	0.7	$7.0143 \cdot 10^{-1}$	$1.4301 \cdot 10^{-2}$
2	0.5	0.73	$7.3715 \cdot 10^{-1}$	$1.4301 \cdot 10^{-2}$
3	0.8	0.78	$7.8144 \cdot 10^{-1}$	$1.4301 \cdot 10^{-2}$

Make a projection of the data points of this system on a plane  $zOx$ . It will yield the usual rubidium–strontium isochron (Fig. 2.2). The data points are scattered and the regression line  $y = 0.1129x + 0.6873$  is defined as a fictitious value of the age:

$$t = \frac{1}{1.42 \cdot 10^{-11}} \ln(0.1142 + 1) = 7 \text{ Ga with initial } {}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.6873$$

**Fig. 2.2** Projection of points of the isochron plane on the  $xOz$  plane. This is an ordinary Rb–Sr isochron. In our case, due to extremely contrasting data, it determines a meaningless age of ca. 7 Ga and an underestimated initial strontium isotope ratio. These features may more or less exhibit themselves in cases of ordinary distorted Rb–Sr isochrons. The points do not lie on a straight line



Solve a reverse task:

$$A_{\max 1} = \frac{z_1 - 0.7}{x_1} = \frac{7.0143 \cdot 10^{-1} - 0.7}{0.1} = 1.43 \cdot 10^{-2}$$

$$A_{\max 2} = \frac{z_2 - 0.7}{x_2} = \frac{7.3715 \cdot 10^{-1} - 0.7}{0.5} = 7.43 \cdot 10^{-2}$$

$$A_{\max 3} = \frac{z_3 - 0.7}{x_3} = \frac{7.8144 \cdot 10^{-1} - 0.7}{0.8} = 1.018 \cdot 10^{-1}$$

$A_{\max 1}$ —the least of three values—lies close to the true value (in our case, it coincides with the true one, but this does not influence our conclusions).

The age  $t = (1/1.42 \cdot 10^{-11}) \ln(1.43 \cdot 10^{-2} + 1) = (1/1.42 \cdot 10^{-11}) \ln(1.43 \cdot 10^{-2} + 1) \approx 1$  Ga

The closeness to the true value is caused by specific initial data. Find the initial isotope ratios:

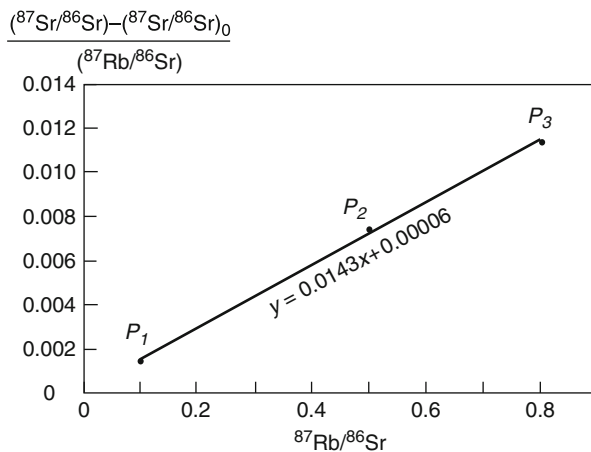
$$y_0 = z_0 - Ax_0$$

$$y_1 = z_1 - Ax_1 = 7.0143 \cdot 10^{-1} - 1.4301 \cdot 10^{-2} = 0.7$$

$$y_2 = 7.371 \cdot 10^{-1} - 7.1506 \cdot 10^{-3} = 0.73$$

$$y_3 = 7.8144 \cdot 10^{-1} - 1.144 \cdot 10^{-2} = 0.78$$

Find a track of the isochron plane, defined by new points, on a plane  $yOz$ . The regression line  $y = 0.0143x + 6 \cdot 10^{-5}$  (Fig. 2.3) with a value of multiplier  $x = 0.0143$ , designating a slope of a line relative to the axis of abscissa, determines an age  $t = (1/1.42 \cdot 10^{-11}) \ln(0.0143 + 1) \approx 1$  Ga. The small difference of the free member from zero is caused, obviously, by low precision of calculation. The initial isotope ratios with precisely fixed differences coincide with the given values.



**Fig. 2.3** A track of an isochron plane on the  $yOz$  plane. Three data points lie on a straight line, which is directed to the origin of the coordinates. The slope of the line determines an age of 1 Ga. A satisfactory approximation is obtained

At any quantity of coeval data points, the number of unknowns will exceed by one the number of equations. It is necessary to involve an age obtained by some other method or at least one initial ratio. Even the approximate solution is valuable in reaching a conclusion on differences of the initial isotope ratios that remain constant at any fictitious age. Therefore, the method of the isochron plane allows checking sin-genetic series of data points.

### 2.1.2 Common Rb–Sr Isochron

We have seen that after introduction of the requirement for synchronism to a set of data points, the system of the equations remains insoluble all the same. Enter one more condition: all points of the system should be sin-genetic, i.e. should have the same initial strontium isotope ratio:

$$z_1 - y - Ax_1 = 0$$

$$z_2 - y - Ax_2 = 0$$

$$z_n - y - Ax_n = 0$$

All points of this system should lie on one straight line:

$$z = Ax + y$$

The line has a slope  $A = e^{\lambda \cdot t} - 1$  and cuts a segment  $y$  on the axis of ordinate. The system becomes soluble. For its definition, one should know two points:  $x_1 z_1$  and  $x_2 z_2$ . Then:

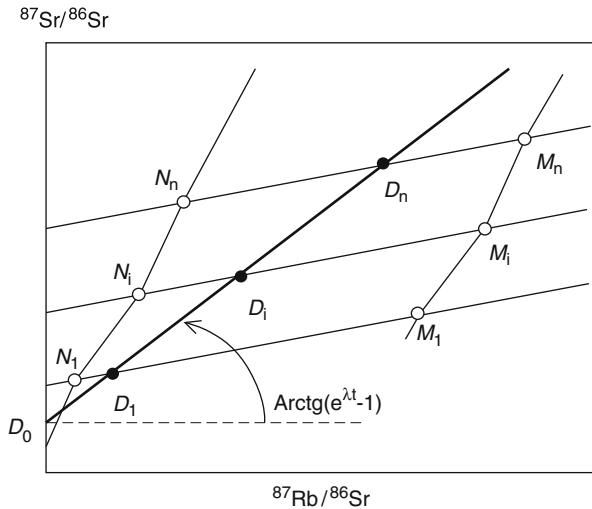
$$A = \frac{z_1 - z_2}{x_1 - x_2} \quad \text{and} \quad y = \frac{z_2 x_1 - z_1 x_2}{x_1 - x_2}$$

The isochron represents a projection of the data points on a plane  $xOz$ . This kind of two-dimensional isochron has been widely used for age determinations in all isotope systems.

Examine the geochronometric sense of isochrones, derived from whole-rock and mineral fractions (for example, granites and their micas, amphiboles etc.).

The locus of data points  $D_1, D_2, \dots, D_n$  of magmatic differentiates in the isochron coordinates of Fig. 2.4 is a straight line subjected to the equation  $^{87}\text{Sr}/^{86}\text{Sr} = (^{87}\text{Sr}/^{86}\text{Sr})_0 + (^{87}\text{Rb}/^{86}\text{Sr})(e^{\lambda \cdot t} - 1)$ . The intersection of the line with the axis of ordinates determines the initial strontium isotope ratio  $D_0$  and the slope of the line yields an age of the series. Whole-rock compositions define an external isochron that is not consistent with distribution of mineral points. The latter, designated as phases  $N_1, N_i, N_n$ , and  $M_1, M_i, M_n$  for respective samples, show isochrons with a gentle slope and elevated initial values. The slope of the mineral isochrons determines the moment of metamorphism, which has resulted in homogenization of the strontium isotope system in all mineral fractions of each probe  $D_i$ . Respectively, intersection of each mineral isochron with an axis of ordinates reflects the strontium isotope composition of the probe  $D_i$  at the moment of metamorphism.

**Fig. 2.4** Relation between whole-rock and intrinsic (mineral) isochrons in coordinates of the Rb–Sr isotope system



Hence, the isochron construction of minerals (for example, micas) from various differentiates is unacceptable. Crystallization of different fractions might differ and connecting data points of their minerals ( $N_1$ – $N_i$ – $N_n$ ;  $M_1$ – $M_i$ – $M_n$ ) by common lines can show misleading results.

We have considered ideal cases of points with fixed values. Actually, a researcher receives a series of points, each of which is characterized by an analytical error. In a regression line, the statistical model (most often the model of York (1969)) is used:

$$A = \frac{\sum_i Z_i^2 (y_i - \bar{y}) \left[ \frac{x_i - \bar{x}}{\omega(x_i)} + \frac{A(y_i - \bar{y})}{\omega(x_i)} - \frac{r_i(y_i - \bar{y})}{\alpha_i} \right]}{\sum_i Z_i^2 (x_i - \bar{x}) \left[ \frac{x_i - \bar{x}}{\omega(y_i)} + \frac{A(y_i - \bar{y})}{\omega(x_i)} - \frac{A r_i(y_i - \bar{y})}{\alpha_i} \right]}$$

where  $\omega_i(x_i) = 1/\sigma_{x_i}^2$ ,  $\omega_i(y_i) = 1/\sigma_{y_i}^2$ ,  $r_i$  – parameter of correlation between errors of the  $i$ -th measurements (calculated similar to the coefficient of linear correlation (Müller et al. 1982; Size 1987)):

$$\alpha_i = \sqrt{\omega(x_i)\omega(y_i)}, \quad \bar{x} = \frac{\sum Z_i x_i}{\sum Z_i}, \quad \bar{y} = \frac{\sum Z_i y_i}{\sum Z_i}, \quad Z = \frac{\alpha_i^2}{\omega(x_i) + \omega(y_i) - 2A r_i}$$

This equation is solved by iteration. Programs for use of the York algorithm are available in easily approached form (Ludwig 1990, 1999).

The isochron quality is estimated from values of Mean Squared Weighted Deviates (MSWD), representing the relation given from a line regression to the expected disorder calculated from correlation of errors. The data are interpreted in the framework of the isochron model, if  $\text{MSWD} = 1$ . Frequently, MSWD value exceeds 1, which means distortion of the measured values in comparison with their analytical errors,

probably because of unknown analytical problems or natural geologic scattering of data points. For rocks and minerals with distorted Rb–Sr isotope systems, more than four data points cannot yield an isochron with an acceptable MSWD value and, on the contrary, if  $\text{MSWD} \sim 1$ , the isotope system of the analyzed series of samples is not distorted (Kostitsyn 2002).

Brooks et al. (1972) showed that a regression line cannot be accepted as an isochron with a confidence interval of 95% at  $\text{MSWD} > 2.5$ . Taking into account this rule, researchers accept frequently as the true isochron a regression line with  $\text{MSWD} = 2.5$ . Actually, it is not correct, because this regression line corresponds to only 5% confidence (e.g. Dickin 1997). At a quantity of data points less than four, the MSWD value reveals a tendency to artificial understating depending on the particular algorithm used.

Besides the York algorithm, other ways of age calculations have been proposed (e.g. Faure 1989; Dickin 1997). For instance, Lepin and Brandt have suggested calculating ages for each separate pair of data points, taking into account their errors and displaying the received age values as probability functions (Makagon et al. 2000). Satisfactory results are obtained by simultaneous application of the York and Lepin–Brandt methods (Vladimirov et al. 2003).

## 2.2 Pb–Pb Isochron

In the Rb–Sr isotope system, we have seen that the isochron defines the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  with a low limit determined by BABI. For the Th, U–Pb system, the least isotope ratios were measured in a troilite of the meteorite Canyon Diablo (Tatsumoto et al. 1973):

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 = 9.307; \quad \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 = 10.294; \quad \left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_0 = 29.476$$

This lead, referred to as primeval, has never been in contact with uranium or thorium.

Assume that radiogenic leads began accumulating  $t$  years ago and before this moment had only primeval composition. Then the equations are valid:

$$\begin{aligned} \frac{^{207}\text{Pb}}{^{204}\text{Pb}} - 10.294 &= \frac{^{235}\text{U}}{^{204}\text{Pb}}(e^{\lambda_{5t}} - 1) \\ \frac{^{206}\text{Pb}}{^{204}\text{Pb}} - 9.307 &= \frac{^{238}\text{U}}{^{204}\text{Pb}}(e^{\lambda_{8t}} - 1) \end{aligned}$$

Dividing the former ratio by the latter and taking into account  $^{238}\text{U}/^{235}\text{U} = 137.88$ , we obtain a transcendent equation:

$$\frac{^{207}\text{Pb} - 10.294}{^{206}\text{Pb} - 9.307} = \frac{e^{\lambda_{5t}} - 1}{137.88(e^{\lambda_{8t}} - 1)}$$

For age definition, this method requires measurements of only one pair of isotope ratios for one probe:  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$ .

In this respect, the model is elementary. Assumption of equality of the initial lead to primeval values is not substantiated, however. Therefore, the method has not received a wide distribution. The only exception is dating of Ca–Al inclusions in the meteorite Allende on fractions enriched by radiogenic isotopes (Allègre et al. 1995).

Assume now that a captured lead had some composition at the moment of a system closure. Enter designations:

$$\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} = a; \quad \frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} = b; \quad \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} = c$$

Designate the appropriate initial ratios by an index “0”. Then:

$$a - a_0 = \frac{c}{137.88}(e^{\lambda_{5t}} - 1); \quad b - b_0 = c(e^{\lambda_{8t}} - 1)$$

Express  $c$  and combine the equations:

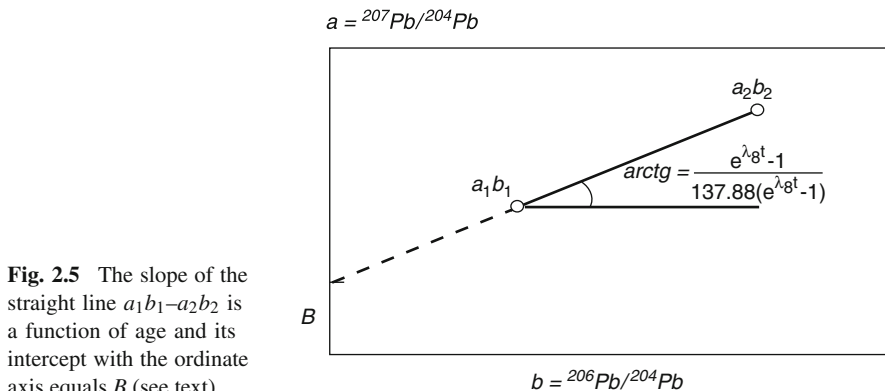
$$c = \frac{137.88(a - a_0)}{e^{\lambda_{5t}} - 1} = \frac{b - b_0}{e^{\lambda_{8t}} - 1}$$

After transformations, we obtain:

$$a = kb + a_0 - kb_0 = kb + B$$

The equation corresponds to a straight line that has a slope  $k = (e^{\lambda_{8t}} - 1)/137.88(e^{\lambda_{5t}} - 1)$  and cuts a segment  $B$  on an axis of ordinates (Fig. 2.5).

The locus of data points  $a = f(b)$  in the isochron and sin-genetic uranium–lead system is a straight line that can be defined by two pairs of data points:  ${}^{207}\text{Pb}/{}^{204}\text{Pb} = a$ ;  ${}^{206}\text{Pb}/{}^{204}\text{Pb} = b$ . Such an isochron does not give, however, an opportunity to define values, which are included in the expression for initial values:  $a_0$  and  $b_0$ . The latter has no practical application.



**Fig. 2.5** The slope of the straight line  $a_1b_1$ – $a_2b_2$  is a function of age and its intercept with the ordinate axis equals  $B$  (see text)



### 2.3 Concordia–Discordia Model

This model has been developed for isotopes of U and Pb. Uranium consists of two radioactive isotopes:  $^{235}\text{U}$  and  $^{238}\text{U}$ . The former turns to  $^{207}\text{Pb}$  through a series of radioactive nuclides, releasing  $(235 - 207)/4 = 7\alpha$ -particles with the constant  $\lambda_5 = 9.8 \cdot 10^{-10}$ . The latter turns to  $^{206}\text{Pb}$  with similar releasing  $(238 - 206)/4 = 8\alpha$ -particles with the constant  $\lambda_8 = 1.55 \cdot 10^{-10}$  (Jaffey et al. 1971). The present-day uranium has  $^{238}\text{U}/^{235}\text{U} = 137.88$ . Temporally, this ratio is growing. Both isotopes of uranium are closely connected to each other in kinetic processes due to the value  $\sqrt{238/235} = 1.0063$ , which is close to 1.

Similarity of the isotope properties assumes coincidence of age values calculated from  $^{207}\text{Pb}/^{235}\text{U}$  and  $^{206}\text{Pb}/^{238}\text{U}$  ratios. Discordant values, obtained in practice, have resulted in development of the Concordia–Discordia model.

This model describes an open system with losses of radiogenic lead in accessory minerals (zircons, monazites, apatites etc.) assuming their crystallization during any geologic process (magmatic, metamorphic etc.).

We deduce the basic relations. As a parametric curve of the consent, the Concordia means a locus of equal ages in coordinates:

$$x = \frac{^{206}\text{Pb}}{^{238}\text{U}} = e^{\lambda_8 t} - 1; \quad y = \frac{^{207}\text{Pb}}{^{235}\text{U}} = e^{\lambda_5 t} - 1 \quad (2.4)$$

The parameter is the age (Fig. 2.6). This line has essential curvature.

Practical measurements have revealed the tendency to a discordant arrangement of data points (points showing various ages on axes  $x$  and  $y$ ) along straight lines intersecting the Concordia that is unexpected for the system subjected to complex transcendent dependences. The suggested explanations are known as the Wetherill and Wasserburg models.

The Wetherill model assumes that zircons, accumulated radiogenic lead since  $t_1$  (Fig. 2.6), were subjected to a metamorphic impact  $t_2$ , at which they lost radiogenic lead partially or completely, whereas some zircons kept the radiogenic lead of the point  $t_1$ .

Where will be the point of the zircon in case of complete loss of radiogenic lead? To find out, consider the expression (2.4) as:

$$^{206}\text{Pb} = ^{238}\text{U}_0(1 - e^{-\lambda_8 t}) \text{ and } ^{207}\text{Pb} = ^{235}\text{U}_0(1 - e^{-\lambda_5 t}) \quad (2.5)$$

The loss of lead  $t_2$  years ago resulted in:

$$^{238}\text{U}_0(1 - e^{-\lambda_8(t_1 - t_2)}); \quad ^{235}\text{U}_0(1 - e^{-\lambda_5(t_1 - t_2)})$$

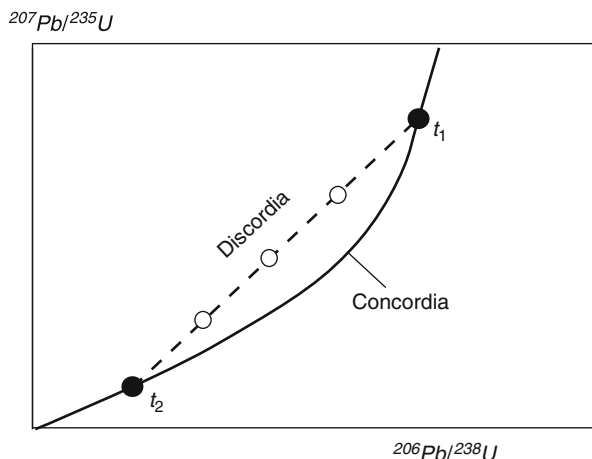
Subtract the loss from the expression (2.5):

$$^{206}\text{Pb} = ^{238}\text{U}_0(1 - e^{-\lambda_8 t_1} - 1 + e^{-\lambda_8(t_1 - t_2)}) = ^{238}\text{U}_0(e^{-\lambda_8(t_1 - t_2)} - e^{-\lambda_8 t_1})$$

and

$$^{207}\text{Pb} = ^{235}\text{U}_0(1 - e^{-\lambda_5 t_1} - 1 + e^{-\lambda_5(t_1 - t_2)}) = ^{235}\text{U}_0(e^{-(t_1 - t_2)} - e^{-\lambda_5 t_1})$$

**Fig. 2.6** Concordia diagram. The Concordia is a parametric locus of equal  $^{207}\text{Pb}/^{235}\text{U}$  and  $^{206}\text{Pb}/^{238}\text{U}$  ages. Filled circles on the Concordia show an age  $t_1$  for crystallization of a system that had experienced a metamorphic impact at an instant  $t_2$  with total loss of radiogenic lead. Open circles on a straight line correspond to portions of 25, 50, and 75% of radiogenic lead losses



Proceed now to modern uranium:  ${}^iUe^{\lambda_i t} = {}^iU_0$  and we get:

$$\frac{{}^{206}\text{Pb}}{{}^{238}\text{U}} = e^{\lambda_8 t_2} - 1; \frac{{}^{207}\text{Pb}}{{}^{235}\text{U}} = e^{\lambda_5 t_2} - 1$$

We see that the point of the probes, which have lost all radiogenic lead at the time of the metamorphic impact, lies on the Concordia and marks the moment of loss  $t_2$ .

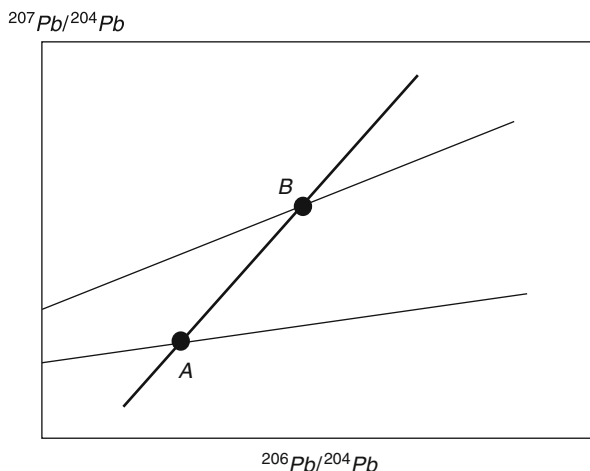
Where will be the intermediate points that have lost 25, 50, and 75% of radiogenic lead? According to the accepted hypothesis, the loss of the isotopes  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  took place instantly and congruently. Therefore, allocation will occur along a straight line connecting the points  $t_1$  and  $t_2$  (Fig. 2.6). In general, lead, possessing a small ion radius, is extremely mobile in host Si-, OH-structures, entering as a ligand into an alloy of intrusion, not an alloy of replacement. This very property is used in the model. The manuals on geochronometry show many examples of complete conformity of the model to the requirements. However, experience has shown even more often deviations from the model.

First of all, it concerns the lower intersection of the Concordia and Discordia (point  $t_2$  in Fig. 2.6). It is not observed frequently and is not substantiated by any geologic evidence. No traces of the late metamorphic influence are detected. Respectively, the alternative (Wasserburg) model that was based on diffusion of lead from zircons without the lower intersection has been proposed (Chap. 14).

Data points could reveal also significant dispersion without reference to any line. This requires explanations by involvement of multiple metamorphic impacts, which can complicate searching of possible concordant ages.

Now consider a series of probes corresponding to an isochron in coordinates:  ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ ;  ${}^{207}\text{Pb}/{}^{204}\text{Pb}$ . What geometrical image will the series represent in coordinates:  ${}^{206}\text{Pb}/{}^{238}\text{U}$ ;  ${}^{207}\text{Pb}/{}^{235}\text{U}$ ? And on the contrary, consider a series of probes that precisely meets the Discordia by two intersections with the Concordia. What

**Fig. 2.7** Interpretation of data points of the U–Pb coordinates on the Pb–Pb diagram shows a relation between isochrones corresponding to the older and younger Concordia ages (respectively, thin lines B and A) and fictitious overestimated age derived from the Discordia (heavy line AB)



geometrical image will it represent in coordinates:  $^{206}\text{Pb}/^{204}\text{Pb}$ ;  $^{207}\text{Pb}/^{204}\text{Pb}$ ? Can we tell whether these images make sense?

The name “isochron” itself presumes a locus of data points displaying the same age. From definition of the Discordia by a parameter “age”, a set of isochron points will represent a unique point of repeatability  $i$ .

Consider a case when the points belong to the two-stage Discordia  $t_1 t_2$  (Fig. 2.6). The point  $t_2$  corresponds to the younger concordant age and will belong to an isochron with a smaller slope  $A$  in Pb–Pb coordinates (Fig. 2.7). The point  $t_1$  corresponds to the older concordant age and will lie, therefore, on the steeper isochron  $B$ . The line  $AB$  has a steeper slope than either isochron. If the experimenter derives an age from the line  $AB$  in Fig. 2.7, he will receive some fictitious overestimated age value, which has no geochronological sense.

Radiogenic Pb is formed in monazite, zircon, apatite, and other accessory minerals due to radioactive decay of Th and U. The lead quantity depends on time. Is it possible to calculate age precisely by measurements in such minerals with only U, Th, and Pb concentrations?

An isotopic age was first calculated this way by Boltwood in 1907. Later on, ages were calculated from Th, U, and Pb concentrations using the procedure of Th translation to an equivalent quantity of U by multiplying constants  $\lambda_U$  and  $\lambda_{\text{Th}}$ . Up to 200 million years, approximate ages were obtained with diversity about 2%. The older ages were calculated with corrections for: (1) daughter nuclides formed due to decay in the actinium series, which ends with stable  $^{207}\text{Pb}$ , (2) decay of parent substance for the passed time, and (3) various rates of decay for U and Th, resulting in wrong values of their equivalent expression. From experience, it was inferred that age determinations by the U–Pb method without isotope analysis of Pb did not yield reliable results (Starik 1961).

Recently, age determinations were reported again using high quality microprobe analyses. The developed Chemical Isochron Method (CHIME) was based on assumed

relative variations of Th, U, and Pb on the Concordia. The complete deduction of equations for age calculations and results of dating were reported by Suzuki et al. (1991, 1994, 1996) and Suzuki and Adachi (1994):

$$^{208}\text{Pb}_{\text{rad}} = ^{208}\text{Pb}_{\text{init}} + ^{232}\text{Th}(\exp(\lambda_{232}t) - 1) \quad (2.6)$$

$$^{207}\text{Pb}_{\text{rad}} = ^{207}\text{Pb}_{\text{init}} + ^{235}\text{U}(\exp(\lambda_{235}t) - 1) \quad (2.7)$$

$$^{206}\text{Pb}_{\text{rad}} = ^{206}\text{Pb}_{\text{init}} + ^{238}\text{U}(\exp(\lambda_{238}t) - 1) \quad (2.8)$$

where  $\lambda_{232}$ ,  $\lambda_{235}$ , and  $\lambda_{238}$  are decay constants of  $^{232}\text{Th}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ , respectively. The total concentration of lead in a mineral is the sum of all lead isotopes:

$$\text{Pb} = ^{208}\text{Pb}_{\text{init}} + ^{208}\text{Pb}_{\text{rad}} + ^{207}\text{Pb}_{\text{init}} + ^{207}\text{Pb}_{\text{rad}} + ^{206}\text{Pb}_{\text{init}} + ^{206}\text{Pb}_{\text{rad}} \quad (2.9)$$

Taking into account the ratio  $^{235}\text{U}/^{238}\text{U} = 137.88$  (except for natural nuclear reactor Oklo), the Eqs. (2.6–2.9) are transformed to equation:

$$\text{Pb} = \text{Pb}_{\text{ini}} + \text{Th} \times \left[ \frac{\exp(\lambda_{235}t) + 137.88 \exp(\lambda_{238}t)}{138.88} - 1 \right] \quad (2.10)$$

For the measured concentrations of  $\text{UO}_2$ ,  $\text{ThO}_2$ , and  $\text{PbO}$  (wt%) in the mineral (neglecting initial concentration of lead ( $\text{Pb}_{\text{init}}$ ), at first approximation), the Eq. (2.10) is transformed to the equation:

$$\begin{aligned} \frac{\text{PbO}}{W_{\text{Pb}}} &= \frac{\text{ThO}_2}{W_{\text{Th}}} (\exp(\lambda_{232}t_{\text{app}}) + 1) + \frac{\text{UO}_2}{W_{\text{U}}} \\ &\times \left( \frac{\exp(\lambda_{235}t_{\text{app}}) + 137.88 \exp(\lambda_{238}t_{\text{app}})}{138.88} - 1 \right) \end{aligned} \quad (2.11)$$

where  $W$  – molecular mass of each oxide ( $W_{\text{Pb}} = 224$ ,  $W_{\text{Th}} = 264$ , and  $W_{\text{U}} = 270$ ), and  $t_{\text{app}}$  – apparent age estimate without taking into account initial lead concentrations. The designed apparent age is used for estimation of initial concentration of  $\text{ThO}_2$  or  $\text{UO}_2$ , respectively, for monazite or zircon:

$$\begin{aligned} ^*\text{ThO}_2 &= \text{ThO}_2 + \frac{\text{UO}_2 W_{\text{Th}}}{W_{\text{U}} (\exp(\lambda_{232}t_{\text{app}}) - 1)} \\ &\times \left( \frac{\exp(\lambda_{235}t_{\text{app}}) + 137.88 \exp(\lambda_{238}t_{\text{app}})}{138.88} - 1 \right) \end{aligned} \quad (2.12)$$

or

$$^*\text{UO}_2 = \text{UO}_2 + \frac{138.88 \times \text{ThO}_2 W_{\text{U}} (\exp(\lambda_{232}t_{\text{app}}) - 1)}{W_{\text{Th}} (\exp(\lambda_{235}t_{\text{app}}) + 137.88 \exp(\lambda_{238}t_{\text{app}}) - 138.88)} \quad (2.13)$$

If coeval monazites or zircons have identical concentrations of  $\text{Pb}_{\text{init}}$ , in coordinates  $\text{PbO}$  (wt%) –  $^*\text{ThO}_2$  (wt%) or  $\text{PbO}$  (wt%) –  $^*\text{UO}_2$  (wt%), data points fall on a straight line, where  $^*\text{ThO}_2$  – sum of  $\text{ThO}_2$  that was measured and calculated as

equivalent to the quantity of formed radiogenic particles of lead to the measured  $UO_2$  or, respectively,  $*UO_2$  – sum of  $UO_2$  that was measured and calculated as equivalent to the quantity of formed radiogenic particles of lead to the measured  $ThO_2$ .

For the first approximation, the slope of a line ( $m$ ) corresponds to the age of a mineral crystallization or time of complete homogenization of the isotope system:

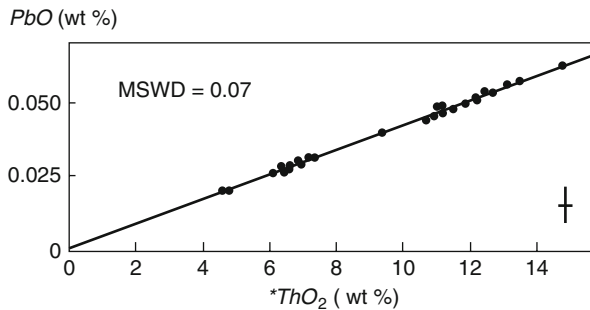
$$t = \frac{1}{\lambda_{232}} \ln \left( 1 + m \frac{W_{Th}}{W_{Pb}} \right) \quad (2.14)$$

or

$$m \frac{W_U}{W_{Pb}} = \frac{\exp(\lambda_{235}t) + 137.88 \exp(\lambda_{238}t_{app})}{138.88} \quad (2.15)$$

For the second approximation, the obtained age  $t$  is substituted in the appropriate equation (2.12) or (2.13). Iteration is done up to coincidence of  $t_{app}$  and  $t$ . Concentration of initial lead in a mineral is obtained from intersection of the regression line with an axis  $PbO$  (wt%). Any distortion of Th, U–Pb isotope system results in loss of data point linearity.

Monazites of a gneiss, sampled from the Ryoke metamorphic belt (southwest Japan), showed intervals of  $ThO_2$  2.7–9.8 wt%,  $UO_2$  0.4–3.3 wt%, and  $PbO$  0.020–0.056 wt%. Concentrations of thorium and uranium oxides were recalculated to conventional units  $*ThO_2$ . Linearity of points in  $PbO$  –  $*ThO_2$  coordinates was obtained with a low MSWD value (Fig. 2.8). The slope of the line with the age of  $98.9 \pm 2.1$  Ma was interpreted as timing of metamorphism. Similar data were obtained for zircons in coordinates of lead and conventional uranium (Suzuki et al. 1996).



**Fig. 2.8** Isochron plot for monazites of a gneiss from the Ryoke metamorphic belt (SW Japan) (Suzuki et al. 1996).  $*ThO_2$  is the sum of  $ThO_2$  measured and of  $ThO_2$  equivalent to  $UO_2$ . 36 analyses on 20 monazite grains were performed. In the lower right corner of the diagram, the interval of analytic uncertainty ( $2\sigma$ ) of measurements is shown. For age calculations without determination of Pb isotope ratios on presented relations between parent and daughter substances, however, additional corrections are required (Starik 1961). This isochron age is overestimated as compared with the Concordia age

A prominent feature of the Th, U–Pb system is its open evolution. The CHIME measurements do not provide any criterion for concordant age relations. Therefore, linearity might have a discordant nature. As shown on Fig. 2.7, U and Pb isotopes, controlled in accessory minerals by the Concordia–Discordia model, yield discordant linearity of data points with the fictitious overestimated age.

Direct comparisons between results obtained by the Concordia–Discordia and Chemical Isochron methods have never been done. For such purpose, we used concentrations of U, Th, and Pb measured in five monazites of the Proterozoic migmatites from the Grand Canyon, Arizona, USA (UG–78.0–6) (Hawkins and Bowring 1999). The data points of the fractions, obtained by air abrasion of grains, have given an interval of the oldest  $^{207}\text{Pb}/^{206}\text{Pb}$  ages from 1706 to 1698 Ma. Using the Eqs. (2.12–2.15) on a linear series of points, we have calculated an unreal age of 17 Ga.

On the one hand, the CHIME dating does not assume corrections required for age calculations from element concentrations. On the other hand, the results of age calculations from microprobe data are useful for age estimates of samples younger than 200 Ma (Starik 1961). The results of measurements, performed by this method by Suzuki et al, largely for the late Mesozoic magmatic and metamorphic rocks of southwest Japan, have been interpreted in general agreement with results obtained by other isotope systems.

## 2.4 Summary: Models for Open and Closed Parent–Daughter Systems

Geochronometry is based on the preserved conformity between parent and daughter nuclides, satisfying the Law of Radioactivity of Rutherford–Soddy. The conformity must be substantiated by models applied both to open and closed isotope systems.

For the open system, reliable dating is provided by the U–Pb method with interpretation of data points for accessory minerals in the Concordia–Discordia model. This model is applied to an isotope system, in which not less than two nuclides of one element transform to nuclides of another element. Ages are determined through comparisons of results on kinetically equivalent pairs of nuclides. In interpretation of the Discordia as an isochron, the age is overestimated.

For the closed system, data points are interpreted in terms of an isochron model that assumes two unknown variables: the age and the initial isotope ratio. In three-dimensional coordinates, all data points of coeval probes belong to a single isochron plane, which, however, cannot be constructed a priori. We have not found a way of direct calculations of the plane from the measured data, because the number of unknowns exceeds by one the number of equations at any quantity of probes. To present interpretation at the isochron plane, one should know the age or the initial ratio for at least one probe. Conventionally, data on the closed system are interpreted in isochron coordinates representing a projection of data points on the plane  $xOz$ . For practical purposes, reliability of the isochron model is estimated statistically in terms of data point deviations using the algorithm of York and other approaches.

Radiogenic Isotopes in Geologic Processes

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2010, XIII, 306 p., Hardcover

ISBN: 978-90-481-2998-0