

1 Constants

1.1 Molar mass

H: 1.00794, He: 4.002602, C: 12.0107, O: 15.9994, Al: 26.98154, Si: 28.0855, K: 39.0983, Ar: 39.948, Ca: 40.078, Rb: 85.4678, Sr: 87.62, I: 126.904, Xe: 131.293, Nd: 144.242, Sm: 150.36, Eu: 151.964, Lu: 174.967, Hf: 178.49, W: 183.84, Re: 186.207, Os: 190.23, Pb: 207.2, Th: 232.04, U: 238.04

1.2 Isotopic ratios

K: $^{40}\text{K}/\text{K} = 0.01167\%$
 Ar: $^{40}\text{Ar}/^{36}\text{Ar} (\text{atm}) = 298.5$; $^{38}\text{Ar}/^{36}\text{Ar} = 0.187$
 Rb: $^{85}\text{Rb}/^{87}\text{Rb} = 2.59337$
 Sr: $^{84}\text{Sr}/^{86}\text{Sr} = 0.056584$; $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$
 Sm: $^{147}\text{Sm}/\text{Sm} = 14.99\%$
 U: $^{238}\text{U}/^{235}\text{U} = 137.818$;
 $\text{A}(^{234}\text{U})/\text{A}(^{238}\text{U})[\text{modern ocean}] \approx 1.15$.

1.3 Half-lives and decay constants

C: $t_{1/2}(^{14}\text{C}) = 5730 \text{ yr}$
 K: $\lambda_{\beta^-} = 4.962 \times 10^{-10} \text{ yr}^{-1}$; $\lambda_e = 0.581 \times 10^{-10} \text{ yr}^{-1}$;
 $t_{1/2}(e + \beta^-) = 1.248 \text{ Gyr}$
 Rb: $t_{1/2}(^{87}\text{Rb}) = 48.8 \text{ Gyr}$
 Sm: $t_{1/2}(^{147}\text{Sm}) = 106 \text{ Gyr}$
 U: $t_{1/2}(^{238}\text{U}) = 4.468 \text{ Gyr}$; $t_{1/2}(^{235}\text{U}) = 703.8 \text{ Myr}$;
 $t_{1/2}(^{234}\text{U}) = 245.5 \text{ kyr}$; $\lambda_f = 8.46 \times 10^{-17} \text{ yr}^{-1}$
 Th: $t_{1/2}(^{232}\text{Th}) = 14.05 \text{ Gyr}$; $t_{1/2}(^{230}\text{Th}) = 75.38 \text{ kyr}$

2 Basic notions

2.1 Radioactivity

The decay equation:

$$\frac{dP}{dt} = -\lambda P \quad (1)$$

Its solution:

$$P = P_0 e^{-\lambda t} \quad (2)$$

The fundamental age equation:

$$t = \frac{1}{\lambda} \ln \left(\frac{D^*}{P} + 1 \right) \quad (3)$$

where D^* marks the radiogenic daughter component. Half-life vs. decay constant:

$$\frac{P_0}{2} = P_0 e^{-\lambda t_{1/2}} \Rightarrow t_{1/2} = \frac{\ln(2)}{\lambda} \quad (4)$$

2.2 Decay series

$$\text{for } P: dP/dt = -\lambda_P P \quad (5)$$

$$\text{for } D_1: dD_1/dt = \lambda_P P - \lambda_1 D_1 \quad (6)$$

$$\text{for } D_*: dD_*/dt = \lambda_1 D_1 \quad (7)$$

Assuming that $D_1 = 0$ at $t = 0$:

$$D_1 = \frac{\lambda_P}{\lambda_1 - \lambda_P} P_0 [e^{-\lambda_P t} - e^{-\lambda_1 t}] \quad (8)$$

Secular equilibrium:

$$D_1 \lambda_1 = P \lambda_P \quad (9)$$

or, equivalently:

$$\frac{P}{D_1} = \frac{t_{1/2}(P)}{t_{1/2}(D_1)} \quad (10)$$

3 Analytical techniques

3.1 Mass spectrometry

Kinetic energy of single-charged ion of m a.m.u. in a mass spectrometer:

$$E = eV = \frac{mv^2}{2} \quad (11)$$

With $e = 1.60219 \times 10^{-19} \text{ C}$ and $1 \text{ a.m.u.} = 1.660538 \times 10^{-27} \text{ kg}$. The mass analyser deflects the ions according to the following equation:

$$Hev = \frac{mv^2}{r} \quad (12)$$

from which it follows that:

$$r = \frac{1}{H} \sqrt{\frac{2mV}{e}} \quad (13)$$

3.2 Isotope dilution

Will not be part of the exam.

3.3 Sample-standard bracketing

Will not be part of the exam.

4 Simple parent-daughter pairs

4.1 ^{14}C dating

$$\frac{d^{14}\text{C}}{dt} = -\lambda_{14} \times ^{14}\text{C} \quad (14)$$

where $\lambda_{14} = 0.120968 \text{ kyr}^{-1}$.

$$t = -\frac{1}{\lambda_{14}} \ln \left[\frac{d^{14}\text{C}/dt}{(d^{14}\text{C}/dt)_0} \right] \quad (15)$$

4.2 The Rb-Sr method

Ingrowth equation:

$$^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb}(e^{\lambda_{87}t} - 1) \quad (16)$$

where $^{87}\text{Sr}_0$ is the initial ^{87}Sr content. $^{87}\text{Rb}/^{86}\text{Sr}$ -ratio is calculated as:

$$\frac{^{87}\text{Rb}}{^{86}\text{Sr}} = \frac{\text{Rb}}{\text{Sr}} \frac{Ab(^{87}\text{Rb})M(\text{Sr})}{Ab(^{86}\text{Sr})M(\text{Rb})} \quad (17)$$

where $Ab(\cdot)$ signifies ‘abundance’.

4.3 Isochrons

The universal isochron equation:

$$\frac{D}{d} = \left(\frac{D}{d} \right)_0 + \frac{P}{d} (e^{\lambda_P t} - 1) \quad (18)$$

where P = the parent isotope, D = the daughter isotope, d = a non-radiogenic sister isotope of the radiogenic daughter. For the Rb-Sr method:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda_{87}t} - 1) \quad (19)$$

4.4 The Sm-Nd method

The age equation:

$$^{143}\text{Nd} = ^{143}\text{Nd}_o + ^{147}\text{Sm}(e^{\lambda_{147}t} - 1) \quad (20)$$

Isochron equation:

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}} = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_o + \frac{^{147}\text{Sm}}{^{144}\text{Nd}} (e^{\lambda_{147}t} - 1) \quad (21)$$

5 The U-Pb system

$$\begin{aligned} ^{238}\text{U} &\rightarrow ^{206}\text{Pb} + 8\alpha + 6\beta + 47\text{MeV} \\ ^{235}\text{U} &\rightarrow ^{207}\text{Pb} + 7\alpha + 4\beta + 45\text{MeV} \\ ^{232}\text{Th} &\rightarrow ^{208}\text{Pb} + 6\alpha + 4\beta + 40\text{MeV} \end{aligned} \quad (22)$$

6 The U-(Th-)Pb method

Ingrowth equations:

$$\begin{aligned} ^{206}\text{Pb}^* &= ^{238}\text{U}(e^{\lambda_{238}t} - 1) \\ ^{207}\text{Pb}^* &= ^{235}\text{U}(e^{\lambda_{235}t} - 1) \\ ^{208}\text{Pb}^* &= ^{232}\text{Th}(e^{\lambda_{232}t} - 1) \end{aligned} \quad (23)$$

where $^{20x}\text{Pb}^*$ is the radiogenic ^{20x}Pb component ($^{20x}\text{Pb} = ^{20x}\text{Pb}^* + ^{20x}\text{Pb}_o$). The corresponding age equations are:

$$\begin{aligned} t_{206} &= \frac{1}{\lambda_{238}} \ln \left(\frac{^{206}\text{Pb}^*}{^{238}\text{U}} + 1 \right) \\ t_{207} &= \frac{1}{\lambda_{235}} \ln \left(\frac{^{207}\text{Pb}^*}{^{235}\text{U}} + 1 \right) \\ t_{208} &= \frac{1}{\lambda_{232}} \ln \left(\frac{^{208}\text{Pb}^*}{^{232}\text{Th}} + 1 \right) \end{aligned} \quad (24)$$

with common Pb correction:

$$\begin{aligned} t_{206} &= \frac{1}{\lambda_{238}} \ln \left(\frac{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right) - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\frac{^{238}\text{U}}{^{204}\text{Pb}}} + 1 \right) \\ t_{207} &= \frac{1}{\lambda_{235}} \ln \left(\frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right) - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\frac{^{235}\text{U}}{^{204}\text{Pb}}} + 1 \right) \\ t_{208} &= \frac{1}{\lambda_{232}} \ln \left(\frac{\left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}} \right) - \left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\frac{^{232}\text{Th}}{^{204}\text{Pb}}} + 1 \right) \end{aligned} \quad (25)$$

6.1 The Pb-Pb method

Age equation:

$$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right) - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right) - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_o} = \frac{1}{137.818} \frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1} \quad (26)$$

where $^{238}\text{U}/^{235}\text{U} = 137.818$. For modern samples:

$$\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_p^* = \frac{\lambda_{235}}{137.818\lambda_{238}} = 0.04607 \quad (27)$$

7 The K-Ar system

Ingrowth equation:

$$\begin{aligned} ^{40}\text{Ar} &= ^{40}\text{Ar}_o + ^{40}\text{Ar}^* \\ \text{where } ^{40}\text{Ar}^* &= \frac{\lambda_e}{\lambda} ^{40}\text{K}(e^{\lambda t} - 1) \end{aligned} \quad (28)$$

7.1 K-Ar dating

Age equation:

$$t = \frac{1}{\lambda} \ln \left[1 + \frac{\lambda}{\lambda_e} \left(\frac{^{40}\text{Ar}^*}{^{40}\text{K}} \right) \right] \quad (29)$$

Isochron equation:

$$\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_o + \frac{\lambda_e}{\lambda} \frac{^{40}\text{K}}{^{36}\text{Ar}} (e^{\lambda t} - 1) \quad (30)$$

7.2 $^{40}\text{Ar}/^{39}\text{Ar}$ dating

Sample:

$$t_x = \frac{1}{\lambda} \ln \left[1 + J \left(\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} \right)_x \right] \quad (31)$$

Standard:

$$t_s = \frac{1}{\lambda} \ln \left[1 + J \left(\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} \right)_s \right] \quad (32)$$

Age equation:

$$\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_o + \frac{^{39}\text{Ar}}{^{36}\text{Ar}} \frac{e^{\lambda t} - 1}{J} \quad (33)$$

8 Thermochronology

8.1 The U-Th-He method

Ingrowth equation:

$$[^4\text{He}] = 8(e^{\lambda_{238}t} - 1)[^{238}\text{U}] + 7(e^{\lambda_{235}t} - 1)[^{235}\text{U}] + 6(e^{\lambda_{232}t} - 1)[^{232}\text{Th}] + (e^{\lambda_{147}t} - 1)[^{147}\text{Sm}] \quad (34)$$

where $[^4\text{He}]$, $[^{238}\text{U}]$, $[^{235}\text{U}]$, $[^{232}\text{Th}]$ and $[^{147}\text{Sm}]$ are concentrations in atoms or moles per unit mass or volume.

Fick's Law:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (35)$$

Arrhenius equation:

$$\ln(D) = \ln(D_o) - \frac{E_a}{RT} \quad (36)$$

where $R = 8.3144621 \text{ J/mol.K}$.

Closure temperature (assuming that $t \propto 1/T$):

$$\frac{E_a}{RT_c} = \ln \left(\frac{ART_c^2 D_o / r^2}{E_a dT/dt} \right) \quad (37)$$

where $A = 55$ for a sphere, 27 for a cylinder and 8.7 for a plane sheet.

8.2 Fission tracks

The volume density n_s (in cm^{-3}) of fission tracks:

$$n_s = \frac{\lambda_f}{\lambda} [^{238}\text{U}] (e^{\lambda t} - 1) \quad (38)$$

The surface density ρ (in cm^{-2}):

$$\rho = gLn_s \quad (39)$$

Where $g = 1$ for internal and $g = 1/2$ for external surfaces, and $L \sim 15 \mu\text{m}$ for apatite. Age equation:

$$t = \frac{1}{\lambda} \ln \left(\frac{\lambda}{\lambda_f} \frac{\rho_s}{[^{238}\text{U}]g_s L} + 1 \right) \quad (40)$$

External detector method:

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{g_i}{g_s} \lambda \zeta \rho_d \frac{N_s}{N_i} \right) \quad (41)$$

where N_s and N_i are the spontaneous and induced track counts. Arrhenius relationship for fading fission tracks:

$$\ln(t) = \frac{E_A}{kT} + \ln \left[\ln \left(\frac{\rho_o}{\rho} \right) \right] - \ln(C) \quad (42)$$

where $k = 8.616 \times 10^{-5} \text{ eV/K}$.

9 Cosmogenic nuclides

Will not be part of the exam.

10 U-series disequilibrium

10.1 The ^{234}U - ^{238}U method

Age equation:

$$\frac{A(^{234}\text{U})}{A(^{238}\text{U})} = 1 + [\gamma_o - 1] e^{-\lambda_{234}t} \quad (43)$$

10.2 The ^{230}Th method

Ingrowth equation:

$$A(^{230}\text{Th}) = A(^{230}\text{Th})_o e^{-\lambda_{230}t} + A(^{238}\text{U})(1 - e^{-\lambda_{230}t}) \quad (44)$$

Isochron equation:

$$\frac{A(^{230}\text{Th})}{A(^{232}\text{Th})} = \frac{A(^{230}\text{Th})_o}{A(^{232}\text{Th})} e^{-\lambda_{230}t} + \frac{A(^{238}\text{U})}{A(^{232}\text{Th})} (1 - e^{-\lambda_{230}t}) \quad (45)$$

10.3 The ^{230}Th -U method

Decay series:

$$A(^{230}\text{Th}) = A(^{230}\text{Th})^s + A(^{230}\text{Th})^x \quad (46)$$

$$\text{with: } A(^{230}\text{Th})^s = A(^{238}\text{U})(1 - e^{-\lambda_{230}t}) \quad (47)$$

$$\text{and: } A(^{230}\text{Th})^x = \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} A(^{234}\text{U})_o^x (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) \quad (48)$$

Age equation:

$$\frac{A(^{230}\text{Th})}{A(^{238}\text{U})} = 1 - e^{-\lambda_{230}t} + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} (\gamma_o - 1) (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) \quad (49)$$

If $\gamma_o = 1$:

$$\frac{A(^{230}\text{Th})}{A(^{238}\text{U})} = 1 - e^{-\lambda_{230}t} \quad (50)$$

11 Error propagation

11.1 Basic definitions

Mean:

$$\begin{cases} \bar{x} \equiv \frac{1}{n} \sum_{i=1}^n x_i \\ \bar{y} \equiv \frac{1}{n} \sum_{i=1}^n y_i \end{cases} \quad (51)$$

Variance:

$$\begin{cases} s[x]^2 \equiv \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \\ s[y]^2 \equiv \frac{1}{n-1} \sum_{i=1}^n (y_i - \bar{y})^2 \end{cases} \quad (52)$$

Covariance:

$$s[x,y] \equiv \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y}) \quad (53)$$

General equation for the error propagation of a function $t = f(x,y)$:

$$s[t]^2 s[x]^2 \left(\frac{\partial f}{\partial x} \right)^2 + s[y]^2 \left(\frac{\partial f}{\partial y} \right)^2 + 2 s[x,y] \frac{\partial f}{\partial x} \frac{\partial f}{\partial y} \quad (54)$$

In matrix form:

$$s[t]^2 = \begin{bmatrix} \frac{\partial t}{\partial x} & \frac{\partial t}{\partial y} \end{bmatrix} \begin{bmatrix} s[x]^2 & s[x,y] \\ s[x,y] & s[y]^2 \end{bmatrix} \begin{bmatrix} \frac{\partial t}{\partial x} \\ \frac{\partial t}{\partial y} \end{bmatrix} \quad (55)$$

11.2 Examples

Let x and y indicate measured quantities associated with analytical uncertainty. And let a and b be some error free parameters.

1. addition ($t = ax + by$):

$$s[t]^2 = a^2 s[x]^2 + b^2 s[y]^2 + 2ab s[x,y] \quad (56)$$

2. subtraction ($t = ax - by$):

$$s[t]^2 = a^2 s[x]^2 + b^2 s[y]^2 - 2ab s[x,y] \quad (57)$$

3. multiplication ($t = axy$):

$$\left(\frac{s[t]}{t} \right)^2 = \left(\frac{s[x]}{x} \right)^2 + \left(\frac{s[y]}{y} \right)^2 + 2 \frac{s[x,y]}{xy} \quad (58)$$

4. division ($t = a \frac{x}{y}$):

$$\left(\frac{s[t]}{t} \right)^2 = \left(\frac{s[x]}{x} \right)^2 + \left(\frac{s[y]}{y} \right)^2 - 2 \frac{s[x,y]}{xy} \quad (59)$$

5. exponentiation ($t = a e^{bx}$):

$$s[t]^2 = (bt)^2 s[x]^2 \quad (60)$$

6. logarithms ($t = a \ln(bx)$):

$$s[t]^2 = a^2 \left(\frac{s[x]}{x} \right)^2 \quad (61)$$

7. power ($t = ax^b$):

$$\left(\frac{s[t]}{t} \right)^2 = b^2 \left(\frac{s[x]}{x} \right)^2 \quad (62)$$

11.3 Standard error of the mean

If $cov(x_i, x_j) = 0 \forall i, j$:

$$s[\bar{x}]^2 = \frac{1}{n} \sum_{i=1}^n s[x_i]^2 = \frac{s[x]^2}{n} \Rightarrow s[\bar{x}] = \frac{s[x]}{\sqrt{n}} \quad (63)$$

11.4 Poissonian counting statistics

$$s[N]^2 = N \quad (64)$$