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

1.3 Half-lives and decay constants

C: $t_{1/2}(^{14}\mathrm{C})$ = 5730 yr
K: $\lambda_{\beta^-} = 4.962 \times 10^{-10}\mathrm{yr}^{-1}$; $\lambda_e = 0.581 \times 10^{-10}\mathrm{yr}^{-1}$; $t_{1/2}(e+\beta^-)=1.248$ Gyr
Rb: $t_{1/2}(^{87}\mathrm{Rb})$ = 48.8 Gyr
Sm: $t_{1/2}(^{147}\mathrm{Sm})$ = 106 Gyr
U: $t_{1/2}(^{238}\mathrm{U})$ = 4.468 Gyr; $t_{1/2}(^{235}\mathrm{U})$ = 703.8 Myr; $t_{1/2}(^{234}\mathrm{U})$ = 245.5 kyr; $\lambda_f = 8.46\times10^{-17}\mathrm{yr}^{-1}$
Th: $t_{1/2}(^{232}\mathrm{Th})$ = 14.05 Gyr; $t_{1/2}(^{230}\mathrm{Th})$ = 75.38 kyr

2 Basic notions

2.1 Radioactivity

The decay equation:

$$\frac{dP}{dt} = -\lambda P \tag{1}$$

Its solution:

$$P = P_\circ e^{-\lambda t} \tag{2}$$

The fundamental age equation:

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

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

$$\frac{P_\circ}{2} = P_\circ e^{-\lambda t_{1/2}} \Rightarrow t_{1/2} = \frac{\ln(2)}{\lambda} \tag{4}$$

2.2 Decay series

$$\text{for } P: dP/dt = -\lambda_P P \tag{5}$$

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

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

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

$$D_1 = \frac{\lambda_P}{\lambda_1-\lambda_P}P_\circ\left[e^{-\lambda_P t} - e^{-\lambda_1 t}\right] \tag{8}$$

Secular equilibrium:

$$D_1\lambda_1 = P\lambda_P \tag{9}$$

or, equivalently:

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

3 Analytical techniques

3.1 Mass spectrometry

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

$$E = eV = \frac{mv^2}{2} \tag{11}$$

With $e = 1.60219\times10^{-19}$C and 1 a.m.u. = 1.660538×10^{-27}kg. The mass analyser deflects the ions according to the following equation:

$$Hev = \frac{mv^2}{r} \tag{12}$$

from which it follows that:

$$r = \frac{1}{H}\sqrt{\frac{2mV}{e}} \tag{13}$$

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

$$\frac{d^{14}C}{dt} = -\lambda_{14}\times{}^{14}C \tag{14}$$

where λ_{14} = 0.120968 kyr^{-1}.

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

4.2 The Rb-Sr method

Ingrowth equation:

$$^{87}Sr = {}^{87}Sr_\circ + {}^{87}Rb(e^{\lambda_{87}t}-1) \tag{16}$$

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

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

where $Ab(\cdot)$ signifies 'abundance'.

4.3 Isochrons

The universal isochron equation:

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

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

$$\frac{^{87}Sr}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_\circ + \frac{^{87}Rb}{^{86}Sr}(e^{\lambda_{87}t}-1) \tag{19}$$

4.4 The Sm-Nd method

The age equation:

$$^{143}Nd = ^{143}Nd_\circ + ^{147}Sm(e^{\lambda_{147}t} - 1) \tag{20}$$

Isochron equation:

$$\frac{^{143}Nd}{^{144}Nd} = \left(\frac{^{143}Nd}{^{144}Nd}\right)_\circ + \frac{^{147}Sm}{^{144}Nd}(e^{\lambda_{147}t} - 1) \tag{21}$$

5 The U-Pb system

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

6 The U-(Th-)Pb method

Ingrowth equations:

$$\begin{array}{l} ^{206}Pb^* = ^{238}U\left(e^{\lambda_{238}t} - 1\right) \\ ^{207}Pb^* = ^{235}U\left(e^{\lambda_{235}t} - 1\right) \\ ^{208}Pb^* = ^{232}Th\left(e^{\lambda_{232}t} - 1\right) \end{array} \tag{23}$$

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

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

with common Pb correction:

$$\begin{array}{l} t_{206} = \frac{1}{\lambda_{238}}\ln\left(\frac{\left(\frac{^{206}Pb}{^{204}Pb}\right) - \left(\frac{^{206}Pb}{^{204}Pb}\right)_\circ}{\frac{^{238}U}{^{204}Pb}} + 1\right) \\ t_{207} = \frac{1}{\lambda_{235}}\ln\left(\frac{\left(\frac{^{207}Pb}{^{204}Pb}\right) - \left(\frac{^{207}Pb}{^{204}Pb}\right)_\circ}{\frac{^{235}U}{^{204}Pb}} + 1\right) \\ t_{208} = \frac{1}{\lambda_{232}}\ln\left(\frac{\left(\frac{^{208}Pb}{^{204}Pb}\right) - \left(\frac{^{208}Pb}{^{204}Pb}\right)_\circ}{\frac{^{232}Th}{^{204}Pb}} + 1\right) \end{array} \tag{25}$$

6.1 The Pb-Pb method

Age equation:

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

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

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

7 The K–Ar system

Ingrowth equation:

$$\begin{array}{rl} ^{40}Ar & = ^{40}Ar_\circ + ^{40}Ar^* \\ \text{where } ^{40}Ar^* & = \frac{\lambda_e}{\lambda}{}^{40}K\left(e^{\lambda t} - 1\right) \end{array} \tag{28}$$

7.1 K-Ar dating

Age equation:

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

Isochron equation:

$$\frac{^{40}Ar}{^{36}Ar} = \left(\frac{^{40}Ar}{^{36}Ar}\right)_\circ + \frac{\lambda_e}{\lambda}\frac{^{40}K}{^{36}Ar}\left(e^{\lambda t} - 1\right) \tag{30}$$

7.2 ^{40}Ar/^{39}Ar dating

Sample:

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

Standard:

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

Isochron equation:

$$\frac{^{40}Ar}{^{36}Ar} = \left(\frac{^{40}Ar}{^{36}Ar}\right)_\circ + \frac{^{39}Ar}{^{36}Ar}\frac{e^{\lambda t} - 1}{J} \tag{33}$$

8 Thermochronology

8.1 The U-Th-He method

Ingrowth equation:

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

where [^{4}He], [^{238}U], [^{235}U] [^{232}Th] and [^{147}Sm] are concentrations in atoms or moles per unit mass or volume.
Fick's Law:

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

Arrhenius equation:

$$\ln(D) = \ln(D_\circ) - \frac{E_a}{RT} \tag{36}$$

where R = 8.3144621 J/mol.K.

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

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

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:

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

The surface density ρ (in cm^{-2}):

$$\rho = gLn_s \tag{39}$$

Where $g=1$ for internal and $g=1/2$ for external surfaces, and $L \sim 15$µm for apatite. Age equation:

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

External detector method:

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

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

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

where $k = 8.616\times10^{-5}$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:

$$\frac{A(^{234}U)}{A(^{238}U)} = 1+[\gamma_\circ-1]e^{-\lambda_{234}t} \tag{43}$$

10.2 The ^{230}Th method

Ingrowth equation:

$$A(^{230}Th) = A(^{230}Th)_\circ e^{-\lambda_{230}t} + A(^{238}U)(1-e^{-\lambda_{230}t}) \tag{44}$$

Isochron equation:

$$\frac{A(^{230}Th)}{A(^{232}Th)} = \frac{A(^{230}Th)_\circ}{A(^{232}Th)}e^{-\lambda_{230}t} + \frac{A(^{238}U)}{A(^{232}Th)}(1-e^{-\lambda_{230}t}) \tag{45}$$

10.3 The ^{230}Th-U method

Decay series:

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

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

$$\text{and: } A(^{230}Th)^x = \frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}}A(^{234}U)^x_\circ\left(e^{-\lambda_{234}t}-e^{-\lambda_{230}t}\right) \tag{48}$$

Age equation:

$$\frac{A(^{230}Th)}{A(^{238}U)} = 1-e^{-\lambda_{230}t} + \frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}}(\gamma_\circ-1)\left(e^{-\lambda_{234}t}-e^{-\lambda_{230}t}\right) \tag{49}$$

If $\gamma_\circ = 1$:

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

11 Error propagation

11.1 Basic definitions

Mean:

$$\begin{cases} \overline{x} \equiv & \frac{1}{n}\sum_{i=1}^{n}x_i \\ \overline{y} \equiv & \frac{1}{n}\sum_{i=1}^{n}y_i \end{cases} \tag{51}$$

Variance:

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

Covariance:

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

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

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

In matrix form:

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

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 ($t = ax+by$):

$$s[t]^2 = a^2s[x]^2 + b^2s[y]^2 + 2ab\ s[x,y] \tag{56}$$

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

$$s[t]^2 = a^2s[y]^2 + b^2s[y]^2 - 2ab\ s[x,y] \tag{57}$$

3. multiplication ($t = axy$):

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

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

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

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

$$s[t]^2 = (bt)^2s[x]^2 \tag{60}$$

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

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

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

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

11.3 Standard error of the mean

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

$$s[\overline{x}]^2 = \frac{1}{n^2}\sum_{i=1}^{n}s[x_i]^2 = \frac{s[x]^2}{n} \Rightarrow s[\overline{x}] = \frac{s[x]}{\sqrt{n}} \tag{63}$$

11.4 Poissonian counting statistics

$$s[N]^2 = N \tag{64}$$