Online Appendix B

Equations of the open-system production of total ^{206}Pb at secular equilibrium

Following the example given in Albarède (1995), the rate of change of the numbers of atoms of ^{238}U, ^{234}U and ^{230}Th radionuclides can be written:

$$\frac{d}{dt}\begin{bmatrix} {}^{238}N \\ {}^{234}N \\ {}^{230}N \end{bmatrix} = \begin{bmatrix} -\lambda_{238} & 0 & 0 \\ \lambda_{238} & -\lambda_{234} & 0 \\ 0 & \lambda_{234} & -\lambda_{230} \end{bmatrix} \begin{bmatrix} {}^{238}N \\ {}^{234}N \\ {}^{230}N \end{bmatrix} + \begin{bmatrix} j_{238} \\ j_{234} \\ j_{230} \end{bmatrix} \tag{1}$$

where j is the rate of gain or loss of U and Th. By converting into activity ratios, Eq.1 becomes:

$$\frac{d}{dt}\begin{bmatrix} \left[{}^{238}\mathrm{U}\right] \\ \left[{}^{234}\mathrm{U}\right] \\ \left[{}^{230}\mathrm{Th}\right] \end{bmatrix} = \begin{bmatrix} -\lambda_{238} & 0 & 0 \\ \lambda_{234} & -\lambda_{234} & 0 \\ 0 & \lambda_{230} & -\lambda_{230} \end{bmatrix} \begin{bmatrix} \left[{}^{238}\mathrm{U}\right] \\ \left[{}^{234}\mathrm{U}\right] \\ \left[{}^{230}\mathrm{Th}\right] \end{bmatrix} + \begin{bmatrix} \lambda_{238} j_{238} \\ \lambda_{234} j_{234} \\ \lambda_{230} j_{230} \end{bmatrix} \tag{2}$$

which is of the form $d\mathbf{x}/dt = \boldsymbol{A}\boldsymbol{x} + \boldsymbol{j}$ with:

$$\mathbf{A} = \begin{bmatrix} -\lambda_{238} & 0 & 0 \\ \lambda_{234} & -\lambda_{234} & 0 \\ 0 & \lambda_{230} & -\lambda_{230} \end{bmatrix} \quad \text{and} \quad \mathbf{j} = \begin{bmatrix} \lambda_{238} j_{238} \\ \lambda_{234} j_{234} \\ \lambda_{230} j_{230} \end{bmatrix} \tag{3}$$

This system has a unique set of solutions:

$$\mathbf{x} = e^{\mathbf{A}t}\mathbf{x}_0 + \int_0^t e^{\mathbf{A}(t-t')}\mathbf{j}(t')\,dt' = -\mathbf{A}^{-1}\mathbf{j} + e^{\mathbf{A}t}\left(\mathbf{x}_0 + \mathbf{A}^{-1}\mathbf{j}\right) \tag{4}$$

where $e^{\boldsymbol{At}}$ equals:

$$e^{\mathbf{A}t} = e^{-\lambda_{238}t}\mathbf{C}_{238} + e^{-\lambda_{234}t}\mathbf{C}_{234} + e^{-\lambda_{230}t}\mathbf{C}_{230} \tag{5}$$

with:

$$\mathbf{C}_{238} = \begin{bmatrix} 1 & 0 & 0 \\ \frac{\lambda_{234}}{\lambda_{234}-\lambda_{238}} & 0 & 0 \\ \frac{\lambda_{230}\,\lambda_{234}}{(\lambda_{234}-\lambda_{238})(\lambda_{230}-\lambda_{238})} & 0 & 0 \end{bmatrix} \tag{6}$$

$$\mathbf{C}_{234} = \begin{bmatrix} 0 & 0 & 0 \\ -\frac{\lambda_{234}}{\lambda_{234}-\lambda_{238}} & 1 & 0 \\ -\frac{\lambda_{230}\,\lambda_{234}}{(\lambda_{234}-\lambda_{238})(\lambda_{230}-\lambda_{234})} & \frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}} & 0 \end{bmatrix} \tag{7}$$

$$\mathbf{C}_{230} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \frac{\lambda_{230}\,\lambda_{234}}{(\lambda_{230}-\lambda_{238})(\lambda_{230}-\lambda_{234})} & -\frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}} & 1 \end{bmatrix} \tag{8}$$

When ^{234}U and ^{230}Th are at secular equilibrium with ^{238}U, then $e^{-\lambda_{230}t} \approx e^{-\lambda_{234}t} \approx 1$, and Eq.(4) thus reduces to:

$$\mathbf{x}_{sec} \approx -\mathbf{A}^{-1}\mathbf{j} + e^{-\lambda_{238}t}\mathbf{C}_{238}\left(\mathbf{x}_0 + \mathbf{A}^{-1}\mathbf{j}\right) \tag{9}$$

Given that:

$$\mathbf{A}^{-1}\mathbf{j} = -\begin{bmatrix} j_{238} \\ j_{238} + j_{234} \\ j_{238} + j_{234} + j_{230} \end{bmatrix} \tag{10}$$

Eq.(9) can be developed as:

$$\begin{aligned} \begin{bmatrix} \left[^{238}\mathrm{U}\right]_{sec} \\ \left[^{234}\mathrm{U}\right]_{sec} \\ \left[^{230}\mathrm{Th}\right]_{sec} \end{bmatrix} &= \begin{bmatrix} j_{238} \\ j_{238} + j_{234} \\ j_{238} + j_{234} + j_{230} \end{bmatrix} \\ +e^{-\lambda_{238}t} \begin{bmatrix} 1 & 0 & 0 \\ \frac{\lambda_{234}}{\lambda_{234}-\lambda_{238}} & 0 & 0 \\ \frac{\lambda_{230}\,\lambda_{234}}{(\lambda_{234}-\lambda_{238})(\lambda_{230}-\lambda_{238})} & 0 & 0 \end{bmatrix} & \begin{bmatrix} \left[^{238}\mathrm{U}\right]_0 - j_{238} \\ \left[^{234}\mathrm{U}\right]_0 - j_{238} - J_{234} \\ \left[^{230}\mathrm{Th}\right]_0 - j_{238} - j_{234} - j_{230} \end{bmatrix} \end{aligned} \tag{11}$$

Leading to:

$$\left[{}^{238}\mathrm{U}\right]_{sec} = \left[{}^{238}\mathrm{U}\right]_0 e^{-\lambda_{238}t} + \left(1 - e^{-\lambda_{238}t}\right) j_{238} \tag{12}$$

$$\left[{}^{234}\mathrm{U}\right]_{sec} = \left[{}^{238}\mathrm{U}\right]_0 e^{-\lambda_{238}t} + \left(1 - e^{-\lambda_{238}t}\right) \left(j_{238} + j_{234}\right) \tag{13}$$

$$\left[{}^{230}\mathrm{Th}\right]_{sec} = \left[{}^{238}\mathrm{U}\right]_0 e^{-\lambda_{238}t} + \left(1 - e^{-\lambda_{238}t}\right) \left(j_{238} + j_{234} + j_{230}\right) \tag{14}$$

Or:

$$\left[{}^{238}\mathrm{U}\right]_0 - \left[{}^{238}\mathrm{U}\right]_{sec} = \left(\left[{}^{238}\mathrm{U}\right]_0 + j_{238}\right) \left(1 - e^{-\lambda_{238}t}\right) \tag{15}$$

$$\left[{}^{238}\mathrm{U}\right]_0 - \left[{}^{234}\mathrm{U}\right]_{sec} = \left(\left[{}^{238}\mathrm{U}\right]_0 + j_{238} + j_{234}\right) \left(1 - e^{-\lambda_{238}t}\right) \tag{16}$$

$$\left[{}^{238}\mathrm{U}\right]_0 - \left[{}^{230}\mathrm{Th}\right]_{sec} = \left(\left[{}^{238}\mathrm{U}\right]_0 + j_{238} + j_{234} + j_{230}\right) \left(1 - e^{-\lambda_{238}t}\right) \tag{17}$$

By subtracting Eq.(16) from Eq.(15), Eq.(17) from Eq.(16) and Eq.(17) from Eq.(15), we obtain:

$$\left[{}^{234}\mathrm{U}\right]_{sec} - \left[{}^{238}\mathrm{U}\right]_{sec} = \left(1 - e^{-\lambda_{238}t}\right) j_{234} \tag{18}$$

$$\left[{}^{230}\mathrm{Th}\right]_{sec} - \left[{}^{234}\mathrm{U}\right]_{sec} = \left(1 - e^{-\lambda_{238}t}\right) j_{230} \tag{19}$$

$$\left[{}^{230}\mathrm{Th}\right]_{sec} - \left[{}^{238}\mathrm{U}\right]_{sec} = \left(1 - e^{-\lambda_{238}t}\right) \left(j_{230} + j_{234}\right) \tag{20}$$

However, the total production of ${}^{206}Pb$ can be obtained by integrating $\mathbf{x}$ in Eq.4. This gives:

$$\int_0^t \mathbf{x}\left(t'\right) dt' = -\mathbf{A}^{-1}\mathbf{j}t + \left[\int_0^t e^{\mathbf{A}t'} dt'\right] \left(\mathbf{x}_0 + \mathbf{A}^{-1}\mathbf{j}\right) \tag{21}$$

With:

$$\int_0^t e^{\mathbf{A}t'} dt' = \frac{1 - e^{-\lambda_{238}t_s}}{\lambda_{238}} \mathbf{C}_{238} + \frac{1 - e^{-\lambda_{234}t}}{\lambda_{234}} \mathbf{C}_{234} + \frac{1 - e^{-\lambda_{230}t}}{\lambda_{230}} \mathbf{C}_{230} \tag{22}$$

When ${}^{234}U$ and ${}^{230}Th$ are at secular equilibrium with ${}^{238}U$, then $1 - e^{-\lambda_{230}t} \approx 1 - e^{-\lambda_{234}t} \approx 0$, and Eq.(22) thus reduces to :

$$\int_0^{t_s} e^{\mathbf{A}t'} dt' = \frac{1 - e^{-\lambda_{238}t_s}}{\lambda_{238}} \mathbf{C}_{238} + \frac{1}{\lambda_{234}} \mathbf{C}_{234} + \frac{1}{\lambda_{230}} \mathbf{C}_{230} \tag{23}$$

Moreover:

$$\frac{\mathbf{C}_{238}}{\lambda_{238}} \gg \frac{\mathbf{C}_{234}}{\lambda_{234}} \quad \text{and} \quad \frac{\mathbf{C}_{238}}{\lambda_{238}} \gg \frac{\mathbf{C}_{230}}{\lambda_{230}} \tag{24}$$

Eq.(21) can be rewritten as:

$$\int_0^{t_s} \mathbf{x}(t')\,dt' = -\mathbf{A}^{-1}\mathbf{j}t_s + \frac{1-e^{-\lambda_{238}t_s}}{\lambda_{238}} \begin{bmatrix} \left[{}^{238}\mathrm{U}\right]_0 - j_{238} \\ \left[{}^{238}\mathrm{U}\right]_0 - j_{238} \\ \left[{}^{238}\mathrm{U}\right]_0 - j_{238} \end{bmatrix} \tag{25}$$

From the radioactive decay equation $N = N_0 e^{-\lambda t}$, it can be deduced that:

$$\left[{}^{238}\mathrm{U}\right]_0 - j_{238} = \left(\left[{}^{238}\mathrm{U}\right]_{sec} - j_{238}\right) e^{\lambda_{238}t} \tag{26}$$

Which reintroduced into Eq.(25) gives:

$$\int_0^{t_s} \mathbf{x}(t')\,dt' = -\mathbf{A}^{-1}\mathbf{j}t_s + \frac{e^{\lambda_{238}t_s}-1}{\lambda_{238}} \begin{bmatrix} \left[{}^{238}\mathrm{U}\right]_{sec} - j_{238} \\ \left[{}^{238}\mathrm{U}\right]_{sec} - j_{238} \\ \left[{}^{238}\mathrm{U}\right]_{sec} - j_{238} \end{bmatrix} \tag{27}$$

When the ^{234}U and ^{230}Th radionuclides are at secular equilibrium with ^{238}U, then $(e^{\lambda t} - 1)/\lambda \approx t$, and the total production of ^{206}Pb is:

$$^{206}\mathrm{Pb}(t_s) - {}^{206}\mathrm{Pb}(0) = \left[{}^{238}\mathrm{U}\right]_{sec} \frac{\left(e^{\lambda_{238}t_s}-1\right)}{\lambda_{238}} + \left(j_{234} + j_{230}\right) t_s \tag{28}$$

Using Eq.(23) leads to:

$$^{206}\mathrm{Pb}(t_s) - {}^{206}\mathrm{Pb}(0) = \left[{}^{238}\mathrm{U}\right]_{sec} \frac{\left(e^{\lambda_{238}t_s}-1\right)}{\lambda_{238}} + \frac{\left[{}^{230}\mathrm{Th}\right]_{sec} - \left[{}^{238}\mathrm{U}\right]_{sec}}{1-e^{-\lambda_{238}t_s}} t_s \tag{29}$$

Using the approximation $(1 - e^{-\lambda t})/\lambda \approx t$ and the activity excess definition of $[^{230}Th]_{sec}$ relative to $[^{238}U]_{sec}$ we obtain:

$$^{206}\mathrm{Pb}(t_s) - {}^{206}\mathrm{Pb}(0) = \frac{\left[{}^{238}\mathrm{U}\right]_{sec}}{\lambda_{238}} \left(e^{\lambda_{238}t_s}-1\right) + \frac{\left[{}^{238}\mathrm{U}\right]_{sec}}{\lambda_{238}} \left[{}^{230}\mathrm{Th}\right]_{xs} \tag{30}$$

Finally, the total production of ^{206}Pb equals:

$$^{206}\mathrm{Pb}(t_s) - {}^{206}\mathrm{Pb}(0) = {}^{238}\mathrm{U}_{sec}\left(\lambda_{238}t_s + \left[{}^{230}\mathrm{Th}\right]_{xs}\right) \tag{31}$$

Reference

Albarède (1995) Introduction to Geochemical Modeling. Cambridge University Press, 543 p.