`PbIso`: an R package and web app for calculating and plotting Pb isotope data

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Abstract

The package `PbIso` is a free and open R toolbox for commonly used calculations and plots of Pb-Pb isotope data and for generating Pb evolution models. In this paper, we review Pb isotope systematics and the calculations that are commonly used, such as model age, model source μ ($^{238}U/^{204}Pb$), time-integrated κ ($^{232}Th/^{238}U$), and initial Pb isotope ratios. These complicated equations are implemented into simple R functions in the package `PbIso`. In addition, functions are provided for generating Pb evolution models, isochron lines, and time-dependent slopes. This allows users to apply calculations to their data in a straightforward way, while providing transparency and flexibility of the calculations used. We have implemented some basic features of the `PbIso` package into an online shiny application (https://shereearmistead.shinyapps.io/PbIsoApp/), which makes it easy for users without any R experience to use these calculations with their own data and to generate plots.

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1 Introduction

Pb isotopes are used in a range of science applications including, plate tectonics, studies of early Earth evolution and archaeometry. Despite their widespread applications, there are few tools readily available to users, to calculate and plot these data, and to generate Pb evolution models. Pb isotopes are routinely used in studies of ore deposit geology (Eglington 2018), and are often used by geologists who are not specialists in isotope geochemistry. This presents a challenge as there are few tools available to process, plot and interpret Pb isotope data. In recent years, tools have been developed and adapted for various isotopic and geochemical datasets, including, `IsoplotR` (Vermeesch 2018) and `provenance` (Vermeesch, Resentini, and Garzanti 2016) in R, and `pyrolite` (Williams et al. 2020) in Python. Some of these packages have a linked graphic user interface (GUI), which allows users of various programming experience to use them. The power of these tools is the ability to apply them to large datasets, and integrate them with other powerful statistical and

visualisation packages, which is becoming increasingly important as many disciplines within Earth Sciences involve big data analytics.

Typically Pb isotope calculations and Pb evolution models are performed in makeshift spreadsheets with little transparency of how they are actually calculated. The methods for calculating these different values also vary among publications, often with poor documentation, making reproducibility difficult. Our aim is to provide a review of Pb isotope systematics and how these are incorporated into various Pb isotope calculations. We document the different calculations used for Pb isotope data and Pb evolution models and how they have been implemented into the `PbIso` R package. The `PbIso` functions allow for simplicity in only requiring minimal Pb isotope measurements as inputs, while also allowing users the flexibility of setting optional input values, or defining their own Pb evolution models.

`PbIso` is intended for users interested in modelling the evolution of various earth systems from Pb isotopes, such as calculating model age, model source μ, and initial isotope ratios. These calculations are particularly applicable to a wide range of ore deposit studies (e.g. Huston et al. (2010)), and plate tectonic studies (e.g. Blichert-Toft et al. (2016)). `PbIso` also allows rapid modelling of user-defined Pb evolution curves, which is important for understanding Earth evolution as well as the evolution of many ore-forming regions around the world. For individual samples, we recommend using the functions withing `IsoplotR` (Vermeesch 2018), which allows more detail on the individual sample level such as factoring in uncertainties, performing regressions and sample statistics.

1.1 Pb isotope systematics

The decay of ^{238}U to ^{206}Pb; ^{235}U to ^{207}Pb and ^{232}Th to ^{208}Pb and the non-radiogenic ^{204}Pb can be used to understand the isotopic compositions of the environments in which a mineral/rock formed. The abundance of the radiogenic isotopes increases with time (Figure 1), so comparison of samples with significantly different ages cannot easily be compared using the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb ratios. To allow easy comparison of samples across broad time periods, the model source μ (^{238}U/^{204}Pb) and κ (^{232}Th/^{238}U) values can be used, calculated using an independently constrained age for each sample. These also allow us to compare samples/deposits of varying ages to modelled reservoirs such as upper crust, mantle and lower crust (Zartman and Doe 1981); Bulk Silicate Earth (Maltese and Mezger 2020); or region specific models (e.g. Abitibi-Wawa in Superior Province (Thorpe 1999)).

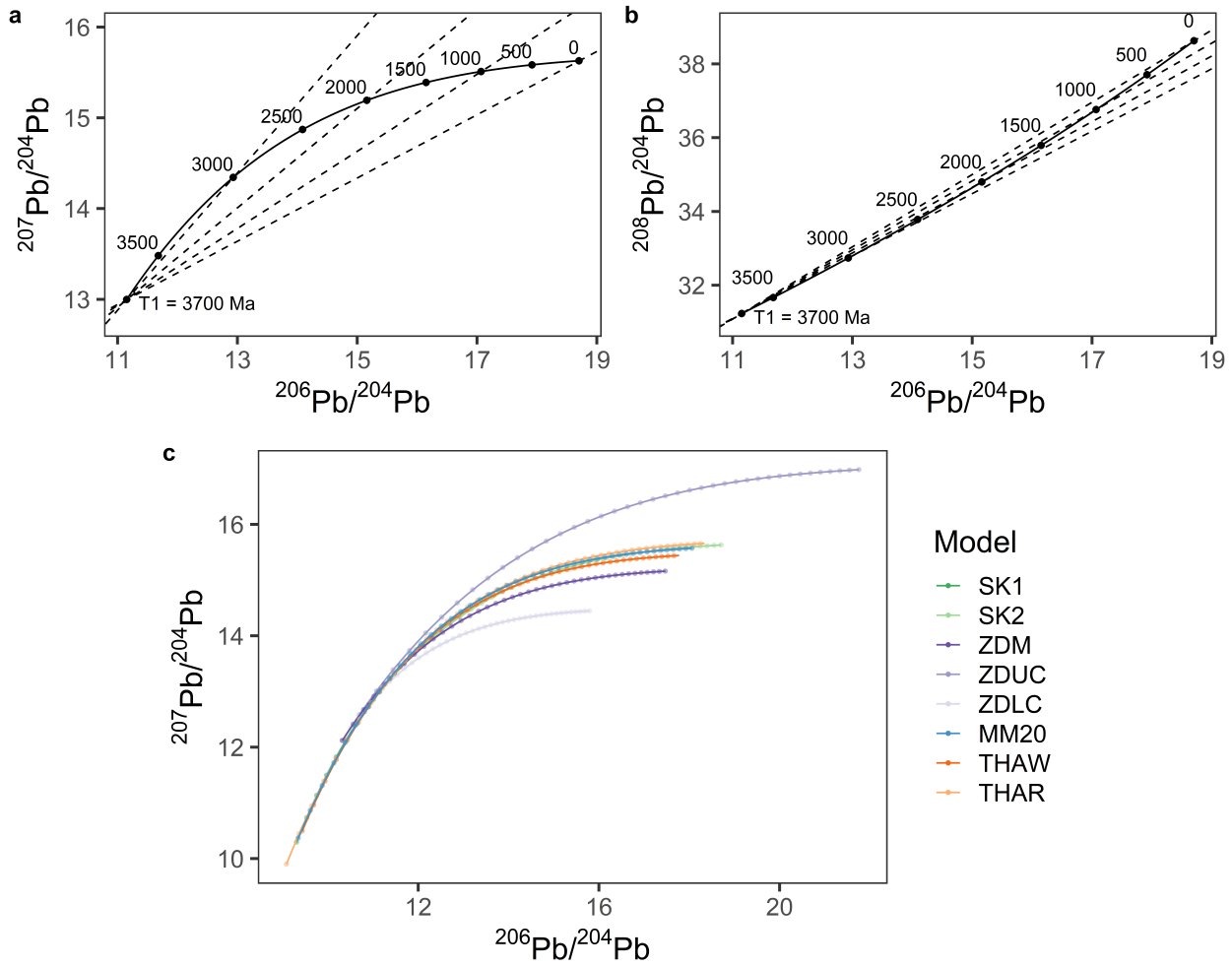

Figure 1: Pb isotopic evolution through time, a) evolution of $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$; b) evolution of $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$; both using the 2nd stage model parameters from Stacey and Kramers (1975). Isochrons for 3000 Ma, 2000 Ma, 1000 Ma and 0 Ma are shown as dashed lines in both plots. c) Pb evolution curves using models packaged within `PbIso`, see Table 3 for model parameters and references. Points are shown along each curve at 100 Ma intervals. See section 4 for how to generate the model curves and section 5.2.1 for the isochron lines shown in (a) and (b).

2 Using `PbIso` in R

We introduce an R package `PbIso`, which includes functions for calculating initial Pb isotope ratios, model age, model source μ ($^{238}U/^{204}Pb$) and time-integrated κ ($^{232}Th/^{238}U$), as well as plotting parameters such as model curves, geochron lines and y-intercepts, and time-dependent slopes. Using the package within R allows the most flexibility in applying the functions to the user's own datasets and the ability to use the wide array of plotting and statistical tools available in R.

Alternatively, we have implemented some of the basic features of `PbIso` into an online Shiny application (https://shereearmistead.shinyapps.io/PbIsoApp/), which requires no knowledge of R, making this very accessible for many users. The app allows input of user data including sample name/ID, age, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios. Users can then export the processed data as a .xlsx file, which will include the calculated columns for initial Pb isotope ratios, model age, model source μ ($^{238}U/^{204}Pb$) and time-integrated κ ($^{232}Th/^{238}U$), as well as a sheet containing the model parameters. Four basic plots are

automatically generated in the Shiny application based on the user data, and can be downloaded as .pdf figures.

All of the functions in `PbIso` take one or more of the basic input parameters t (time (Ma)), x ($^{206}Pb/^{204}Pb$), y ($^{207}Pb/^{204}Pb$) and z ($^{208}Pb/^{204}Pb$) to perform the calculations. For advanced usage, the functions can also optionally take the values for different model parameters (summarised in Table 1). The calculations and functions used in `PbIso` assume a starting composition and model following Stacey and Kramers (1975) 2nd stage model. These values can be overridden in R if an alternative model (e.g. Stacey and Kramers (1975) 1st stage; Maltese and Mezger (2020) Bulk Silicate Earth or others) is preferred.

Table 1: Default model parameters used in `PbIso` functions. These can be manually changed if an alternative model is preferred.

Parameter	Description	Default value	Reference
T1	Model start time (Ma)	3700	Stacey and Kramers (1975)
X1	$^{206}Pb/^{204}Pb$ model starting composition	11.152	Stacey and Kramers (1975)
Y1	$^{207}Pb/^{204}Pb$ model starting composition	12.998	Stacey and Kramers (1975)
Z1	$^{208}Pb/^{204}Pb$ model starting composition	31.23	Stacey and Kramers (1975)
Mu1	$^{238}U/^{204}Pb$ model (μ_1)	9.74	Stacey and Kramers (1975)
Ka1	$^{232}Th/^{238}U$ model (κ_1)	3.78	Stacey and Kramers (1975)
W1	$^{232}Th/^{204}Pb$ model (ω_1)	36.84	Stacey and Kramers (1975)
L5	^{235}U decay constant (λ_5)	$9.8485 * 10^{-10}$	Jaffey et al. (1971)
L8	^{238}U decay constant (λ_8)	$1.55125 * 10^{-10}$	Jaffey et al. (1971)
L2	^{232}Th decay constant (λ_2)	$0.49475 * 10^{-10}$	Le Roux and Glendenin (1963)
U8U5	Present-day $^{238}U/^{235}U$ ratio	137.88	Stacey and Kramers (1975)
E1	ϵ_1 rate factor for change in μ over time	0	see Cumming and Richards (1975)
E2	ϵ_2 rate factor for change in κ over time	0	see Cumming and Richards (1975)

2.1 Installation

The package can be downloaded from https://github.com/ShereeArmistead/PbIso or can be installed within R by running the following:

```
install.packages(devtools)
devtools::install_github("shereearmistead/PbIso")
library(PbIso)
```

Note: the first two lines only need to be run once to install the package on a user's computer. The third line needs to be run every time a user wants to use PbIso in a new R session.

2.2 Running functions

All of the functions in `PbIso` are designed for ease of use, while also allowing flexibility in changing model parameters. The required inputs are outlined in subsequent sections of this manuscript, but we have included a brief overview of the different ways these functions can be used below, using the `Calc64()` function as an example, which only requires one input (age).

The most basic usage is to simply include the one required input parameter, in this case age:

```
Calc64(2700)
```

```
[1] 13.63662
```

2.3 Customising model parameters

As stated previously, the default starting parameters are based on Stacey and Kramers (1975) 2nd stage model, however, these can be manually overridden by specifying them in the function. Further information about how to generate a table with values for a customised Pb evolution model, see section 4. The optional parameters, in this case, T1, X1, Mu1, can be specified as:

```
Calc64(2700, T1 = 4000, X1 = 9.5, Mu1 = 7)
```

```
[1] 11.87765
```

Not all of the optional parameters need to be defined. For example, accepting the defaults for T1 and X1, but modifying Mu1 to 8:

```
Calc64(2700, Mu1 = 8)
```

```
[1] 13.19276
```

Table 2 summarises the `PbIso` functions and their required and optional input parameters. See Table 1 for the descriptions and default values for these model parameters. Note that the decay constants are included as optional arguments in `PbIso` functions for maximum flexibility, however, we advise against modifying these unless there are good constraints on alternative values.

Rather than setting the optional parameters manually for every calculation, a predefined model can be used. We have incorporated several commonly used models (see Table 3), for example the Stacey and Kramers (1975) 1st stage model:

```
Calc64(2700, model = SK1)
```

```
[1] 12.98544
```

Or the Maltese and Mezger (2020) Bulk Silicate Earth Model:

```
Calc64(2700, model = MM20)
```

```
[1] 13.57078
```

Alternatively, users may define starting parameters for their own Pb evolution models, which is particularly useful if this is needed for multiple calculations, and to generate model curves (see section 4). To define your own model, use the `list()` function in R to define the starting parameters:

```
my_model <- list(T1 = 4000, X1 = 10.5, Y1 = 11.5, Z1 = 30, Mu1 = 10, W1 = 33)
Calc64(2700, model = my_model)
```

```
[1] 13.89664
```

Note, that for `Calc64()`, only age, T1, X1 and Mu1 are required (not Y1, Z1 or W1), however to make the user-defined model applicable to other `PbIso` functions, it is best to include parameters required for all functions of interest.

Models that we have included as options in `PbIso` are given in Table 3.

Table 2: Summary of 'PbIso' functions and their input parameters

Function	Description	Required inputs	Optional inputs
`Calc64()`	Calculates $^{206}Pb/^{204}Pb$ at a given time, for a given model	t	T1, X1, Mu1, L8, model
`Calc74()`	Calculates $^{207}Pb/^{204}Pb$ at a given time, for a given model	t	T1, Y1, Mu1, U8U5, L5, model
`Calc84()`	Calculates $^{208}Pb/^{204}Pb$ at a given time, for a given model	t	T1, Z1, W1, L2, model
`CalcModAge()`	Calculates the model age	x, y	T1, X1, Y1, U8U5, L5, L8, model
`CalcMu()`	Calculates the model source μ_1	t, x, y	T1, X1, Y1, U8U5, L5, L8, model
`CalcKa()`	Calculates the time-integrated κ_1	t, z, x	T1, X1, Z1, L2, L8, model
`Calc64in()`	Calculates the initial $^{206}Pb/^{204}Pb$ ratio	t, x, y	T1, X1, Y1, U8U5, L5, L8, model
`Calc74in()`	Calculates the initial $^{207}Pb/^{204}Pb$ ratio	t, x, y	T1, X1, Y1, U8U5, L5, L8, model
`Calc84in()`	Calculates the initial $^{208}Pb/^{204}Pb$ ratio	t, x, y, z	T1, X1, Y1, Z1, U8U5, L5, L8, L2, model
`modelcurve()`	Generates a dataframe for a Pb evolution model	t	T1, X1, Y1, Z1, Mu1, W1, U8U5, L5, L8, L2, E1, E2, model
`geochron76slope()`	Isochron slope on a $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ plot	t	T1, X1, Y1, Mu1, U8U5, L5, L8, model
`geochron76yint()`	Isochron y-intercept on a $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ plot	t	T1, X1, Y1, Mu1, U8U5, L5, L8, model
`geochron86slope()`	Isochron slope on a $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ plot	t	T1, X1, Z1, Mu1, W1, L8, L2, model
`geochron86yint()`	Isochron y-intercept on a $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ plot	t	T1, X1, Z1, Mu1, W1, L8, L2, model
`LeastRad()`	Filters a dataset for the least radiogenic value	df, group, value	

Table 3: Predefined models that can be used in the `PbIso` functions

Model	R name	T1	X1	Y1	Z1	Mu1	W1
Stacey and Kramers (1975) single stage model	SK1	4570	9.307	10.294	29.487	7.19	33.21
Stacey and Kramers (1975) 2nd stage model	SK2	3700	11.152	12.998	31.23	9.74	36.84
Zartman and Doe (1981) mantle	ZDM	4000	10.32	12.12	30.56	8.316	29.211
Zartman and Doe (1981) upper crust	ZDUC	4000	10.32	12.12	30.56	13.301	45.34
Zartman and Doe (1981) lower crust	ZDLC	4000	10.32	12.12	30.56	6.364	37.403
Maltese and Mezger (2020) Bulk Silicate Earth	MM20	4500	9.345	10.37	29.51	8.63	34.9515
Thorpe (1999) Abitibi-Wawa	THAW	4490	9.431	10.495	29.681	8.29	33.91439
Thorpe et al. (1992) Archean Sulphide	THAR	4560	9.0818	9.9002	29.343	9	34

3 A review of Pb isotopes and how to perform calculatons with `PbIso`

3.1 The evolution of radiogenic Pb isotopes with time

The following equations describe the evolution of Pb isotopes with time:

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_t = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{T_1} + \mu_1(e^{\lambda_8 T_1} - e^{\lambda_8 t}) \quad (1)$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_t = \left(\frac{^{207}Pb}{^{204}Pb}\right)_{T_1} + \frac{\mu_1}{137.88}(e^{\lambda_5 T_1} - e^{\lambda_5 t}) \quad (2)$$

$$\left(\frac{^{208}Pb}{^{204}Pb}\right)_t = \left(\frac{^{208}Pb}{^{204}Pb}\right)_{T_1} + \omega_1(e^{\lambda_2 T_1} - e^{\lambda_2 t}) \quad (3)$$

Note that ω (^{232}Th/^{204}Pb) in equation (3) can also be expressed as $\mu \cdot \kappa$, which is equivalent to ^{238}U/^{204}Pb . ^{232}Th/^{238}U.

The above equations are implemented in `PbIso` by the functions `Calc64()`, `Calc74()` and `Calc84()`, respectively. These functions can be used in a number of ways. For simply calculating the value of each isotope ratio on the Stacey and Kramers (1975) average ore lead curve at a given time, only the age is required.

For example, the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios on the Stacey and Kramers (1975) curve at a given time, say 2700 Ma, is given by:

```
Calc64(2700)
```

```
[1] 13.637
```

```
Calc74(2700)
```

```
[1] 14.69
```

```
Calc84(2700)
```

```
[1] 33.366
```

See Table 2 for the optional parameters for each of these functions to allow a different Pb evolution model to be used.

3.2 Model age

Pb-Pb model ages are calculated by assuming a starting composition (typically Stacey and Kramers (1975) 2nd stage values), and calculating the time needed to reach the present-day measured values. To visualise this, in Figure 2a, the line connecting the model starting composition (X1, Y1 at T1) and the sample (red circle) intersects the Stacey and Kramers (1975) curve at the model age for this sample. This is numerically given by the following equation:

$$\frac{\frac{^{207}Pb}{^{204}Pb}_{t_{sample}} - \frac{^{207}Pb}{^{204}Pb}_{T_1}}{\frac{^{206}Pb}{^{204}Pb}_{t_{sample}} - \frac{^{206}Pb}{^{204}Pb}_{T_1}} = \frac{1}{137.88} \cdot \frac{e^{\lambda_5 T_1} - e^{\lambda_5 t_{sample}}}{e^{\lambda_8 T_1} - e^{\lambda_8 t_{sample}}} \tag{4}$$

It is not possible to solve this equation directly for the model age (t_{sample}), so a Newton-Raphson iterative calculation is implemented using the `uniroot()` function in the `stats` package in R. This is implemented in `PbIso` using the `CalcModAge()` function. Only the $^{206}Pb/^{204}Pb$ (x) and $^{207}Pb/^{204}Pb$ (y) ratios are needed to solve for the model age.

To apply `CalcModAge()` to a hypothetical sample with $^{206}Pb/^{204}Pb = 13.5$ and $^{207}Pb/^{204}Pb = 14.5$:

```
CalcModAge(13.5, 14.5)
```

```
[1] 2510
```

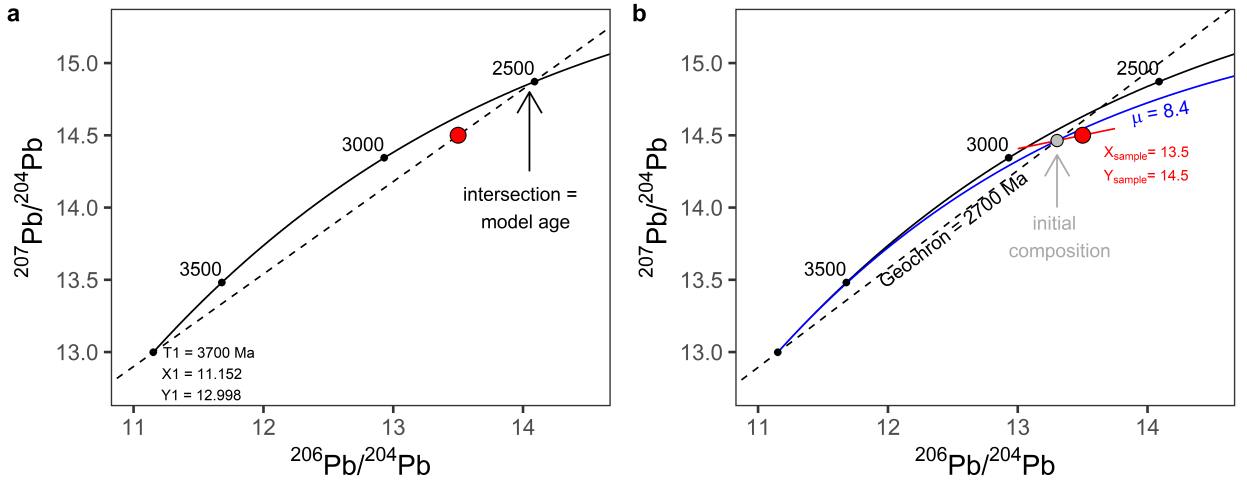

Figure 2: Hypothetical sample (red circle) plotted on a standard Stacey and Kramers (1975) 2nd stage model curve (black line), showing a) that a line connected between a model starting composition and the sample composition, will project onto the Stacey and Kramers (1975) model curve at the corresponding model age, and b) additional values that can be calulcated if the actual sample age (in this case 2700 Ma) is known. Grey circle represents the calculated initial ratios, the blue curve represents the corresponding model source μ value for this sample, and the dashed line is the sample age (2700 Ma) isochron.

3.3 Model source μ ($^{238}U/^{204}Pb$)

All calculations from here onwards require that the sample age is known. Preferably an independently obtained age, such as a zircon U–Pb age is used. When comparing Pb isotope signatures across different time periods, it is often more useful to compare the model source μ ($^{238}U/^{204}Pb$) rather than the Pb isotope ratios, as μ does not vary with time in a closed system.

Rocks or minerals that formed within the same reservoir will have Pb isotopic compositions that cluster along a line on a $^{206}Pb/^{204}Pb$ vs $^{207}Pb^{204}Pb$ plot (red line in Figure 2b). The least radiogenic samples will fall near the lower left end of this line, while more radiogenic samples will fall near the upper right end. One way to calculate a rock's age is to define a line joining multiple sample analyses. The slope of this line is directly related to its mineralisation age. A more robust way of doing this though is to use the known age of a sample, whereby the slope (m) for a sample with a known age (t_{sample}) is defined by:

$$m_{sample} = \frac{e^{\lambda_5 t_{sample}} - 1}{137.88(e^{\lambda_8 t_{sample}} - 1)} \tag{5}$$

This is implemented in `PbIso` by the function `mslope()`, which takes the argument t and additional optional arguments (see documentation). Substituting equation (5) into the following equation gives us the model source μ ($^{238}U/^{204}Pb$) (Harmer, Auret, and Eglington (1995), Eglington (2018)):

$$\mu = \frac{m_{sample}(X_1 - X_{sample}) + Y_{sample} - Y_1}{\frac{e^{\lambda_5 T_1} - e^{\lambda_5 t_{sample}}}{137.88} - m_{sample}(e^{\lambda_8 T_1} - e^{\lambda_8 t_{sample}})} \tag{6}$$

This is implemented in `PbIso` by the function `CalcMu()`, using the sample age (t) in Ma, $^{206}Pb/^{204}Pb$ (x) and $^{207}Pb/^{204}Pb$ (y) ratios. Optional arguments T1, X1, Y1, U8U5, L5 and L8 can also be applied in the format `CalcMu(t, x, y, T1, X1, Y1, U8U5, L5, L8)`. For example, if we have a sample with a known deposit age (independently obtained using a robust method such as U-Pb zircon crystallisation) of t = 2700 Ma; $^{206}Pb/^{204}Pb$ = 13.5, and $^{207}Pb/^{204}Pb$ = 14.5, and accepting the default Stacey and Kramers (1975) model values, we can calculate the model source μ by:

```
CalcMu(2700, 13.5, 14.5)
```

```
[1] 8.43
```

These calculations can be visualised in Figure 2b. The intersection of the age dependent slope (m_{sample}; red line in Figure 2b), the geochron associated with the sample age (2700 Ma in this case), and the model source μ curve of 8.43 (blue curve in Figure 2b), mark the initial Pb isotope composition of the sample. For samples with very low U concentrations, such as galena, the initial compositions will be approximately the same as the measured values. See section 3.5 for calculating initial Pb isotope ratios, and section 5.2 for generating the model curves and geochron lines shown in Figure 2b.

3.4 Time-integrated κ ($^{232}Th/^{238}U$)

Somewhat similar to using the model source μ ($^{238}U/^{204}Pb$) for a sample, we can use the time-integrated κ ($^{232}Th/^{238}U$) to look at thorogenic Pb isotopic trends for samples or regions over different time scales.

The time-integrated κ ($^{232}Th/^{238}U$) is given by:

$$\kappa = \frac{Z_{sample} - Z_1}{X_{sample} - X_1} \times \frac{e^{\lambda_8 T_1} - e^{\lambda_8 t_{sample}}}{e^{\lambda_2 T_1} - e^{\lambda_2 t_{sample}}} \tag{7}$$

This is implemented in `PbIso` as the `CalcKa()` function, using the sample age (t), $^{208}Pb/^{204}Pb$ (z) and $^{206}Pb/^{204}Pb$ (x). Again, let's assume a sample with $^{206}Pb/^{204}Pb$ = 13.5; t = 2700 Ma and now with $^{208}Pb/^{204}Pb$ = 33:

```
CalcKa(2700, 33, 13.5)
```

```
[1] 3.32
```

This calculation can be visualised in Figure 3, where the red circle is the sample, the blue curve is evolution of the sample κ, and the grey circle is the initial Pb isotope ratio.

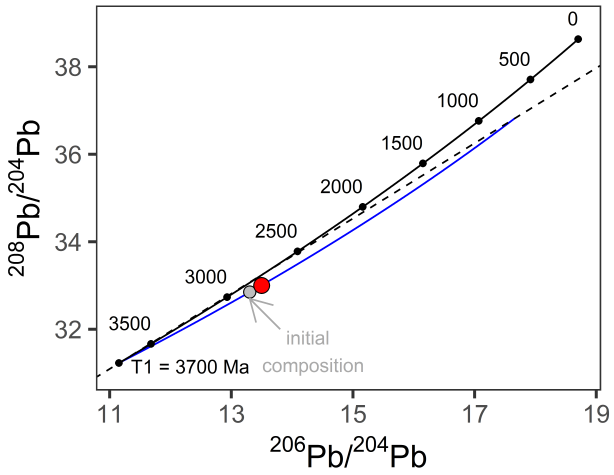

Figure 3: Plot of $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ with the same hypothetical sample as previous plots, with the 2700 Ma isochron (dashed line), corresponding kappa curve (blue) and initial isotope composition (grey circle)

3.5 Initial Pb isotope ratios

Often we are interested in the initial Pb isotope composition of a sample at the time of formation, particularly for more radiogenic samples.

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_{initial} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{T_1} + \mu_{sample}(e^{\lambda_8 T_1} - e^{\lambda_8 t_{sample}}) \tag{8}$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_{initial} = \left(\frac{^{207}Pb}{^{204}Pb}\right)_{T_1} + \frac{\mu_{sample}}{137.88}(e^{\lambda_5 T_1} - e^{\lambda_5 t_{sample}}) \tag{9}$$

$$\left(\frac{^{208}Pb}{^{204}Pb}\right)_{initial} = \left(\frac{^{208}Pb}{^{204}Pb}\right)_{T_1} + \omega_{sample}(e^{\lambda_2 T_1} - e^{\lambda_2 t_{sample}}) \tag{10}$$

The above equations are identical to the Pb isotope equations in section 3.1, so we could use those same functions, but substitute the sample μ (or ω) in. However, this would require two steps: 1) calculate the model source μ (or ω) using the `CalcMu()` (or `CalcMu()`·`CalcKa()` for ω), which requires t_{sample}, X_{sample}, Y_{sample} (and Z_{sample} for equation (10) as input parameters, and 2) use that calculated μ (or ω) value to

input into equations `Calc64()`, `Calc74()` and `Calc84()`. To eliminate the need to do this in two steps, we have added the functions `Calc64in()`, `Calc74in()` and `Calc84in()` to calculate the initial Pb isotope ratios directly. Note: the X_{sample}, Y_{sample} and Z_{sample} are compulsory arguments because these are required to calculate μ and/or κ. The initial Pb isotope ratios can be calculated using our hypothetical sample as follows:

```
Calc64in(2700, 13.5, 14.5)
```

```
[1] 13.304
```

```
Calc74in(2700, 13.5, 14.5)
```

```
[1] 14.464
```

```
Calc84in(2700, 13.5, 14.5, 33)
```

```
[1] 32.852
```

4 Pb evolution models

Pb evolution models can be generated using the `modelcurve()` function in `PbIso`. This function takes the arguments for time (t) – usually given as a time interval e.g. 0:3700 – as well as optional arguments for model starting parameters, μ_1, ω_1 values and decay constants (see Table 2). Additionally, parameters ϵ_1 and ϵ_2 can be specified to allow a variable μ with time (see Cumming and Richards (1975) for further information). These two ϵ parameters are rate factors that account for accelerated or decelerated Pb isotope evolution, and therefore the changes in μ of a Pb source over time. The `modelcurve()` function will generate a dataframe with columns t, x, y, z. These correspond to time, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, respectively. The values x, y and z are calculated following equations (1), (2) and (3) in section 3.1, with the added parameters ϵ_1 and ϵ_2 to allow a variable μ through time. The model curves shown in Figure 1c and Figure @ref(fig:4are generated using the `modelcurve()` function, and we have detailed the steps to do this below.

To generate a simple (Stacey and Kramers 1975) 2nd stage Pb evolution model, only the time (t) is needed in the function `modelcurve()`. The 'SKcurve' dataframe will have 3701 rows of data, each corresponding to a 1 Ma time interval (Table 4).

```
SKcurve <- modelcurve(0:3700)
```

Table 4: First ten rows of the 'SKcurve' dataframe produced using the `modelcurve()` function.

t	x	y	z
0	18.703	15.629	38.631
1	18.702	15.629	38.629
2	18.700	15.629	38.627
3	18.699	15.629	38.625
4	18.697	15.629	38.623
5	18.696	15.629	38.621
6	18.694	15.628	38.620
7	18.693	15.628	38.618

t	x	y	z
8	18.691	15.628	38.616
9	18.690	15.628	38.614

The `modelcurve()` function can be used to produce model curves with different model parameters. For example the 'modelex1' curve in Figure 4, which corresponds to a model μ of 8 is generated by the following:

```
modelex1 <- modelcurve(0:3700, Mu1 = 8)
```

Using the same parameters as above, but using a variable μ with time (specified by parameters ϵ_1 and ϵ_2)

```
modelex2 <- modelcurve(0:3700, Mu1 = 8, E1 = 0.05 * 10^-9, E2 = 0.037 * 10^-9)
```

The `modelcurve()` function can be used to produce model curves over different time ranges with optional arguments. For example, in the code below, 'modelex3' is a hypothetical model using a custom model 'my_model'. These three example curves are shown in Figure 4.

```
my_model <- list(T1 = 4000, X1 = 10.5, Y1 = 11.5, Z1 = 30, Mu1 = 10, W1 = 33)
modelex3 <- modelcurve(0:3500, model = my_model)
```

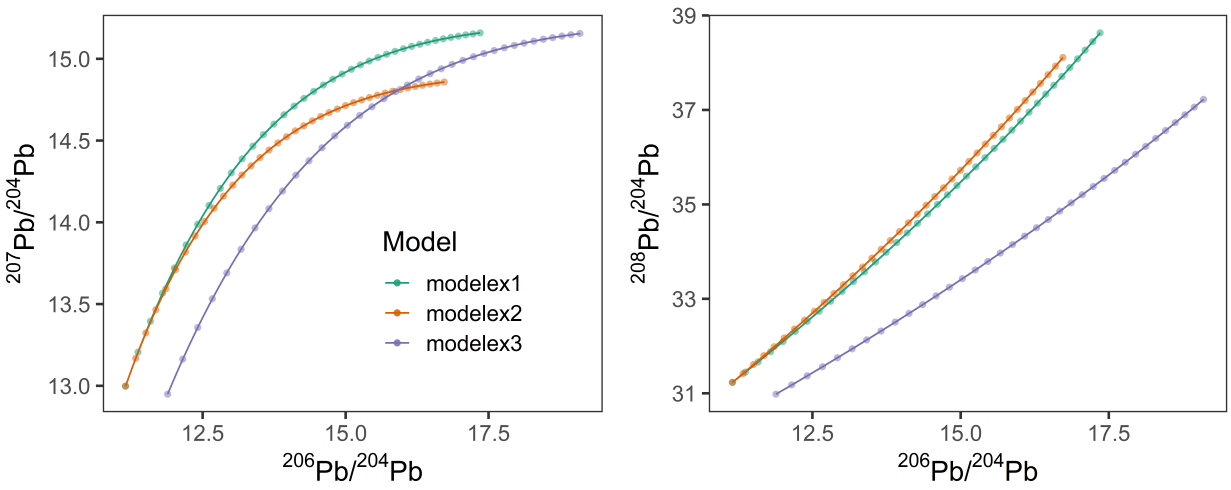

Figure 4: Model curves generated using the `modelcurve()` function for three hypothetical models. Points on curves are shown for every 100 Ma.

5 Other `PbIso` functions

5.1 Least radiogenic calculation

Usually in Pb isotope studies of ore deposits, multiple samples will be obtained from an individual deposit, which produce analyses with a range of Pb isotope values. When doing large regional-scale studies, often only the least radiogenic sample from each deposit will be used.

In `PbIso` we have implemented the function `LeastRad()` which filters a dataset (e.g. df), based on the lowest analysis of an isotope ratio (e.g. $^{207}Pb/^{204}Pb$ or $^{206}Pb/^{204}Pb$) from each group (e.g. ore deposit), in the format: `LeastRad(df, group, value)`.

For example, to filter a sample dataset 'df', based on the lowest $^{207}Pb/^{204}Pb$ analysis from each deposit we would use:

```
LeastRad(df, DepositName, Pb74)
```

Note that this function can only be applied to a dataframe in R, not to individual measurements. More information on using `PbIso` with dataframes is included in the sections below.

5.2 Plotting parameters

In addition to plotting sample data, there are also several plotting features that are usually plotted such as isochron/geochron lines.

5.2.1 Isochrons

To generate isochron/geochron lines for a given time (t), the slope and y-intercept are needed. To calculate the slope of a geochron line on a $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ plot, the function `geochron76slope()` is used, which takes the argument t as well as optional arguments (see documentation). The associated y-intercept for that geochron is given by the function `geochron76yint()`. These can then be used to plot the geochron line along with a model curve. Similarly, to calculate the geochron slope and y-intercept on a $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ plot, the functions `geochron86slope()` and `geochron86yint()` can be used. Geochron lines in Figure 1 are plotted using the below functions for t = 3000 Ma, t = 2000 Ma, t = 1000 Ma and t = 0 Ma. These values can then be used to plot geochron lines, or the function can be called directly, for example by using `abline(a = geochron76yint(2700), b = geochron76slope(2700))` in base R plotting, or `geom_abline(slope = geochron76slope(2700), intercept = geochron76yint(2700))` in ggplot2 (this command is used to produce the black dashed line in 2b). For a $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ plot, the ggplot2 command would be `geom_abline(slope = geochron86slope(2700), intercept = geochron86yint(2700))` (black dashed line in 3). To use this function to generate the slope and y-intercept of a geochron at time 2700 Ma:

```
geochron76slope(2700)
```

```
[1] 0.681
```

```
geochron76yint(2700)
```

```
[1] 5.4
```

```
geochron86slope(2700)
```

```
[1] 0.86
```

```
geochron86yint(2700)
```

```
[1] 21.6
```

6 Applying `PbIso` functions to a dataset, case study: Superior Province, Canada

We have shown above that the `PbIso` package allows for straightforward calculations of various Pb isotope parameters such as model age, model source μ ($^{238}U/^{204}Pb$), time-integrated κ ($^{232}Th/^{238}U$) and initial Pb isotope ratios. However, usually we will want to apply these calculations to an entire dataset rather than to just one sample. Using the standard base R function `mapply()` we can apply the `PbIso` functions to a dataframe. `PbIso` is packaged with a sample dataset, which is a subset of sulphide Pb isotope analyses from the Superior Province in Canada obtained from the DepIso database (see: https://sil.usask.ca/databases.php and Eglington (2018)). We briefly document below how to apply functions to this dataset, using the 'SampleData.csv'.

Import the SampleData.csv file:

```
df <- read.csv("SampleData.csv")
```

The dataframe that we have imported as 'df', before any calculations have been applied, is shown in Table 5.

Table 5: First ten rows of sample data input with sample information and measured Pb isotope ratios

DepositName	age	DepClan	Pb64	Pb74	Pb84
Bachelor Lake	2697	Lode Au	13.492	14.544	33.219
Bachelor Lake	2697	Lode Au	13.607	14.547	33.252
Birchtree Mine	1880	Ni-PGE-Cr	17.318	15.463	37.435
Birchtree Mine	1880	Ni-PGE-Cr	17.320	15.480	36.723
Birchtree Mine	1880	Ni-PGE-Cr	17.320	15.480	36.723
Bousquet	2698	VMS	13.335	14.473	33.200
Bousquet	2698	VMS	13.273	14.448	33.117
Chibougamau	2726	VMS	13.262	14.441	33.186
Chibougamau	2726	VMS	13.279	14.422	33.172
Chibougamau	2726	VMS	13.444	14.477	33.306

We can now apply the `PbIso` functions to the dataframe in the same way we do to individual analyses. Each of the new calculations below will be added as separate columns to the 'df' dataframe.

```
df$Mu     <- CalcMu(df$age, df$Pb64, df$Pb74)
df$Ka     <- CalcKa(df$age, df$Pb84, df$Pb64)
df$Pb64in <- Calc64(df$age, df$Pb64, df$Pb74)
df$Pb74in <- Calc74in(df$age, df$Pb64, df$Pb74)
df$Pb84in <- Calc84in(df$age, df$Pb64, df$Pb74, df$Pb84)
```

Like applying the functions to individual analyses, we can specify optional arguments (e.g. T1, X1, Y1) or specify a predefined or user-defined model (see section 2.2 for defining your own model 'my_model'):

```
df$Mu2 <- CalcMu(df$age, df$Pb64, df$Pb74, T1 = 4570)
df$Mu3 <- CalcMu(df$age, df$Pb64, df$Pb74, model = SK1)
df$Mu4 <- CalcMu(df$age, df$Pb64, df$Pb74, model = my_model)
```

The model age function is slightly more complex, so we need to use the base R function `mapply()`. Instead of using 'model' to add a predefined or user-defined model, we need to use 'MoreArgs'.

```
df$ModAge  <- mapply(CalcModAge, df$Pb64, df$Pb74)
df$ModAge2 <- mapply(CalcModAge, df$Pb64, df$Pb74, T1 = 4570)
df$ModAge3 <- mapply(CalcModAge, df$Pb64, df$Pb74, MoreArgs = SK1)
df$ModAge4 <- mapply(CalcModAge, df$Pb64, df$Pb74, MoreArgs = my_model)
```

The resulting 'df' dataframe with calculations applied (we have removed the extra columns demonstrating the optional arguments and models) is now shown in Table 6:

Table 6: First ten rows of dataframe after the `PbIso` functions have been applied

DepositName	age	DepClan	Pb64	Pb74	Pb84	Mu	Ka	Pb64in	Pb74in	Pb84in	ModAge
Bachelor Lake	2697	Lode Au	13.49	14.54	33.22	8.8	3.7	13.64	14.53	33.14	2608
Bachelor Lake	2697	Lode Au	13.61	14.55	33.25	8.6	3.6	13.64	14.50	33.05	2467
Birchtree Mine	1880	Ni-PGE-Cr	17.32	15.46	37.44	9.7	4.2	15.41	15.24	35.49	721
Birchtree Mine	1880	Ni-PGE-Cr	17.32	15.48	36.72	9.8	3.8	15.41	15.26	35.04	753
Birchtree Mine	1880	Ni-PGE-Cr	17.32	15.48	36.72	9.8	3.8	15.41	15.26	35.04	753
Bousquet	2698	VMS	13.34	14.47	33.20	8.5	4.0	13.64	14.47	33.18	2676
Bousquet	2698	VMS	13.27	14.45	33.12	8.3	3.9	13.64	14.45	33.13	2711
Chibougamau	2726	VMS	13.26	14.44	33.19	8.4	4.1	13.58	14.44	33.17	2712
Chibougamau	2726	VMS	13.28	14.42	33.17	8.2	4.0	13.58	14.41	33.10	2648
Chibougamau	2726	VMS	13.44	14.48	33.31	8.4	4.0	13.58	14.44	33.13	2537

The dataframe is now ready to use for plotting various parameters against each other or for performing a wide range of statistical analysis that is possible with other R functions and packages.

Users may wish to only use the least radiogenic sample from each deposit, which can be performed using the `LeastRad()` function, either as the first step in this workflow (immediately after importing the dataset) or the last (after running the various calculations above).

In either case:

```
dfLR <- LeastRad(df, DepositName, Pb74)
```

6.1 Pb evolution models for Superior Province

Often regional Pb isotope models are developed to help understand the evolution of Pb isotopes in particular regions. Two models are commonly referred to when dealing with Superior Province data, the Abitibi-Wawa model (Thorpe (1999)) and an Archean model based on sulphide data from the Pilbara Craton in Australia and other Archean terranes (Thorpe et al. (1992)). We refer to these below as the 'Abitibi Model' and 'Archean Model', respectively.

```
AbitibiModel <- modelcurve(4000:0, model = THAW, Mu1 = 8)
ArcheanModel <- modelcurve(4000:0, model = THAR, Mu1 = 9)
```

With `PbIso`, it's very straight forward to generate your own multi-stage models. In the hypothetical example below, let's assume we want to model an extraction event from the Stacey and Kramers (1975) 2nd stage model curve at 3200 Ma, with a new μ value of 5. First, the starting parameters need to be obtained. To do this, we can just filter the 'SK2model' dataframe for our starting time, t=3200 Ma, as follows:

```
SK2model <- modelcurve(3700:0)
new_start_params <- filter(SK2model, t == 3200)
new_start_params
```

```
     t           x           y           z
1 3200 12.44246395 14.04849329 32.31097509
```

The new_start_params values are now the starting composition for our 'NewSuperior' model below, using our desired μ value of 5. We can then use the `modelcurve()` function to generate the dataframe for this model and plot it on Figure 5.

```
new_Superior_model <- list(T1 = 3200, X1 = 12.442, Y1 = 14.048, Z1 = 32.311, Mu1=5)
new_Superior_curve <- modelcurve(3200:0, model = new_Superior_model)
```

The above steps can be repeated indefinitely to generate additional model 'stages'. By plotting the Pb isotope data along with the model curves, we can begin to interrogate different Pb evolution models for what might be realistic for the source of Pb in sulphides from the Superior Province. Note that the 'NewSuperior' model is very much a hypothetical example to demonstrate how this can be done in the `PbIso` package, and is not being suggested here as a suitable model for Pb isotope evolution in the Superior Province.

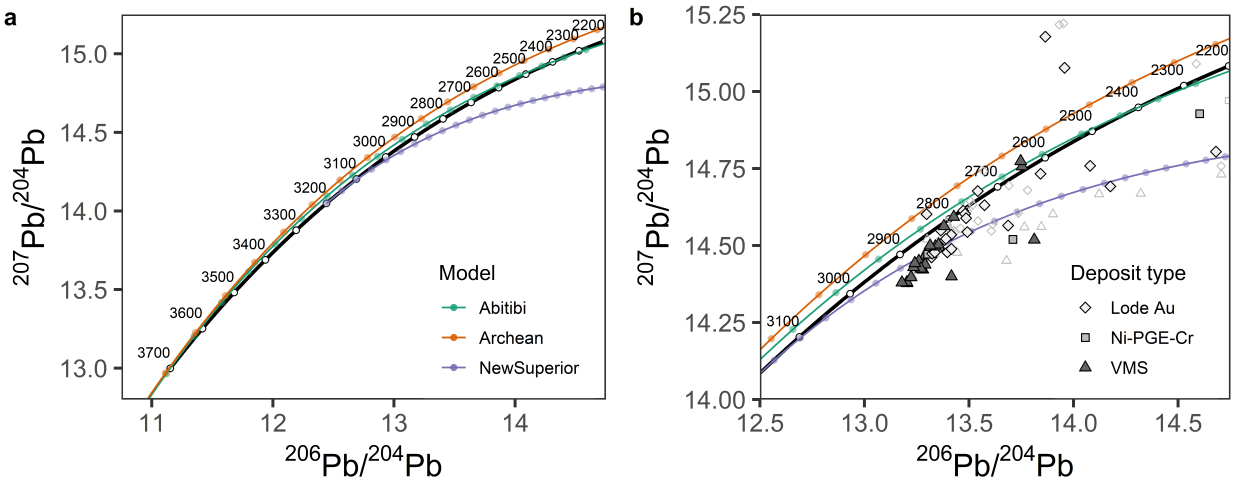

Figure 5: a) Stacey and Kramers (1975) model curve (black line) with three Pb evolution model curves, including two published models (Thorpe (1999) and Thorpe et al. (1992)), and a hypothetical NewSuperior model; and b) the same model curves as (a) but showing the extent of Superior Province Pb isotope data from selected ore deposits. Filled symbols are the least radiogenic value from each deposit and the unfilled symbols include all data from deposits. Circles along model curves are shown at 100 Ma intervals.

7 Shiny application

Using the above functions within R allows for flexibility in applying them to different datasets and using models that are appropriate for specific regions of interest. For a quick and easy to use approach, and to demonstrate some of the capabilities of `PbIso`, we have deployed the `PbIso` package into a Shiny application (https://shereearmistead.shinyapps.io/PbIsoApp/). The app allows users to add their own data by simply copying and pasting data into an excel-like spreadsheet. The app will then automatically generate the values for model age, model source μ ($^{238}U/^{204}Pb$), time-integrated κ ($^{232}Th/^{238}U$) and the three initial Pb isotope

ratios. The app also plots these data onto a series of standard plots. These include; 1) model source μ ($^{238}U/^{204}Pb$) vs. age; 2) time-integrated κ ($^{232}Th/^{238}U$) vs. age; 3) $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$; and 4) $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$. The app also allows users to modify the model parameters such as T1, X1, Y1 and decay constants. We advise caution before modifying these values unless there are good model constraints available.

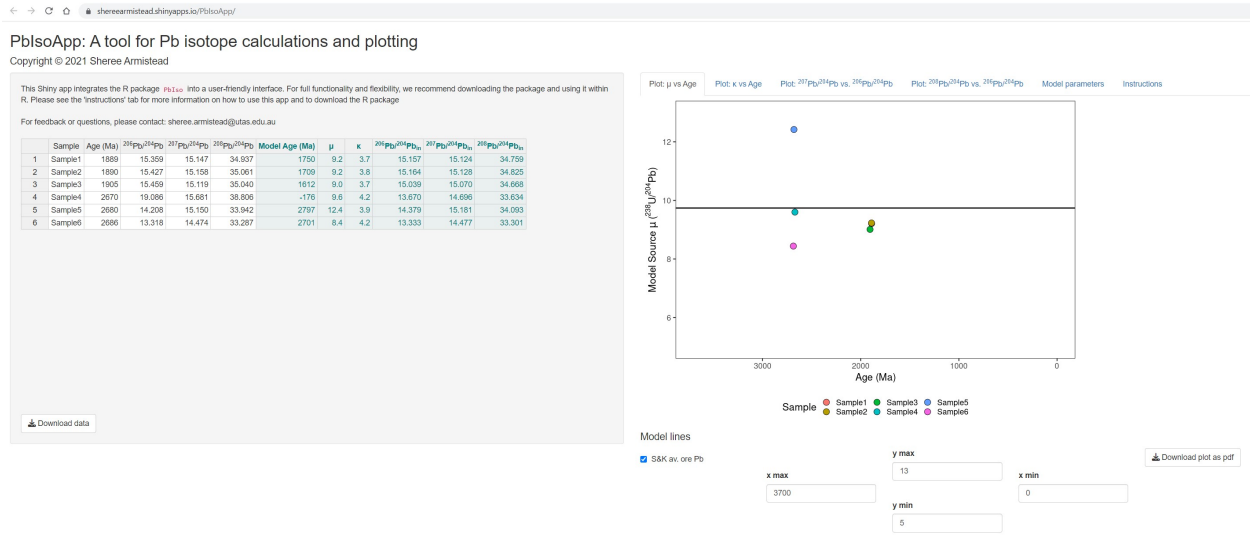

Figure 6: Screenshot of the PbIso shiny application. Left side is where the user can copy and paste data, and values are subsequently calculated. The right side has a series of tabs that include four commonly used Pb isotope plots and a tab for modifying the model parameters

The spreadsheet with newly calculated values can be exported as a .xlsx file by clicking the 'Download data' button. The downloaded spreadsheet contains two tabs, the 'DataOutput' tab contains the input data with the new calculations as shown on the left hand side of the Shiny App screen. The second tab in the .xlsx spreadsheet is the 'ModelParameters' tab and contains all of the values from the 'Model parameters' tab in the Shiny App that were used to generate the calculated values. The four plots can be downloaded separately as .pdf files by clicking the 'Download plot as pdf' button in the lower right corner. If the input sample data is 12 samples or less, these will be differentiated by colour and the sample ID included in a legend below the plots. For more than 12 samples, differentiating by colour becomes difficult and so these will simply be plotted as the same colour points. Optional lines and curves for different Pb isotopic models can be selected or deselected using the controls in the lower panel. The x and y axis limits can be specified either by typing a number or using the up/down arrows in the y min, y max, x min and x max fields. The two isotopic plots have the option of adding a 95% filled contour behind the data.

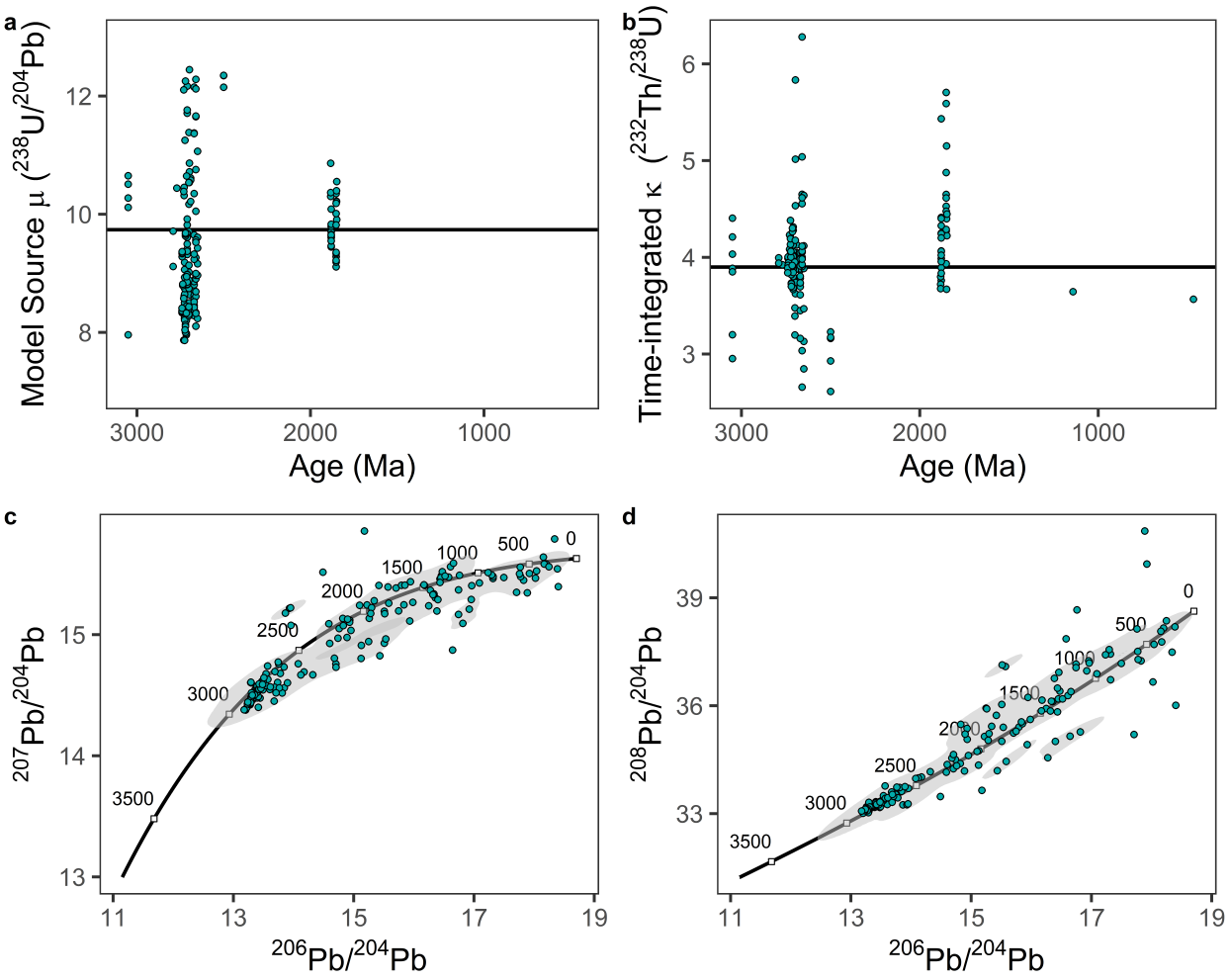

Figure 7: PbIso Shiny app plots that are produced based on user input data

8 Conclusion

We have provided a user-friendly R package for dealing with Pb isotope data. The functions allow maximum flexibility in that they can be used in a very simple way accepting the default values for the Stacey and Kramers (1975) 2nd stage model, or the user can change individual parameters or apply a user-defined model. This toolset adds to the growing number of open-source software packages that help with processing and interpreting geological data. This package may continue to have features added beyond the publication of this manuscript, and all updates will be managed and maintained through: https://github.com/ShereeArmistead/PbIso .

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- Metal Earth publication number ####TBA
- Ryan Ickert and Michael Anenburg are thanked for feedback that improved the Shiny Application
-

10 Code availability section

Name of the code/library: PbIso

Contact: sheree.armistead@utas.edu.au

Hardware requirements: …

Program language: R

Software required: R

Program size: 1MB

The source codes are available for downloading at the link: https://github.com/ShereeArmistead/PbIso

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