IsoFishR: An application for reproducible data reduction and analysis of strontium isotope ratios ($^{87}$Sr/$^{86}$Sr) obtained via laser-ablation MC-ICP-MS

Malte Willmes1,*, Katherine M. Ransom1,2, Levi S. Lewis1, Christian T. Denney1, Justin J. G. Glessner3, James A. Hobbs1

1 Department of Wildlife, Fish and Conservation Biology, UC Davis, Davis, California, United States of America, 2 Department of Land, Air, and Water Department, UC Davis, Davis, California, United States of America, 3 Interdisciplinary Center for Plasma Mass Spectrometry, UC Davis, Davis, California, United States of America

* mwillmes@ucdavis.edu

Abstract

The IsoFishR application is a data reduction and analysis tool for laser-ablation strontium isotope data, following common best practices and providing reliable and reproducible results. Strontium isotope ratios ($^{87}$Sr/$^{86}$Sr) are a powerful geochemical tracer commonly applied in a wide range of scientific fields and laser-ablation inductively coupled mass spectrometry is considered the method of choice to obtain spatially resolved $^{87}$Sr/$^{86}$Sr isotope ratios from a variety of sample materials. However, data reduction and analyses methods are variable between different research groups and research communities limiting reproducibility between studies. IsoFishR provides a platform to standardize these methods and can be used for both spot and time-resolved line transects. Furthermore, it provides advanced data analysis tools and filters for outlier removal, noise reduction, and visualization of time resolved data. The application can be downloaded from GitHub (https://github.com/MalteWillmes/IsoFishR) and the source code is available, encouraging future development and evolution of this software.

Introduction

Strontium is a lithophile alkaline earth metal and substitutes easily for Ca$^{2+}$ in the structures of minerals such as plagioclase feldspar, gypsum, calcite, dolomite, aragonite and apatite [1]. As a trace element, it is found in many igneous, metamorphic and sedimentary rock types, in the ocean, rivers and groundwater, in soils, plants, and animal soft and hard tissues. It has four naturally occurring isotopes, all of which are stable, namely $^{84}$Sr (~0.56%), $^{86}$Sr (~9.87%), $^{87}$Sr (~7.04%) and $^{88}$Sr (~82.53%) [2]. The isotopic abundance of $^{87}$Sr varies because of the production of radiogenic $^{87}$Sr by the decay of $^{87}$Rb by emission of a negative $\beta$-particle with a half-life...
products constitute endorsement or
recommendation for use. Kathrine Ransom was
funded from the California Department of Water
Resources contract #460001196 to James
Hobbs. The funders had no role in study design,
data collection and analysis, decision to publish, or
preparation of the manuscript.

Competing interests: The authors have declared
that no competing interests exist.

of ~4.88 x 10^{10} \text{ years} (\text{Eq} \ 1).

\begin{equation}
\frac{^{87}\text{Rb}}{^{37}} \rightarrow \frac{^{87}\text{Sr} + \beta^- + \nu + Q}{^{38}}
\end{equation}

\beta^- \ \text{beta particle}

\nu \ \text{antineutrino}

Q \ \text{decay energy}

\text{^{87}Sr/^{86}Sr} \ \text{composition of materials found in nature can vary based on the age and Rb/Sr}
composition of the underlying bedrock geology. Through weathering, this bedrock strontium
is transferred into the environment: the soils, plants, and waterbodies of a region. Thus,
the \text{^{87}Sr/^{86}Sr} isotope ratios measured in minerals and tissues such as teeth, bones, otoliths,
shells, feathers, and speleothems, reflect the available sources of strontium that were present
during their formation. This also applies to geologically derived materials, such as pottery or
flint, that were sourced locally. Consequently, it can be possible to trace the origin of materials
and reconstruct a time resolved record of movement and transport across geologically differ-
ent regions.

Due to the natural variation in strontium isotope ratios (\text{^{87}Sr/^{86}Sr}), they are a widely applied
geochemical tracer across scientific fields including geology [3,4], ecology [5–7], paleoclimate
sciences [8,9], archaeology [10,11], food sciences [12,13], and forensic sciences [14].

Laser-ablation (LA) mass spectrometry is considered the method of choice for many of
these applications because it provides a high spatial sampling resolution (on the order of ~10s
of \mu m) and a high sample throughput. The analytical methods to apply laser-ablation to a vari-
ety of natural materials were developed early on [15–17] and are constantly evolving and
improving [18–24]. Recently, large amounts of effort have been placed on producing accurate
and reliable data even from analytically problematic materials, such as bioapatite, that have
direct interferences on the \text{^{87}Sr/^{86}Sr} isotope ratio [25–27]. However, with a few exceptions
such as the commercial program “Iolite” [28,29], software developed to process and
analyze \text{^{87}Sr/^{86}Sr} isotope ratios has been limited. Consequently, data reduction and data analy-
ses methods are variable between laboratories, making direct data comparisons and aggrega-
tion challenging. Furthermore, evaluating the quality of strontium isotope data relies on
proper reporting of data reduction procedures, interference corrections, and analyses paramet-
ers [19,21,26]. Finally, most conventional software is geared towards non-time resolved spot
analysis, where each analysis is treated as a single homogenous sample. However, one of the
great advantages of laser ablation analysis is the time-resolved continuous track method,
where the laser traverses across a heterogeneous sample to identify changes in the \text{^{87}Sr/^{86}Sr}
isotope ratio at a high spatial resolution. In the case of continuous track analysis, a single aver-
aged \text{^{87}Sr/^{86}Sr} value is not appropriate, rather the full time-resolved data profile is of interest.
This is also important for applications using laser-ablation for depth profiling, where the laser
is used to drill into the sample to obtain a time-resolved record from the outside of the sample
without prior cutting [18,30].

To address the need for consistent data reduction and reporting as well as useful analysis of
continuous track laser-ablation mass spectrometry \text{^{87}Sr/^{86}Sr} data, we developed the IsoFishR
application. The aim of this application is to provide rapid, reliable, and reproducible data
reduction and analysis of laser-ablation strontium isotope ratios, that can be applied across dif-
ferent scientific disciplines and sample materials. In contrast to a software such as Iolite, that is
aimed at analyzing a whole range of different element ratios and isotopes, our tool is specific
to strontium isotopes (\text{^{87}Sr/^{86}Sr}) which allows a focused and targeted solution for high sample
throughput. Additionally, our software is open source, so it can be adapted by its users to fit
their data reduction and data analyses preferences.
Program architecture

Overview
The IsoFishR application is written in the statistical programming language R, which is an open source language that is supported across all major operating systems [31]. R was chosen because it will ensure the usability and longevity of the application due to the large amounts of data manipulation and statistical packages already available, including packages directly aimed at isotope and elemental analyses [32–35]. The backbone of the IsoFishR application is the R package shiny [36], which allows for the creation of an interactive graphical user interface (GUI) connected to a running R session. This allows the user to perform complex operations without directly having to interact with the underlying R commands. IsoFishR utilizes several other established R packages (Table 1), which are available on the Comprehensive R Archive Network; CRAN (http://cran.rproject.org) and are installed and loaded automatically when running IsoFishR. The source code is maintained using Git version control and hosted online (https://github.com/MalteWillmes/IsoFishR), which allows for issue tracking, and development and dissemination of new features and updates. In GitHub, users can create their own branch of the application and modify it to fit their study protocols while staying connected to any improvements made to the base version of the application. This paper describes the master branch, stable release version 1.0. Changes to the application will be reflected in the version number and listed in the readme document on GitHub.

Layout
The IsoFishR application is divided into a navigation menu (left sidebar) and a main window that displays the different pages. Five pages can be accessed through the navigation window; About, Projects, Data Reduction, Data Analysis, and Data Reporting.

The “About” page consists of a short introduction section and describes the functionality of the application, including links to the tutorial, GitHub issue tracker, as well as funding sources, and license information. The “Projects” page allows users to create and manage projects. Projects are used in the application to group similar types of analyses together (for example a set of samples). They define the import settings from the mass spectrometer and set the default data reduction parameters to apply to each sample. Creating a new project creates a set of folders in the app root directory where all settings, data, and plots are stored. The “Data Reduction” page (Fig 1A) is used to process the data files from the mass spectrometer and to provide a quick overview of the data quality. After the data has been reduced it can be edited and manipulated

Table 1. List of the R packages currently utilized by IsoFishR. More information for each package is available on their respective CRAN sites or on GitHub.

| R package name | Use | Reference |
|----------------|-----|-----------|
| ‘shiny’        | A web application framework for R | [36] |
| ‘shinydashboard’ | Creating dashboards in shiny | [37] |
| ‘shinyWidgets’ | Custom inputs widgets | [38] |
| ‘tidyverse’    | Collection of compatible R packages for advanced data cleaning, manipulation, and plotting | [39] |
| ‘broom’        | Convert statistical objects into tidy data frames | [40] |
| ‘changepoint’  | Changepoint analysis | [41] |
| ‘colourpicker’ | Color picking for shiny | [42] |
| ‘mgcv’         | Generalized Additive Models | [43] |
| ‘DT’           | Data objects and data table in R | [44] |
| ‘zoo’          | Advanced moving average functions | [45] |

https://doi.org/10.1371/journal.pone.0204519.t001
using the “Data Analysis” page (Fig 1B). Finally, the “Data Reporting” page provides a quick overview of the current analysis.

Features

The standard workflow is shown in Fig 2 and the following section explains the available features of the IsoFishR application (version 1.0) in detail. Data are imported in the “Data Reduction” page and multiple files from a single folder can be selected for import. There is no limit to the individual data files that make up a project but loading times increase significantly past ~500 individual sample files. Once data has been reduced it can be imported in the "Data analysis" page and can be reimported multiple times as long as the original columns are not

https://doi.org/10.1371/journal.pone.0204519.g001
changed (e.g. outside of R). This allows the user to work on data analysis iteratively and save the changes. The project and datafiles include all the relevant analysis information so that a project can be transferred between different users or could be included as supplementary material in publications which would allow any user to recalculate and evaluate the presented data.

**Data import**

Data import format, such as the number and order of columns in the mass spectrometer export file, varies between different mass spectrometers, labs, and projects. For data reduction in IsoFishR several specific measurements are required (Table 2). To facilitate the import of different data files into the IsoFishR application the project page allows the user to change and select the order of columns and the format of the original data file. Once a new data import format has been developed it is saved together with the project file and is available for any future analyses.

**Data reduction**

Depending on the analyzed material, there are a number of potential isobaric interferences on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio including double charged rare earth elements (REEs), Kr, Rb, Ca dimers, Ca...
argides, and polyatomic interferences, see Table 3 [19,21,46]. Data reduction procedures in IsoFishR follow established protocols for Kr and Rb corrections using known isotope ratios [47]. No corrections are currently applied for interferences from rare earth elements, Ca dimers, Ca argides, or polyatomic interferences. These interferences are complex and occur only in some sample materials (e.g., biogenetic apatite) and consequently are not included in the default data reduction schema. For these applications the interferences could be monitored (e.g., $^{89}$Y for REEs), and corrected as needed by either peak stripping (Ca dimers, Ca argides) or controlled analytical conditions and instrument modifications (polyatomic interferences). The Ca dimer and Ca argide peak stripping could be a valuable extension of the current data reduction procedure, because while it does not significantly affect the $^{87}$Sr/$^{86}$Sr isotope ratio in most applications, it does lead to a shift in the $^{84}$Sr/$^{86}$Sr isotope ratio, which can be used as a monitor for data quality [19,21,46].

1. **Averaging integration**: The first step is to use the "integration time" value to average the raw data to a one data point per second resolution. For example, an integration time set to five indicates that the instrument collected five raw data points per second (0.2s per raw data point) and the application will average these to a single value.

2. **Baseline correction**: Correcting for the krypton interference originating from the argon supply ($^{86}$Kr) is achieved by monitoring the background level before the analysis and subtracting the background from the data. In the default configuration, the data background is defined as any value below a user defined mass 88-voltage (V) cutoff, default is set to 0.05 V during a set blank time at the beginning of the measurement, default is 30 seconds.

3. **Detector cutoff value**: A maximum 88 V cutoff is applied to the entire data to exclude any values that went over voltage, default 9.8 V. This should be adjusted to the detectors used on the instrument.

4. **Mass bias correction**: The mass bias induced from the laser and the instrument mass discrimination is calculated using an exponential correction to the stable $^{86}$Sr/$^{88}$Sr ratio of 0.1194 (Eqs 2 and 3).

\[
\frac{^{87}\text{Sr}}{^{86}\text{Sr}}(\text{corrected}) = \frac{^{87}\text{Sr}}{^{86}\text{Sr}}(\text{measured}) \times \frac{m_{87}}{m_{86}}^f
\]

\[
f = \text{Sr mass bias}
\]

\[
m_{87} = 86.9088775
\]
\[ m_{86} = 85.9092607 \]

\[ f = \frac{\ln \left( \frac{m_{86}^{\text{true}}}{m_{86}^{\text{measured}}} \right)}{\ln \left( \frac{m_{88}}{m_{87}} \right)} \]  

(3)

\[ \frac{m_{87}^{\text{true}}}{m_{88}} = 0.1194 \]

\[ m_{88} = 87.9056123 \]

5. **Rubidium correction**: The direct interference of \(^{87}\text{Rb}\) on the \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio is corrected by monitoring \(^{85}\text{Rb}\) and subtracting the appropriate amount from the signal at mass 87 assuming the natural \(^{85}\text{Rb}/^{87}\text{Rb}\) ratio of 2.59712. The \(^{85}\text{Rb}/^{87}\text{Rb}\) ratio is corrected for mass bias, using the mass discrimination factor calculated from strontium (Eqs 4 and 5). Next, the strontium mass bias is applied to the Rb corrected \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio from Eq 5 using Eqs 2 and 3.

\[ \frac{^{87}\text{Rb}_{\text{measured}}}{^{87}\text{Sr}/^{86}\text{Sr}} = \frac{^{87}\text{Rb}_{\text{true}}}{^{87}\text{Sr}/^{86}\text{Sr}} \times \frac{^{85}\text{Rb}_{\text{measured}}}{^{85}\text{Rb}_{\text{measured}}} \]  

(4)

\[ m_{85} = 84.9117897 \]

\[ m_{87} = 86.9091805 \]

\[ ^{87}\text{Sr}_{\text{measured}} = ^{87}\text{Sr}_{\text{Intensity}} - ^{87}\text{Rb}_{\text{measured}} \]  

(5)

6. **Outlier detection and removal**: Outliers in the data are the result of potentially many different sources such as surface features, cracks, or residues from resins, dust, or other materials. They are removed based on the median and a multiplicate of the standard deviation, default is 2, calculated over a user defined moving median window.

7. **Distance calculation**: The run speed value is used to calculate the length of the analysis based on the time of the analysis. This results in a distance resolved \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope profile as shown in the main plot window on the "Data Reduction" page.

8. **Smoothing**: Laser-ablation strontium isotope data is typically accompanied by more signal noise than traditional solution-based work both from instrumental conditions (laser pulses, gas uptake), as well as actual changes within the sample’s physical properties and composition (e.g., zones within an otolith). Statistical smoothing of reduced data has the aim to minimize noise while keeping the important changes in the profile. This is achieved in IsoFishR using a moving average or applying a thin plate spline fit. Both functions allow the user to vary the degree of smoothing appropriate for different instruments and sample materials.

9. At this stage data can be saved (either appending to an existing project or overwriting any present files) and moved outside of the IsoFishR application for further analysis or imported into the "Data analysis" page.

**Data analysis**

First the reduced data needs to be reimported (e.g., Project_name_03_reduced_data.csv). Then a variety of data analysis options are available, and they should be carried out in the sequence as denoted on the “Data Analysis” page.
**Data selection.** Trimming of data is a common task as the laser ablation analysis is time dependent and sometimes starts and/or ends outside of the bounds of the sample material. Additionally, the laser and mass spectrometer are often given time to stabilize before collecting important data. Trimming at the beginning of the profile will recalculate the distance based on the new zero position (if enabled), while trimming at the end of the profile will remove the entered distance in μm from the end of the profile. Since trimming removes data from the analysis file it is important to perform the trimming step before doing any further qualitative or quantitative data analysis.

**Profile orientation.** Next the profile can also be reversed (inverting the x-direction of the analysis). This can be useful if some of the profiles were analyzed in different directions, but the same orientation is required for further analysis.

**Data filtering.** The IsoFishR application has three options for calculating summary statistics of the distance resolved $^{87}$Sr/$^{86}$Sr isotope profile: (i) no distinct defined regions (homogeneous sample case), (ii) user defined manual regions, and (iii) statistically defined regions.

(i). Homogenous sample, for example a reference material, a simple average across the trimmed data is most appropriate and this is automatically calculated for any analyzed sample.

(ii). Heterogeneous types of samples require different approaches. For example, in a case where the sample material has a distinctive physically observable pattern (such as the rings in an otolith, or layers in a speleothem), performing summary statistics within distinct regions along the profile may be more appropriate. Within IsoFishR, regions can be manually defined using the known distances from the start of the profile.

(iii). In other cases, it may be more appropriate to determine distinct ranges within a sample based on some statistical test. In IsoFishR this can be achieved by implementing changepoint analysis [41]. The changepoint analysis is a statistical approach in which the variability in the $^{87}$Sr/$^{86}$Sr isotope ratio along the profile is used to define significant regions. IsoFishR calculates summary statistics for sample points that fall within each user defined or changepoint defined region. There are many other pattern detection methods available in R that can easily be implemented in IsoFishR, if required.

**Saving analyzed data.** Changes to each profile are saved using the “save edits to profile button” and at the end of the data analysis the complete data can be exported using the “Export analyzed data” option. Previously analyzed data can be reimported and edited.

**Data reporting**
The analyzed data from IsoFishR is saved in “long” format, where each row is one observation of the sample. This allows for easy data transfer for additional analyses either in R or python. More extensive data analyses and reporting should be done outside of IsoFishR (see next section on data exporting). However, for a quick overview the “Data Reporting” tab can be used. It includes a list of data tables and a grouping tab for creating a summary data table.

**Data export**
Data is exported as comma delimited (.csv) files which can be imported into a variety of software programs (including R) for further data analysis. For each step and each analyzed profile, the application saves to a summary file and creates plot files in PDF format. Data exports are organized in tiers, starting with raw data at T1, background data T2, Reduced data T3 from the...
“Data Reduction” page, and analyzed data T4 from the “Data Analysis” page. A metadata file is included in the application folder which contains the detailed descriptions for each column of data.

Example data

Line scan/transect analysis

Here we include a case study to illustrate the work flow for a typical application in IsoFishR. The case study uses $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analysis of otoliths (“earbones”) to identify the life history of a Chinook salmon ($\text{Oncorhynchus tshawytscha}$) from the Central Valley, California. Otoliths consist of calcium carbonate (aragonite) and accrete continuously throughout the life of a fish, providing a life-long archive of physiological and environmental conditions. The accretions typically form banded microstructures that are identifiable under a microscope and are commonly used for aging the fish. This physical information can be used to filter the strontium isotope data obtained from laser ablation analyses (Fig 3).

The five sagittal otoliths provided in this case study were collected in 2016 during carcass surveys on Putah Creek, a small river between UC Davis and the city of Winters, CA. Salmon were previously extirpated from this river and consequently identifying their origin is of great interest. The example data analysis encompasses the following steps:

---

Fig 3. An image of a Chinook salmon ($\text{Oncorhynchus tshawytscha}$) otolith and the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ isotope profile. The otolith was aged, and microstructures were visually identified to inform the selection of discrete ranges within the strontium isotope profile that relate to different life stages of the salmon.

https://doi.org/10.1371/journal.pone.0204519.g003
Step 1) Create a new project called “Putah Creek Salmon” and adjust the default data reduction settings. The otoliths were analyzed using a run speed of 5 μm/s and a moving average of 20 points. The otoliths were analyzed from the dorsal to the ventral lobe capturing the full life history in duplicate. Update the project settings and add a comment ("Initial Putah Creek data reduction").

Step 2) From the “Data reduction” page it is now possible to import the five runfiles, located in the “Example runfiles” folder within the app directory. Data reduction should only take a few seconds for this example data but can take much longer for a large number of raw data files.

Step 3) The sample selector tool enables the user to view each of the sample profiles individually. For an initial idea of the data quality, measurement parameters such as Sr (V), 83Kr, and 85Rb/88Sr plots are displayed and can be checked. The button next to the main 87Sr/86Sr graph enables various graphing options. Next, clicking on the “save reduced data” button will create three .csv files (Project_name_01_raw_data; Project_name_02_background_data; Project_name_03_reduced_data), as well as four plot types for each analyzed otolith (83Kr, 85Rb, 87Sr/86Sr_reduced, and totalSr). At this stage further processing could be performed outside of IsoFishR or we can continue with data reduction and analysis within the app.

Step 4) Change to the “Data Analysis” page and import the Project_name_03_reduced_data.csv file. After the data is loaded individual samples can be selected with the sample selector. These example otoliths require data trimming to remove erroneous data points due to laser ablation analysis of the sample holder at the beginning and the end of the transect. A trim distance of 10 μm from both the left and right removes the erroneous data points for all samples except “PC_2016_01_B4_11R” which requires a 40 μm left trim. Trimming is either subjectively based on the quality of the data or can be estimated from measuring the laser scar under the microscope after the analyses.

Step 5) Adult salmon otoliths contain a core, a natal region, and an adult region. The core often shows a maternal influence (from the parent maturing in the ocean), the natal region should reflect the stream the fish spawned and reared in, and the adult region should reflect the ocean habitat. This ocean habitat is particular useful because the global marine 87Sr/86Sr ratio is well known at 0.70918 [49,50]. Consequently, this can be used as an internal reference in each of the samples. The core is visible under the microscope and was measured for each fish. The natal region is often assumed to be at roughly ~150–200 μm from the core but can vary between individuals depending on their growth. The adult region encompasses the rest of the otolith. Each of these regions can be marked using the manual region selection (Fig 3) by typing in the numbers or selecting the ranges on the graph (Table 4). The adult region can be defined by either the remaining section of the otolith after the natal portion, or alternatively, only the ocean habitat that displays a stable 87Sr/86Sr ratio around 0.70918. The final step is to save edits to each graph and then export the analyzed data.

### Spot data analysis

Spot data collection is also frequently used in laser ablation analysis. Here we include an example from one of our commonly used internal reference materials, a White seabass (Atractoscion nobilis) otolith. The white sea bass spends most of its life in the ocean and therefore any spot on the otolith from this fish should reflect the modern average global ocean 87Sr/86Sr ratio of...
0.70918. For the example spot analysis create a new project named “reference_materials”, change the analysis type in the project settings to spot, and then click update project settings. Load the runfile in the “data reduction” tab. Here it is visible that multiple spot analyses were saved within a single run file and that the data reduction automatically picked out the correct areas to average over (Fig 4). Edits can then be exported and saved. The reduced data can be loaded in the “data analysis” tab for further processing, if needed, in order to trim and manually select spot regions.

Conclusions and future directions

IsoFishR aims to provide a fast, reproducible, and transparent data reduction application for laser-ablation strontium isotope analysis. Since the application was programmed in R, it combines a robust framework with the ability for users to customize and adapt the program. Furthermore, many additional R packages for data smoothing and data filter processing are available and can be utilized for more advanced data exploration and analysis. We expect that the IsoFishR application will continue to evolve and we encourage contributions from other researchers and developers.

Table 4. Measured microstructure features on otolith images for the core and natal regions of the five Chinook salmon (Oncorhynchus tshawytscha) example otoliths. The adult regions for these examples are based on the section of otolith for which the strontium isotope profile remains stable at around 0.70918.

| Sample ID       | Left trim | Right trim | Core (μm)   | Natal (μm)   | Adult (μm)   |
|-----------------|-----------|------------|-------------|--------------|--------------|
| PC_2016_01_A2_4R | 10        | 10         | 1980–2030   | 2164–2684    | 2870–5654    |
| PC_2016_01_A3_6R | 10        | 10         | 1520–1570   | 1810–2145    | 2355–4444    |
| PC_2016_01_B4_11R | 40        | 10         | 1564–1614   | 1790–2204    | 2424–4590    |
| PC_2016_01_C3_15R | 10        | 10         | 1525–1585   | 2070–2185    | 2425–4490    |
| PC_2016_01_C4_16R | 10        | 10         | 1977–2027   | 2262–2707    | 2932–5646    |

https://doi.org/10.1371/journal.pone.0204519.t004

Fig 4. $^{87}\text{Sr}/^{86}\text{Sr}$ results from 3 discrete spot analyses on the White Seabass (Atractoscion nobilis) otolith. Average values for each of the spots are shown and are in good agreement with the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern ocean water (0.70918) [49,50]. The red data points indicate outlier values (2σ).

https://doi.org/10.1371/journal.pone.0204519.g004
Access to IsoFishR

IsoFishR is available under the MIT license from GitHub (https://github.com/MalteWillmes/IsoFishR) or by contacting Malte.willmes@googl email.com. New versions of the application will be released on GitHub. Installation requires an up to date R installation. Please report any bugs and problems on GitHub.

Acknowledgments

The authors would like to thank Julie Griffin, Rachel Fichman, Mackenzie Gilliam, James Chhor, and Brian Healey for testing the application and providing helpful comments. We would also like to thank Chris Donohoe for his important work on the original strontium otolith method excel-macro. The Chinook salmon otoliths were collected by the Biotelemetry lab at UC Davis as part of an ongoing research project funded by the Solano County Water Agency. Finally, we would like to acknowledge the reviewers and the editor for providing valuable feedback which improved the quality of this manuscript.

Author Contributions

Conceptualization: Malte Willmes, Katherine M. Ransom, Justin J. G. Glessner, James A. Hobbs.

Data curation: Malte Willmes, Christian T. Denney, Justin J. G. Glessner.

Formal analysis: Justin J. G. Glessner.

Funding acquisition: James A. Hobbs.

Methodology: Malte Willmes, Katherine M. Ransom, Levi S. Lewis, Christian T. Denney, Justin J. G. Glessner.

Project administration: Malte Willmes, James A. Hobbs.

Software: Katherine M. Ransom.

Supervision: James A. Hobbs.

Validation: Levi S. Lewis.

Visualization: Malte Willmes, Katherine M. Ransom, Levi S. Lewis.

Writing – original draft: Malte Willmes, Katherine M. Ransom, Levi S. Lewis, Christian T. Denney, Justin J. G. Glessner, James A. Hobbs.

Writing – review & editing: Malte Willmes, Katherine M. Ransom, Levi S. Lewis, Christian T. Denney, Justin J. G. Glessner, James A. Hobbs.

References

1. Faure G, Mensing TM. Isotopes: Principles and Applications. 3rd ed. Hoboken, New Jersey: John Wiley and Sons Inc.; 2005.

2. de Laeter JR, Böhlke JK, De Bièvre P, Hidaka H, Peiser HS, Rosman KJR, et al. Atomic weights of the elements. Review 2000 (IUPAC Technical Report). Pure Appl Chem. 2003; 75: 689–800. https://doi.org/10.1351/pac200375060683

3. Davidson J, Tepley F, Palacz Z, Meffan-Main S. Magma recharge, contamination and residence times revealed by in situ laser ablation isotopic analysis of feldspar in volcanic rocks. Earth Planet Sci Lett. 2001; 184: 427–442. https://doi.org/10.1016/S0012-821X(00)00333-2

4. Zhang L, Ren Z-Y, Wu Y-D, Li N. Strontium isotope measurement of basaltic glasses by laser ablation multiple collector inductively coupled plasma mass spectrometry based on a linear relationship between
analytical bias and Rb/Sr ratios. Rapid Commun Mass Spectrom. 2018; 32: 105–112. https://doi.org/10.1002/rcm.8011 PMID: 29027292

5. Brennan SR, Zimmerman CE, Fernandez DP, Cerling TE, McPhee M V., Wooler MJ. Strontium isotopes delineate fine-scale natal origins and migration histories of Pacific salmon. Sci Adv. 2015; 1: e1400124–e1400124. https://doi.org/10.1126/sciadv.1400124 PMID: 26601173

6. Vogel JC, Eglington B, Aurel JM. Isotope fingerprints in elephant bone and ivory. Nature. 1990; 346: 747–749. https://doi.org/10.1038/346747a0

7. Hobson KA, Barnett-johnson R, Cerling TE. Chapter 13: Using Isoscapes to Track Animal Migration. In: West JB, Bowen GJ, Dawson TE, Tu KP, editors. Isoscapes: Understanding Movement, Pattern, and Process on Earth Through Isotope Mapping. Springer Netherlands. 2010. pp. 1–487.

8. Bell R, Borsato A, Fria S, Drysdale R, Maas R, Greig A. Investigating the hydrological significance of stalagmite geochemistry (Mg, Sr) using Sr isotope and particulate element records across the Late Glacial-to-Holocene transition. Geochim Cosmochim Acta. Elsevier Ltd; 2017; 199: 247–263. https://doi.org/10.1016/j.gca.2016.10.024

9. Wortham BE, Wong CI, Silva LCR, McGee D, Montañez IP, Troy Rasbury E, et al. Assessing response of local moisture conditions in central Brazil to variability in regional monsoon intensity using speleothem 87Sr/86Sr values. Earth Planet Sci Lett. Elsevier B.V.; 2017; 463: 310–322. https://doi.org/10.1016/j.epsl.2017.01.034

10. Bentley RA. Strontium Isotopes from the Earth to the Archaeological Skeleton: A Review. J Archaeol Method Theory. 2006; 13: 135–187. https://doi.org/10.1007/s10816-006-9009-x

11. Slovak NM, Paytan A. Handbook of Environmental Isotope Geochemistry. Baskaran M, editor. Handbook of Environmental Isotope Geochemistry. Berlin, Heidelberg: Springer; 2012. https://doi.org/10.1007/978-3-642-10637-8

12. Kelly S, Heaton K, Hoogewerff J. Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis. Trends Food Sci Technol. 2005; 16: 555–567. https://doi.org/10.1016/j.tifs.2005.08.008

13. Voerkelius S, Lorenz GD, Rummel S, Qué tel CR, Heiss G, Baxter M, et al. Strontium isotopic signatures of natural mineral waters, the reference to a simple geological map and its potential for authentication of food. Food Chem. Elsevier Ltd; 2010; 118: 933–940. https://doi.org/10.1016/j.foodchem.2009.04.125

14. Beard BL, Johnson CM. Strontium isotope composition of skeletal material can determine the birth place and geographic mobility of humans and animals. J Forensic Sci. 2000; 45: 899–904. https://doi.org/10.1039/Ja9961100899

15. Arrowsmith P. Laser Ablation of Solids for Elemental Analysis by Inductively Coupled Plasma Mass Spectrometry. Anal Chem. 1987; 59: 1437–1444. https://doi.org/10.1021/acs.ja00137a014

16. Christensen JN, Halliday AN, Lee D-C, Hall CM. In situ Sr isotopic analysis by laser ablation. Earth Planet Sci Lett. 1995; 136: 79–85. https://doi.org/10.1016/0012-821X(95)00181-6

17. Longerich HP, Jackson SE, Günther D. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. J Anal At Spectrom. 1996; 11: 899–904. https://doi.org/10.1039/Ja9661100899

18. Sanborn M, Telmer K. The spatial resolution of LA-ICP-MS line scans across heterogeneous materials such as fish otoliths and zoned minerals. J Anal At Spectrom. 2003; 18: 1231–1237. https://doi.org/10.1016/j.jaas.2003.03.008

19. Woodhead JD, Swearer S, Hergt J, Maas R. In situ Sr-isotope analysis of carbonates by LA-MC-ICP-MS: interference corrections, high spatial resolution and an example from otolith studies. J Anal At Spectrom. 2005; 20: 22. https://doi.org/10.1039/b412730g

20. Woodhead JD, Hallstrom J, Hergt JM, Greig A, Maas R. Isotopic and elemental imaging of geological materials by laser ablation inductively coupled plasma-mass spectrometry. Geostand Geoanalytical Res. 2007; 31: 331–343. https://doi.org/10.1111/j.1751-908X.2007.00104.x

21. Vroon PZ, van der Wagt B, Koornneef JM, Davies GR. Problems in obtaining precise and accurate Sr isotope analysis from geological materials using laser ablation MC-ICPMS. Anal Bioanal Chem. 2008; 390: 465–476. https://doi.org/10.1007/s00216-007-1742-9 PMID: 18080118

22. Pozebon D, Scheffler GL, Dressler VL, Nunes M a. G. Review of the applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to the analysis of biological samples. J Anal At Spectrom. 2014; 29: 2204–2228. https://doi.org/10.1039/C4JA00250D

23. Irgehejer J, Gallier P, Prohaska T. 87Sr/86Sr isotope ratio measurements by laser ablation multicollector inductively coupled plasma mass spectrometry: Reconsidering matrix interferences in bioapatites and biogenic carbonates. Spectrochim Acta Part B At Spectrosc. Elsevier B.V.; 2016; 125: 31–42. https://doi.org/10.1016/j.sab.2016.09.008
24. Fox M, Tripathy-Lang A, Shuster DL. Improved spatial resolution of elemental maps through inversion of LA-ICP-MS data. Chem Geol. Elsevier; 2017; 467: 30–41. https://doi.org/10.1016/j.chemgeo.2017.07.001

25. Lewis J, Coath CD, Pike AWG. An improved protocol for 87Sr/86Sr by laser ablation multi-collector inductively coupled plasma mass spectrometry using oxide reduction and a customised plasma interface. Chem Geol. Elsevier B.V.; 2014; 390: 173–181. https://doi.org/10.1016/j.chemgeo.2014.10.021

26. Müller W, Anczkiewicz R. Accuracy of laser-ablation (LA)-MC-ICPMS Sr isotope analysis of (bio)apatite—a problem reassessed. J Anal At Spectrom. 2016; 31: 259–269. https://doi.org/10.1039/C5JA0311C

27. Willmes M, Kinsley L, Moncel M-H, Armstrong RA, Aubert M, Egging S, et al. Improvement of laser ablation in situ micro-analysis to identify diagenetic alteration and measure strontium isotope ratios in fossil human teeth. J Archaeol Sci. Elsevier Ltd; 2016; 70: 102–116. https://doi.org/10.1016/j.jas.2016.04.017

28. Paton C, Hellstrom J, Paul B, Woodhead J, Hergt J. Iolite: Freeware for the visualisation and processing of mass spectrometric data. J Anal At Spectrom. 2011; 26: 2508. https://doi.org/10.1039/c1ja10172b

29. Paul B, Paton C, Norris A, Woodhead J, Hellstrom J, Hergt J, et al. CellSpace: A module for creating spatially registered laser ablation images within the Iolite freeware environment. J Anal At Spectrom. 2012; 27: 700–706. https://doi.org/10.1039/c2ja10383d

30. Benson A, Kinsley L, Willmes M, Defleur AR, Kokkonen H, Musi M, et al. Laser ablation depth profiling of U-series and Sr isotopes in human fossils. J Archaeol Sci. Elsevier Ltd; 2013; 40: 2991–3000. https://doi.org/10.1016/j.jas.2013.02.028

31. R Core Team. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; 2018; http://www.r-project.org/

32. Mischel SA, Mertz-Kraus R, Joehum KP, Scholz D. TERMITE: An R script for fast reduction of laser ablation inductively coupled plasma mass spectrometry data and its application to trace element measurements. Rapid Commun Mass Spectrom. 2017; 31: 1079–1087. https://doi.org/10.1002/rcm.7895 PMID: 28488735

33. Rittner M, Müller W. 2D mapping of LA-ICPMS trace element distributions using R. Comput Geosci. 2012; 42: 152–161. https://doi.org/10.1016/j.cageo.2011.07.016

34. Sirot C, Ferraton F, Panfili J, Childs AR, Guilhaumon F, Darnaude AM. elementr: An R package for reducing elemental data from LA-ICPMS analysis of biological calcified structures. Methods Ecol Evol. 2017; 8: 1659–1667. https://doi.org/10.1111/2041-210X.12822

35. Solari LA, Tanner M. U-Pb, age, a fast data reduction script for LA-ICP-MS U-Pb geochronology. Rev Mex Ciencias Geol. 2011; 28: 83–91.

36. Chang W, Cheng J, Allaire J, Xie Y, McPherson J. shiny: Web Application Framework for R. R package version 1.0.3. 2017; https://cran.r-project.org/web/packages/shiny/index.html

37. Chang W, Ribeiro BB. shinydashboard: Create Dashboards with “Shiny,” 2018;

38. Perrier V, Meyer F. shinyWidgets: Custom Inputs Widgets for Shiny. 2018; https://cran.r-project.org/package=shinyWidgets

39. Wickham H. tidyverse: Easilly Install and Load “Tidyverse” Packages. 2017; https://cran.r-project.org/package=tidyverse

40. Robinson D. broom: Convert Statistical Analysis Objects into Tidy Data Frames. 2018; http://github.com/tidyverse/broom

41. Killick R, Eckley I. changepoint: An R Package for Changepoint Analysis. J Stat Softw. 2014; 58: 1–19.

42. Attali D. colourpicker: A Colour Picker Tool for Shiny and for Selecting Colours in Plots. 2017; https://cran.r-project.org/package=colourpicker

43. Wood SN. Generalized Additive Models: An Introduction with R. CRC Press Inc.; 2017.

44. Xie Y, DT: A Wrapper of the JavaScript Library “DataTables”. 2018; https://cran.r-project.org/package=DT

45. Zeileis A, Grothendieck G. zoo: S3 Infrastructure for Regular and Irregular Time Series. J Stat Softw. 2005; 14: 1–30. Available: http://arxiv.org/abs/math/0505527

46. Simonetti A, Buzon MR, Creaser RA. In-situ elemental and Sr isotope investigation of human tooth enamel by Laser Ablation-(MC)-ICP-MS: Successes and pitfalls. Archaeometry. 2008; 50: 371–385. https://doi.org/10.1111/j.1475-4754.2007.00351.x

47. Rosman KJR, Taylor PDP. Isotopic compositions of the elements 1997 (Technical Report). Pure Appl Chem. 1998; 70: 217–235. https://doi.org/10.1351/pac19987005217

48. Horstwood MSA, Evans JA, Montgomery J. Determination of Sr isotopes in calcium phosphates using laser ablation inductively coupled plasma mass spectrometry and their application to archaeological
tooth enamel. Geochim Cosmochim Acta. Elsevier Ltd; 2008; 72: 5659–5674. https://doi.org/10.1016/j.gca.2008.08.016

49. McArthur JM, Howarth RJ, Bailey TR. Strontium Isotope Stratigraphy: LOWESS Version 3: Best Fit to the Marine Sr-Isotope Curve for 0–509 Ma and Accompanying Look-up Table for Deriving Numerical Age. J Geol. 2001; 109: 155–170. https://doi.org/10.1086/319243

50. Mokadem F, Parkinson IJ, Hathorne EC, Anand P, Allen JT, Burton KW. High-precision radiogenic strontium isotope measurements of the modern and glacial ocean: Limits on glacial–interglacial variations in continental weathering. Earth Planet Sci Lett. Elsevier B.V.; 2015; 415: 111–120. https://doi.org/10.1016/j.epsl.2015.01.036