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The IRHUM (Isotopic Reconstruction of Human Migration) database – bioavailable strontium isotope ratios for geochemical fingerprinting in France

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Abstract

Strontium isotope ratios (^{87}Sr/^{86}Sr) are a key geochemical tracer used in a wide range of fields including archaeology, ecology, food and forensic sciences. These applications are based on the principle that the Sr isotopic ratios of natural materials reflect the sources of strontium available during their formation. A major constraint for current studies is the lack of robust reference maps to evaluate the source of strontium isotope ratios measured in the samples. Here we provide a new dataset of bioavailable Sr isotope ratios for the major geologic units of France, based on plant and soil samples (Pangaea data repository doi:10.1594/PANGAEA.819142). The IRHUM (Isotopic Reconstruction of Human Migration) database is a web platform to access, explore and map our dataset. The database provides the spatial context and metadata for each sample, allowing the user to evaluate the suitability of the sample for their specific study. In addition, it allows users to upload and share their own datasets and data products, which will enhance collaboration across the different research fields. This article describes the sampling and analytical methods used to generate the dataset and how to use and access of the dataset through the IRHUM database. Any interpretation of the isotope dataset is outside the scope of this publication.

1 Introduction

Strontium isotope ratios (^{87}Sr/^{86}Sr) can be used as a geochemical tracer in a wide range of fields, including archaeology (Bentley, 2006; Slovak and Paytan, 2011), ecology (Hobson et al., 2010), food (Kelly and Heaton, 2005; Voerkelius et al., 2010) and forensic sciences (Beard and Johnson, 2000). The Sr isotopic ratios of natural materials reflect the sources of strontium available during their formation. Sr isotope ratios in bedrock are a function of age and composition of the rock and thus vary between geologic units (Faure and Mensing, 2005). Through weathering Sr is released and transported into the soil, ground and surface water, where it becomes available for uptake

by plants and eventually enters the food cycle (Bentley, 2006; Capo et al., 1998). Due to their large atomic mass, Sr isotope ratios are not measurably affected by kinetic and equilibrium fractionations during processes at low temperatures and biologic processes (Faure and Mensing, 2005). The isotopic composition of bioavailable Sr (the Sr taken up into the food cycle) can differ from the bulk Sr isotopic composition of the bedrock, mainly through to the preferential weathering of different minerals (Sillen et al., 1998). However, the bioavailable Sr isotope ratios can also be influenced by processes like precipitation, dryfall, seaspray, and in modern context by fertilizer application (Bentley, 2006; Evans et al., 2010; Frei and Frei, 2013; Maurer et al., 2012; Price et al., 2002; Slovak and Paytan, 2011). In addition, the range of Sr isotope compositions varies not only laterally between different regions, but also with depth and time as the local environmental conditions change. In summary, a direct connection exists between the measured Sr isotope ratio of a material and its source region, but determining the Sr isotope composition of different regions is complicated by the diverse range of possible influences on the bioavailable Sr isotope ratio composition.

2 Mapping strontium isotopes

The choice of sample material to constrain the bioavailable isotope ratio is a fundamental consideration and is discussed in detail in the literature (Bentley, 2006; Maurer et al., 2012; Price et al., 2002; Slovak and Paytan, 2011). In general three different approaches can be distinguished:

1. Fauna or human samples that are local to a region are considered to represent a robust average bioavailable Sr isotope composition over their feeding area (Bentley, 2006; Price et al., 2002). However, these samples are restricted in their availability in the context of a country wide study. In addition, fossil samples are subject to diagenetic overprint, while modern samples might be influenced by non-local food sources and fertilizer (Bentley, 2006; Maurer et al., 2012).

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2. The bioavailable Sr isotope ratio for different geologic units can be determined by analysing a number of soils, plants, ground and surface waters (Evans et al., 2010; Hodell et al., 2004; Maurer et al., 2012; Price et al., 2002; Sillen et al., 1998). Overall, surface and groundwater samples provide a good estimate of the bioavailable Sr isotope signal over their catchment area, but are influenced by seasonal changes and changes in precipitation (e.g. Shand et al., 2009). Soils and plants average Sr over a very small area and are readily available in many different environments and easily analysed. The use of soil leachates to determine the local bioavailable Sr isotope ratio has shown varying degrees of success in different regions (Bentley, 2006; Frei and Frei, 2011, 2013; Hodell et al., 2004; Maurer et al., 2012; Price et al., 2002; Sillen et al., 1998; Slovak and Paytan, 2011). Plant samples are generally considered to be a better sample choice across different environments and can also offer insights into the variation of the Sr isotope ratio with depth, as different plant samples source Sr from different soil depths.

3. The bioavailable Sr isotope ratio can also be modelled based on the bedrock lithology, age, and weathering rates (Bataille and Bowen, 2012; Bataille et al., 2012; Beard and Johnson, 2000). These models have shown significant potential and the next step is to assess their predictive ability across different geologic and geographic regions using direct measurements.

In many regions mineral weathering is the dominant influence on the bioavailable Sr isotope ratio and thus different geologic units can be differentiated. However, as there are other processes including atmospheric Sr input (seaspray, dryfall), and in modern context fertilizers and other anthropogenic influences that can significantly affect the Sr isotope ratio. In addition, in regions with exogenic surface deposits (loess, glacial deposits) the local bioavailable Sr isotope ratio can be completely disconnected from the underlying geology. In conclusion, the choice of sample location and material and its value as a reference for mapping the geologic unit need to take these effects into

consideration. This interpretative step will also depend on the focus of the study e.g., modern studies in contrast to archaeological studies.

Strontium isoscapes have been published on a country scale for Mesoamerica (Hodell et al., 2004), UK (Evans et al., 2010), and Denmark (Frei and Frei, 2011, 2013), using a combination of directly sampled materials. Modelling of the bioavailable Sr isotope ratio has been undertaken for the contiguous USA (Bataille and Bowen, 2012; Beard and Johnson, 2000) and the Circum-Caribbean region (Bataille et al., 2012). Sr data also exist as smaller scale maps from different archaeological studies summarized in Slovak and Paytan (2011). While data is still lacking for many regions a robust approach is to combine as many different sample materials as possible to investigate their differences. Moreover, where possible, strontium isotope analyses should be undertaken in conjunction with other lines of evidence, including other isotope systems such as oxygen and lead, to validate a samples provenance. As a final note, a fundamental limitation of provenance studies is that it is only possible to disprove a source hypothesis, not to prove origin from a specific source.

3   Dataset of bioavailable Sr isotope ratios of France

The bioavailable Sr isotope ratio dataset of France is based on plant and soil samples. By sampling both sample types over a wide range of geologic units and large geographic regions, we hope to reliably constrain the local bioavailable Sr isotope ratios and gain insight into the possibly different sources of Sr to plants and soils. Ground and surface water samples would be a valuable addition to this dataset and are being considered for future sample collection.

The dataset presently contains 840 sample locations, covering the major geologic units of France (Fig. 1, Table 1). As only small amounts of the collected sample material have been used for our analysis we have established a large archive of plant, soil and rock samples that is available to the scientific community for further investigation. The analysis of these samples is ongoing and new results will be added to the database as

they become available with the aim of analysing all major geologic units of France within the next year. Finally, because the geology of France is varied and incorporates some of Europe's dominant geologic units, the data gathered for France might be useable to infer Sr isotope values for similar geologic regions across Europe.

4 Methods

4.1 Sample collection

The selection and density of the sample sites is based on the distribution of the geologic units on the 1 : 1M Geologic map of France (Chantraine et al., 2005). There is a wide spacing of sample sites in sedimentary basins, where the geology does not change over large areas, and closer spacing in geologically complex regions. Some geologic units contain several very different lithologies and our sampling was aimed at covering each of these lithologies. Areas where the bioavailable Sr isotope ratios are likely to be detached from the bedrock geology, like coastal areas influenced by seaspray, areas covered with glacial or loess deposits, swamps and peat deposits, were targeted to investigate these processes. In addition, close-spaced samples were taken around sites of special interest, such as archaeological sites and we collected a number of samples from agricultural fields to investigate the possible influence of fertilizers in France. Typical sample sites include roadcuts, outcrops, fields, areas of forest, and shallow pits. At each site plant, soil and rock samples were collected in close proximity to each other. Each sample site was photographed and described in detail, including information about the rock, soil and plant type collected, as well as an assessment of possible recent geomorphic and anthropogenic influences.

4.2 Analytical methods

Strontium is abundant in many materials in the environment. While this is an advantage for its use as a tracer it also increases the potential of contamination during sam-

ple preparation, especially for samples with low natural Sr concentrations. The samples were transported in sealed containers to Australia and irradiated at 50 Gy by the Australian Quarantine and Inspection Service to comply with quarantine procedures. All work is carried out under clean laboratory conditions. Only ultrapure reagents are used, and blanks are monitored at each step during the laboratory procedures to check for possible contamination. A summary of the sample preparation steps is illustrated in Fig. 2 and described in detail in this section.

4.2.1 Sample treatment

A $\sim$ 30 g subsample of each soil sample was dried overnight at 60 °C and then sieved through a 2 mm sieve. A 1 g aliquot was subsampled and leached by adding 2.5 mL 1M ammonium nitrate (NH_4NO_3) following the protocol DIN ISO 19730 and shaking for 8 h. Samples are then centrifuged at 3000 rpm for 15 min, the supernatant extracted ($\sim$ 1–2 mL) and evaporated to dryness and then redissolved in 2 mL 2M nitric acid (HNO_3). Plant samples were placed in heat resistant ceramic crucibles and ashed in an oven at 800 °C for 8 h. A 0.1 g aliquot of each sample was then digested in 1 mL ultrapure concentrated nitric acid (HNO_3) for at least 1 h, before being evaporated to dryness overnight and redissolved in 2 mL 2M nitric acid (HNO_3). A 0.1 mL subsample was extracted and placed in a vial with 4.9 mL 2 % nitric acid (HNO_3). These solutions were then analysed using the ICP-AES to determine Sr and other major and trace element concentrations. The samples are further processed by ion exchange chromatography to isolate Sr from other interfering elements, in particular [87]Rb (isobaric interference), using two sets of columns filled with Eichrom Sr specific resin (pre-filter and Sr spec resin). In order to reach a target concentration of Sr in each sample volume eluted (600 ng in 2 mL) the amount of sample added to the ion exchange columns is adjusted based on the Sr concentration determined by ICPAES. The samples were finally diluted by a factor of 4 prior to MC-ICP-MS analysis to allow for reanalysis if necessary.

4.2.2   Neptune MC-ICP-MS measurements

Sr isotope ratios were measured in the Environmental Geochemistry and Geochronology Laboratory at the Research School of Earth Sciences, ANU, using a Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). MC-ICP-MS was chosen over TIMS due to the requirement of high sample throughput for this project. A Quartz Dual Cyclonic Spray Chamber, PFA 100 µL nebulizer and standard Ni cones were used for sample introduction, and the instrument was tuned for maximum signal strength, stability and peak shape. The isotopes and Faraday cup configuration employed for analysis is shown in Table 2. Data reduction is performed offline in Microsoft Excel and includes Kr and ^{87}Rb isobar corrections, an exponential mass bias correction, and 3 sigma outlier rejection.

4.2.3   Quality control

To assure dataset precision, accuracy, reproducibility and comparability to other international data sources we record and report blank and standard analyses as a long-term reference for our laboratory in the database. Total procedural blanks vary between 50–250 pg Sr, and were analysed by isotope dilution with an ^{84}Sr enriched isotope spike using a TRITON Plus Thermal Ionisation Mass Spectrometer (TIMS) at RSES, ANU. These blank levels represent insignificant contributions to the amount of sample Sr measured (i.e. > 100 ng). We tested the reproducibility of our analysis by running duplicate samples through the entire procedure and found differences between ^{87}Sr/^{86}Sr ratios measured for the same sample to be < 0.004 % (n = 42).

Biases between measured ^{87}Sr/^{86}Sr ratios in different laboratories relate to differences in instrument design, problems of resolution of mass peaks and differences in measurement protocols (Faure and Mensing, 2005). Measurements of the Sr carbonate standard SRM987 (National Institute of Standards and Technology) on the Neptune MC-ICP-MS gave an average ^{87}Sr/^{86}Sr value of 0.71023 ± 0.00001 (n = 167, 2 s.e.). This is in excellent agreement with measurements of the same standard by TIMS at

RSES, ANU, which gave an average $^{87}Sr/^{86}Sr$ value of 0.71023 ± 0.00002 (n = 99, 2 s.e). It is also in agreement with the accepted $^{87}Sr/^{86}Sr$ value for SRM987 of 0.71025 (Faure and Mensing, 2005), and is within uncertainty of the original, albeit imprecise, certified value of 0.71034 ± 0.00026 (Moore et al., 1982).

5   To assess the comparability of our dataset we carried out a blind test on a grazing soil standard from the GEMAS project (Geochemical Mapping of Agricultural and Grazing Land Soil). Measurements at RSES gave an average value of 0.70631 ± 0.00005 (n = 10, 2 s.e) which is in agreement with the GEMAS value of 0.70638 ± 0.00003 (n = 39, 2 s.e) (Reimann et al., 2013). For future comparability studies we have commenced

10   measuring an in-house soil standard which will be made available upon request.

5   Database architecture

The IRHUM (Isotopic Reconstruction of Human Migration) database is a web platform to explore and share strontium isotope datasets and data products. It is built upon a highly flexible open source software stack (Opengeosuite, Geonode) maintained by

15   Boundless (http://boundlessgeo.com) and follows common web standards. Its current functionality allows the user to explore our datasets, upload their own data, and create basic isotope maps. It is also possible to connect to an external WMS server to load background data such as geologic and soil maps. In addition to the spatial isotope data the IRHUM website stores metadata and allows the user to upload documents to

20   describe their project and methods. This will enable others to assess the suitability of specific data for their study. Finally, the data can be exported in a variety of formats (.csv, .kml, .shp, .pdf) for GIS analysis. In summary IRHUM provides easy access to datasets, which facilitate the reuse of data and collaborative development of isotope maps at a variety of scales.

6 Data access

The dataset can be viewed and downloaded on the IRHUM webpage (http://rses. anu.edu.au/research-areas/archaeogeochemistry/tracing-human-migration or http:// irhumdatabase.com). The full dataset is also available through the Pangaea data repository (doi:10.1594/PANGAEA.819142). Updates of the dataset are added to the IRHUM webpage as soon as they become available and will be passed on to the Pangaea data repository at the end of the project in 2014.

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Table 1. Metadata available for each sample site.

Sample ID	The sample ID can be used to identify the sample in our data tables and archives. Current standard is F-year-sample#, for example F11-02 means the second sample collected in 2011.
Researcher	Names of the researchers collecting the samples
Latitude, Longitude, Elevation	Coordinates of the sample site
Site image	If available, a picture of the outcrop or sampling site will be shown here
Outcrop type	We distinguish different types of outcrops: – Outcrop: A natural outcrop of rock, as far as we could identify. Not uncovered through recent human activity. – Roadcut: Along a major road, rocks unearthed by human activity. – Quarry: Outcrop created by human activity, often no longer in use. – Field: A sample collected from a field or meadow. – Turned over tree: A sample collected from or beneath a turned over tree that has excavated some fresh soil layers. – Shallow pit: A sample collected from ~ 10–20 cm deep hole dug by us.
Setting	This is a short description of our observations in the field, such as the proximity of human activities (agriculture, forest plantations) or clear indications of other recent influences.
Sample descriptions	Field observations during sample collection, such as rock, soil and plant type and characteristics.
^{87}Sr/^{86}Sr	Bioavailable strontium isotope ratios
Geologic setting	Summary of the geologic information from the 1 : 1M BRGM geologic map including the geologic region, rock type, geologic unit, major lithologies and age ranges.

Table 2. Standard cup configuration and analysed masses (amu or isotope mass) employed for solution Sr isotope analysis on the Neptune MC-ICP-MS at RSES.

L4	L3	L2	L1	C	H1	H2	H3	H4
82.152	^{83}Kr	83.466	^{84}Sr	^{85}Rb	^{86}Sr	86.469	^{87}Sr	^{88}Sr
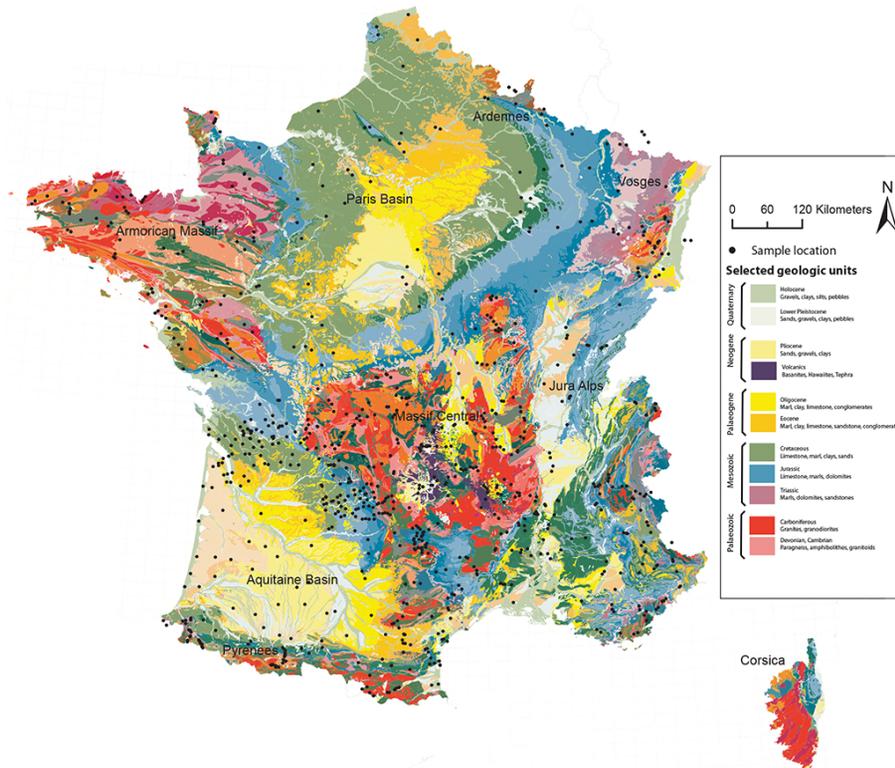
Fig. 1. Map showing the sample locations (black dots) overlain on the 1 : 1M Geologic map of France (Chantraine et al., 2005).

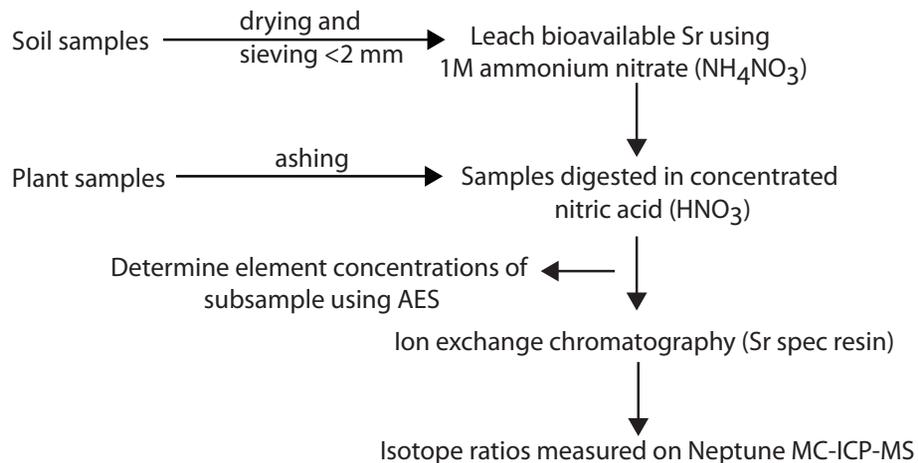Soil samples —— drying and sieving <2 mm ——▶ Leach bioavailable Sr using 1M ammonium nitrate (NH_4NO_3)

Plant samples —— ashing ——▶ Samples digested in concentrated nitric acid (HNO_3)

Determine element concentrations of subsample using AES ◀——

Ion exchange chromatography (Sr spec resin)

Isotope ratios measured on Neptune MC–ICP–MS

Fig. 2. Overview of the preparation procedure for Sr analysis of plant and soil samples.