Bioavailable Soil and Rock Strontium Isotope Data from Israel

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Abstract. Strontium isotope ratios ($^{87}$Sr/$^{86}$Sr) of biogenic carbonates such as bones and teeth reflect the local sources of strontium ingested as food and drink during their formation. This has led to the use of strontium isotope ratios as a geochemical tracer in a wide range of fields including archaeology, ecology, food studies and forensic sciences. In order to utilise strontium as a geochemical tracer, baseline data of bioavailable $^{87}$Sr/$^{86}$Sr in the region of interest is required, and a growing number of studies have developed reference maps for this purpose in various geographic regions, and over varying scales. This study presents a new data set of bioavailable strontium isotope ratios across Israel, from rock and soil samples. This data set may be viewed and accessed both in an Open Science Framework repository (doi:10.17605/OSF.IO/XKJ5Y (Moffat et al., 2020)) or via the IRHUM (Isotopic Reconstruction of Human Migration) database (Willmes et al. 2014).

1 Introduction

Strontium (Sr) isotope geochemistry has applications in many fields of research including archaeology (Bentley, 2006; Slovak and Paytan, 2012), ecology (Barnett-Johnson et al., 2008; Hobson et al., 2010), food traceability (Voerkelius et al., 2010) and forensic sciences (Beard and Johnson, 2000). Strontium is widely distributed within geological and biological materials, and the strontium isotope ratios ($^{87}$Sr/$^{86}$Sr) of these materials reflect the sources of strontium in the environment during their formation (Dasch, 1969). The use of traditional isotope systems such as hydrogen and oxygen systems in provenance studies is limited by their broad gradients across the Earth’s surface, whereas $^{87}$Sr/$^{86}$Sr ratios show predictable geographic variability determined by geologic units, with some temporal variability (Aggarwal et al., 2008; Willmes et al., 2018). To utilise the potential of strontium isotopes as a geochemical tracer, prior knowledge of baseline data in the region of interest is required. Bedrock strontium isotope ratios are a product of the age, mineralogy, and origin of source material. The strontium isotope composition of regolith is principally derived from local weathering of bedrock (Capo et al., 1998), but may be augmented by windblown marine, mineral and anthropogenic aerosols, differential mineral weathering rates, transportation of regolith and pore water chemistry (Frumkin and Stein, 2004; Goede et al., 1998). Bioavailable strontium is
the component of strontium present in an environment which is available for incorporation into biological systems. Regolith, in combination with water, is the principal source of bioavailable strontium, although processes including precipitation, sea spray and fertiliser use may also affect the isotopic composition of bioavailable strontium (Bentley, 2006; Frei and Frei, 2011; Price et al., 2002; Slovak and Paytan, 2012).

1.1 Strontium isotope mapping

There are range of approaches to mapping bioavailable strontium, as summarised below and in greater detail in Bentley (2006) Maurer et al. (2012), Slovak and Paytan (2012) and Bataille et al. (2020). Archaeological human or faunal samples are considered to be one of the best indicators of the local bioavailable range, although their geographic origin may be uncertain (Maurer et al., 2012; Price et al., 2002). Modern faunal samples from known localities may also be used, although non-local food sources and fertiliser use must be considered (Bentley, 2006; Maurer et al., 2012). Soils, plants, and water may also be measured for local bioavailable strontium isotope ratios (Evans et al., 2010; Maurer et al., 2012; Price et al., 2002). While soils and plants average strontium over a smaller area, ground water and surface waters may provide an estimate of bioavailable strontium over a wider area, depending on catchment size (Evans et al., 2010; Willmes et al., 2014).

As discussed previously, the strontium isotope ratios of plants, soils and water may be affected by numerous factors including precipitation, sea spray and fertiliser use, which may vary over seasonal timescales (Bentley, 2006; Hoogewerff et al., 2019; Price et al., 2002). Local bioavailable strontium isotope ratios may also be modelled from bedrock, considering age, mineralogy and weathering rates (Bataille et al., 2012; Bataille and Bowen, 2012). In the case of soil and rock samples, an ammonium acetate or ammonium chloride digestion method, which removes cations from electrostatically bound pore water in addition to exchange sites on minerals and organic matter, is used as a means of extracting the bioavailable component of these samples (Stewart et al., 1998). At a country scale, strontium isoscapes have been developed for Mesoamerica (Hodell et al., 2004), the United Kingdom (Evans et al., 2010), France (Willmes et al., 2014, 2018) and Denmark (Frei and Frei, 2011) from a combination of bedrock, soil, plant and water samples. Isoscapes of bioavailable strontium have also been modelled for the contiguous USA (Bataille and Bowen, 2012), Western Europe (Bataille et al., 2018; Hoogewerff et al., 2019) and the Caribbean region (Bataille et al., 2012). At a larger scale, Voerkelius et al. (2010) sampled mineral waters across Western Europe to predict bedrock $^{87}\text{Sr}/^{86}\text{Sr}$ but found local processes to result in unexpected values.

1.2 Strontium isotope studies and mapping in Israel

Previous studies in Israel and across the Levant region have utilised strontium isotope analyses in a variety of applications in addition to undertaking small scale mapping of bioavailable strontium. Herut et al. (1993) measured the $^{87}\text{Sr}/^{86}\text{Sr}$ values of rainwater samples across Israel, and used these results in conjunction with the chemical composition of the sample to determine the sources of Sr and soluble salts. Shewan (2004) developed a map of bioavailable strontium throughout Israel using modern faunal bones and grass samples, for comparison to bones from archaeological sites in the region. The work of
Shewan (2004) and Perry et al. (2008), who measured $^{87}\text{Sr}/^{86}\text{Sr}$ from archaeological faunal dental samples in western Jordan, was collated to create a bioavailable strontium map for Israel and Jordan, combining modern flora and fauna with material from archaeological sites (Perry et al., 2009). These studies highlight several distinct provinces in the region, with samples along the Jordan Valley distinguished from those in the Eastern highlands of Israel and the Western Highlands in Jordan, as well as several smaller areas with varying isotopic signatures in the north of the study area (Perry et al., 2009). Rosenthal et al. (1989) report the strontium isotope composition of gastropod shells to reconstruct water sources in the Dead Sea Rift area of the Jordan Valley. Spiro et al. (2011) measured $^{87}\text{Sr}/^{86}\text{Sr}$ values of water and mollusc shells in the Hula catchment in the Upper Jordan Valley, adjacent to the Golan Heights, and found distinct water sources and aquifers. Stein et al. (1997) sampled water and sediments around the Dead Sea to determine water sources and the evolution of the Dead Sea and its precursor, Lake Lisan, identifying two distinct periods of lake evolution. Hartman and Richards (2014) sampled plants and invertebrates in Northern Israel and the Golan Heights to produce a map of modern bioavailable strontium isotope ratios, and to investigate potential sources of variability, including inter-site variability and the influence of precipitation. Arnold et al. (2016) sampled plants in the vicinity of Tell es-Safi/Gath to create a local bioavailable strontium map as a baseline for use in interpreting the mobility of domestic animals from archaeological sites in the region. Moffat et al. (2012) undertook spatially resolved strontium isotope analysis using laser ablation techniques to demonstrate annual migration using a bovid tooth from the archaeological site of Skhul. These studies have highlighted the value and potential of bioavailable strontium mapping in this region, and the data presented in this study aims to add to this growing knowledge base.

2 Methods

2.1 Sample collection

Soil and rock samples were collected throughout Israel in September and October 2008. Sample locations were chosen with reference to a digital 1:200000 geological map of Israel using the Old Israel Grid co-ordinate system (Sneh et al., 1998). Soil samples were collected for each visible soil layer, with grain size, sphericity, roundness, grain sorting, Munsell colour and pH recorded in the field. Rock samples were taken for the principle geological unit present at each site and a brief description of the lithology made in the field.

2.2 Analytical methods

2.2.1 Sample treatment

Rock and soil samples were heated to 60°C for a minimum of 24 hours prior to sample preparation to comply with Australian quarantine procedures. After heating, rock samples were crushed to a medium powder using a hand piston. Rock and soil samples were passed through a 2 mm sieve, and 1 g aliquot of the sieved sample was leached by adding 2.5 ml of 1M
ammonium nitrate (NH₄NO₃), following DIN (German Industrial Standard) ISO (International Organization for Standardization) 197310 (2009). Samples were shaken for 24 h and subsequently centrifuged at 3000 rpm for 5–10 min. 1 ml of supernatant was extracted and evaporated until dry, before being dissolved in 2 ml of 2 M high purity nitric acid (HNO₃), evaporated until dry and then dissolved in 2 ml of 2 M high purity nitric acid (HNO₃).

The concentrations of strontium and other major and trace elements were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry). Ion exchange chromatography was then used to isolate strontium from other elements, particularly ⁸⁷Rb to prevent isobaric interference with ⁸⁷Sr (Dickin, 2000), using two columns filled with Eichrom strontium specific resin (prefilter resin and strontium specific resin). The strontium concentration determined by ICP-AES was used to determine the amount of sample added to the ion exchange column. Samples were diluted prior to MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry) analysis to allow for reanalysis if necessary.

2.2.2 Neptune MC-ICP-MS analysis

A Neptune MC-ICP-MS was used to measure strontium isotope ratios in the Environmental Geochemistry and Geochronology Laboratory at the Research School of Earth Sciences, Australian National University (ANU). The isotopes measured and Faraday cup configuration used for the analysis are shown in Table 1. Data reduction was performed offline and includes a blank, ⁸⁷Rb isobar and an exponential mass bias correction. To ensure precision, accuracy and reproducibility in the data produced, the samples were run in a sequence, which included blank and standard samples. The strontium carbonate standard SRM987 (National Institute of Standards and Technology) was measured on the Neptune MC-ICP-MS during the sample sequence to quantify instrument drift.

3 Results

60 soil samples and 48 rock samples were analysed for ⁸⁷Sr/⁸⁶Sr. The ⁸⁷Sr/⁸⁶Sr ratios of the soil samples range from 0.705772 ± 0.000011 to 0.710199 ± 0.000034. The ⁸⁷Sr/⁸⁶Sr ratios of the rock samples range from 0.705291 ± 0.000006 to 0.740718 ± 0.000014. These results are illustrated on satellite images of Israel in Figure 1 (rock samples) and Figure 2 (soil samples). Gross lithologies, defined by observations in the field and geological maps of the region (Sneh et al., 1998), are used to group the results of Sr isotope analysis. Soil and rock ⁸⁷Sr/⁸⁶Sr values show some correlation with lithology, as illustrated in Figure 3. Figure 3a displays all samples analysed, while 3b displays an inset removing a high ⁸⁷Sr/⁸⁶Sr granite sample (site IS044, sample number 134) to display the rest of the data set more clearly. Basalt units are less radiogenic in ⁸⁷Sr/⁸⁶Sr value than other lithologies for both soil and rock samples. Soil samples from carbonate (limestone, dolostone, chalk and marl), granite, kurkar (aeolian quartz sandstone with carbonate cement), rhyolite, siliciclastic lithologies and areas with no bedrock have comparable ⁸⁷Sr/⁸⁶Sr values (Figure 3b). The median ⁸⁷Sr/⁸⁶Sr values from rock samples are slightly lower than those from soils for basalt, carbonate and kurkar samples (Figure 3b). The ⁸⁷Sr/⁸⁶Sr values measured from granite rock samples
(two samples), and the rhyolite rock sample, are substantially elevated compared to other units, and compared to the soil samples from the same lithologies.

At 43 of the sample locations, both soil and rock samples were collected, and the $^{87}\text{Sr}/^{86}\text{Sr}$ values of these samples are compared in Figure 4. As with Figure 3, Figure 4a illustrates the entire data set, while Figure 4b has the granite rock sample (site IS044) removed to better display the variation in the rest of the data set. The variation between soil and rock $^{87}\text{Sr}/^{86}\text{Sr}$ values range from 0.000003 to 0.031304. This offset between rock and soil samples is also visualised in Figure 5, in which the reference line indicates where rock and soil samples have the same $^{87}\text{Sr}/^{86}\text{Sr}$ values for both rock and soil samples ($y=x$). Points which lie above this reference line have higher $^{87}\text{Sr}/^{86}\text{Sr}$ values for soil samples than for rock samples, which in this study is the case for most basalt, carbonate, siliciclastic and kurkar samples. Points which lie below the $y=x$ reference line have higher $^{87}\text{Sr}/^{86}\text{Sr}$ values for rock samples compared to soil samples, in this study this is the case for granite and rhyolite samples. The mean offsets from rock to soil $^{87}\text{Sr}/^{86}\text{Sr}$ values of samples collected from the same sites are shown in Table 2 grouped by lithology.

4 Discussion

4.1 Comparison between rock and soil values

The variation between $^{87}\text{Sr}/^{86}\text{Sr}$ values of soil and rock sampled from the same site is in most cases greater than error (Figure 4), which may be due to inputs to the soil other than bedrock, such as sea spray or Saharan aeolian dust ($^{87}\text{Sr}/^{86}\text{Sr}$ values in the range of 0.7160–0.7192 (Krom et al., 1999)). The input of aeolian dust is expected to be particularly important in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of these soil samples, as it has been reported that aeolian material may make up to 50% of soils formed on hard limestone rocks in Israel (Yaalon, 1997). The Sr isotope value of dust in the region is known to have varied over time, which is an important consideration in the use of modern isoscapes for the interpretation of older sample material. $^{87}\text{Sr}/^{86}\text{Sr}$ values of dust in this region varied from 0.711–0.712 during MIS 2 and 4, and 0.709–0.710 during MIS 1, 3 and 5 (Haliva-Cohen et al., 2012). The delivery of aeolian dust is also affected by climate variations (Frumkin et al., 2011), with Sr isotope values found to increase at major climate transitions that correspond to sapropel formation in the Mediterranean (Stein et al., 2007). Speleothem analyses have shown that glacial periods have a higher aeolian Sr isotope contribution than interglacial periods (Frumkin and Stein, 2004).

4.2 Comparison with regional datasets

Several previous studies of bioavailable strontium have been undertaken in Israel, particularly in Northern Israel and the Golan Heights region. The results obtained in this study of soils derived from basalts in the Golan Heights region have $^{87}\text{Sr}/^{86}\text{Sr}$ values in the range of 0.705772 to 0.706810 for samples (sample numbers: 175, 203, 204, 205 and 216) with robust geological provenance. Basalt rock samples (sample numbers: 119, 143, 144, 147 and 278) in this study from the Golan Heights region have $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.705291 to 0.706807. For the same region, Shewan (2004) report
$^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.70529 to 0.70571 (n=4), while the results of Spiro et al. (2011) of $^{87}\text{Sr}/^{86}\text{Sr}$ measured from water samples in the Hula Valley and Golan Heights region range from 0.70467 to 0.70790 (n=37). The small disparity between the results of this study and those of Shewan (2004) may reflect the limited number of samples analysed, as the larger data set of Spiro et al. (2011) encompasses the results of both this study and Shewan (2004). Hartman and Richards (2014) measured bedrock $^{87}\text{Sr}/^{86}\text{Sr}$ from basalt units in the region, ranging from 0.7031 to 0.7033, lower than those measured in this study. Hartman and Richards (2014) also measured $^{87}\text{Sr}/^{86}\text{Sr}$ values from plants and invertebrates, and for basalt bedrock, ligneous (woody) plants were found to have $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.704558 to 0.708513, non-ligneous plants ranging from 0.704728 to 0.70872, and invertebrates from 0.70494 to 0.708677. Rosenthal et al. (1989) summarise Sr isotope sampling of basalt derived groundwater in the Jordan Valley, with $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7045 to 0.705. Rainwater in the Golan Heights region was found to have a Sr isotope composition in the range of 0.70804 to 0.70923 (Herut et al., 1993).

The wide range of Sr isotope results in the Golan Heights region may be explained by the rapid depletion of Sr from rocks and soil in this region due to weathering and the large contribution of aeolian dust to soil profiles (Singer, 2007: 202-206). Carbonate units were the most sampled lithology in this study, due to their widespread distribution across the country. This lithology groups a range of carbonate units (limestones, dolostones, chalk and marl), and the $^{87}\text{Sr}/^{86}\text{Sr}$ values of rock samples range from 0.707328 to 0.709112, while soil $^{87}\text{Sr}/^{86}\text{Sr}$ values range from 0.708025 to 0.710199. Hartman and Richards (2014) report bedrock $^{87}\text{Sr}/^{86}\text{Sr}$ values from Northern Israel for carbonate units to range from 0.7073 to 0.7078, comparable to the lower values in the range of rock samples measured in this study. Ligneous plant samples have $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.707889 to 0.709095, non-ligneous plants from 0.70791 to 0.709181 and invertebrates from 0.708064 to 0.708761 (Hartman and Richards, 2014), comparable to the results of this study from rock and soil samples. Rosenthal et al. (1989) summarise Sr isotopes from carbonate derived water sources in the Jordan Valley as having $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.7070 to 0.7080.

Arnold et al. (2016) sampled plants in the vicinity of Tell es-Safi/Gath to create a local biavailable strontium map as a baseline for use in interpreting the mobility of domestic animals from archaeological sites in the region. Of the 10 plant samples collected, four were from kurkar soils, with $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.708631 to 0.708810. The kurkar soil $^{87}\text{Sr}/^{86}\text{Sr}$ values reported in this study are slightly more elevated, ranging from 0.708944 to 0.709344. Hartman and Richards (2014) also measured $^{87}\text{Sr}/^{86}\text{Sr}$ values from plants and invertebrates from kurkar units, ligneous plants ranged from 0.708992 to 0.709027, non-ligneous plants ranged from 0.708998 to 0.709034, and two mollusc shells were measured with $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.708968 and 0.709043, comparable to the kurkar soil samples reported in this study. Coastal plain grasses were analysed by Shewan (2004) in the region of El Wad cave, south of Haifa. These $^{87}\text{Sr}/^{86}\text{Sr}$ values ranged from 0.70886 to 0.70965, with an outlying value of 0.71003 attributed to influence from the road base (Shewan, 2004). The results from the kurkar samples in this study are comparable to those of coastal plain grasses as reported by Shewan (2004).

Samples from granite, rhyolite and siliciclastic lithologies, as well as samples from regions with no bedrock, are also reported in this study. Hartman and Richards measured $^{87}\text{Sr}/^{86}\text{Sr}$ values from plants growing in alluvium, with a range of 0.707124 to 0.708303 for combined ligneous and non-ligneous (n=4) plants. From this study, samples sites where no
bedrock was found had $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.707834 to 0.709524, comparable to the results of Hartman and Richards (2014). There are no comparable studies which sample $^{87}\text{Sr}/^{86}\text{Sr}$ for the granite and rhyolite samples included in this study.

5 Conclusion

This data set provides the first comprehensive database of bioavailable soil and rock $^{87}\text{Sr}/^{86}\text{Sr}$ values for Israel. The $^{87}\text{Sr}/^{86}\text{Sr}$ results are shown to be principally controlled by lithology and in broad agreement with previous, smaller scale, studies in the region. Soil and rock $^{87}\text{Sr}/^{86}\text{Sr}$ values from the same site are generally offset.

6 Data availability

The data set can be viewed and downloaded on the IRHUM (Isotopic Reconstruction of Human Migration) database (http://www.irhumdatabase.com). The IRHUM database architecture and functionality is described by Willmes et al. (2014). The data is also available at the Open Science Framework data repository “Data Associated with Bioavailable Soil and Rock Strontium isotope data from Israel” doi:10.17605/OSF.IO/XKJ5Y (Moffat et al., 2020)

7 Acknowledgements

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References


Haliva-Cohen, A., Stein, M., Goldstein, S. L., Sandler, A. and Starinsky, A.: Sources and transport routes of fine detritus


Table 1: Standard cup configuration and analysed masses (amu or isotope mass) employed for solution strontium isotope analysis on the Neptune MC-ICP-MS at RSES.

<table>
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<th>L3</th>
<th>L2</th>
<th>L1</th>
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Figure 1: Bioavailable $^{87}$Sr/$^{86}$Sr of rock samples overlain on Landsat image of Israel (Provided by Dr Stephen Savage, Arizona State University 2010)
Figure 2: Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ of soil samples overlain on Landsat image of Israel (Provided by Dr Stephen Savage, Arizona State University 2010)
Figure 3: Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ of rock and soil samples in Israel, grouped by gross lithology observed in the field. Points indicate individual samples. a) all data, b) subset of data with high $^{87}\text{Sr}/^{86}\text{Sr}$ granite sample (site IS044) removed to better display variability between other samples.
Figure 4: Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ of rock and soil samples collected from the same sample locations displayed with 2σ error bars. Sample locations are grouped based on gross lithology observed in the field. a) all data, b) subset of data with high $^{87}\text{Sr}/^{86}\text{Sr}$ granite sample (site IS044) removed to display variability between other samples.
Figure 5: Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ of rock and $^{87}\text{Sr}/^{86}\text{Sr}$ of soil samples collected from the same sample locations. Sample locations are grouped based on gross lithology observed in the field. Points which lie along the reference line ($y=x$) have the same $^{87}\text{Sr}/^{86}\text{Sr}$ values for both soil and rock samples from the same sample site, while points above the line indicate a higher soil $^{87}\text{Sr}/^{86}\text{Sr}$ value than rock, and points which lie below this line indicate a rock $^{87}\text{Sr}/^{86}\text{Sr}$ value higher than the soil sample from the same site.

Table 2: Mean offset by lithology from rock to soil $^{87}\text{Sr}/^{86}\text{Sr}$ values collected from the same sample locations.

<table>
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<th>Basalt (6)</th>
<th>Carbonate (31)</th>
<th>Granite (2)</th>
<th>Kurkar (2)</th>
<th>Rhyolite (1)</th>
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