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Lead and strontium isotopes as palaeodietary indicators in the Western Cape of South Africa

We analysed the isotopic compositions of bioavailable strontium (Sr) and lead (Pb) in 47 samples of animals and plants derived from the various geological substrates of southwestern South Africa, to explore the utility of these isotope systems as dietary tracers. Measurements were made using high-resolution multi-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS). $^{87}Sr/^{86}Sr$ could efficiently discriminate between geologically recent sediments of marine origin in near-coastal environments and older geologies further inland. However, $^{87}Sr/^{86}Sr$ was not able to distinguish between the Cape Granite Suite and the Cape System (Table Mountain sandstones), whereas Pb isotopes could, demonstrating the utility of this hitherto underused isotope system. Bioavailable $^{87}Sr/^{86}Sr$ in near-coastal terrestrial environments is influenced by marine input, whereas Pb isotopic ratios are not, because of low concentrations of Pb in seawater. There is considerable potential to use Pb isotopes as a dietary and palaeodietary tracer in near-coastal systems in fields as diverse as archaeology, palaeontology, wildlife ecology and forensics.

Significance:

- This study is the first investigation of the potential of Pb isotopes as a dietary tracer in southwestern South Africa.

- Pb isotopes are a valuable dietary tracer; used in combination with $^{87}Sr/^{86}Sr$, they can extend our knowledge of landscape usage in coastal-marine environments.

- Pb isotopes have also shown to be useful in samples from the 1980s, collected during the time when leaded petrol was in use in South Africa; however, these samples were from remote areas with low motor vehicle emissions.

Introduction

We examined strontium ($^{87}Sr/^{86}Sr$) and lead ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) isotopes as biogeochemical tracers for studying diet and landscape usage in the (semi-)arid, coastal regions of southwestern South Africa, with application in both contemporary and ancient (archaeological and palaeontological) contexts. Consumer body tissues record the isotopic composition of food and water ingested in life.[1] Where these isotopes vary across the landscape, they provide a natural tracer of diet and migration. We measured Sr and Pb concentrations and isotopic compositions in animals and isotope compositions in plants collected from the major geological substrates of southwestern South Africa (shales, sandstones, granites and recent marine-derived sands), ranging in age from pre-Cambrian to Quaternary (Figure 1). We were thus able to characterise isotope ratios of bioavailable Sr and Pb for each substrate. Our work expands on previous studies of $^{87}Sr/^{86}Sr$ isotopes as a (palaeo)dietary indicator in this region[2-5]; however, this study is the first to investigate Pb isotopes for this purpose. In addition, we aimed to determine the utility of Pb isotope measurements on archival samples that were collected during the time when leaded petrol was in use in South Africa. This is important because there is a large body of materials in museum and other collections that can be drawn from in future studies.

Sr isotopes in the geosphere and biosphere

Sr^{2+} substitutes for Ca^{2+} in minerals including plagioclase feldspar, calcite, dolomite, aragonite, gypsum and, most importantly regarding archaeological materials, apatite in bones and teeth. $^{87}Sr/^{86}Sr$ in biological materials is increasingly widely used to track animal migrations[1], in forensics[6], and in archaeology and palaeontology[7]. ^{87}Sr is radiogenic ($^{87}Rb \rightarrow ^{87}Sr$, $t_{1/2} = 88 \times 10^{10}$ years), whereas ^{86}Sr is not.[8,9] $^{87}Sr/^{86}Sr$ therefore increases gradually through time and is highest in geologically ancient rocks, and those with high Rb contents relative to Sr.[9,10] Sr is released from rocks through chemical weathering and moves (without fractionation of $^{87}Sr/^{86}Sr$) from the source rock into the soils and groundwater.[9,11,12] Different components of rocks with different $^{87}Sr/^{86}Sr$ may weather at different rates, so bioavailable $^{87}Sr/^{86}Sr$ may differ from the average underlying bedrock.[13] Measurement of local animals and plants is the best way to characterise bioavailable $^{87}Sr/^{86}Sr$[13,14] because Sr passes through the food chain from plants to animals and humans without significant fractionation of its isotopes.[7,11,15]

$^{87}Sr/^{86}Sr$ in soil and water may be altered by admixing of non-local Sr from rivers flowing through different geologies, precipitation and wind-blown dust.[16] Sr is homogeneously distributed in the ocean, with a residence time of 2×10^7 years and a concentration of 7.62 ppm.[12] An important limitation of the Sr isotope system worldwide is the tendency of coastal terrestrial areas to have $^{87}Sr/^{86}Sr$ values reflecting the composition of present-day seawater at 0.709241 ± 0.000032.[17] This is due to the presence of geologically recent marine-derived calcareous sediments with high fractions of shell[3,4], and Sr contributed by sea spray and mists[16].

Pb isotopes in the geosphere and biosphere

Pb has four stable, naturally occurring isotopes, of which ^{206}Pb ($^{238}U \rightarrow ^{206}Pb$, $t_{1/2} = 4.47 \times 10^9$ years)[9], ^{207}Pb ($^{235}U \rightarrow ^{207}Pb$, $t_{1/2} = 0.70 \times 10^9$ years)[9], and ^{208}Pb ($^{232}Th \rightarrow ^{208}Pb$, $t_{1/2} = 14.01 \times 10^9$ years)[9] are all radiogenic. ^{204}Pb is not radiogenic and is therefore a good reference isotope. $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ can increase over geological timescales and are highest in geologically ancient rocks, and those with high elemental U and Th content relative to Pb.[18] ^{204}Pb may suffer isobaric interference from ^{204}Hg which, if not corrected for, can pose a problem in inductively-coupled-plasma mass spectrometry (ICP-MS). That being the case, Pb isotopic ratios over ^{206}Pb are often used.
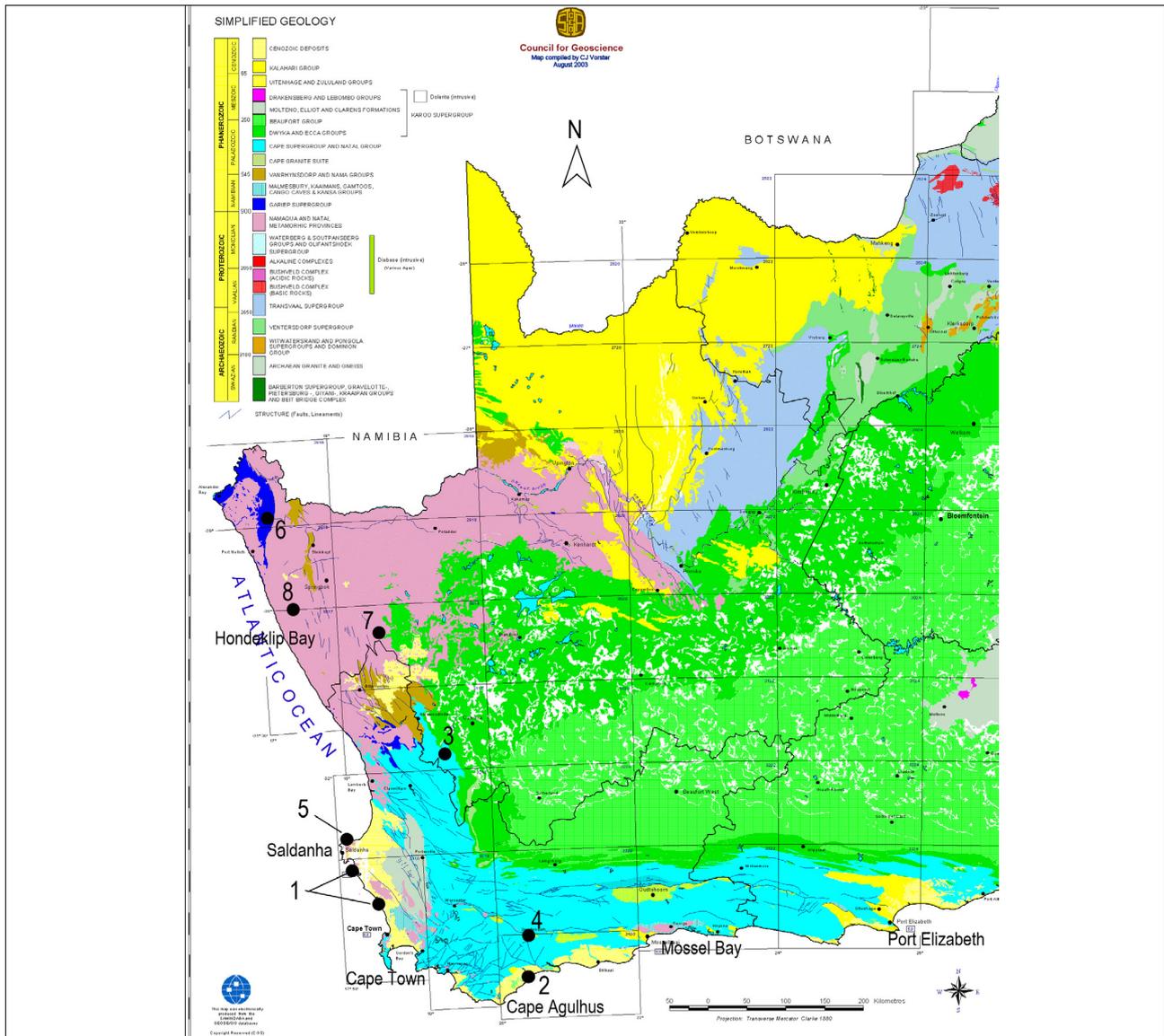
Figure 1: Geological map (base map derived from the Council for Geoscience) showing sample collection locations: 1. Churchhaven and Koeberg Nature Reserve consist mainly of unconsolidated calcareous sand (modern coastal-marine sands); 2. De Hoop Nature Reserve with some Table Mountain sandstone, and mostly Wankoe/Waenhuiskrans limestones of the Bredasdorp Group; 3. Doringbos (between Clanwilliam and Calvinia) with Karoo sedimentary deposits of mostly sandstones and shales, with some mudrock and siltstone; 4. Bontebok National Park with Table Mountain sandstone and Malmesbury shale; 5. Rooiheuwel farm with granite rocks of the Vredenburg pluton of the Cape Granite Suite; 6. Richtersveld National Park with volcanic, igneous, metamorphic and sedimentary rock formations (e.g. granites, syenites, pegmatites, schists, quartzites, shales, greywackes and conglomerates); 7. Dabidas farm with granites of the Namaqua-Natal Metamorphic Province; 8. Namaqua National Park with ultrametamorphic rocks, gneisses, schists, quartzites, granites and conglomerates of the Namaqua-Natal Metamorphic Province .

Like Sr, bioavailable Pb moves through the food chain without significant fractionation of its isotopes[19,20] from the source bedrock via chemical weathering to soils and groundwater, and is then taken up by plants through their roots[21]. Industrial discharges and atmospheric transport and deposition of airborne Pb increase the Pb levels in soils, surface waters and the food chain.[22] Pb in modern rainwater seems to be mainly from airborne particles derived from industrial sources, most of which appears to be taken up by surface soils.[23] The introduction of alkyl-lead as an anti-knock agent in petrol resulted in raised atmospheric Pb levels worldwide.[24] In South Africa, leaded petrol reached its peak between the 1980s and 1990s.[25] Since 1996, unleaded petrol has been available to motorists and its use gradually increased until 2006, when all leaded petrol was phased out and only lead-free petrol was available in South Africa.

In the oceans, Pb is not homogeneously distributed and has a much shorter residence time (80–100 years)[26] than Sr (2×10^7 years)[12], resulting in Pb fluctuating with time as well as space. When comparing the Pb concentration and isotopic ratios of current surface waters in the South Atlantic Ocean to those measured in the 1990s, a decrease in the Pb concentration can be observed from 29 pmol/kg in 1990[27] to 17.7 pmol/kg in 2010[28]. Also, the $^{206}Pb/^{204}Pb$ ratio has decreased from 18.3800 in May/June 1996[29] to 18.0730 in October 2010[28]. Conversely, the $^{208}Pb/^{206}Pb$ ratio has increased from 2.0900 in May/June 1996[29] to 2.1040 in October 2010[28].

Pb and Sr as palaeodietary tracers in southwestern South Africa

A number of archaeological and palaeontological studies have analysed Pb isotopes in bones and teeth for examining past mobility and geographical origins of archaeological specimens.[30-33] Progressively more studies are comparing Pb with Sr isotopes, and concluding that whilst Pb and Sr isotopic systems alone can provide valuable information, a combination of the two techniques is a very powerful tool.[30,32,33]

Extensive research has been done on the bioavailable and whole-rock $^{87}Sr/^{86}Sr$ in southwestern South Africa (Table 1). Allsopp and Kolbe[34] analysed whole-rock $^{87}Sr/^{86}Sr$ from the Malmesbury shale (0.7208–0.7873) and Cape Granite (0.7701–1.1602) for geological age determination. Sealy et al.[2] analysed animal bones to estimate bioavailable $^{87}Sr/^{86}Sr$. They reported values for shales (0.7178–0.7179) and sandstones (0.7154–0.7175) based on a limited number of samples from carefully chosen sites some distance from the coast, where the soils derived from the underlying geological formations. As a result, this study showed a clear separation between the values for shales and sandstones, and those for near-coastal marine sands (0.7094–0.7117).[2] Copeland et al.[4] and Lehmann et al.[5] also assessed bioavailable $^{87}Sr/^{86}Sr$ by analysing plants from the south coast and animal bone and teeth samples from the west coast of southern Africa. They employed much wider-ranging sampling strategies and included samples from shales, granites and sandstones near the coast, with significant marine Sr input. This is reflected in the very broad $^{87}Sr/^{86}Sr$ ranges, with marine Sr input contributing to the lower extremes: 0.7095–0.7204 for the Malmesbury shales, 0.7095–0.7236 for the Cape Granite Suite and 0.7092–0.7237 for the Cape Supergroup.

Radloff et al.[3] reported bioavailable $^{87}Sr/^{86}Sr$ values of different geological substrates in the De Hoop Nature Reserve in southwestern South Africa, measured on modern rodent teeth. There is a distinction between higher values for shales (0.7101–0.7104) and sandstones (0.7098–0.7100) and lower values for the coastal sands (0.7092–0.7093) and limestones (0.7091–0.7099)[3], but the values for shales and sandstones are very low, reflecting a substantial contribution from seawater-derived Sr.

Limited research has been done on whole-rock or bioavailable Pb isotopic ratios in southwestern South Africa. Soderberg and Compton[35] reported $^{206}Pb/^{207}Pb$ (1.141±0.008) and $^{208}Pb/^{207}Pb$ (2.404±0.017) for a protea sample derived from the Table Mountain substrate of the Cape Floristic Region.

Methods

Sample collection

The details of the samples analysed are given in Supplementary table 1. Those collected specifically for this project comprise a variety of bones and teeth from animals that had recently died natural deaths, as well as some plants. As the goal of this study was to characterise bioavailable Pb and Sr isotopic ratios, diversity in the plant and animal species is irrelevant. It is, however, important to avoid cultivated areas where artificial fertilisers may have been used. Most samples were collected in the last few years, and therefore date from the post-2006 era of unleaded petrol. The sample set includes a few samples from the 1980s, when leaded petrol was still in use in South Africa, but these samples are from remote areas where there is likely to have been little influence from motor vehicle emissions. Small mammals from De Hoop Nature Reserve were trapped and euthanised in 2010 for a previous study.[3] The set of samples was derived from all of the major geological substrates of

the Western Cape. Figure 1 is a geological map showing the sample collection locations.

Sample preparation

Bones and teeth were lightly sanded to remove superficial contamination. Pieces weighing approximately 50 mg were placed in vials filled with MilliQ-water in an ultrasonic bath for about 10 min, then left to dry on watch glasses in an oven at 40 °C overnight, after which they were ready for chemical processing. As most teeth were from small animals, they were processed as 'whole-tooth' samples. In only two cases (both antelope teeth) were dentine and enamel separated and processed individually.

Plant samples were placed in quartz crucibles (uncovered) in a muffle furnace at an initial temperature of 300 °C and the temperature was increased by 100 °C every hour until a temperature of 650 °C was reached; thereafter the samples were left overnight. Possible Pb loss through volatilisation was minimised by increasing the temperature of the furnace gradually and keeping it well below the boiling point of Pb (1749 °C). The resulting ashed samples were ground to a fine powder using a mortar and pestle. Approximately 50 mg of each ash was weighed out (masses were recorded) and placed in a 7-mL Teflon vial.

The combined Sr-Pb elemental separation method used in this study is based on that of Pin et al.[36], with minor modifications (see supplementary material for laboratory protocol). Sr and Pb, present in only trace amounts, were concentrated and matrix elements were removed by passing the samples through Savillex Teflon columns filled with Sr.Spec resin (Eichrom), using 0.05 M HNO_3. Samples were processed in batches of eight, along with a total procedural blank and a reference material (NM95 in-house carbonate standard for the bone and tooth samples, and ALR33G in-house basalt standard for the plant-derived mineral ash samples).

Measuring Sr and Pb concentrations and isotope ratios

Elemental concentrations of Sr and Pb were determined on a Thermo X-series II quadrupole ICP-MS, to assess the quantity of sample required for isotopic analysis. Because there is no published Sr or Pb concentration data for NM95, the in-house standard solutions were run as unknowns to assess accuracy. Calibration curves were obtained using artificial multi-element standards, from which standard solutions were made.

Isotopic ratios of Sr and Pb were determined on a NuPlasma HR multi-collector (MC)-ICP-MS from Nu Instruments. Samples were introduced into the MC-ICP-MS as solutions, using the Nu Instruments DSN-100 desolvating nebuliser. Solution analysis typically requires at least 50 ng of the element of interest, achieved through Sr-Pb elemental separation chemistry as described above.

The separated Sr fraction for each sample, dissolved in 2 mL 0.2% HNO_3, was diluted to 200 ppb Sr for isotope analysis. Analyses were referenced to bracketing analyses of NIST SRM987, using an $^{87}Sr/^{86}Sr$ reference value of 0.710255. All Sr isotope data were corrected for

Table 1: Previously published $^{87}Sr/^{86}Sr$ in biological and geological samples from southwestern South Africa

Study	Sample type	Location in South Africa	Malmesbury shales	Cape Granite Suite	Cape Supergroup	Karoo Supergroup	Bredasdorp Group	Quaternary coastal sands
Allsopp and Kolbe[34]	Rocks	Cape Peninsula	0.7208–0.7873	0.7701–1.1602				
Sealy et al.[2]	Modern bone of mammals	Southwestern coast	0.7178–0.7179		0.7154–0.7175			0.7094–0.7117
Soderberg and Compton[35]	Plant and soil	Cape Floristic Region			Plants = 0.722 and 0.724; Soil = 0.735			
Radloff et al.[3]	Modern teeth of rodents	De Hoop Nature Reserve	0.7101–0.7104		0.7098–0.7100		0.7091–0.7099	0.7092–0.7093
Copeland et al.[4]	Plants	Southern Cape	0.7095–0.7157	0.7095–0.7177	0.7092–0.7237	0.7124–0.7237	0.7092–0.7101	
Lehmann et al.[5]	Modern bone and teeth, and plants	Southwestern coast	0.7141–0.7204	0.7114–0.7236	0.7141–0.7204			0.7094–0.7117

Rb interference using the measured signal for [85]Rb and the natural [85]Rb/[87]Rb ratio. Instrumental mass fractionation was corrected using the measured [86]Sr/[88]Sr ratio, the exponential law, and a true [86]Sr/[88]Sr value of 0.1194. Analytical error associated with measurements by solution is ± 0.000020 (2 σ). Sr isotope results for repeat analyses of the in-house reference materials agreed well with long-term results obtained in this facility. NM95 for this study: [87]Sr/[86]Sr=0.708938$\pm$0.000022 (n=5) and long-term values: [87]Sr/[86]Sr=0.708911$\pm$0.000040 (n=414). ALR33G for this study: [87]Sr/[86]Sr=0.704890$\pm$0.000014 (n=1) and long-term values: [87]Sr/[86]Sr=0.704901$\pm$0.000040 (n=72).

The separated Pb fraction, dissolved in 1 mL 2% HNO_3, was diluted to 50 ppb for isotope analysis. NIST SRM997 Tl (thallium) was added to all standards and samples to give a Pb:Tl ratio of approximately 10:1. NIST SRM981 was used as the reference standard, with [208]Pb/[204]Pb, [207]Pb/[204]Pb and [206]Pb/[204]Pb normalising values of 36.7219, 15.4963 and 16.9405, respectively.[37] All Pb isotope data were corrected for Hg isobaric interference by subtraction of on-peak background measurements. Instrumental mass fractionation was corrected using the exponential law, and a [205]Tl/[203]Tl value of 2.3889. Lead isotope results for repeat analyses of the in-house reference materials agreed well with long-term results obtained in this facility. NM95 for this study: [208]Pb/[204]Pb=38.1897$\pm$0.2386 (n=5), [207]Pb/[204]Pb=15.7898$\pm$0.0319 (n=5), [206]Pb/[204]Pb=20.5553$\pm$0.5133 (n=5) and long-term values: [208]Pb/[204]Pb=38.2295$\pm$0.0436 (n=11), [207]Pb/[204]Pb=15.7892$\pm$0.0360 (n=11), [206]Pb/[204]Pb=20.6682$\pm$0.1521 (n=11). ALR33G for this study: [208]Pb/[204]Pb=38.8608$\pm$0.0028 (n=1), [207]Pb/[204]Pb=15.6174$\pm$0.0010 (n=1), [206]Pb/[204]Pb=18.4264$\pm$0.0010 (n=1) and long-term values: [208]Pb/[204]Pb=38.8510$\pm$0.0140 (n=16), [207]Pb/[204]Pb=15.6152$\pm$0.0031 (n=16), [206]Pb/[204]Pb=18.4248$\pm$0.0069 (n=16).

Results and discussion

Elemental concentrations and isotopic ratios of Sr and Pb for all samples in this study are listed in Supplementary table 1.
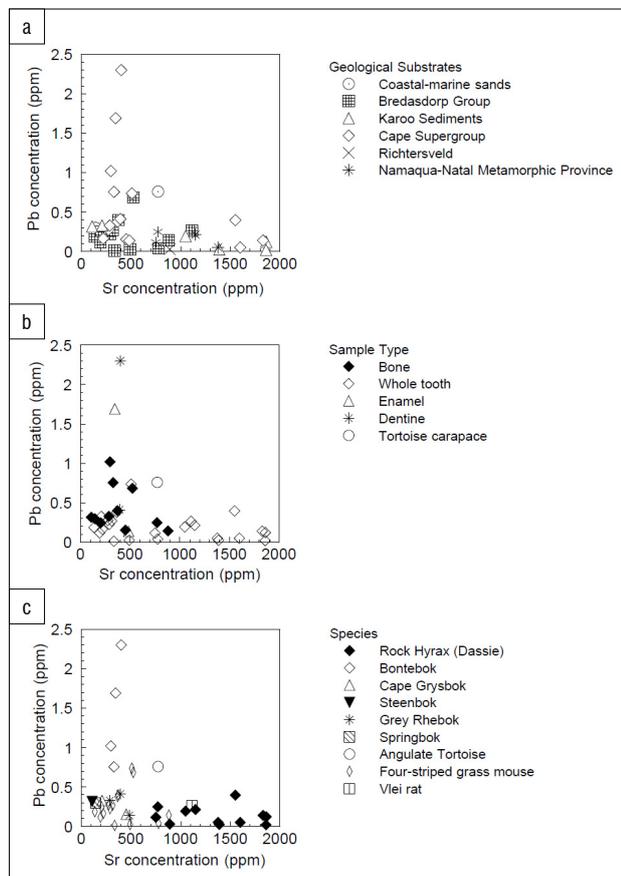

Figure 2:   Sr vs Pb concentrations (ppm), grouped according to (a) geological substrate, (b) sample type and (c) species.

Sr and Pb concentrations

Sr concentrations of samples analysed here were in the range of 111–1862 ppm, while Pb concentrations were in the range of 0.012–2.30 ppm. As shown in Figure 2, all bone samples had Sr concentrations below 900 ppm and Pb concentrations below 1 ppm, while the whole-tooth samples had Sr concentrations up to about 1900 ppm with Pb concentrations below 0.8 ppm. This finding is as expected, given that whole-tooth samples consist largely of enamel, with a much higher mineral content than bone. The 10 samples with [Sr]>1000 ppm were rock hyrax (dassie) whole-tooth samples from the Cape Supergroup, Karoo sediments and Namaqua-Natal metamorphic province, as well as the vlei rat tooth from Bredasdorp sediments. Of the entire sample set, only seven samples had Pb concentrations above 0.5 ppm. In the two cases in which the dentine and enamel of the tooth were separated, Pb concentrations were higher in dentine than in enamel, as seen in previous studies.[30] In addition, the Pb concentrations were higher in the dentine compared with the individual's bone. Sr and Pb concentrations were patterned by geological substrate. All samples from regions underlain by Karoo sediments had Pb concentrations below 0.4 ppm, with Sr concentrations ranging from 111 ppm for bone samples to 1862 ppm for the tooth samples. The samples from regions underlain by Bredasdorp limestones and coastal terrestrial substrates had relatively low Pb (<0.7 ppm) and moderate Sr concentrations (<700 ppm), compared with the rest of the sample set.

Sr isotopic ratios

Figure 3 illustrates the new bioavailable [87]Sr/[86]Sr values obtained for the major geological substrates of southwestern South Africa. The bioavailable [87]Sr/[86]Sr ranges for each geological substrate were as follows (from youngest to oldest geological age): 0.709282–0.709483 for the Cenozoic coastal sands, 0.709141–0.709942 for the Bredasdorp limestones, 0.715184–0.718972 for the Late Carboniferous Karoo sediments, 0.709925–0.713088 for the Ordovician Table Mountain sandstones of the Cape Supergroup, and 0.711469–0.714618 for the Late Precambrian to Early Cambrian granitoids of the Cape Granite Suite.
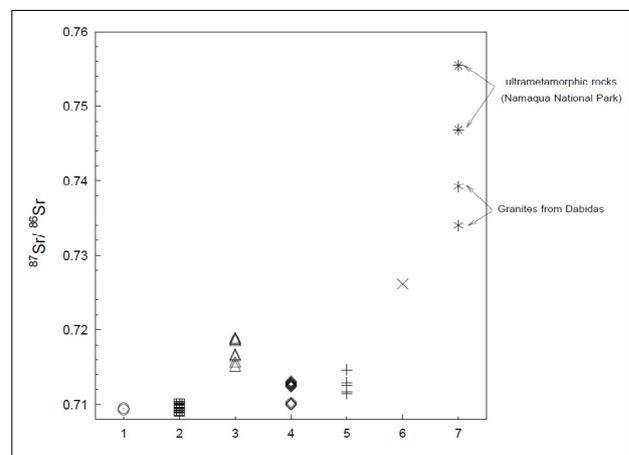

Figure 3:   Bioavailable [87]Sr/[86]Sr values of the samples collected from the various geological substrates in the Western and Northern Cape Province: 1. Coastal sands; 2. Bredasdorp limestones; 3. Karoo sediments; 4. Cape Supergroup (e.g. Table Mountain sandstones); 5. Cape Granite Suite; 6. Richtersveld, 7. Namaqua-Natal Metamorphic Province. Errors are included within the sizes of the points as plotted.

Samples from coastal marine sands ('Cenozoic deposits' in Figure 1) had [87]Sr/[86]Sr close to the marine value of 0.7092[17], reflecting the marine-shell-rich coastal sands and the influence of sea spray. It is clear from Figure 4 that the [87]Sr/[86]Sr values of the samples from the Table Mountain sandstones in De Hoop Nature Reserve (closed symbols at 2.5–5 km from coastline) are much lower than those from Gifberg and Bontebok National Park (40–50 km from coast). Copeland et al.[4] also reported lower [87]Sr/[86]Sr values for samples collected near the coast (as shown in their Figure 5). They did not, however, distinguish different geologies. Plotting

$^{87}Sr/^{86}Sr$ of both their and our samples from Table Mountain sandstones against distance from the coast shows increasing $^{87}Sr/^{86}Sr$ as one moves further inland (Figure 4), i.e. falling off of marine-derived Sr. The effect of marine-derived Sr appears to extend as far as 40 km inland. Similar results have been reported by other researchers[38,39]; the magnitude of the effect depends on atmospheric circulation and is greater in soils with low Sr concentrations. Setting aside samples from older substrates close to the coast (e.g. Cape granites at Vredenburg Peninsula), the older substrates (Cape granites, Table Mountain sandstones, Malmesbury shales) show higher $^{87}Sr/^{86}Sr$ than the Cenozoic sands and Bredasdorp formation, which have values closer to seawater.

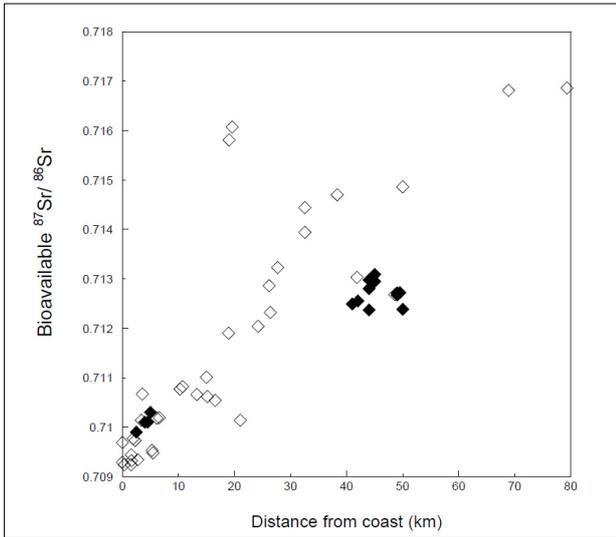**Figure 4:** Bioavailable $^{87}Sr/^{86}Sr$ values compared to distance from coast for rodent and plant samples collected from the Table Mountain sandstones in this study (closed symbols) and Copeland et al.'s[4] study (open symbols).

Figure 5 shows the ranges of bioavailable $^{87}Sr/^{86}Sr$ found in this study compared with those found in previous studies. We report much narrower Sr isotopic ranges for each substrate than Copeland et al.[4] and Lehman et al.[5], although the same analytical methods were applied using the same analytical facility. In this study, the ranges of the Cape and Karoo geologies are distinct, whereas Copeland et al.[4] found them to overlap. This difference may in part be a sample population effect, as sample

populations in this study ($n=8$ for the Karoo, 15 for Cape Supergroup) were smaller than those of Copeland et al.[4] (50 and 35 respectively).

The bioavailable $^{87}Sr/^{86}Sr$ ranges for the older geological substrates from northwestern South Africa were as follows: 0.734004–0.755445 for the Namaqua-Natal metamorphic province and 0.726132 for the sample from the Richtersveld. High values are consistent with the underlying older Mesoproterozoic rocks, comprising highly deformed ultrametamorphic rocks, gneisses and migmatites.[40]

Pb isotopic ratios

The new bioavailable $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ranges for the geological substrates from the Western Cape (from youngest to oldest geological age) are given in Table 2.

Table 2: Bioavailable Pb isotope ranges for the geological substrates from the Western Cape

Geological substrate	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
Cenozoic coastal sands	36.99 and 37.16	15.53 and 15.55	17.17 and 17.41
Bredasdorp limestones	37.38–38.46	15.56–15.65	17.49–18.51
Karoo and Cape Supergroup	37.10–38.25	15.48–15.64	17.28–18.39
Cape granites	37.32–38.11	15.61–15.66	17.37–18.06

The Cape granites at Rooiheuwel farm have narrower bioavailable Pb isotopic ranges compared with the Karoo and Cape samples and show a slight offset from the rest of the samples. This offset is only seen in Figure 6a ($^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}P$) and not in Figure 6b ($^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$). This result is not unexpected, as the Cape granites are known to have high concentrations of U and Th relative to Pb.[41,42] The half-life of $^{235}U \rightarrow ^{207}Pb$ (0.70×10^9 years) is much shorter than that of $^{238}U \rightarrow ^{206}Pb$ (4.47×10^9 years) and $^{232}Th \rightarrow ^{208}Pb$ (14.01×10^9 years), therefore the initial production of ^{207}Pb is much more rapid than ^{206}Pb and ^{208}Pb.[43] This results in the initial rapid increase in the $^{207}Pb/^{204}Pb$ ratio of a geological system, as observed here for the Cape granites. For the Namaqua-Natal metamorphic province, the two samples from the granites on Dabidas farm plot between the Cape granites and the rest of the samples, while the two samples from the ultrametamorphic rocks of the Namaqua National Park had very different Pb isotopic ratios from the rest of the samples (Figure 6).
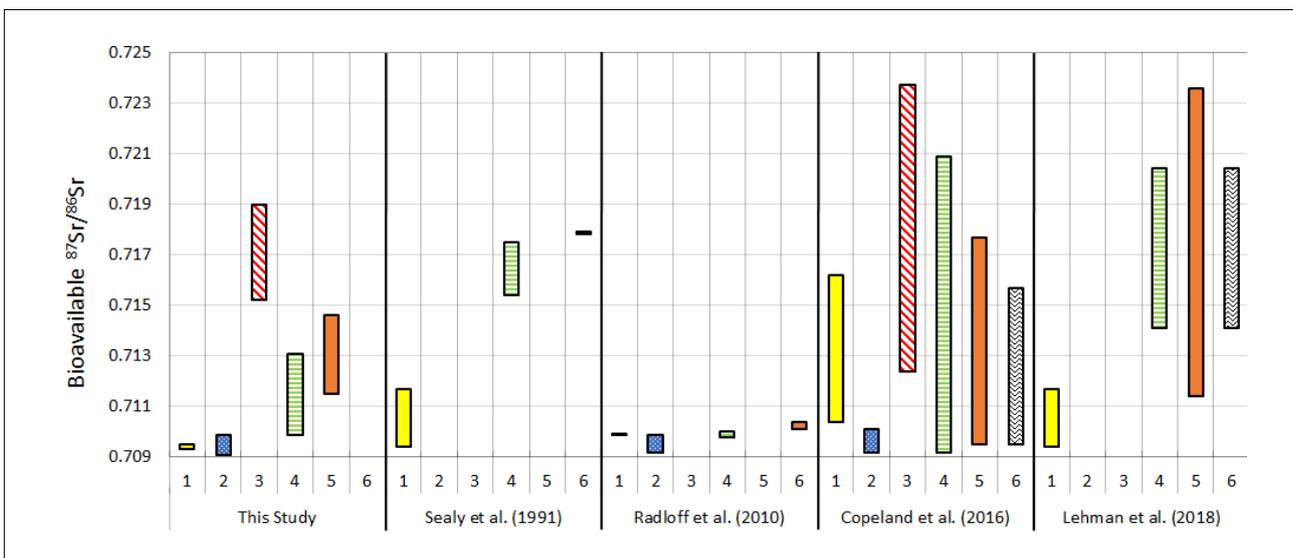

Figure 5: Comparisons between the bioavailable $^{87}Sr/^{86}Sr$ ranges found in this study and those from previous studies, for each geological substrate: 1. Coastal sands; 2. Bredasdorp limestones; 3. Karoo sediments; 4. Cape Supergroup; 5. Cape Granite Suite; 6. Malmesbury shales.
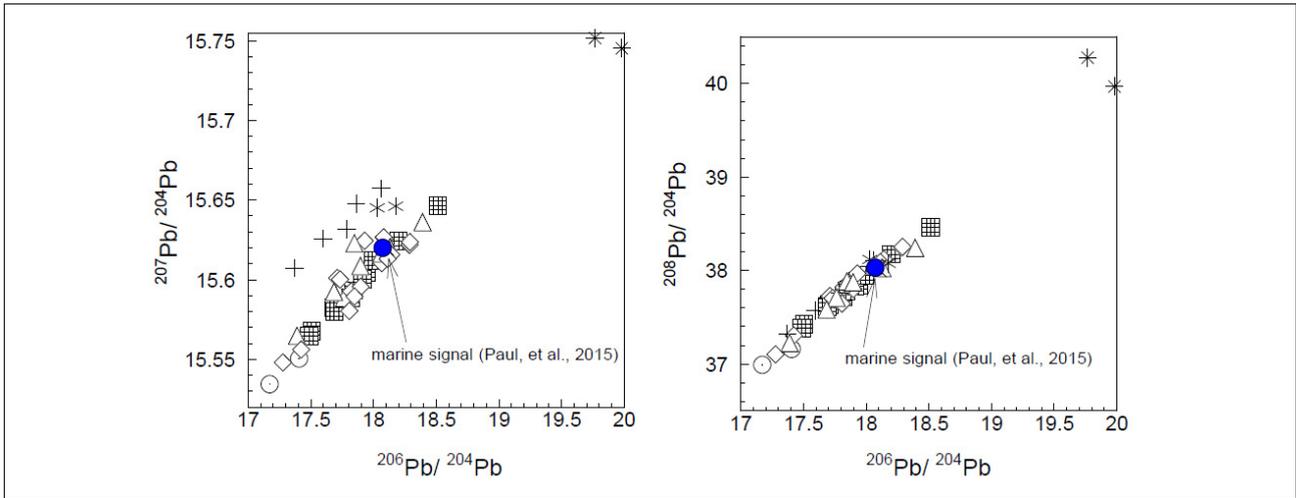
Figure 6: (a) $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ and (b) $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ of the samples collected from various geological substrates of the Western and Northern Cape Provinces, compared with the marine Pb isotopic signal, as measured in South Atlantic surface water sampled in 2010.[28] Errors are included within the sizes of the points as plotted. Refer to Figure 3 for geological substrates.

Figure 6 presents the new bioavailable Pb isotopic data of samples collected from various geological substrates of the Western and Northern Cape Provinces compared with the marine Pb isotopic signal, as measured in South Atlantic surface water sampled in 2010.[28] Figure 7 compares the bioavailable $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ values with the respective marine values. Although samples from the Cenozoic coastal marine sands exhibited strongly marine Sr signals, their Pb isotopic ratios were quite unlike the marine Pb signal. The $^{206}Pb/^{204}Pb$ values for the Bredasdorp limestones are more varied, ranging between 17.49 and 18.51, compared with their $^{87}Sr/^{86}Sr$ values which range between 0.709141 and 0.709942. The marine contribution to bioavailable Sr in the terrestrial environment is much greater than the contribution to bioavailable Pb, due to the higher concentration of Sr (7.62 ppm)[12] compared with Pb (5.22x10^{-6} ppm) in seawater.[28]
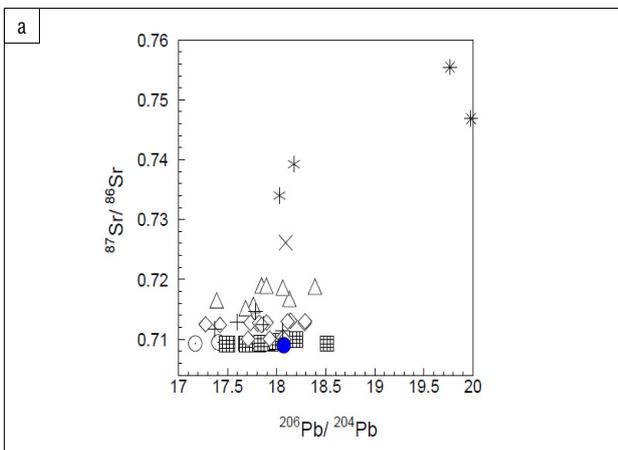
signature. The lowest $^{208}Pb/^{207}Pb$ (2.3812) and $^{206}Pb/^{207}Pb$ (1.1054) values were measured in a tortoise from Koeberg (coastal terrestrial substrate), collected in 1982. Figure 8 shows that the red circled points (samples from the 1980s leaded petrol era) cover the same range as the non-circled points, so there appears to be no contribution from leaded petrol. These 1980s samples were collected from national parks in the Western Cape, or in coastal areas where emissions from motor vehicles are much lower than in urban areas.
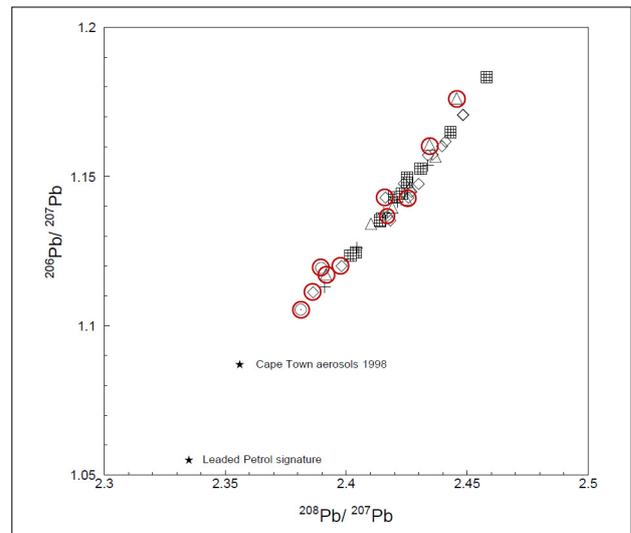

Figure 7: Bioavailable $^{87}Sr/^{86}Sr$ vs $^{206}Pb/^{204}Pb$ values of the samples collected from various geological substrates of the Western and Northern Cape Provinces, compared with the marine Pb isotopic signal (blue circle), as measured in South Atlantic surface water sampled in 2010.[28] Errors are included within the sizes of the points as plotted. Refer to Figure 3 for geological substrates.

Some samples in this study were collected during the 1980s, when leaded petrol was still in use (it was phased out in 2006). The $^{208}Pb/^{207}Pb$ (2.353–2.358) and $^{206}Pb/^{207}Pb$ (1.085–1.090) ratios of Cape Town aerosols in 1998[24] were somewhat higher than the leaded petrol signature of 2.335 and 1.055[24], respectively (Figure 8). The 1980s samples had $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ values distinctly higher than Cape Town's aerosols in 1998 and even higher than the leaded petrol

Figure 8: Bioavailable $^{208}Pb/^{207}Pb$ vs $^{206}Pb/^{207}Pb$ values of all the samples collected within the various geological substrates of the Western Cape region of South Africa, compared with the values for leaded petrol and for aerosols in Cape Town in 1998. Samples collected in the 1980s (leaded petrol era) are circled in red. Refer to Figure 3 for geological substrates.

Conclusions

This study has added to our database of measurements of bioavailable $^{87}Sr/^{86}Sr$ from the Western Cape Province of South Africa. $^{87}Sr/^{86}Sr$ can efficiently discriminate between coastal-marine environments and older geological substrates lying further inland. Organisms living on older geological substrates close to the coast have lowered $^{87}Sr/^{86}Sr$ as a result of marine Sr input. This decreases with increasing distance from the coast; the effects may be seen up to 40 km inland.[4] $^{87}Sr/^{86}Sr$ measurements alone cannot distinguish between the Cape Granite Suite and the Cape

Supergroup (Table Mountain sandstones), whereas Pb isotopes can, as shown in this study. Pb isotopic ratios of terrestrial plants and animals living close to the coast are distinct from seawater values. There does not appear to be significant alteration from marine-derived Pb in sea spray or similar sources. Pb is much less abundant in seawater than Sr[12,28], which could explain why the marine contribution to bioavailable Sr in the terrestrial environment is much greater than the contribution to bioavailable Pb. Ultimately, Pb isotope data can give valuable information on palaeolandscape usage, and can be used as an additional isotope system to extend interpretations based solely on Sr isotopes.

Samples collected from relatively remote localities in the 1980s had Pb isotope ratios similar to those of more recent samples from the same geologies, and distinct from leaded petrol. They do not appear to be compromised by contamination from leaded petrol. It should therefore be possible to use historical samples, e.g. from museum collections, in studies of this kind.

In conclusion, we have demonstrated the value of using a combination of both $^{87}Sr/^{86}Sr$ and Pb isotope systems in coastal terrestrial environments to trace mobility or migration and landscape usage. This use has applications in archaeology, palaeontology, studies of animal migration, wildlife forensics and more.

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Authors' contributions

M.S.: Methodology; data collection; sample collection; data analysis; validation; data curation; writing – the initial draft; writing – revisions; project leadership and management. P.l.R.: Conceptualisation; methodology; validation; data curation; writing – revisions; student supervision; project leadership and management. J.S.: Conceptualisation; data curation; writing – revisions; student supervision; project leadership and management. R.P.: Data curation; writing – revisions; student supervision; project leadership and management.

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