

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of tooth enamel: a comparison of solution and laser ablation multicollector inductively coupled plasma mass spectrometry methods

Sandi R. Copeland^{1,2*}, Matt Sponheimer², Petrus J. le Roux³, Vaughan Grimes^{1,4}, Julia A. Lee-Thorp⁵, Darryl J. de Ruiter⁶ and Michael P. Richards^{1,7}

¹Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology, Deutscher Platz 6, Leipzig D-04103, Germany

²Department of Anthropology, University of Colorado at Boulder, 233 UCB, Boulder, CO 80309, USA

³AEON EarthLAB, Department of Geological Sciences, University of Cape Town, Rondebosch 7701, South Africa

⁴Department of Anthropology and Archaeology, Memorial University of Newfoundland, St. John's, NL A1C 5S7 Canada

⁵Division of Archaeological, Geographical and Environmental Sciences, University of Bradford, Bradford BD7 1DP, UK

⁶Department of Anthropology, Texas A&M University, College Station, TX 77843-4352, USA

⁷Department of Archaeology, Durham University, South Road, Durham DH1 3LE, UK

Received 3 June 2008; Revised 13 August 2008; Accepted 16 August 2008

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) in tooth enamel provide a means to investigate migration and landscape use in humans and other animals. Established methods for measuring $^{87}\text{Sr}/^{86}\text{Sr}$ in teeth use bulk sampling (5–20 mg) and labor-intensive elemental purification procedures before analysis by either thermal ionization mass spectrometry (TIMS) or multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). Another method for measuring $^{87}\text{Sr}/^{86}\text{Sr}$ is laser ablation MC-ICP-MS, but concerns have been expressed about its accuracy for measuring tooth enamel. In this study we test the precision and accuracy of the technique by analyzing 30 modern rodent teeth from the Sterkfontein Valley, South Africa by laser ablation MC-ICP-MS and solution MC-ICP-MS. The results show a mean difference in $^{87}\text{Sr}/^{86}\text{Sr}$ measured by laser ablation and by solution of 0.0003 ± 0.0002 . This degree of precision is well within the margin necessary for investigating the potential geographic origins of humans or animals in many areas of the world. Because laser ablation is faster, less expensive, and less destructive than bulk sampling solution methods, it opens the possibility for conducting $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of intra-tooth samples and small and/or rare specimens such as micromammal and fossil teeth. Copyright © 2008 John Wiley & Sons, Ltd.

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) provide a means by which to investigate migration and landscape use in humans and other animals, and they are increasingly important in archaeological,¹ ecological,² and paleontological³ applications. Local rock $^{87}\text{Sr}/^{86}\text{Sr}$ composition is determined largely by its rubidium/strontium ratio and its age, and therefore $^{87}\text{Sr}/^{86}\text{Sr}$ differs among rock types.⁴ Strontium isotope ratios are incorporated into the biosphere without isotopic fractionation due to their very small relative mass differences. Thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in plants directly reflect those of the local geology, with some hydrological and atmospheric inputs, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of animals in turn reflect those of local plants.^{5–8} Strontium substitutes for calcium in enamel apatite, and the $^{87}\text{Sr}/^{86}\text{Sr}$ of tooth enamel becomes fixed at

the time of enamel mineralization. Thus, if an animal moves from one geological substrate to another during the years in which its teeth mineralize, one can potentially reconstruct this move by comparing teeth that formed at different times.

Commonly employed solution methods for measuring strontium isotope ratios in teeth involve the physical removal of about 5 to 20 mg of tooth enamel, digestion in acid, variable chemical isolation of strontium, followed by thermal ionization mass spectrometry (TIMS) or multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) analysis. This approach is precise and accurate, but nonetheless destructive, which precludes its use for sampling small, rare, or otherwise important specimens. A potentially less destructive method for measuring strontium isotopes in tooth samples is laser ablation MC-ICP-MS. This *in situ* technique is increasingly being applied in geochemical studies to obtain the strontium isotope compositions of high Sr/low Rb minerals. e.g.,^{9,10} Although laser ablation MC-ICP-MS is generally less precise than conventional TIMS analysis, its advantages are the ability to perform *in situ* analysis, no requirement for chemical preparation, rapid data acquisition,

*Correspondence to: S. R. Copeland, Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology, Deutscher Platz 6, Leipzig D-04103, Germany.

E-mail: sandi_copeland@eva.mpg.de

Contract/grant sponsor: National Science Foundation (USA);

contract/grant number: 0609963.

Contract/grant sponsor: The Max Planck Society.

and lower costs. Laser ablation is also far less destructive than bulk sampling in that a tooth sampling area is typically around $250 \times 750 \mu\text{m}$ and barely visible to the naked eye.

Although laser MC-ICP-MS has been successfully applied to determine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in strontium-rich minerals, there has been little effort or success in applications using relatively strontium-rich/rubidium-poor tooth enamel. Simonetti *et al.*¹¹ compared solution and laser MC-ICP-MS measurements of strontium isotope ratios for 36 specimens of archaeological human tooth enamel from ancient Nubia. In nearly all cases their laser measurements gave more radiogenic values (higher $^{87}\text{Sr}/^{86}\text{Sr}$) than the solution values, and the mean difference was 0.0013 ± 0.0006 (1σ). Following a suggestion by Batey *et al.*,¹² Simonetti *et al.*¹¹ argued that molecular interference of $\text{Ca} + \text{P} + \text{O}$ with ^{87}Sr probably caused the higher $^{87}\text{Sr}/^{86}\text{Sr}$ laser values. Simonetti *et al.*¹¹ concluded that laser ablation MC-ICP-MS of tooth enamel was too inaccurate to be used for deciphering historical population migrations. Richards *et al.*¹³ also reported laser and solution strontium isotope ratios for archaeological cattle enamel and found a difference of 0.0015, rather similar to the results of Simonetti *et al.*¹¹

Thus, for the studies reported so far, laser ablation has not been demonstrated to measure the strontium isotope ratios in tooth enamel with acceptable precision or accuracy compared with solution methods. The technique is worthy of further investigation, however, as these studies were very few in number and because the studies were conducted on archaeological, rather than modern enamel. This is particularly important as test cases should exclude the possible contaminating effects of diagenesis which are likely to vary significantly from site to site. *e.g.*,¹⁴ Here, we report on our investigation of the utility of this technique by analyzing laser ablation and solution MC-ICP-MS measurements of strontium isotope ratios in 30 modern rodent teeth from the Sterkfontein Valley, South Africa.

EXPERIMENTAL

Study area

The rodent teeth were collected from a modern owl roost at Gladysvale Cave, Gauteng, South Africa. Gladysvale Cave is located within the Cradle of Humankind World Heritage Site on the John Nash Nature Reserve about 13 km northeast of Sterkfontein Cave, and like several caves in this area it is known for its fossil-bearing breccias.¹⁵ Barn owls, *Tyto alba*, roost in the cave (L. R. Berger, personal communication), and drop micromammal remains which collect at the base of a shaft about 50 m from the cave entrance. This owl species typically uses roosts repeatedly^{16,17} and has a hunting radius of about 1–2 km from the roost site.¹⁸

Gladysvale Cave is situated within the Precambrian dolomites of the Eccles formation in the Malmani subgroup of the Transvaal Supergroup. The Timeball Hill shale formation in the Pretoria Group of the Transvaal Supergroup outcrops along the northeastern border of the dolomite, and is exposed about 0.8 km northwest of Gladysvale Cave. Given the approximate size of the owl hunting radius, the modern rodents are likely to derive from both the Eccles dolomite and the Timeball Hill shale.

Analytical methods

Thirty rodent skulls were collected from the top of the debris pile below the owl roost in January 2007, July 2007, and January 2008, and an upper incisor was extracted from each skull and analyzed. Each tooth was cleaned manually with a brush and distilled water. The outer layer of the labial surface of the tooth was gently cleaned by abrasion with a dental drill equipped with a 1 mm spherical diamond drill bit, and sonicated for at least 30 min in double distilled H_2O . Prior to performing laser ablation, the enamel surface was swabbed with acetone and then swabbed once with 0.1 M acetic acid.

Laser ablation MC-ICP-MS

All teeth were analyzed using a 213 nm laser ablation unit (New Wave Research, Fremont, CA, USA) coupled to a NuPlasma HR MC-ICP-MS instrument (Nu Instruments, Wrexham, UK) in the Africa Earth Observatory Network EarthLAB Facility at the University of Cape Town, South Africa (operational parameters are given in Table 1). This is a double-focusing ICP-MS instrument fitted with twelve Faraday detectors, three discrete dynode ion counters and one channeltron ion counter in a fixed-position collector array. Unique variable zoom optics manipulate the ion beam to achieve coincidence and alignment of ion beams of interest. All data from this instrument presented here were collected on five of the twelve Faraday detectors ($^{88}\text{Sr}:\text{H}4$, $^{87}\text{Sr}+^{87}\text{Rb}:\text{H}2$, $^{86}\text{Sr}+^{86}\text{Kr}:\text{A}x$, $^{85}\text{Rb}:\text{L}1$, $^{84}\text{Sr}+^{84}\text{Kr}:\text{L}2$). Regular Faraday amplifier gain calibrations ensured relative stability between detectors.

The laser ablation sample chamber was flooded with helium as a sweep gas, and mixed with argon using a y-connector prior to injection into the plasma. Any potential surface contamination was removed just before analysis by rapidly sweeping the laser along the path of the analysis ($250 \mu\text{m}$ spot size, $750 \mu\text{m}$ line length, 10 Hz repetition rate, $50 \mu\text{m}/\text{s}$ translation rate, $\sim 0.25 \text{ mJ}$ energy and $\sim 0.5 \text{ J}/\text{cm}^2$ fluency). This resulted in the removal of approximately the top 2–5 μm of tooth material along this line. Subsequent analysis followed this pre-cleaned path, but with a narrower beam, higher energy and slower speed ($200 \mu\text{m}$ spot size, $750 \mu\text{m}$ line length, 20 Hz repetition rate, $5 \mu\text{m}/\text{s}$ translation rate, $\sim 1.35 \text{ mJ}$ energy and $\sim 4.35 \text{ J}/\text{cm}^2$ fluency) and removed a further 20–30 μm deep layer of material along this line.

The on-peak background gas composition was measured on all relevant detectors for 30 s before each analysis with all settings the same as during data acquisition, but with no laser firing. These background measurements, including any krypton present in the argon gas (^{84}Kr and ^{86}Kr overlap with ^{84}Sr and ^{86}Sr), were subtracted from the signals measured during laser ablation. Typical total Kr backgrounds measured during this study were $<5 \text{ mV}$. Periodic monitoring of potential oxide formation found SrO at $<0.1\%$ of the Sr signal, *i.e.* $<<4 \text{ mV } ^{88}\text{Sr}^{16}\text{O}$ at $\sim 4 \text{ V } ^{88}\text{Sr}$. Instrumental mass fractionation was corrected using the exponential law and a fractionation factor based on the measured $^{86}\text{Sr}/^{88}\text{Sr}$ ratio and the accepted $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194.

A major complicating factor in all strontium isotope analyses is the overlap of ^{87}Rb with ^{87}Sr . For solution analysis (by means of TIMS or MC-ICP-MS) Rb is effectively removed by selective ion exchange chemistry, but for laser ablation analysis this is not possible. Hence, for the laser ablation Sr

Table 1. Operating parameters for MC-ICP-MS solution and laser ablation analyses used in this study at the University of Cape Town (UCT) and Max Planck Institute for Evolutionary Anthropology (MPI-EVA) facilities

Parameters	UCT	MPI-EVA
Solution		
MC-ICP-MS	Nu Instruments NuPlasma HR	Thermo Fisher Neptune™
RF power	1300 W	1200 W
Cool gas flow rate	13 L/min	15 L/min
Aux gas flow rate	0.8 L/min	0.8 L/min
Sample gas	37.2 psi	1.17 L/min
Interface cones	Ni	Ni
Mass resolution	Low	Low (400)
Lens settings	Optimized for maximum signal intensity	Optimized for maximum signal intensity
Nebulizer	Glass expansion, MicroMist 200 $\mu\text{L}/\text{min}$, borosilicate glass	Elemental Scientific Inc., Microflow 100 $\mu\text{L}/\text{min}$, perfluoroalkoxy (PFA)
Sensitivity on ^{88}Sr	40–50 V/ppm	50 V/ppm
Cup configuration	L3 (^{84}Sr); L2 (^{85}Rb); Ax (^{86}Sr); H2 (^{87}Sr); H4 (^{88}Sr)	L4 (^{82}Kr); L3 (^{83}Kr); L2 (^{84}Sr); L1 (^{85}Rb); Ax (^{86}Sr); H1 (^{87}Sr); H2 (^{88}Sr)
Data collection	3 blocks, 20 cycles, 10 s integrations	1 block, 50 cycles, 2 s integrations
Laser ablation		
Laser	New Wave™ Research UP213	
Wave length (nm)	213 UV	
Line raster length	750 μm	
Ar flow rate	0.50–0.55 L/min	
He flow rate	0.25–0.30 L/min	
<i>Pre-ablation</i>		
Frequency	10 Hz	
Translation rate	50 $\mu\text{m}/\text{s}$	
Beam width	250 μm	
<i>Ablation</i>		
Frequency	20 Hz	
Translation rate	5 $\mu\text{m}/\text{s}$	
Beam width	200 μm	
Sample	1.35 mJ	
Fluence	4.35 J/cm ²	
<i>Data collection</i>		
Gas background	30 s	
Sample	180 s	
Integration	0.2 s	

isotope data reported here, the potential contribution of ^{87}Rb on the measured signal at mass 87 was monitored by measuring the interference-free ^{85}Rb signal, correcting for instrumental mass fractionation, and using the natural abundance ratio of 0.38506 for $^{87}\text{Rb}/^{85}\text{Rb}$.

No correction was made for the presence of Ca argides/dimers which can be a significant interference on mass 84, raising the invariant $^{84}\text{Sr}/^{86}\text{Sr}$ ratio from the accepted 0.0565 to approximately 0.0575 (see e.g.¹⁹ for a discussion). We monitored the $^{84}\text{Sr}/^{86}\text{Sr}$ ratio which allows assessment of the applied instrumental mass fractionation correction. Ca argide/dimer interference does not significantly affect the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.¹⁹

The typical duration of data acquisition during laser firing was 180 s, with a measurement every 0.2 s. Following data acquisition, the start and end of the data reduction interval were adjusted for each analysis based on a visual assessment of signal stability. This typically meant discarding data collected during the initial few seconds of laser firing and during the final seconds as the signal declined when laser firing ended. Visual assessment of the measured signals against time (using manufacturer supplied Time Resolved software) also aided in detecting and avoiding signal anomalies associated with cracks, fractures and sundry defects in the analyzed sample area. When sampling the rodent

teeth, each sampling line was oriented parallel to the long axis of the tooth. Some individuals were sampled multiple times and some were sampled only once (Table 2). A rodent tooth (either specimen 26-to10z or specimen 26-r29x, depending on availability) was used as a working standard and was measured prior to and after all of the other measurements during a session in order to check for consistency. These rodent tooth standards were also analyzed by solution (see below), and the solution data are referenced to the international Sr isotope standard SRM 987 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710255$) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA). Since the laser $^{87}\text{Sr}/^{86}\text{Sr}$ values of the rodent tooth standards consistently agreed with the SRM 987-referenced solution $^{87}\text{Sr}/^{86}\text{Sr}$ data of these rodent tooth standards, it was not necessary to make further corrections to the laser $^{87}\text{Sr}/^{86}\text{Sr}$ data of rodent tooth samples relative to the bracketing rodent tooth standards in each laser session.

Solution MC-ICP-MS

The preparation of the tooth samples for solution MC-ICP-MS strontium isotope analysis followed a modified version of the method described by Deniel and Pin.²⁰ A piece of each tooth weighing approximately 20 mg was used. Since rodent incisors are very small, it was not possible to manually

Table 2. Results of the analyses of modern rodent teeth from Gladysvale Cave, South Africa. For laser internal error, laser external error, total Sr (V) and $^{85}\text{Rb(V)}/\text{Sr(V)}$, if the number of laser runs was greater than one, the result given is the mean of all runs for that specimen. * = insufficient strontium signal intensity (V) for accurate laser analysis

Rodent tooth specimen	Solution				Laser ablation				total Sr (V)	$^{85}\text{Rb(V)}/\text{Sr(V)}$	Difference (laser-solution)
	solution $^{87}\text{Sr}/^{86}\text{Sr}$	solution internal error (2 σ)	Sr (ppm)	laser $^{87}\text{Sr}/^{86}\text{Sr}$	laser internal error (2 σ)	laser external error (2 σ)	# laser runs (n =)				
26-to10z	0.72972	0.000012		0.72989	0.000045	0.000028	72	5.146	0.03%	0.00017	
26-to5z	0.75005	0.000012		0.75074	0.000086		3	5.467	0.03%	0.00069	
26-r1	0.73785	0.000008	408	0.73760	0.000048		1	3.010	0.03%	-0.00025	
26-r2	0.72854	0.000026	61	0.72892	0.000220		1	0.440	0.38%	0.00037	
26-r3	0.73595	0.000008	338	0.73631	0.000085		3	1.810	0.06%	0.00036	
26-r5	0.72815	0.000008	394	0.72832	0.000036		1	3.820	0.04%	0.00018	
26-r7	0.71978	0.000006	422	0.71979	0.000044		1	4.070	0.02%	0.00001	
26-r8	0.74924	0.000020	93	0.74923	0.000126		1	0.690	0.18%	-0.00001	
26-r9	0.72981	0.000012	233	0.73003	0.000092		1	1.110	0.06%	0.00023	
26-r10	0.72666	0.000014	115	0.72707	0.000154		1	0.460	0.09%	0.00041	
26-r23x	0.73121	0.000016	25	0.73146	0.000162		1	0.321	0.60%	0.00025	
26-r26x	0.73013	0.000010	43	0.73092	0.000100		1	0.860	0.17%	0.00079	
26-r29x	0.73262	0.000014	145	0.73293	0.000081	0.000036	10	1.887	0.03%	0.00031	
26-r33x	0.73191	0.000012	71	0.73171	0.000084		1	0.930	0.08%	-0.00020	
26-r34x	0.75067	0.000012	189	0.75088	0.000072		2	2.040	0.04%	0.00021	
26-r36x	0.73038	0.000012	54	0.73040	0.000132		1	0.380	0.12%	0.00002	
26-to4z	0.73057	0.000012	185	0.73094	0.000041		3	6.100	0.05%	0.00037	
26-to8z	0.73313	0.000012	85	0.73367	0.000088		2	4.200	0.13%	0.00054	
26-to9z	0.73191	0.000012	78	0.73206	0.000174		4	0.431	0.35%	0.00016	
26-r39x	0.72883	0.000016	133	0.72875	0.000126		1	0.770	0.05%	-0.00008	
26-r4	0.74407	0.000012	71	0.74368	0.000388		2	0.312	0.11%	-0.00039	
26-r20x	0.73507	0.000014	28	0.73556	0.000240		2	0.320	0.54%	0.00049	
26-r21x	0.72710	0.000018	88	0.72730	0.000058		2	1.300	0.09%	0.00020	
26-r22x	0.73235	0.000016	55	0.73313	0.000116		1	0.918	0.13%	0.00078	
26-r6*	0.72958	0.000012	25	0.72965	0.000340		1	0.250	0.80%	0.00007	
26-r24x*	0.72802	0.000018	22	0.72940	0.000240		1	0.283	0.31%	0.00138	
26-r25x*	0.72851	0.000026	17	0.72993	0.000320		1	0.296	0.55%	0.00142	
26-to3z*	0.72878	0.000012	41	0.73080	0.000710		2	0.100	1.11%	0.00202	
26-to7z*	0.72804	0.000030	11	0.73138	0.000400		1	0.150	1.00%	0.00334	
26-r42x*	0.72915	0.000020	19	0.73249	0.000760		1	0.101	0.53%	0.00334	

separate the enamel from the dentine, so each solution tooth sample includes both enamel and dentine. The $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentrations are both very similar for enamel and dentine in teeth that have not been subject to burial (and therefore potential diagenetic contamination).²¹

Each tooth sample was sonicated for at least 30 min in a clean lab (PicoTrace GmbH, Bovenden, Germany) at the Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology (MPI-EVA), Leipzig, Germany. The sample was then rinsed three times with high-purity deionized (18.2 M Ω) water (Milli-Q[®] Element A10 ultrapure water purification system, Millipore GmbH, Schwalbach, Germany), rinsed with acetone (GR for analysis grade, $\geq 99.8\%$, Merck KGaA, Darmstadt, Germany), and dried overnight. Each tooth sample was weighed into clean 3 mL Savillex[™] (Minnetonka, MN, USA) vials and closed-vessel digested on a heating block (120°C) in 1 mL of 14.3 M nitric acid (HNO₃) before it was evaporated to dryness. The resulting residue was re-dissolved in 3 M HNO₃ and then transferred into clean 2 mL columns containing preconditioned Sr-Spec[™] resin (EiChrom Technologies, Inc., Darien, IL, USA; cleaned following the procedure in Charlier *et al.*²²) with a bead size of 50–100 μm suspended in ultrapure deionized water.²³ After several washes with 3 M HNO₃, strontium was eluted in ultrapure deionized water and dried, then re-dissolved in 3% HNO₃ for MC-ICP-MS analysis. All acids used in this procedure were made from SupraPur[®] grade (Merck KGaA) stock solutions and diluted using ultrapure deionized H₂O.

Solution measurements were made using a Thermo Fisher Neptune[™] (Thermo Fisher Scientific Inc., Dreieich, Germany) MC-ICP-MS instrument at MPI-EVA (operational parameters given in Table 1). The Neptune[™] is a high-resolution, double-focusing mass spectrometer equipped with nine Faraday detectors fitted with 10¹¹ Ω resistors (four movable detectors (H1–H4; L1–L4) on either side of a fixed axial detector) and a Virtual Amplifier[™] system which eliminates possible amplifier-detector bias and provides a dynamic range of 5 mV to 50 V on each detector.^{12,24} Solutions were diluted in 3% HNO₃ to give ^{88}Sr signal intensities of 20–25 V and were introduced into the plasma source of the mass spectrometer using a 100 $\mu\text{L}/\text{min}$ self-aspirating capillary and Microflow PFA (perfluoroalkoxy) ST-nebulizer (Elemental Scientific Inc., Omaha, NE, USA).

Strontium isotope measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ were made in static mode using a collector configuration similar to that described in Batey *et al.*¹² (Table 1). During each analysis, baselines were first measured for 30 s at half mass positions (85.6 and 86.5) of the axial cup mass (^{86}Sr), followed by data collection involving 50 cycles of 2 s integration in one block. Corrections for interferences from Kr in the carrier gas (argon) and Rb in the carrier gas and samples, as well as mass bias normalization (using $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$, exponential law), followed an inverse mass bias correction procedure described in Nowell *et al.*²⁴ The data were externally corrected to SRM 987 (strontium carbonate isotope standard dissolved in 3% HNO₃), which was run concurrently with the samples. The MPI-EVA Neptune[™] long-term (10 months) average for $^{87}\text{Sr}/^{86}\text{Sr}$ in SRM 987 was 0.710273 ± 0.000033 (46 ppm, 2σ , $n = 97$), while the average internal error of any

given measurement was 0.000006 ± 0.000004 (8 ppm, 2σ , $n = 97$). Typically, in an analytical run samples were corrected by -0.00002 to be in agreement with an accepted TIMS $^{87}\text{Sr}/^{86}\text{Sr}$ value in SRM 987 of 0.710240.^{25,26} Total procedural blanks were considered negligible ($^{88}\text{Sr} = 0.040$ to 0.070 V) at $<0.4\%$ of the analyte signal intensity ($^{88}\text{Sr} = \sim 20$ V).

The strontium concentration (ppm) was calculated by measuring the ^{88}Sr signal intensity (V) in three diluted solutions of SRM 987 with stoichiometrically determined strontium concentrations (100, 400 and 700 ppb) at the beginning, middle and end of the sample run. A regression equation was created for these data points (^{88}Sr (V) as a function of Sr concentration (ppb)), and the ^{88}Sr (V) signal of the samples was then used to calculate the Sr concentration (ppb) in the sample solutions. By employing the dilution factor and the starting mass of the sample we then converted the determined concentrations from ppb into ppm levels. This method has an accuracy of 90% (± 31 ppm, 1σ , $n = 14$) compared with the isotope dilution TIMS concentration data from an in-house tooth enamel standard.

Two rodent tooth samples (26-to10z and 26-to5z) were analyzed by solution MC-ICP-MS in the AEON EarthLAB Facility at the University of Cape Town (Table 1). After being cleaned as outlined above, the teeth were dissolved in 1 mL of 14.3 M HNO₃, re-dissolved twice in 6.2 M HNO₃ and finally dissolved in 2.5 M HCl. The strontium was then isolated from this solution using individually calibrated 10 mL Dowex AG50W-X8 (200–400 mesh) cation-exchange columns. The samples were loaded in 0.5 mL 2.5 M HCl, followed by 12–13 mL washes of 2.5 M HCl, before the Sr fraction was collected in 6 mL of 2.5 M HCl. After being dried down the final strontium fraction was dissolved in 0.2% HNO₃ and a 200 ppb solution taken for MC-ICP-MS analysis.

The approximately 200 ppb Sr sample and standard solutions were aspirated into a micro-cyclonic spray chamber using a 200 $\mu\text{L}/\text{min}$ nebulizer (both from Glass Expansion, Melbourne, Australia) and the resulting aerosol introduced into the plasma. The Faraday detector configuration and data reduction routine were the same as those used for the laser ablation analysis. The background measurement was taken for 120 s while aspirating the same 0.2% HNO₃ used to dilute the sample and standard solutions.

The total Sr voltage measured during the analyses of the SRM 987 and sample solutions varied between 6 and 11 V. The external, measured 2σ reproducibility of the SRM 987 was 0.000040 ($n = 2$) on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

RESULTS

The results of the laser and solution measurements for the modern rodent teeth are given in Table 2. Twenty-four of the 30 rodent teeth had acceptable signal strength (see below) and their mean difference in $^{87}\text{Sr}/^{86}\text{Sr}$ measured by laser and solution ($\Delta_{\text{laser-solution}}$) was 0.00031 ($1\sigma = 0.00022$) (Fig. 1). The long-term, external 2σ reproducibility was calculated from the two specimens that were analyzed multiple times with the laser, 26-to10z ($n = 72$) and 26-r29x ($n = 10$), giving a mean external error of 0.0003 (Table 2).

The strontium signal intensity of rodent tooth enamel measured during laser ablation was highly variable, ranging

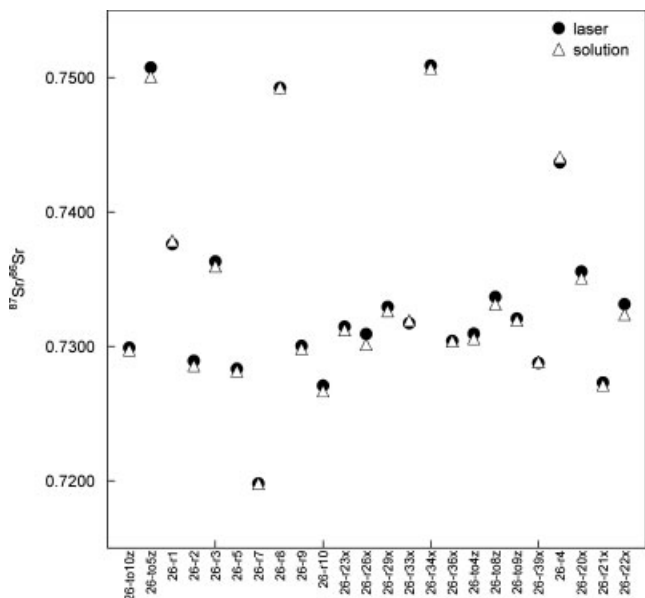


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$ of modern rodent teeth from Gladysvale Cave, South Africa, measured by solution and laser ablation MC-ICP-MS. The external errors for the laser values (2σ , ± 0.0003) and the solution values (<0.0001) are smaller than the symbols.

from 0.1 to 6.1 V. This reflects both the variation in strontium concentration among the teeth and the slight daily variations in the optimization of the MC-ICP-MS instrument. At total laser ablation Sr signal intensities below 0.3 V, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio deteriorated, as seen by the lack of agreement between the laser ablation and solution derived values (Fig. 2). We therefore selected 0.3 V as a conservative minimum accepted

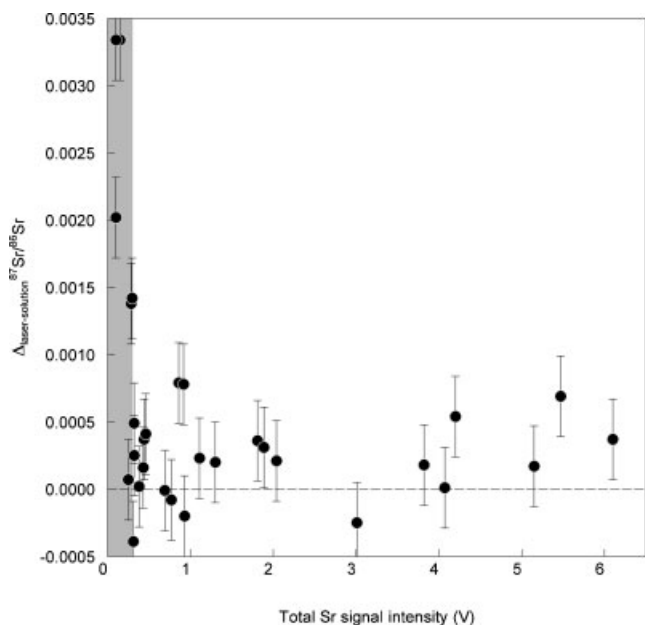


Figure 2. The total strontium signal intensity (V) versus the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ based on laser ablation and solution MC-ICP-MS for the modern rodent teeth. Error bars represent the laser external error (2σ , ± 0.0003). Shaded area encompasses measurements for which the signal intensity was less than 0.3 V and measurement precision degraded rapidly.

total Sr voltage, below which the calculated fractionation factor is compromised by the larger uncertainty in measuring ^{86}Sr . Teeth with strontium signal intensities below 0.3 V are thus not considered hereafter. When the total strontium signal intensity was above our minimum acceptable level, which was the case in 24 of the 30 rodent teeth, the absolute offset from solution values was never greater than 0.0008. In addition, $\Delta_{\text{laser-solution}}$ does not decrease with higher strontium signal intensities, but scatters randomly to positive and negative offsets ($R^2 = 0.07$; Fig. 2).

The uncorrected average $^{84}\text{Sr}/^{86}\text{Sr}$ value of the 26-to10z tooth standard was as expected 0.0576 ± 0.0012 (2σ external), higher but still within error from the accepted value. The laser ablation Sr isotope analyses, shown in Table 2, with total Sr signals >0.9 V all have $^{84}\text{Sr}/^{86}\text{Sr}$ values within the range of the above tooth standard. At total Sr signals <0.9 V, the signals measured at mass 84 after background subtraction (<5 mV) become progressively more unreliable, and uncorrected $^{84}\text{Sr}/^{86}\text{Sr}$ values increase substantially. Because the $^{87}\text{Sr}/^{86}\text{Sr}$ data for the solution analyses and laser ablation analyses correspond for total Sr signals down to 0.3 V, we feel that the correction for instrumental mass fractionation is robust, irrespective of the behavior of the $^{84}\text{Sr}/^{86}\text{Sr}$ ratio, due to the uncorrected Ca argide/dimer interference discussed in the Analytical methods section.

There was no relationship between $\%^{85}\text{Rb}/\text{Sr}$ and $\Delta_{\text{laser-solution}}$ for our 24 samples with acceptable Sr intensity ($R^2 = 0.03$; Fig. 3).

DISCUSSION

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the rodent teeth range from 0.720 to 0.751, values which are consistent with our analysis of plants

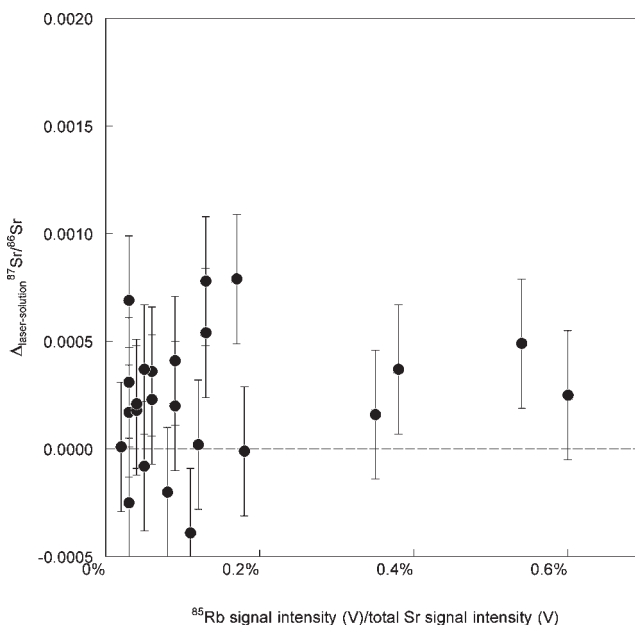


Figure 3. The potential interference of Rb in laser ablation measurements of the modern rodent teeth was monitored by comparing relative Rb signal strength, ^{85}Rb (V)/total Sr (V), with the accuracy of the laser measurement (the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ based on laser ablation and solution MC-ICP-MS). Error bars represent the laser external error (2σ , ± 0.0003).

collected from the Eccles dolomite and Timeball Hill shale, the two geological zones that fall within the likely hunting area of owls roosting at Gladysvale Cave. Plant values on dolomite have a mean value of 0.72935 ± 0.00421 (2σ , $n = 23$), whereas plants on the Timeball Hill shale have a mean value of 0.74964 ± 0.01306 (2σ , $n = 9$). Twenty-nine of the 30 rodents have solution (and laser) values that fall within two standard deviations of the mean plant values in both regions, and are consistent with being derived from these substrates. The large difference in biologically available strontium between the two geological zones within the owl hunting radius near Gladysvale Cave means that the precision level of the laser measurements (external error) of ± 0.0003 on tooth enamel is well within the margin of error required to interpret the geographic origins of the rodents. This can be seen clearly when solution versus laser values are plotted for the modern rodents ($R^2 = 0.998$; Fig. 4).

In the laser ablation study on Nubian archaeological human tooth enamel, Simonetti *et al.*¹¹ found a mean difference between laser and solution measurements of 0.0013, which is more than four times greater than the mean difference found in our study of modern rodents. Their data also suggested that laser measurements were closer to solution measurements with increasing strontium concentration ($R^2 = 0.36$), but that trend is not seen in the modern rodent teeth ($R^2 = 0.09$) despite the fact that the range of strontium concentrations in both sets of samples is broadly similar (Fig. 5). This observation is confirmed by the fact that there is no relationship between Sr signal intensity and $\Delta_{\text{laser-solution}}$ in the rodent teeth (Fig. 2), except for teeth with signal intensities below the threshold of 0.3 V. Thus, our results are inconsistent with the suggestion by Simonetti *et al.*¹¹ that a strontium concentration of ~ 1900 ppm would be necessary to offset a proposed molecular interference of $^{40}\text{Ca} + ^{31}\text{P} + ^{16}\text{O}$. Our data reveal no evidence of molecular interference of

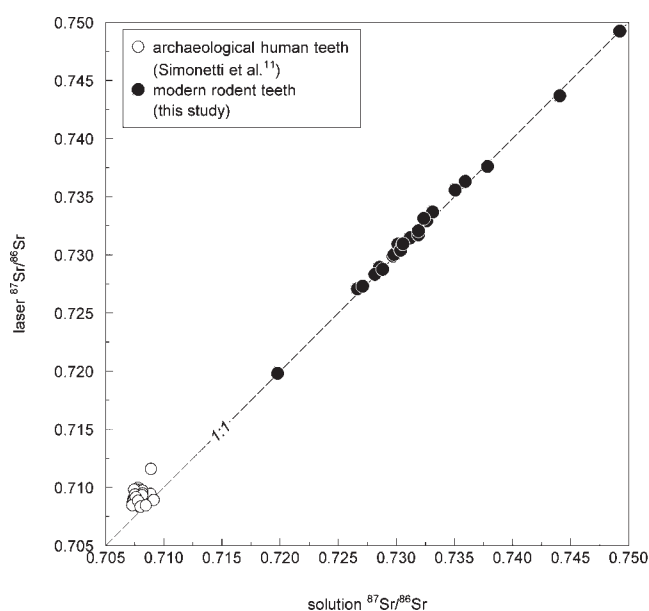


Figure 4. $^{87}\text{Sr}/^{86}\text{Sr}$ measured by solution and laser ablation MC-ICP-MS for the modern rodent teeth analyzed in this study ($R^2 = 0.998$) and the teeth from ancient Nubia (data from Simonetti *et al.*¹¹; $R^2 = 0.034$).

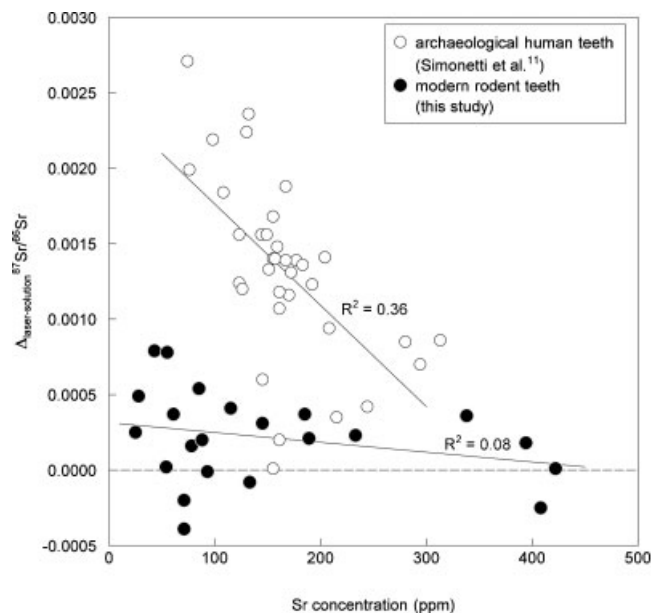


Figure 5. The accuracy of laser $^{87}\text{Sr}/^{86}\text{Sr}$ measurements (the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ based on laser ablation and solution MC-ICP-MS) is shown relative to the concentration of strontium in tooth enamel (Sr ppm) for the modern rodent teeth from this study and the archaeological human teeth analyzed by Simonetti *et al.*¹¹

$^{40}\text{Ca} + ^{31}\text{P} + ^{16}\text{O}$, even in several cases where the strontium concentration is relatively low. Importantly, our data scatter towards both positive and negative $\Delta_{\text{laser-solution}}$ values, which is not consistent with the impact of any particular interfering agent.

The difference between the maximum and minimum values of the $^{87}\text{Sr}/^{86}\text{Sr}$ of archaeological human teeth measured by Simonetti *et al.*¹¹ was only 0.0018, so the mean $\Delta_{\text{laser-solution}}$ in their study of 0.0013 was close to the entire range of variation among their tooth values. Clearly, the conclusion drawn by Simonetti *et al.*¹¹ that $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained by laser ablation "cannot be used for accurately deciphering historical population migrations" was appropriate within the context of their study (for their solution versus laser values $R^2 = 0.034$; Fig. 4). However, it is a considerable overstatement with regard to studies from other places where the geology leads to much higher differences in enamel $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

The $\Delta_{\text{laser-solution}}$ values found in the archaeological cattle tooth reported by Richards *et al.*¹³ and in the archaeological human teeth reported in Simonetti *et al.*¹¹ suggest that it is possible that the accuracy and precision of measured $^{87}\text{Sr}/^{86}\text{Sr}$ values by laser MC-ICP-MS may differ in enamel arising from different contexts. It is possible that subtle differences in the matrix composition of the enamel due to diagenesis affect the accuracy of laser MC-ICP-MS measurements in some cases, and this must be tested in the future. It is worth bearing in mind, however, that even the lower precision found in these studies would be sufficient to determine differences in geographic origin for individuals in many localities around the world, including the Sterkfontein Valley, South Africa.

CONCLUSIONS

Our results from modern South African rodent teeth show that laser ablation MC-ICP-MS can be used to obtain $^{87}\text{Sr}/^{86}\text{Sr}$ ratios quickly, with much less expense than bulk solution methods, and with an acceptable degree of accuracy and precision in at least some circumstances. These results open the possibility of obtaining $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of samples that have previously been limited or excluded from analysis due to concerns about destructive sampling or prohibitive costs. Since laser ablation requires very little enamel surface area, it can be used to measure $^{87}\text{Sr}/^{86}\text{Sr}$ in extremely small teeth such as those of micromammals without the need to destroy the whole tooth. Laser ablation is also ideal for taking intra-tooth measurements of $^{87}\text{Sr}/^{86}\text{Sr}$, and can be used, for example, to sample along incrementally growing structures within tooth enamel. Laser ablation may also be ideal for measuring rare and fossil specimens without causing appreciable damage.

Acknowledgements

We would like to thank Lee Berger and the John Nash Nature Reserve for access to Gladysvale Cave and the rodent specimens. For help in the laboratory, access to facilities, and useful discussions we thank Daryl Codron, Jacqui Codron, Andy Duncan, Shireen Govender, John Lanham, Janet Montgomery, Ian Newton, Fayrooza Rawoot, Judith Sealy, Colin Smith, Andreas Späth, Annette Weiske, and Maarten de Wit. For help in the field we thank Lee Berger, Juliet Brophy, Daryl Codron, Jacqui Codron, Ethan Codron, Jack and Karen of the Kenjara Guest Lodge, and the Kloofzicht Little Foot Bar. Comments from the editor and three reviewers helped us to improve the manuscript. We gratefully acknowledge our funding sources: the National Science Foundation (USA) grant # 0609963 and the Max Planck Society. This is AEON contribution number 56.

REFERENCES

- Price TD, Johnson CM, Ezzo JA, Ericson J, Burton JH. *J. Archaeol. Sci.* 1994; **21**: 315.

- Feranec RS, Hadly EA, Paytan A. *Oecologia* 2007; **153**: 943.
- Hoppe KA, Koch PL, Carlson RW, Webb SD. *Geology* 1999; **27**: 439.
- Faure G, Powell T. *Strontium Isotope Geology*. Springer-Verlag: New York, 1972.
- Hurst R, Davis TE. *Environ. Geol.* 1981; **3**: 363.
- Gosz JR, Brookins DG, Moore DI. *BioScience* 1983; **33**: 23.
- Graustein WC. In *Stable Isotopes in Ecological Research*, Rundel PW, Ehleringer JR, Nagy KA (eds). Springer-Verlag: New York, 1989; 491.
- Blum JD, Taliaferro EH, Weisse MT, Holmes RT. *Biogeochemistry* 2000; **49**: 87.
- Bizzarro M, Simonetti A, Stevenson RK, Kurszlaukis S. *Geochim. Cosmochim. Acta* 2003; **67**: 289.
- Outridge PM, Chenery SR, Babaluk JA, Reist JD. *Environ. Geol.* 2002; **42**: 891.
- Simonetti A, Buzon MR, Creaser RA. *Archaeometry* 2008; **50**: 371.
- Batey JH, Prohaska T, Horstwood MSA, Nowell GM, Goenaga-Infante H, Eiden GC. In *ICP Mass Spectrometry Handbook*, Nelms S (ed). Blackwell: Oxford, 2005; 26.
- Richards M, Harvati K, Grimes V, Smith C, Smith T, Hublin J-J, Karkanas P, Panagopoulou E. *J. Archaeol. Sci.* 2008; **35**: 1251.
- Sponheimer M, Lee-Thorp JA. *Geochim. Cosmochim. Acta* 2006; **70**: 1644.
- Berger LR, Keyser AW, Tobias PV. *Am. J. Phys. Anthropol.* 1993; **92**: 107.
- Bunn DS, Warburton AB, Wilson RDS. *The Barn Owl*. Buteo Books: Vermillion, South Dakota, 1982.
- Reed DN. *J. Archaeol. Sci.* 2005; **32**: 1669.
- Taylor I. *Barn Owls*. Cambridge University Press: Cambridge, 1994.
- Woodhead J, Swearer S, Hergt J, Maas R. *J. Anal. At. Spectrom.* 2005; **20**: 22.
- Deniel C, Pin C. *Anal. Chim. Acta* 2001; **426**: 95.
- Montgomery J, Evans JA, Cooper RE. *Appl. Geochem.* 2007; **22**: 1502.
- Charlier BLA, Ginibre C, Morgan D, Nowell GM, Pearson DG, Davidson JP, Ottley CJ. *Chem. Geol.* 2006; **232**: 114.
- Horwitz EP, Chiarizia R, Dietz ML. *Solvent Extraction and Ion Exchange* 1992; **10**: 313.
- Nowell GM, Pearson DG, Ottley CJ, Schwieters J, Dowall D. In *Plasma Source Mass Spectrometry: Applications and Emerging Technologies*, Holland G, Tanner SD (eds). Royal Society of Chemistry: Cambridge, 2003; 307.
- Terakado Y, Shimizu H, Masuda A. *Contrib. Mineral. Petrol.* 1988; **99**: 1.
- Johnson CM, Lipman PW, Czamanske GK. *Contrib. Mineral. Petrol.* 1990; **104**: 99.