

IN-SITU ELEMENTAL AND Sr ISOTOPE INVESTIGATION OF HUMAN TOOTH ENAMEL BY LASER ABLATION-(MC)-ICP-MS: SUCCESSES AND PITFALLS*

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Trace element and Sr isotope data were obtained by laser ablation- and solution mode-(MC)-ICP-MS analysis for tooth enamel from remains excavated at the New Kingdom period Egyptian colonial and Nubian cemetery site of Tombos (Sudan). Elemental abundances determined by both methods of ICP-MS analysis yielded comparable values; however, ⁸⁷Sr/⁸⁶Sr values obtained by laser ablation were higher compared to their solution mode counterparts. This discrepancy is related to the production of a molecular interference—Ca + P + O (overlaps ⁸⁷Sr); hence the higher ⁸⁷Sr/⁸⁶Sr values recorded during ablation analyses. Laser ablation studies of enamel may provide relatively precise ⁸⁷Sr/⁸⁶Sr values rather quickly but cannot be used for accurately deciphering historical population migrations.

KEYWORDS: Sr ISOTOPE ANALYSIS, LASER ABLATION, ICP-MS, TOOTH ENAMEL, ANCIENT NUBIA

INTRODUCTION

Numerous previous investigations have demonstrated the effective use of strontium isotope analysis of human tissue (e.g., bone, teeth) as an important tool for examining ancient human migration. For example, ⁸⁷Sr/⁸⁶Sr values have been used to identify immigrants in locations such as ancient Maya communities (e.g., Wright 2005), the North American Southwest and Mexico (e.g., Ezzo *et al.* 1997; Price *et al.* 2006), Central Europe and Britain (e.g., Grupe *et al.* 1997; Bentley *et al.* 2003; Schweissing and Grupe 2003; Price *et al.* 2004), Bolivia and Peru (e.g., Knudson *et al.* 2004, 2005), South Africa (e.g., Cox and Sealy 1997; Sillen *et al.* 1998), and Egypt–Sudan (Buzon *et al.* 2007). This technique is particularly effective in regions of the Earth where the ‘background’ Sr isotope signatures are sufficiently varied in order to indicate differences between potential places of origin. Strontium present in soil and groundwater is incorporated into local plants and animals, and hence the Sr isotopic composition of an individual’s diet will be reflected in his or her hard tissues (Ericson 1985). Strontium commonly substitutes for calcium in the hydroxyapatite of teeth and bone (Nelson *et al.* 1986). The tooth enamel of permanent adult teeth forms in early childhood, during the first 12 years of life (at different times for various teeth), and is considered dead tissue since it is not penetrated by any organic structures (Steele and Bramblett 1988). Thus, tooth enamel will reflect the ⁸⁷Sr/⁸⁶Sr

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composition of the environment in which a person lived while the tooth was forming. Minerals may be taken up by the surface of the tooth during life or after burial, although these materials seldom penetrate deep into the enamel (e.g. Budd *et al.* 2000; Price *et al.* 2004; Wright 2005).

Previous studies dealing with the Sr isotope investigation of human tissue have typically been conducted using sample digestion followed by chemical separation of Sr (ion exchange chromatography), and measurement by thermal ionization mass spectrometry (TIMS; e.g., Knudson *et al.* 2004). This methodology is somewhat labour-intensive and time-consuming, with the Sr isotope analysis of an individual sample alone taking 1–2 h to complete. The relatively recent development of multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) instruments for isotopic analysis has significantly improved sample volume throughput given that analysis time has been reduced to ~15 min/sample with little (if any) detriment to the quality of individual sample measurements. In general, Sr isotope analyses obtained by solution mode-MC-ICP-MS analysis are characterized by internal uncertainties (2σ) for samples and external reproducibility (2σ standard deviation) based on repeated measurement of accepted isotopic standards similar to those obtained by isotope dilution (ID)-TIMS (e.g., Schmidberger *et al.*, 2003; Buzon *et al.* 2007). Moreover, recent advances in microanalytical techniques, such as laser ablation-ICP-MS, now provide the opportunity to quantify elemental abundances within individual specimens of tooth enamel and bio-apatite with both high sensitivity and at high spatial resolution (100s of micron scale; e.g., Budd *et al.* 1998; Kang *et al.* 2004; Dolphin *et al.* 2005; Trotter and Eggins 2006).

The recent coupling of both laser ablation system and ICP source to a multicollector magnetic sector mass spectrometer (MC-ICP-MS) has produced an instrument configuration that yields radiogenic isotope data for in-situ isotopic measurements of geological materials comparable in precision to that offered by TIMS. There presently exist quite a number of previous investigations that report comparisons between data obtained by TIMS and laser ablation-MC-ICP-MS (several also including solution mode-MC-ICP-MS data) for various radiogenic isotope systems—some examples include: Sr isotope analysis of magmatic and biogenic carbonates and apatite (Bizzarro *et al.* 2003; Schmidberger *et al.* 2003; Woodhead *et al.* 2005); Hf isotope analysis of zircons (Griffin *et al.* 2000, Bizzarro *et al.* 2002, Woodhead *et al.* 2004); Pb isotope analysis of silicate minerals (Paul *et al.* 2005); U/Pb dating of accessory minerals (Simonetti *et al.* 2005, 2006). All of these studies clearly demonstrate that laser ablation-MC-ICP-MS analysis can produce accurate in-situ, isotopic data (compared to TIMS results)—thus validating its use for examining the isotopic signatures of various types of samples at high spatial resolution. Jackson *et al.* (2001) provide an excellent summary of the various laser ablation-MC-ICP-MS instrument configurations available and their analytical capabilities relative to the different radiogenic isotope systems.

We report here elemental abundances and Sr isotope ratios of tooth enamel obtained from remains at the New Kingdom period Egyptian colonial site of Tombos, located in ancient Nubia (modern-day Sudan). Sr isotope ratios measured by solution mode-MC-ICP-MS (following sample digestion and ion exchange chromatography) on the same teeth are reported in our recent study (Buzon *et al.* 2007); whereas in-situ laser ablation-multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) Sr isotope analyses are reported here. The relatively rapid nature of an individual laser ablation Sr isotope analysis (~2 min including wash-out time; e.g., Bizzarro *et al.* 2003; Schmidberger *et al.* 2003), if successful, would substantially increase sample throughput and possibly revolutionize the manner in which migration studies of ancient civilizations are carried out in the future. Thus, the accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ values recorded during laser ablation-MC-ICP-MS analysis were evaluated by

comparing these results to those obtained by solution mode analysis (Buzon *et al.* 2007). In addition, elemental abundances of the enamel samples were determined by both solution mode and laser ablation analyses using a quadrupole-ICP-MS instrument. These were used to examine possible matrix effects on the in-situ Sr isotope data (e.g., Budd *et al.* 2000), and evaluate the accuracy of the in-situ laser ablation protocol for quantifying elemental abundances within enamel at high spatial resolution.

MATERIALS AND ANALYTICAL METHODS

Enamel samples

The principal inorganic constituent of enamel is calcium phosphate in the form of hydroxyapatite [$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaX}$, where X can represent a mixture of F, Cl, CO_2 , OH] (e.g., Bowes and Murray 1935); this is similar to the chemical composition of the mineral apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$]. The importance of this similarity is demonstrated below in obtaining accurate elemental abundances by laser ablation-ICP-MS analysis.

Tooth enamel samples investigated here were from 37 individuals and when possible were premolars, which have enamel that forms between the ages of 2 and 6; if missing, another tooth type was substituted. Although tooth enamel is much less susceptible to contamination than bone or dentine, we ensured that the tooth enamel samples were not altered by post-depositional contamination by mechanically and chemically cleaning the surface of the tooth. These techniques have been shown to reduce some diagenetic contamination (Nielsen-March and Hedges 2000). Possible contamination of the Tombos enamel samples by post-depositional strontium was eliminated by the lack of correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ values and strontium concentration (Buzon *et al.* 2007). In addition, the degree of contamination was examined by using the uranium abundances in the enamel, since uranium uptake via groundwater infiltration can occur (Hedges and Millard 1995), and uranium is an element not normally found in skeletal tissues. The low U abundances recorded by the enamel samples (Table 1) also confirm the lack of post-depositional processes.

All of the instrumentation and laboratory facilities used for this study and described below are housed within the Radiogenic Isotope Facility of the Department of Earth and Atmospheric Sciences at the University of Alberta.

Solution mode elemental analysis

Fragments of enamel (between ~0.010 and ~0.060 g) were taken for trace element analysis by solution mode-ICP-MS (Table 1). Sample preparation followed a slightly modified version of that by Gulson and Wilson (1994) for the cleaning of tooth specimens used for elemental and isotopic analysis. Samples were rinsed in milliQ de-ionized water with ultrasonic agitation for 10 min, followed by an overnight 'soaking' in milliQ water. On the following day, samples were soaked in 6% H_2O_2 for 4 h. They were then rinsed with milliQ water and immersed in 8N HNO_3 and placed on a hotplate for several hours; complete digestion normally occurred within the first hour. The samples were then evaporated to dryness followed by the addition of 10 ml of 2% HNO_3 . Prior to the ICP-MS analysis, internal standard solutions were added to a 1 ml aliquot of sample solution.

Sample solutions were analysed using a Perkin Elmer Elan6000 quadrupole ICP-MS, and instrument operating conditions were as follows: RF power = 1200 W; dual detector mode;

blank subtraction performed subsequent internal standard correction; unit of measurement is cps (counts per second); auto lens on; use of 4-point calibration curves (0, 0.25, 0.50 and 1.00 ppm for Ca, Mg and Fe; 0, 0.005, 0.010 and 0.020 ppm for the remaining elements); typical count rates for a 10 ppb Pb solution yields between 150 000 and 200 000 cps; sample uptake rate (using a peristaltic pump) was $\sim 1 \text{ ml min}^{-1}$; sample analysis consisted of 35 sweeps/reading, 1 reading/replicate and 3 replicates; dwell times were 10 ms for Al, Mn and U, and 20 ms for the remaining elements; total integration times (dwell time \times number of sweeps) were 350 ms for Al, Mn and U, and 700 ms for the remaining elements; abundances listed in Table 1 represent the average of three replicates. External reproducibility, based on repeated analysis of international whole rock standards (e.g., BCR-1, BE-N), is 5–10% (2σ level) of the quoted abundances for most elements.

Laser ablation elemental analysis

In-situ trace element analyses of individual tooth enamels were obtained using the Elan6000 quadrupole ICP-MS coupled to a UP213 nm laser ablation system (New Wave Research, USA). The optimization of ICP-MS instrument parameters (RF power 1200 W, peak hopping acquisition, 50 ms dwell time) was achieved by ablating the NIST SRM 612 international glass standard reference material. For trace element determinations, the NIST SRM 612 standard and enamel samples were ablated using a 60 μm spot size, 5 Hz repetition rate and energy density of $\sim 13 \text{ J cm}^{-2}$. Experiments were conducted in a mixed He/Ar atmosphere (ratio of 0.5:0.1 l min^{-1}) within the ablation cell, and mixed with Ar (1.03 l min^{-1}) prior to entering the torch assembly. The laser ablation cell was flushed with a higher flow rate of He (up to 0.9 l min^{-1}) for approximately 1 min in-between laser ablation runs to ensure adequate particle wash-out. The NIST SRM 612 glass standard was used as the external calibration standard. Quantitative results for 11 elements (Tables 1 and 2) were obtained via the external calibration of relative element sensitivities using the NIST SRM 612 standard (preferred concentrations reported by Pearce *et al.* 1997), and normalization of each analysis to the solution mode ICP-MS data for ^{43}Ca as the internal standard (Table 1). Data reduction, including concentration determinations, method detection limits and internal uncertainties were obtained using the GLITTER[®] (XP version, Macquarie University) laser ablation software. A typical analysis consisted of a $\sim 25 \text{ s}$ background measurement followed by data acquisition and ablation for $\sim 40 \text{ s}$ using rapid peak hopping and dwell time of 50 ms for each element reported. Repeated analysis of the NIST SRM 612 glass as an unknown over the course of this study yields relative standard deviations (RSD, 2σ level) of between 0.2 and 8% for most of the elements investigated here (Table 2). The average concentration values obtained for the 'unknown' NIST SRM 612 glass standard analyses deviate $< 2\%$ (most are below 1%) from the accepted values for the elements reported in Table 2. The RSD (2σ level) for most elements measured in the enamels investigated here ranges from 3 to 15%, and detection limits for most trace elements vary between 0.01 and 0.2 ppm (Table 2).

The accuracy of the laser ablation protocol for the enamel samples employed here was assessed through the repeated measurement ($n = 20$ analyses) of a matrix-matched, in-house standard consisting of a gem-quality crystal of Durango apatite (Table 2). This protocol is similar to that employed recently by Trotter and Eggins (2006) for the in-situ analysis of conodont apatite. In addition, three fragments of the Durango apatite (weighing between 0.025 and 0.050 g), obtained from the same large Durango apatite crystal used in the laser ablation experiments, were digested and subsequently analysed by solution mode-ICP-MS. Elemental

Table 1 Elemental abundances for Tombos tooth enamels obtained by solution mode- and laser ablation-ICP-MS analysis

Sample	Mg ppm	Al ppm	P ppm	Ca ppm	Mn ppm	Fe ppm	Ni ppm	Cu ppm	Zn ppm	Rb ppm	Sr ppm	U ppm
DL-SM	0.5	0.02		3.2	0.003	0.37	0.06	0.003	0.008	0.004	0.003	0.003
2-S	2870	2.99		371 422	1.44	11.4	0.69	0.44	139	0.08	170	<b.d.
2-LA	3656	49.0	209 960		1.81	72.3	3.54	18.5	110	0.15	224	0.011
3-S	8056	45.6		435 721	6.62	51.3	3.46	3.07	140	0.11	244	0.005
3-LA	11 759	96.2	207 211		23.6	62.7	3.07	1.66	79.6	0.06	331	<b.d.
5-S	4030	7.94		365 649	1.30	12.8	0.85	0.60	84.7	0.07	192	<b.d.
5-LA	2585	1.17	171 392		0.71	46.5	2.35	0.72	20.2	0.08	205	<b.d.
8-S	3478	2.16		429 987	0.90	14.1	0.60	0.36	47.4	0.08	177	<b.d.
8-LA	4816	13.2	199 197		2.40	62.3	2.97	1.93	37.3	0.05	193	0.004
9-S	3059	20.2		381 549	1.32	11.0	1.59	0.93	168	0.09	144	<b.d.
9-LA	3895	2.40	183 402		4.01	52.1	2.56	1.00	19.1	0.08	168	0.01
10-S	2837	155		406 901	1.86	41.7	2.76	3.19	203	0.24	155	0.011
10-LA	3451	0.55	187 138		0.69	53.2	4.83	2.44	25.6	0.10	207	<b.d.
11-S	3367	20.9		295 930	20.7	40.9	0.82	1.06	108	0.08	98.0	0.003
11-LA	2104	3.49	136 884		0.31	42.7	1.82	0.55	28.8	0.07	97.0	<b.d.
12-S	3578	14.6		357 861	1.41	14.1	0.54	0.40	118	0.04	208	<b.d.
12-LA	2932	2.32	161 408		0.85	51.3	2.46	1.14	41.2	0.02	199	<b.d.
13-S	3550	855		589 465	6.74	264	11.8	11.6	395	0.89	294	0.039
13-LA	19 878	10.3	278 835		1.05	78.5	3.94	1.76	146	0.04	433	<b.d.
15-S	4740	41.0		159 459	0.78	18.3	1.76	1.53	53.4	0.07	65.9	0.242
15-LA	6350	6.72	79 188		0.14	21.3	1.10	0.65	34.9	0.04	67.6	<b.d.
17-S	5159	193		743 794	3.07	23.8	2.74	1.66	239	0.39	313	0.016
17-LA	5221	3.7	325 303		2.12	102	4.80	3.08	51.7	0.15	316	<b.d.
19-S	2743	63.0		453 721	3.17	58.2	1.75	1.00	98.6	0.15	183	<b.d.
19-LA	3461	0.41	213 761		0.54	63.2	3.02	1.98	29.1	0.12	195	<b.d.
22-S	4140	15.4		304 665	0.69	4.12	1.00	0.80	86.7	0.09	123	<b.d.
22-LA	3460	0.56	144 545		0.26	40.9	2.13	1.23	19.9	0.11	109	<b.d.
23-S	2276	8.89		360 621	0.98	2.82	0.74	0.56	127	0.11	172	<b.d.
23-LA	2495	3.80	164 935		0.38	46.1	2.26	0.66	25.1	0.05	175	<b.d.
24-S	4933	3.58		324 941	0.99	7.42	0.39	0.50	62.2	0.10	76.0	<b.d.
24-LA	8590	3.60	159 323		0.42	41.8	2.16	1.28	58.6	0.10	105	<b.d.
29-S	2447	11.9		378 095	1.56	20.8	0.44	0.36	153	0.08	155	<b.d.
29-LA	3098	13.3	176 106		1.29	50.7	2.30	1.11	19.6	0.08	158	<b.d.
31-S	2473	0.82		374 810	0.61	4.26	0.39	0.27	48.9	0.20	157	<b.d.
31-LA	3310	9.30	170 910		0.50	53.2	2.71	1.56	20.8	0.18	155	<b.d.
33-S	4029	6.06		372 838	0.58	10.4	0.51	0.43	76.3	0.10	108	<b.d.
33-LA	2520	8.73	170 811		0.48	53.0	2.65	1.87	47.2	0.10	138	<b.d.
38-S	2661	8.5		358 770	1.96	8.39	0.62	0.37	111	0.10	130	<b.d.
38-LA	2824	14.4	175 064		0.87	50.7	2.47	2.50	39.5	0.19	137	<b.d.
39-S	2509	11.4		379 174	2.86	13.1	0.62	0.65	136	0.13	145	<b.d.
39-LA	2847	6.95	180 672		0.36	50.4	2.64	1.18	28.5	0.13	150	<b.d.
40-S	2709	3.72		389 907	7.13	10.6	0.47	0.33	60.0	0.10	123	<b.d.
40-LA	4220	2.52	183 122		0.26	53.0	2.85	1.48	26.9	0.12	144	<b.d.
41-S	2371	11.8		398 411	1.1	14.9	0.68	0.41	109	0.09	132	<b.d.
41-LA	2460	6.01	178 222		0.7	55.6	2.67	0.83	21.9	0.04	143	<b.d.
42-S	2908	6.78		371 218	7.97	11.8	0.58	0.36	84.6	0.05	280	<b.d.
42-LA	3660	6.14	172 599		0.39	54.8	2.26	0.83	25.4	0.10	223	<b.d.
43-S	2546	2.33		380 002	0.68	7.88	0.59	0.44	71.9	0.14	151	<b.d.
43-LA	2652	3.06	169 909		1.39	55.1	2.56	1.69	74.9	0.09	134	<b.d.

Table 1 (Continued)

Sample	Mg ppm	Al ppm	P ppm	Ca ppm	Mn ppm	Fe ppm	Ni ppm	Cu ppm	Zn ppm	Rb ppm	Sr ppm	U ppm
44-S	2683	44.0		350 168	1.93	12.7	0.49	0.35	46.6	0.15	167	0.005
44-LA	3116	3.69	168 247		0.31	46.1	2.50	1.52	26.4	0.11	101	<b.d.
45-S	3912	4.96		324 124	0.70	9.23	0.37	0.34	47.3	0.13	161	0.006
45-LA	2648	3.57	151 874		0.37	42.1	2.03	1.14	33.6	0.15	158	<b.d.
47-S	2431	14.1		368 768	0.90	13.8	0.52	0.48	106	0.15	167	<b.d.
47-LA	2988	1.12	176 468		0.71	50.8	2.34	1.86	88.8	0.12	172	<b.d.
48-S	2996	10.6		358 289	3.24	13.6	0.57	0.50	149	0.13	204	<b.d.
48-LA	3472	55.8	194 207		<b.d.	<b.d.	4.01	62.5	84.6	2.64	174	<b.d.
49-S	3648	1.77		351 635	0.63	9.22	0.36	0.32	55.7	0.19	159	<b.d.
49-LA	9704	7.12	170 042		0.43	53.8	2.48	1.78	71.2	0.19	214	<b.d.
50-S	4003	3.54		339 296	3.62	7.89	0.28	0.34	102	0.08	126	<b.d.
50-LA	3125	9.62	154 290		1.56	48.7	2.45	1.43	19.3	0.08	106	<b.d.
51-S	3202	1.05		354 139	1.50	3.95	0.28	0.30	68.1	0.13	149	<b.d.
51-LA	3223	3.10	164 884		0.49	47.1	2.18	0.79	21.6	0.13	176	<b.d.
52-S	3791	2.06		342 116	9.15	3.85	0.30	0.28	78.8	0.07	161	<b.d.
52-LA	11 688	138	167 252		19.0	45.5	2.44	1.22	91.2	0.05	235	0.004
53-S	2563	7.44		352 457	0.96	15.2	0.36	0.40	188	0.08	74.1	0.005
53-LA	2491	1.55	164 572		0.71	47.7	2.72	1.86	245	0.19	68.8	<b.d.
54-S	3201	0.98		360 720	0.71	7.55	0.35	0.30	72.5	0.16	161	<b.d.
54-LA	3452	0.75	170 699		0.52	49.4	2.51	0.98	31.4	0.22	178	<b.d.
56-S	3704	43.8		357 822	7.47	43.7	0.43	0.83	110	0.07	215	0.012
56-LA	3244	22.3	168 827		1.32	47.3	2.41	1.05	88.7	0.06	198	0.028
58-S	8087	5.78		277 722	0.43	4.06	0.27	0.43	130	0.01	155	<b.d.
58-LA	2322	8.06	126 607		1.19	40.2	1.94	5.60	20.0	0.09	160	0.034

DL-SM, Detection limit in solution mode; <b.d., below detection limit; S, solution mode; LA, laser ablation mode.

abundances determined by laser ablation analysis were then compared with those obtained by solution mode-ICP-MS analysis (Table 2). The P abundance (55.16 ppm; Pearce *et al.* 1997) in the NIST SRM 612 reference material is many orders of magnitude lower than that found in enamel (~16–18 wt% P; e.g., Bowes and Murray 1935; Frank *et al.* 1966; Curzon and Featherstone 1983) and the Durango apatite (~18 wt% P); therefore, the phosphorus abundances for the enamel samples were calculated relative to the P concentrations determined for the Durango apatite standard using the NIST SRM 612 standardization. By comparing these values to those determined by electron microprobe analysis for the Durango apatite, an average normalization factor was established and applied to the analyses of the tooth enamels. The resultant Ca/P values for almost all of the enamel samples are ~2.1 (Table 3), which is equivalent to the theoretical value for undamaged enamel (e.g., Bowes and Murray 1935), and hence validating the calculation for P abundances outlined above.

Solution mode isotopic analysis

Using a diamond disk saw fitted to a dental drill, an enamel sample (10–20 mg) was cut from the crown with subsequent removal of the pulp and dentine. Enamel samples analysed by solution mode-MC-ICP-MS were digested and chemically treated in a Class 100 cleanroom facility. Samples were sonicated for 15 min in Millipore water (MQ) and then in 5% acetic acid for

Table 2 Trace element analyses of NIST SRM 612 and Durango apatite standards obtained by LA-ICP-MS

Element ppm	DL	Isotope (amu)	NIST SRM 612			Durango apatite				
			Average		RSD %	Average	Std dev.	RSD %	Average	Std. dev.
			This study LA-ICP-MS	Accepted		This study LA-ICP-MS (n = 20)		This study soln. mode-ICP-MS		
Mg	0.08	24	76.89	3.0	77.44	133	9.6	7.2	102	5.7
Al	0.39	27	11286	6.8	11165	<b.d.			3.65	0.89
V	0.08	51	40.03	6.0	39.22	22.7	2.4	10.7	42.97	1.82
Mn	0.16	55	38.66	3.0	38.43	84.2	3.5	4.1	123	22.2
Fe	4.3	57	54.04	8.0	56.33	296	17.9	6.0	375	52.2
Ni	0.19	60	39.36	1.8	38.44	3.20	0.37	11.5	0.83	0.2
Cu	0.08	63	36.56	4.6	36.71	0.71	0.38	53.1	0.47	0.21
Zn	0.22	64	38.25	0.4	37.92	1.46	0.29	19.6	0.19	0.06
Ge	0.95	74	34.70	5.0	34.64	7.24	0.58	8.0	5.77	0.2
Rb	0.05	85	32.27	4.4	31.63	0.13	0.02	16.1	0.12	0.00
Sr	0.02	88	76.39	0.2	76.15	475	11.5	2.4	480	14.1
Y	0.02	89	38.23	1.2	38.25	1232	42	3.4	1058	39.1
Zr	0.05	90	36.03	1.4	35.99	1.35	0.17	12.8	0.75	0.21
Cd	0.05	114	29.05	3.5	28.32	<b.d.			0.01	0.00
Sb	0.16	121	38.46	3.5	38.44	0.12	0.02	12.2	0.15	0.01
Ba	0.01	138	38.27	0.8	37.74	19.42	0.94	4.8	3.12	0.06
La	0.01	139	36.10	0.8	35.77	4140	144	3.5	3965	136
Ce	0.01	140	39.34	2.6	38.35	4464	185	4.1	3019	819
Pr	0.01	141	37.58	1.6	37.16	455	18	4.1	n.a.	
Nd	0.06	146	35.53	1.6	35.24	1538	64	4.2	1507	44.0
Sm	0.24	147	37.08	0.6	36.72	229	14	6.3	241	5.7
Eu	0.02	153	34.84	1.0	34.44	16.3	0.6	3.5	18.5	0.1
Gd	0.09	157	37.39	4.8	36.95	247	13	5.2	234	9.4
Tb	0.01	159	36.22	2.0	35.92	31	2	5.4	28.0	1.1
Dy	0.09	163	36.35	1.8	35.97	189	10	5.3	180	7.2
Ho	0.02	165	38.14	1.6	37.87	39.4	1.7	4.4	37.0	1.6
Er	0.05	166	37.80	3.6	37.43	108	4.7	4.3	103	4.1
Tm	0.02	169	37.33	2.2	37.55	13.54	0.56	4.2	n.a.	
Yb	0.06	172	40.19	4.2	39.95	71.26	2.59	3.6	69.20	2.23
Lu	0.02	175	37.65	3.4	37.71	8.30	0.33	4.0	7.58	0.18
Pb	0.03	208	39.11	2.8	38.96	0.78	0.07	9.1	0.72	0.11
Th	0.01	232	37.97	17.4	37.23	387	8.8	2.3	243	45.2
U	0.01	238	37.69	2.8	37.15	10.98	1.04	9.5	16.59	0.24

DL, detection limit; amu, atomic mass unit; Std dev., standard deviation; <b.d., below detection limit; RSD, relative standard deviation; n.a., not analysed,

Accepted values for NIST SRM 612 reference material from Pearce *et al.* (1997).

15 min. After overnight leaching in 5% acetic acid, the acid was removed and samples were rinsed with MQ prior to transfer to vials. After adding a Rb–Sr spike, the samples were digested in a microwave oven in 4 ml 16N HNO₃ and 1 ml ~10N HCl. Digested samples were dried overnight on a hot plate (80°C). All dried samples were dissolved in 3 ml of 0.75N HCl and then loaded onto 10 cm ion exchange columns containing 1.42 ml of 200–400 mesh AG50W-X8

resin. Samples of 5 ml of 2.5N HCl each were collected into Teflon vials with an added drop of H_3PO_4 and then left to dry overnight on a hot plate (80°C).

Subsequent to ion chromatographic treatment of the samples, the Sr-bearing aliquots were diluted in a 2% HNO_3 solution and aspirated into the ICP torch using a desolvating nebulizing system (DSN-100 from Nu Instruments Inc., Wrexham, UK). Strontium isotope values were determined using a NuPlasma MC-ICP-MS instrument. This technology has led to innovative research studies involving radiogenic isotope systems, due primarily to the overall high ionization efficiency of the ICP source coupled with the simultaneous acquisition of ion beams with flat-topped peak shapes (e.g., Simonetti *et al.* 2005). Strontium isotope data were acquired in static, multicollection mode using five Faraday collectors for a total of 400 s, consisting of 40 scans of 10 s integrations. The 'wash-out' period following the analysis of a sample was approximately 5 min. Prior to the aspiration of a sample, a 30 s measurement of the gas (+ acid) blank was conducted, which is critical for the correction of the ^{86}Kr and ^{84}Kr isobaric (plasma-based) interferences. The isobaric interference of ^{87}Rb was also monitored and corrected for using the ^{85}Rb ion signal; however, the latter was negligible for all of the results reported here. Accuracy and reproducibility of the analytical protocol were verified by the repeated analysis of a 100 ppb solution of the NIST SRM 987 strontium isotope standard during the course of this study; this yielded an average value of 0.710242 ± 0.000041 (2σ standard deviation; $n = 13$ analyses), which is indistinguishable from the accepted value of 0.710245 (Faure and Mensing 2005). The typical internal precision ('error') associated with individual strontium isotopic analysis varies from 0.00001 to 0.00003 (2σ level). The solution mode $^{87}\text{Sr}/^{86}\text{Sr}$ values for the enamel samples from Tombos are listed in Table 3 (from Buzon *et al.* 2007).

Laser ablation Sr isotope analysis

Laser ablation isotopic analyses were obtained using a Nd:YAG UP213 nm laser system coupled to the NuPlasma MC-ICP-MS. The instrument configuration for in-situ Sr isotope analyses follows the method outlined in Schmidberger *et al.* (2003). The sample-out line from the laser ablation cell was 'y'-connected to the sample-out line from the desolvating nebulizing introduction system (DSN-100 from Nu Instruments) to allow for simultaneous aspiration of a 2% HNO_3 solution. At the beginning of each analytical session, parameters for the introduction system and ion optics were optimized by aspirating a 100 ppb solution of the NIST SRM 987 Sr isotope standard. Enamel samples were embedded into 1-inch (circular) epoxy mounts and ablated in a helium atmosphere (1.0 l min^{-1}) using the following parameters: 30–60 s ablation time; 160 μm spot size; 20 Hz repetition rate; $\sim 15 \text{ J cm}^{-2}$ energy density. The accuracy of the laser ablation protocol was verified by repeated analysis ($n = 30$ measurements; 60 μm , 10 J cm^{-2} , 4 Hz; 60 s) of an in-house standard consisting of a modern-day sample of coral from the Indian Ocean. During the course of this study, the average $^{87}\text{Sr}/^{86}\text{Sr}$ value obtained was 0.70924 ± 0.00007 (2σ standard deviation), overlapping the present-day Sr isotope value of modern marine taxa world-wide (0.7090–0.7092; Burke *et al.* 1982). Individual enamel samples were analysed three times by laser ablation and the average $^{87}\text{Sr}/^{86}\text{Sr}$ values and associated 2σ uncertainties obtained by laser ablation are listed in Table 3.

RESULTS AND DISCUSSION

A comparison between elemental concentrations obtained by solution mode and laser ablation-quadrupole-ICP-MS for the enamel samples from Tombos (Table 1) indicates that there is overall

Table 3 Elemental ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ values for Tombos tooth enamels obtained by laser ablation analysis

Sample	Ca/P	(Ca+P)/Sr	^{85}Rb (volts)	$^{87}\text{Sr}/^{86}\text{Sr}$ sol. Mode	2 uncert.	$^{87}\text{Sr}/^{86}\text{Sr}$		Difference
						LA-ICP-MS	2 uncert.	
2	1.8	3428	0.0015	0.70735	0.00002	0.70851	0.00016	0.00116
3	2.1	2639	0.0009	0.70791	0.00002	0.70833	0.00022	0.00042
5	2.1	2799	0.0004	0.70734	0.00002	0.70857	0.00015	0.00123
8	2.2	3561	0.0009	0.70733	0.00002	0.70872	0.00012	0.00139
9	2.1	3924	0.0004	0.70737	0.00002	0.70893	0.00026	0.00156
10	2.2	3831	0.0009	0.70741	0.00003	0.70881	0.00015	0.00140
11	2.2	4417	0.0007	0.70777	0.00002	0.70996	0.00027	0.00219
12	2.2	2501	0.0006	0.70837	0.00003	0.70931	0.00009	0.00094
13	2.1	2954	0.0003	0.70779	0.00006	0.70849	0.00017	0.00070
15	2.0	3623	0.0010	0.70774	0.00008	0.70934	0.00015	0.00160
17	2.2	3413	0.0005	0.70774	0.00001	0.70860	0.00018	0.00086
19	2.1	3651	0.0007	0.70762	0.00002	0.70898	0.00023	0.00136
22	2.1	3641	0.0008	0.70798	0.00007	0.70922	0.00018	0.00124
23	2.2	3053	0.0006	0.70744	0.00003	0.70875	0.00019	0.00131
24	2.0	6369	0.0018	0.70777	0.00002	0.70976	0.00018	0.00199
29	2.1	3586	0.0005	0.70741	0.00002	0.70909	0.00023	0.00168
31	2.2	3475	0.0024	0.70778	0.00002	0.70918	0.00015	0.00140
33	2.2	5047	0.0017	0.70793	0.00002	0.70977	0.00015	0.00184
38	2.0	4096	0.0016	0.70757	0.00002	0.70981	0.00011	0.00224
39	2.1	3851	0.0009	0.70884	0.00003	0.70944	0.00021	0.00060
40	2.1	4667	0.0020	0.70815	0.00003	0.70971	0.00012	0.00156
41	2.2	4364	0.0006	0.70744	0.00001	0.70980	0.00019	0.00236
42	2.2	1945	0.0275	0.70774	0.00006	0.70859	0.00013	0.00085
43	2.2	3632	0.0019	0.70815	0.00003	0.70948	0.00011	0.00133
44	2.1	3099	0.0008	0.70751	0.00003	0.70939	0.00016	0.00188
45	2.1	2954	0.0011	0.70912	0.00001	0.70892	0.00017	0.00020
46	2.1	2163	0.0006	0.70798	0.00003	0.70850	0.00010	0.00052
47	2.1	3260	0.0013	0.70732	0.00003	0.70871	0.00014	0.00139
48	1.8	2704	0.0009	0.70742	0.00002	0.70883	0.00019	0.00141
49	2.1	3273	0.0041	0.70741	0.00002	0.70889	0.00011	0.00148
50	2.2	3928	0.0013	0.70812	0.00002	0.70932	0.00014	0.00120
51	2.1	3476	0.0013	0.70759	0.00002	0.70915	0.00022	0.00156
52	2.1	3169	0.0007	0.70728	0.00002	0.70846	0.00011	0.00118
53	2.1	6977	0.0012	0.70888	0.00005	0.71159	0.00047	0.00271
54	2.1	3295	0.0018	0.70778	0.00003	0.70885	0.00024	0.00107
56	2.1	2447	0.0006	0.70799	0.00002	0.70834	0.00017	0.00035
58	2.2	2616	0.0015	0.70844	0.00003	0.70845	0.00009	0.00001

Ca abundances in (Ca + P)/Sr parameter taken from Table 1; solution mode $^{87}\text{Sr}/^{86}\text{Sr}$ values are from Buzon *et al.* (2007).

good agreement for many of the elements investigated. Figure 1 plots the concentrations of several elements determined by solution mode-ICP-MS analysis versus their corresponding abundances calculated by laser ablation-quadrupole-ICP-MS. Most samples plot on or very close to the 1:1 correspondence line, and confirm that the laser ablation protocol adopted here produces relatively accurate in-situ elemental abundances present within tooth enamel. In

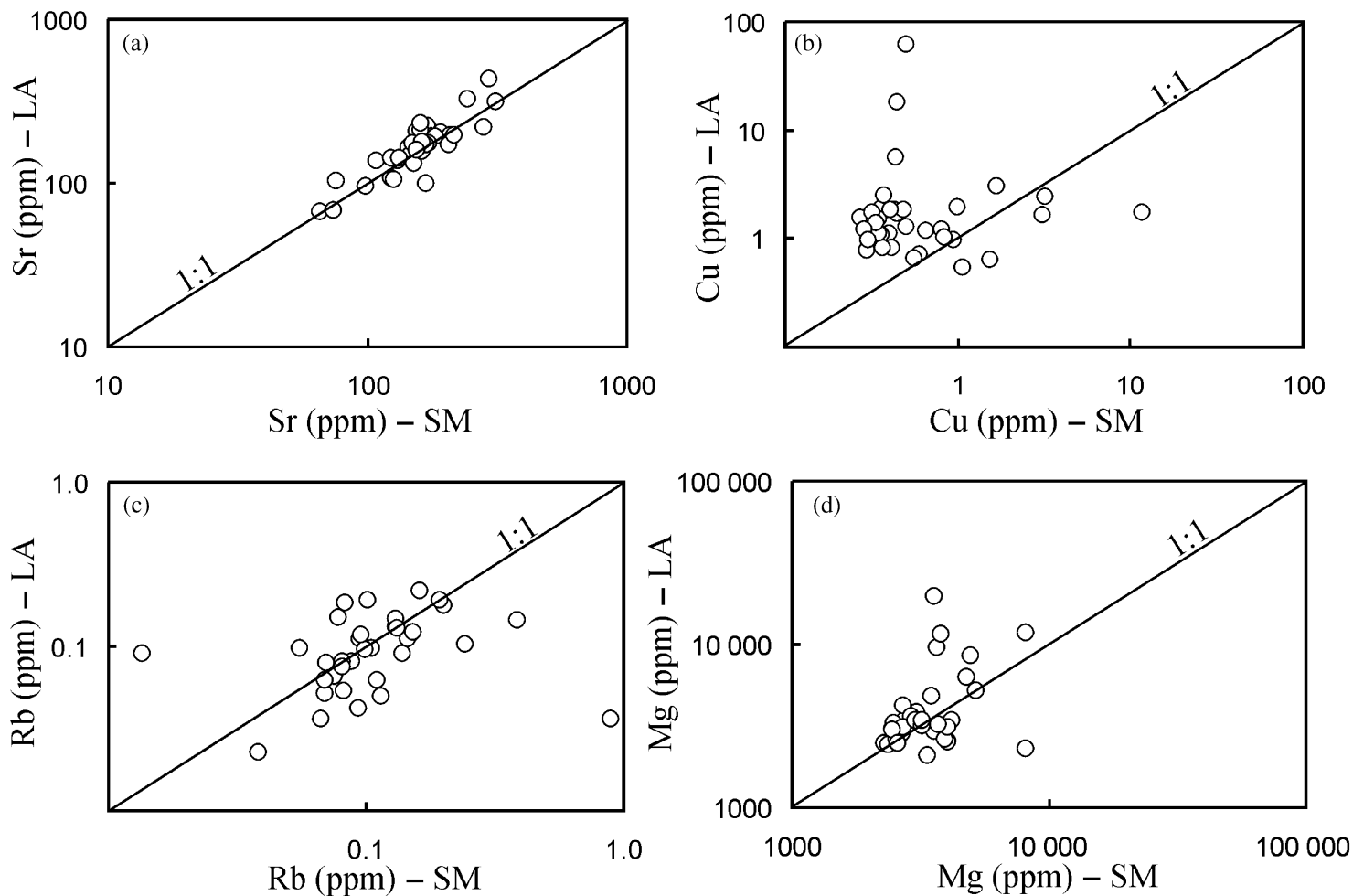


Figure 1 Log-normally distributed plots comparing elemental abundances (ppm) determined by laser ablation (LA) and solution mode (SM) quadrupole ICP-MS analysis for selected elements, (a) Sr, (b) Cu, (c) Rb and (d) Mg, using different fragments of enamel from the same individual. The 1:1 ratio line is drawn in each plot for comparative purposes.

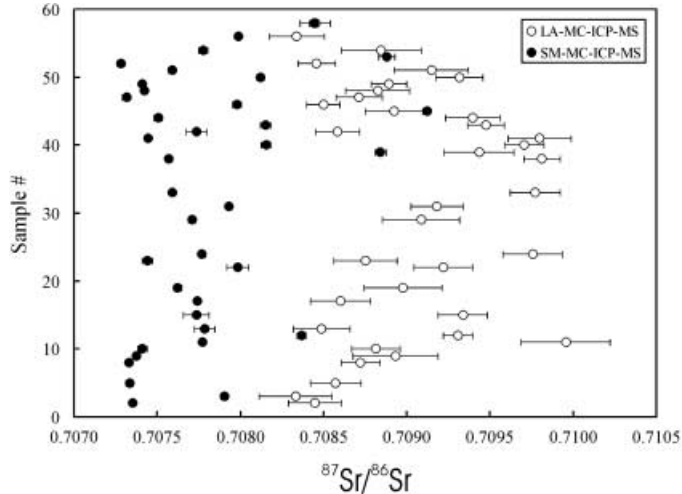


Figure 2 Diagram that compares the Sr isotope values obtained by solution mode-(SM)-MC-ICP-MS versus laser ablation-(LA)-MC-ICP-MS analysis for different fragments of tooth enamel from the same individual. Sample numbers correspond to those listed in Tables 1 and 3. $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained by SM-MC-ICP-MS are from Buzon *et al.* (2007). LA-MC-ICP-MS values represent the mean of three individual laser ablation spot analyses for each sample of enamel. Sr isotope composition (0.71159; Table 3) obtained by LA-MC-ICP-MS for sample #53 is not shown for scaling purposes. Error bars are at 2σ level; for many of the SM-MC-ICP-MS analyses, 2σ error bars are smaller than the symbol size.

addition, the same statement can be made for the elemental abundances obtained for the Durango apatite as the two sets of values overlap (within associated 2σ RSD uncertainties; Table 2). In fact, the abundances of most elements determined here for the Durango apatite are in good agreement with those reported in Trotter and Eggins (2006), despite the fact that the crystals used in both studies are neither one and the same, nor intimately related from a mineralogical/petrological perspective. However, caution must be exercised when examining the chemical composition of enamel since the recent studies of both Kang *et al.* (2004) and Dolphin *et al.* (2005) document a heterogeneous distribution of elemental abundances (e.g., Pb, Zn, Fe) across different developmental regions within a single tooth enamel specimen (and among different teeth from one individual). In fact, the abundances of Cu (Fig. 1 (b)) and those for Fe and Zn (not shown) within the Tombos samples (Table 1) define a much more scattered pattern and confirm the conclusions drawn by Kang *et al.* (2004) and Dolphin *et al.* (2005).

Table 3 and Figure 2 present the Sr isotope values for the Tombos enamel samples obtained by solution mode-MC-ICP-MS analysis (from Buzon *et al.* 2007), and those measured by laser ablation-MC-ICP-MS. It is clear that for a majority of enamel samples, the laser ablation result yields a more radiogenic value (higher $^{87}\text{Sr}/^{86}\text{Sr}$) compared with the corresponding solution mode analysis obtained from a tooth from the same individual (Table 3 and Fig. 2). There is overlap between the two sets of values for just two samples (Fig. 2).

To resolve this apparently systematic difference between Sr isotopes in solution versus laser ablation modes, we conducted a systematic evaluation of the trace element data in conjunction with the laser ablation $^{87}\text{Sr}/^{86}\text{Sr}$ values. The sole parameter that correlates with the offset in

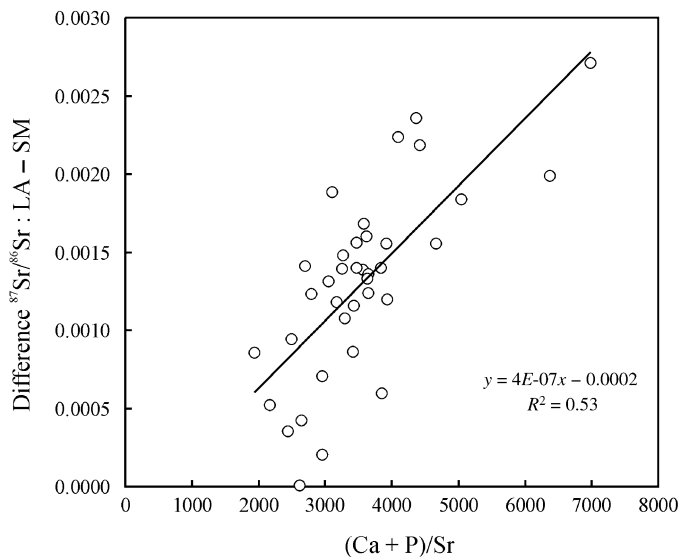


Figure 3 Plot of $(Ca + P)/Sr$ versus the difference between the $^{87}Sr/^{86}Sr$ values obtained by SM-MC-ICP-MS and LA-MC-ICP-MS (i.e., Fig. 2). The line represents a best-fit regression through the data points with its corresponding equation and correlation coefficient.

Sr isotope ratios is the $(Ca + P)/Sr$ value (Fig. 3). Ca and P contents in ‘normal’ tooth enamel can be considered essentially constant; however, Sr contents vary by a factor of ~ 5 (Table 1). A combination of the atomic masses of Ca (40.08) and P (30.97) and O (15.9994)—the latter element is always present to varying degrees in an inductively coupled plasma environment—yields an isobaric molecular interference totalling mass ~ 87 . The production of such a molecule during the laser ablation process will artificially increase the measured $^{87}Sr/^{86}Sr$ ratios. The effect of the Ca–P–O isobaric interference on the Sr isotope composition may be offset with higher Sr contents; according to the positive correlation and calculated best-fit line shown in Figure 3, the Sr abundance required to minimize or negate the effect of this molecular interference is ~ 1900 ppm. However, the Sr abundances for the tooth enamel samples investigated here (Table 1) are substantially lower, with the highest concentration ~ 300 ppm. Of interest, enamel sample #58 contains an anomalously low abundance of P ($\sim 130\,000$ ppm) and is characterized by an almost zero difference associated with its Sr isotope values (Fig. 2; Table 3). The suppression of the Ca–P–O molecular interference produced during laser ablation analysis of apatite with high abundances of Sr was evidenced in the laser ablation study of igneous apatite crystals found within carbonatite complexes (Bizzarro *et al.* 2003). The latter authors report laser ablation $^{87}Sr/^{86}Sr$ values for apatite that overlap with those measured by ID-TIMS and may be a reflection of the high Sr abundances (>3000 ppm) that typically characterize apatites from carbonatite complexes.

As with the solution mode-MC-ICP-MS isotope analyses, the ^{85}Rb ion signal was monitored during the laser ablation analyses in order to apply a correction for the isobaric mass interference of ^{87}Rb on ^{87}Sr . Table 3 lists the intensities of the ^{85}Rb ion signals (average value from three single spot analyses) recorded for the samples investigated here. The data define a complete scatter in a plot of the ^{85}Rb intensity versus the offset in the $^{87}Sr/^{86}Sr$ value (not

shown). Thus, this result indicates that the offset in the Sr isotope values (Table 3) is not a function of the Rb content of the enamel, and that the ^{87}Rb isobaric interference correction is considered effective.

In a recent study, Prohaska *et al.* (2002) report the Sr isotope ratios in prehistoric human bones and teeth using a double-focusing magnetic sector field inductively coupled plasma mass spectrometer (ICP-SFMS, Finnigan MAT Element) coupled to an ablascope 213 nm laser ablation system (Bioptic, Germany). The authors claim that their protocol was successful in determining $^{87}\text{Sr}/^{86}\text{Sr}$ measurements with a precision between 0.1 and 0.2% RSD. In contrast, the Sr isotope measurements reported in Table 3 (solution mode-MC-ICP-MS) are characterized by an average precision that is one order of magnitude higher (i.e., 0.015%). It is important to specify here that a RSD of 0.1–0.2%, as reported by Prohaska *et al.* (2002), corresponds to an absolute uncertainty of ~ 0.00100 for a typical Sr isotope value of >0.70000 . Thus, in their case it becomes extremely difficult to determine the ‘uniqueness’ or ‘distinctiveness’ of individual Sr isotope measurements within a particular data set because of such large associated uncertainties. Moreover, Prohaska *et al.* (2002) determined and compared the laser ablation $^{87}\text{Sr}/^{86}\text{Sr}$ isotope values for bone and tooth samples from each of three different individuals from one excavation site, and these differ from one another by 0.00010 to as much as 0.00100. Once again, these differences are extremely large, especially relative to both the individual, internal (2σ) uncertainties associated with the solution mode results ($\pm \sim 0.00003$; Table 3), and the external reproducibility obtained on repeated measurements of the NIST SRM 987 Sr isotope standard (solution mode) and modern-day coral sample by laser ablation analysis reported here (± 0.000041 and ± 0.000070 , respectively). Prohaska *et al.* (2002) attribute the large difference in the laser ablation Sr isotope values between tooth and bone from a single individual to possible migration during their early childhood. However, given the results presented in this study, their large discrepancies between tooth and bone laser ablation Sr isotope measurements may also be the result of analytical artefact.

CONCLUSIONS

The results from this study clearly indicate that accurate and precise trace element abundances of tooth enamel may be obtained by laser ablation-quadrupole-ICP-MS analysis relatively quickly and at fairly high spatial resolution (e.g., 60 μm). In contrast, the Sr isotope measurements determined by laser ablation-MC-ICP-MS on the same enamel samples at a 160 μm spatial resolution are relatively precise ($\sim 0.02\%$ RSD at 2σ level), but these are deemed inaccurate for almost all of the samples. The Sr isotope values obtained by laser ablation measurement are systematically higher compared to those obtained via solution mode-MC-ICP-MS analysis. We suggest that the higher $^{87}\text{Sr}/^{86}\text{Sr}$ values are related to production of a molecular isobaric interference Ca–P–O with mass of 87 that overlaps the ^{87}Sr signal; hence producing the higher $^{87}\text{Sr}/^{86}\text{Sr}$ values during the laser ablation measurements. It is also possible that the Sr isotopic difference may relate to intrinsic isotopic heterogeneity of the enamel samples, since separate fragments were used for laser ablation versus solution mode analysis. However, the fact that the difference in the two data sets is systematically offset in one direction (i.e., higher for laser ablation) argues against this interpretation. The results reported here highlight the capacity of laser ablation-(MC)-ICP-MS instrument configurations to produce a large quantity of trace element and isotope data in a relatively short period of time. Whereas elemental abundances may be deemed accurate, Sr isotopic results may not be and must be scrutinized carefully in conjunction, if possible, with trace element compositions.

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