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# Simultaneous analysis of stable and radiogenic strontium isotopes in reference materials, plants and modern tooth enamel

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1 **Simultaneous analysis of stable and radiogenic strontium**  
2 **isotopes in reference materials, plants and modern tooth**  
3 **enamel**

4  
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## 14 **Abstract**

15 Radiogenic strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) are a useful tool in forensics, ecology,  
16 bioarcheology and paleoanthropology allowing investigation of present and past migration  
17 and landscape use. The measurement of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio traditionally assumes a constant  
18 stable ( $^{88}\text{Sr}/^{86}\text{Sr}$ ) isotope ratio. However, some studies indicate that these stable Sr isotopes  
19 may display mass-dependent fractionation, suggesting that the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio may  
20 fingerprint previously unknown dietary and physiological information. Here we present a  
21 survey of the variability of  $\delta^{88}\text{Sr}$  values, along with the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, in fourteen  
22 reference materials of geological and biological origin using MC-ICPMS. The measurements  
23 employ a simple sample-standard bracketing method and zirconium external correction.  
24 Comparisons with double-spiked  $\delta^{88}\text{Sr}$  TIMS analyses show a very good agreement (0.014  
25 ‰;  $n = 10$ ). We then applied this method to explore the fractionation of the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio  
26 in tooth enamel of mammals from two modern food-chains (Kruger National Park and  
27 Western Cape, South Africa), and from modern South African chacma baboon populations.  
28 Clear differences in the  $\delta^{88}\text{Sr}$  values are observed between plants and teeth of herbivores  
29 ( $\sim -0.26$  ‰;  $n=5$ ), but the distinction between herbivores and carnivores requires further  
30 investigation. Variations between tooth enamel of young and adult baboons suggests that  
31 the  $\delta^{88}\text{Sr}$  is a promising indicator of weaning behaviors. Our method implementation and  
32 preliminary results highlight the importance of coupled radiogenic and stable Sr isotope  
33 determination in extant and extinct vertebrates.

## 34 **Keywords**

35 Non-traditional isotopes, stable strontium isotopes, radiogenic strontium isotopes, trophic  
36 chain, weaning

37

## 38 **1. Introduction**

39 There are four naturally occurring strontium (Sr) isotopes, all of which are stable  
40 ( $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{88}\text{Sr}$ ,  $^{87}\text{Sr}$ ), but one,  $^{87}\text{Sr}$ , is the radiogenic product of the  $\beta$ -decay radioactivity of  
41 rubidium-87 ( $^{87}\text{Rb}$ ; half-life = 48.8 Ga). Given that the atomic properties of Sr are similar to  
42 those of calcium (Ca), Sr is incorporated into the body as a Ca substitute, undergoing  
43 discrimination processes that lower the Sr/Ca ratio during metabolic processes involving  
44 Ca (Balter, 2004). Multi-collector inductively-coupled plasma mass spectrometers (MC-  
45 ICPMS) and thermal ionization mass spectrometers (TIMS), which are routinely used for  
46 the measurements of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, induce an instrumental mass-bias during  
47 measurement that needs to be corrected, thus the true  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio is traditionally set at  
48 0.1194 to correct the mass-bias on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the body of an  
49 animal records that of the soil/substrate on which the animal lives ( Price et al., 2002;  
50 Lazzarini et al., 2021). By measuring the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in tissues forming at different  
51 periods of life, such as bone and tooth enamel, or within tooth enamel using laser ablation,  
52 it is possible to reconstruct the mobility and range of the animal, with reference to the Sr  
53 isotope ratio of the substrate (Knudson et al., 2004; Martin et al. 2016, Sillen and Balter,  
54 2018).

55           However, with the improvement of MC-ICPMS precision in the last twenty years,  
56 variations of the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio have been increasingly scrutinized in geological materials  
57 since the first measurement of that ratio in seawater (Fietzke and Eisenhauer, 2006).  
58 Variations of this ratio relative to the international standard NIST SRM-987 are expressed  
59 as  $\delta^{88/86}\text{Sr}_{\text{SRM987}}$ , defined as following:

$$60 \quad \delta^{88/86}\text{Sr}_{\text{SRM987}} = \left( \frac{{}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{sample}}}{{}^{88}\text{Sr}/{}^{86}\text{Sr}_{\text{NIST SRM987}}} - 1 \right) \times 1000$$

61 The classical and shorter notation  $\delta^{88}\text{Sr}$  will be used in the following text. There is only  
62 scarce data concerning the  $\delta^{88}\text{Sr}$  value in biological materials. Recent studies suggest that  
63 stable Sr isotopes in bone and tooth enamel may be a good indicator of paleodietary range  
64 and trophic level (Knudson et al., 2010; Lewis et al., 2017; Brazier et al., 2019). Indeed,  $^{86}\text{Sr}$   
65 seems to be preferentially incorporated into biological system compared to  $^{88}\text{Sr}$ . Analyses of  
66 plants show preferred uptake of  $^{86}\text{Sr}$  relative to  $^{88}\text{Sr}$  in the nutrient pathways leading to  
67 lighter isotopic signatures in leaves than in roots and soil (de Souza et al., 2010; Liu et al.,  
68 2016; Guibourdenche et al., 2020). Up trophic chains, the Sr isotope fractionation remains  
69 poorly studied, but it is already noticeable that all  $\delta^{88}\text{Sr}$  values in plants are positive (de  
70 Souza et al., 2010; Liu et al., 2016; Hajj et al., 2017; Brazier et al., 2019), while all  $\delta^{88}\text{Sr}$   
71 values in terrestrial animals are negative (Knudson et al., 2010; Lewis et al., 2017; Brazier  
72 et al., 2019), relative to the SRM-987 standard. In a controlled feeding study on pigs, a shift  
73 of -0.32 ‰ from diet to dental enamel has been observed (Lewis et al., 2017), consistent  
74 with the plant data. Different methods have been developed in order to overcome  
75 instrumental mass bias during measurements of the  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Analyses  
76 with a TIMS use a  $^{84}\text{Sr}/^{86}\text{Sr}$  double spike to correct for the instrumental mass bias

77 (Krabbenhöft et al., 2009; Neymark et al., 2014; Charlier et al., 2017; Lewis et al., 2017;  
78 Brazier et al., 2019) and is the method of reference to achieve the best precision (between  
79 0.01 and 0.02 ‰ (Brazier et al., 2019)). Measurement method using a MC-ICPMS includes  
80 sample-standard bracketing method (SSB) (Fietzke and Eisenhauer, 2006; Ma et al., 2013)  
81 and correction using a zirconium (Zr) internal standard (Ohno and Hirata, 2007; Liu et al.,  
82 2012, 2016, 2017; Xu et al., 2020). Both methods can be used simultaneously (Irrgeher et  
83 al., 2013; Liu et al., 2017; Argentino et al., 2021).

84 A combination of these two methods is used in the present study and we test the  
85 procedure on fourteen reference materials with various mineral and biological matrices.  
86 The robustness and accuracy of this method was assessed in different laboratories. In South  
87 Africa sample preparation was done at the Wits Isotope Geoscience Laboratory (WIGL,  
88 University of the Witwatersrand, Johannesburg, South Africa), while the analytical  
89 measurements were done at the University of Johannesburg (UJ, Johannesburg, South  
90 Africa). Further work was achieved at the Laboratoire de géologie de Lyon (LGLTPE, Ecole  
91 Normale Supérieure de Lyon, France). In addition to the reference materials, we also  
92 measured the  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in animal and plant samples from extant  
93 ecosystems in South Africa to provide a first overview of the Sr stable isotope systematics in  
94 modern ecosystems and to challenge the possible use as a paleodietary indicator.

95

## 96 2. Material and methods

### 97 2.1. Reference material description

98 Eleven reference materials with known  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (biological  
99 matrix: SRM-1400, SRM-1486, BCR-380R, BCR-383 and SRM-1570a; geological matrix: JC-  
100 p1, UB-N, BHVO-2, BCR-1, and GS-N; seawater: IAPSO) and three reference materials with  
101 unknown  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (geological matrix: Granite GA, NBS-120c and SRM-  
102 915b) were analyzed in both labs. The descriptions of the standards are provided in [Table](#)  
103 [1](#). Reference material aliquots were weighed to reach around 5  $\mu\text{g}$  of Sr.

104

105 *Table 1: Description of the reference materials analyzed in this study*

Reference material	Description	Sr ( $\mu\text{g}\cdot\text{g}^{-1}$ )
<b>Animal</b>		
BCR-380R	Whole milk powder	2.72
NIST SRM 1400	Cow bone ash powder	249
NIST SRM 1486	Cow bone meal powder	264
<b>Vegetal</b>		
BCR-383	Green bean powder	5.26
NIST SRM 1570a	Spinach powder	55
<b>Carbonate</b>		
JC-p1	Coral powder ( <i>Porites sp.</i> )	6896
NIST SRM 915b	Calcium carbonate	150
<b>Sea water</b>		
IAPSO	North Atlantic sea water	7.9
<b>Crustal and mantle rocks</b>		
UB-N	Serpentine powder	9
BHVO-2	Basalt powder	389
BCR-1	Basalt powder	330
GS-N	Granite powder	570
Granite GA	Granite powder	310
NIST NBS 120c	Phosphate rock powder	840

106

107

## 108      **2.2. Sample description**

109            We also measure  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in two sets of modern samples. The  
110 first set of samples are from tooth enamel collected from modern chacma baboon (*Papio*  
111 *ursinus*) skulls provided by the Ditsong National Museum of Natural History (Pretoria,  
112 South Africa). Teeth were extracted from sixteen skulls of chacma baboons from a reserve  
113 in Calitzdorp (Western Cape, South Africa). Details for baboons and the geographical  
114 context are available in a previous study (Brand, 1994). The list of sampled individuals is  
115 presented in **Table S1**. The first molar of the upper jaw was sampled in 4 adults (over 6  
116 years old) and 3 sub-adults (around 3 years old). Deciduous teeth (milk incisor, molar and  
117 canine) from 8 sub-adult baboons and the third molar from an adult were also sampled. All  
118 the teeth were washed with distilled water before drilling and the surfaces were cleaned  
119 with an abrasive drill bit. Sampling was located in the mesio- or distobuccal cusps of the  
120 teeth, and drilled using a bit diameter of 0.8 mm. Only the enamel was sampled to avoid  
121 contamination with dentine. Between 5 and 10 mg of powder was recovered. This set of  
122 material has been analyzed at UJ, using the WIGL-UJ method. The second set of samples  
123 consists in tooth enamel of herbivores and carnivores from the Kruger National Park (KNP)  
124 and Western Cape (WC), in South Africa. Details for sex, age and geographical context of  
125 these specimens are given in **Table S2**. The teeth were cleaned with distilled water before  
126 sampling. Plant residues trapped in the dentition of herbivorous mammals were also  
127 collected. The samples were stored at the Ditsong National Museum of Natural History  
128 (Pretoria, South Africa). They were prepared and analyzed at the LGLTPE, using the  
129 LGLTPE-2 analytical method. Around 5 mg of enamel powder was sampled, and the same  
130 quantity was taken from plant residues.



131

### 132 **2.3. Sample digestion**

#### 133 WIGL

134 All sample preparation procedures were carried out in a Class 100 clean room under  
135 laminar flow hoods. Organics present in biological samples were removed via an oxidative  
136 digestion procedure. Thus 2 mL of concentrated HNO<sub>3</sub> (14M) and 0.5 mL of H<sub>2</sub>O<sub>2</sub> (30 %) were added to SRM-1400 and SRM-1486, but also to evaporated IAPSO and baboon tooth  
137 enamel. Beakers were then left on a hotplate for three days at 110 °C. They were opened at  
138 regular 10 minutes intervals during the first hours to allow degassing. The BHVO-2  
139 standard was dissolved using 2 mL of concentrated HNO<sub>3</sub> (14M) and 1 mL concentrated HF.  
140 The closed beakers were left on a hotplate (110 °C) for 48h. After complete dissolution all  
141 the samples were dried down and subsequently taken up with 1 mL of HNO<sub>3</sub> (3M).  
142

143

#### 144 LGLTPE

145 Sample preparation procedures at the LGLTPE were carried out in a clean room  
146 under laminar flow hoods. All the acids used were purified twice by sub-boiling distillation.  
147 As at the WIGL, 4 mL concentrated HNO<sub>3</sub> (15M) and 1 mL H<sub>2</sub>O<sub>2</sub> (30 %) were added to  
148 standards containing organics (i.e., BCR-383, BCR-380R, SRM-1486, SRM-1400 and SRM-  
149 1570a), but also to IAPSO and JC-p1, and closed beakers were left on a hotplate (110 °C) for  
150 48h. They were unscrewed regularly to allow degassing. Tooth enamel samples and plant  
151 residues from the KNP and WC were dissolved using the same protocol. The SRM-915b and  
152 NBS-120c standards were dissolved in 1 mL concentrated HNO<sub>3</sub> (15M) and centrifuged to  
153 remove potential silicate particles. All rock samples (i.e., UB-N, BHVO-2, BCR-1, GS-N and

154 Granite GA) were digested using 2 mL concentrated HNO<sub>3</sub> (15M) and 1 mL concentrated  
155 HF. Closed beakers were left on the hotplate (110 °C) for 48h and evaporated to dryness,  
156 taken up with 6N HCl and a few drops of HClO<sub>4</sub> and evaporated on a hotplate (120 °C) to  
157 eliminate fluorides. This last step was repeated until all fluorides were dissolved. After,  
158 digestion all the samples were dried down and redissolved in 1 mL of 3M HNO<sub>3</sub>.

159

## 160 **2.4. Sample preparation and instrumentation**

### 161 WIGL

162 Isotopic measurements of Sr in biological and geological samples require the  
163 separation of Sr from the matrix with a special attention to avoid any isobaric interference  
164 with <sup>87</sup>Rb and Zr contamination. Strontium must be recovered quantitatively after the  
165 chromatographic separation to ensure the absence of any chemical isotopic mass  
166 fractionation during matrix and Sr elutions. The column chemistry protocol set up at WIGL  
167 was inspired by that of Tacail et al. (Tacail et al., 2014) and De Muynck et al. (De Muynck et  
168 al., 2009). Both protocols use the Sr spec<sup>TM</sup> resin (TrisKem International). 300µL of Sr  
169 spec<sup>TM</sup> resin is loaded into 2 mL polypropylene columns. The elution protocol is given in  
170 **Table 2**. The resin is discarded after a single use.

171

172 *Table 2: Ion exchange protocols for the chromatographic separation of Sr*

Lab	WIGL	LGLTPE
Wash	4 mL 0.5M HNO <sub>3</sub>	4 mL 0.5M HNO <sub>3</sub>
Conditioning	2.5 mL 3M HNO <sub>3</sub>	2.5 mL 3M HNO <sub>3</sub>
Load sample	1 mL 3M HNO <sub>3</sub>	1 mL 3M HNO <sub>3</sub>
Matrix elution	2.5 mL 3M HNO <sub>3</sub>	3.5 mL 3M HNO <sub>3</sub>
Sr elution	16 mL 0.5M HNO <sub>3</sub>	7 mL 0.005M HNO <sub>3</sub>

173

174 [UJ](#)

175 The isotopic analyses were performed on a Nu Plasma II (Nu Instrument) MC-ICPMS  
176 at UJ. The SRM-987 was used as the isotopic reference standard for Sr. On the day of the  
177 analysis session, samples and standards were diluted with 0.05M HNO<sub>3</sub> to reach a  
178 concentration of 500 µg.L<sup>-1</sup>, leading to a typical intensity of 8 V in the H1 collector (<sup>88</sup>Sr). A  
179 high purity Zr solution (Alfa Aesar, 1000 ppm) was diluted and added to the standard and  
180 sample solutions at 500 µg.L<sup>-1</sup>. The true ratio of <sup>91</sup>Zr/<sup>90</sup>Zr is 0.218126 according to the  
181 commission on isotopic abundances IUPAC (Meija et al., 2016). Measurements were carried  
182 out in static mode and a single measurement consisted of one block of 40 cycles with an  
183 integration time of 10 s. Daily calibration was performed to optimize operating conditions  
184 for maximum Sr and Zr signal stability, which was monitored with repeated measurements  
185 on SRM-987. The instrument settings are given in [Table 3](#).

186  
187 *Table 3: Instrument settings and data acquisition parameters for MC-ICP-MS analysis, and*  
188 *main differences between the three measurement methods*

<b>Method</b>	<b>UJ</b>	<b>LGLTPE-1</b>	<b>LGLTPE-2</b>
Element (+internal standard)	Sr(+Zr)	Sr(+Zr)	Sr(+Zr)
MC-ICP-MS	Nu Plasma II	Nu Plasma 500	Nu Plasma 500
RF power (W)	1300	1350	1350
Plasma condition	wet, cyclonic spray chamber	idem	idem
Coolant Ar flow ( <i>L. min</i> <sup>-1</sup> )	13.00	13.00	13.5
Auxiliary Ar flow ( <i>L. min</i> <sup>-1</sup> )	0.80	1.46	1.80
Nebulizer Ar flow ( <i>L. min</i> <sup>-1</sup> )	34.50	37.9	35.1
Mass resolution	300	300	300
Cup configuration	H6: <sup>91</sup> Zr; H5: <sup>90</sup> Zr H1: <sup>88</sup> Sr; L1: <sup>87</sup> Sr L3: <sup>86</sup> Sr; L5: <sup>85</sup> Rb L6: <sup>83</sup> Kr; L7: <sup>82</sup> Kr	H6: <sup>91</sup> Zr; H5: <sup>90</sup> Zr H2: <sup>88</sup> Sr; Ax: <sup>87</sup> Sr L2: <sup>86</sup> Sr; L3: <sup>85</sup> Rb L4: <sup>84</sup> Sr; L5: <sup>83</sup> Kr	H6: <sup>92</sup> Zr; H5: <sup>91</sup> Zr H4: <sup>90</sup> Zr; Ax: <sup>88</sup> Sr L2: <sup>87</sup> Sr; L3: <sup>86</sup> Sr L4: <sup>85</sup> Rb; L5: <sup>84</sup> Sr
Sensitivity	<sup>88</sup> Sr 0.5 ppm: 8V	<sup>88</sup> Sr 0.3 ppm: 8V	<sup>88</sup> Sr 0.3 ppm: 8V

Integration time (s)	10	10	10
Cycles	40	40	20
Isotope ratio used for mass bias correction of $^{88}\text{Sr}/^{86}\text{Sr}$	$^{91}\text{Zr}/^{90}\text{Zr}$	$^{91}\text{Zr}/^{90}\text{Zr}$	$^{92}\text{Zr}/^{90}\text{Zr}$ and $^{91}\text{Zr}/^{90}\text{Zr}$
Baselines	On-peak zero	Deflected beam	On-peak zero
Blank signal	$2.7 \cdot 10^{-3}$ V	$3.5 \cdot 10^{-3}$ V	$3.5 \cdot 10^{-3}$ V
Kr interference correction	None	Yes	None
Rb interference correction	Yes	Yes	Yes

189

190 *Interference correction*

191 Krypton (Kr) contamination of argon (Ar) gas may interfere with  $^{86}\text{Sr}$ . Measurement  
 192 background was determined at the start of each measurement session by analyzing a 0.05M  
 193  $\text{HNO}_3$  laboratory blank. The on-peak background intensities were subtracted from the  
 194 measurement signals during measurement, correcting for possible Kr interference.

195 To calculate the  $^{87}\text{Sr}/^{86}\text{Sr}$  values, the isobaric interference of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$  was corrected  
 196 following the equation:

$$^{87}\text{Rb} = \text{Meas}(^{85}\text{Rb}) \times \text{Ref}(^{87}\text{Rb}/^{85}\text{Rb}) \times \left( \frac{M(^{87}\text{Rb})}{M(^{85}\text{Rb})} \right)^{\text{Fractsr}} \quad \{1\}$$

197

$$^{87}\text{Sr} = \text{Meas}(^{87}\text{Sr}) - ^{87}\text{Rb} \quad \{2\}$$

198

199 With  $\text{Meas}(^{85}\text{Rb})$  and  $\text{Meas}(^{87}\text{Sr})$  being the measured intensity at mass 85 and 87,  
 200 respectively, and  $M(^{87}\text{Rb})$  and  $M(^{85}\text{Rb})$  corresponding to Rb isotopic masses.  $\text{Ref}(^{87}\text{Rb}/^{85}\text{Rb})$   
 201 is the natural abundance ratio extracted from the latest IUPAC report (0.3856, (Meija et al.,  
 202 2016)).  $\text{Fractsr}$  is the fractionation factor defined as in equation 3 that can be used to  
 203 correct for Rb interferences as long as the Rb concentration in the sample is small (Ehrlich

204 et al., 2001). The average measured intensity of mass 85 in the samples was  $2 \times 10^{-05}$  V,  
 205 which is negligible compared to the intensity measured on mass 87 (0.7 V).

206

207 *Normalization of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio*

208 The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was obtained according to classic calculations (Marisa Almeida and  
 209 D. Vasconcelos, 2001). The instrumental mass bias is evaluated by the fractionation factor  
 210  $Fract_{Sr}$ , calculated using Russel's exponential law (Russell et al., 1978):

$$Fract_{Sr} = \frac{\text{Ln} \left( \frac{\text{True} (^{86}\text{Sr}/^{88}\text{Sr})}{\text{Meas} (^{86}\text{Sr}/^{88}\text{Sr})} \right)}{\text{Ln} \left( \frac{M(^{86}\text{Sr})}{M(^{88}\text{Sr})} \right)} \quad \{3\}$$

211

212  $M(^{88}\text{Sr})$  and  $M(^{86}\text{Sr})$  correspond to Sr isotopic masses and  $\text{True} (^{86}\text{Sr}/^{88}\text{Sr})$  equals 0.1194  
 213 (Meija et al., 2016). This fractionation factor can then be used to normalize the  $^{87}\text{Sr}/^{86}\text{Sr}$   
 214 ratio:

$$\text{Norm} (^{87}\text{Sr}/^{86}\text{Sr}) = \text{Meas} (^{87}\text{Sr}/^{86}\text{Sr}) \times \left( \frac{M(^{87}\text{Sr})}{M(^{86}\text{Sr})} \right)^{Fract_{Sr}} \quad \{4\}$$

215 However, the mass bias may change during the analytical session. Thus, a sample-standard  
 216 bracketing method (SSB) was applied to take these variations into account, using the  
 217 equation:

218 {5}

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{sample}} = \text{Norm} (^{87}\text{Sr}/^{86}\text{Sr})_{\text{sample}} \times \frac{\text{Ref} (^{87}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}} \times 2}{\text{Norm} (^{87}\text{Sr}/^{86}\text{Sr})_{\text{stdA}} + \text{Norm} (^{87}\text{Sr}/^{86}\text{Sr})_{\text{stdB}}}$$

220

221 With  $Norm(^{87}\text{Sr}/^{86}\text{Sr})_{std}$  being the measured and normalized  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the  
222 previous (A) and following (B) standards.  $Ref(^{87}\text{Sr}/^{86}\text{Sr})_{SRM987}$  is the “true”  $^{87}\text{Sr}/^{86}\text{Sr}$   
223 value of the NIST SRM-987, set at 0.71024. Although NIST certifies the SRM-987 reference  
224 material  $^{87}\text{Sr}/^{86}\text{Sr}$  value at  $0.71034 \pm 0.00026$ , previous studies have rather been measuring  
225 and using a value of 0.71024, which falls inside the uncertainties of the certified value. This  
226 difference may be explained using 0.1194 as the true  $^{86}\text{Sr}/^{88}\text{Sr}$ , instead of the true value of  
227 this standard (0.119352). For the sake of comparison with other studies (e.g. Weber et al.,  
228 2018; Brazier et al., 2019), it was decided to use in the present study a SRM-987  $^{87}\text{Sr}/^{86}\text{Sr}$   
229 value of 0.71024 as the bracketing standard value.

230 As the measurement method proposed here allows the measurements of the stable  
231  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio corrected from the mass bias and the normalized radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
232 simultaneously, it is possible to use the Zr-corrected  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of a sample to normalize  
233 its  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. However, the  $^{87}\text{Sr}/^{86}\text{Sr}$  value in a biological sample obtained after  
234 normalization to a constant  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194 can solely correspond to the initial  
235  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio i.e., that of the substrate, which depends ultimately on  $^{87}\text{Rb}$  radioactive  
236 disintegration. This constitutes the methodological ground on which are based provenance  
237 and mobility studies. Taking these considerations into account and for the sake of  
238 comparison with previous work, in this study we decided to present only the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
239 normalized with a constant  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194. A comparison of those two corrections  
240 through three analytical sessions can be found in [Figures S1 \(Supplementary material\)](#)  
241 showing, as expected, a strong correlation with a 1:1 slope.

242

243 *Correction of the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio*

244 Given that Zr and Sr have very similar masses, instrumental mass fractionation does not  
245 vary independently for both elements (Maréchal et al., 1999). Therefore, the Zr  
246 fractionation factor can then be used to correct  $^{88}\text{Sr}/^{86}\text{Sr}$  using Russel's exponential law  
247 (Russell et al., 1978). The measured  $^{91}\text{Zr}/^{90}\text{Zr}$  ratio is used to calculate the fractionation  
248 factor of the instrument ( $Fract_{\text{Zr}}$ ) using the equation:

$$Fract_{\text{Zr}} = \frac{\text{Ln}\left(\frac{\text{True}(^{91}\text{Zr}/^{90}\text{Zr})}{\text{Meas}(^{91}\text{Zr}/^{90}\text{Zr})}\right)}{\text{Ln}\left(\frac{M(^{91}\text{Zr})}{M(^{90}\text{Zr})}\right)} \quad \{6\}$$

249

250 With  $M(^{91}\text{Zr})$  and  $M(^{90}\text{Zr})$  corresponding to Zr isotopes isotopic masses. The stable isotopic  
251 composition of Sr is then corrected using the equation:

$$\text{Corr}(^{88}\text{Sr}/^{86}\text{Sr}) = \text{Meas}(^{88}\text{Sr}/^{86}\text{Sr}) \times \left(\frac{M(^{88}\text{Sr})}{M(^{86}\text{Sr})}\right)^{Fract_{\text{Zr}}} \quad \{7\}$$

252

253 We also apply the sample-standard bracketing method (SSB) to correct for the instrumental  
254 mass-bias variations during the measurement session. The sample  $\delta^{88}\text{Sr}$  value is calculated  
255 using the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio averaged from the previous (A) and the following (B) standard:

256 {8}

$$\delta^{88}\text{Sr} = \left(\frac{\text{Corr}(^{88}\text{Sr}/^{86}\text{Sr})_{\text{sample}} \times 2}{\text{Corr}(^{88}\text{Sr}/^{86}\text{Sr})_{\text{stdA}} + \text{Corr}(^{88}\text{Sr}/^{86}\text{Sr})_{\text{stdB}}} - 1\right) \times 1000$$

258

259 This standard must have known Sr isotopic composition. Special care was given to closely  
260 match the concentration between the bracketing standard (SRM-987) and the samples (Ma

261 et al., 2013; Liu et al., 2016). The co-variation between Sr and Zr can be observed in **Figures**  
262 **S2 and S3**, showing the drift of the non-corrected  $^{92}\text{Zr}/^{90}\text{Zr}$  and  $^{88}\text{Sr}/^{86}\text{Sr}$  ratios in SRM-987  
263 through an analytical session.

264

#### 265 **LGLTPE**

266 Strontium was isolated from the matrix using a protocol similar to that set-up at  
267 WIGL with identical resin volume and size column, however the acid molarity for the Sr  
268 elution was slightly modified to reduce acid consumption. As shown in **Table 2**, Sr is eluted  
269 with 7 mL of 0.005M  $\text{HNO}_3$ . A small aliquot (15 $\mu\text{L}$ ) was saved before and after the elution  
270 protocol for the quantitative determination of Sr and other trace element concentrations.

271 The measurement of Sr, Rb and Zr concentrations was performed on a quadrupole  
272 ICPMS (Thermo Scientific, iCap-Q) using the  $^{85}\text{Rb}$ ,  $^{88}\text{Sr}$  and  $^{90}\text{Zr}$  masses. Aliquots were  
273 diluted in 5 mL of 0.5M  $\text{HNO}_3$  with 2  $\mu\text{g}\cdot\text{L}^{-1}$  rhodium (Rh) as an internal standard. Strontium  
274 recovery from the chromatographic separation was found to be  $95.5 \pm 6\%$  (2SD, n=24),  
275 suggesting quantitative yields and therefore absence of any mass-dependent fractionation.  
276 The low amount of Sr in procedural blanks (between 1 and 4 ng) was typically 0.04 % of  
277 total Sr in the samples. After the chromatographic separation of Sr, the Sr/Zr ratio was >  
278 100 on average.

279 Isotopic analyses were performed on a Nu Plasma 500 MC-ICP-MS (Nu Instruments).  
280 On the day of the measurement session, samples and standards were diluted with 0.05M  
281  $\text{HNO}_3$  to reach a Sr concentration corresponding to an intensity of 8 V in the H2 collector  
282 ( $^{88}\text{Sr}$ ) (usually 250 or 300  $\mu\text{g}\cdot\text{L}^{-1}$ ). The solutions were then doped with a high purity Zr  
283 solution (Alfa Aesar) to reach a  $^{90}\text{Zr}/^{88}\text{Sr}$  close to unity. Measurements were carried out in



284 static, multi collection mode and one single measurement consisted in one block of 40  
285 cycles with an integration time of 10 s. Electronic zero by ESA deflection were subtracted  
286 online on each measurement. Krypton possible contribution was monitored by measuring  
287 the intensity at mass 83 ( $^{83}\text{Kr}$ ) and subtracting its influence on mass 86:

$$^{86}\text{Kr} = \text{Meas}(^{83}\text{Kr}) \times \text{Ref}(^{86}\text{Kr}/^{83}\text{Kr}) \quad \{9\}$$

288

$$^{86}\text{Sr} = \text{Meas}(^{86}\text{Sr}) - ^{86}\text{Kr} \quad \{10\}$$

289

290 With  $M(^{86}\text{Kr})$  and  $M(^{83}\text{Kr})$  corresponding to Kr isotopic masses.  $\text{Ref}(^{86}\text{Kr}/^{83}\text{Kr})$  (1.50) is the  
291 ratio of Kr isotopes natural abundances extracted from the latest IUPAC report (Meija et al.,  
292 2016). The isobaric interference of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$  was corrected using equations {1} and {2}.  
293 The typical intensity on mass 85 ( $^{85}\text{Rb}$ ) for the samples was  $2 \times 10^{-4}$  V which is low enough to  
294 use the correction, with a measured intensity of 0.7 V on mass 87. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was  
295 normalized using equations {3} and {4} and the instrumental induced mass-bias on  
296  $^{88}\text{Sr}/^{86}\text{Sr}$  was corrected using equations {6} and {7}. SSB was also applied using equation  
297 {8}. This analytical method is indicated as LGLTPE-1.

298 A second analytical method was tested at LGLTPE, indicated as LGLTPE-2 in [Table 3](#).  
299 This method used an on-peak baseline measurement with 10 s integration time prior to  
300 each measurement session using a 0.05M  $\text{HNO}_3$  blank. The measured intensities were then  
301 subtracted on line during the analytical sequence for all the samples and standards. Thus,  
302 the Kr correction became unnecessary and equations {9} and {10} were not used. The  
303 collector configuration of the LGLTPE-2 method ([Table 3](#)) allowed the measurement of both  
304  $^{91}\text{Zr}/^{90}\text{Zr}$  and  $^{92}\text{Zr}/^{90}\text{Zr}$  ratios. Thus the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio could be corrected for mass bias

305 using the  $^{91}\text{Zr}/^{90}\text{Zr}$  and  $^{92}\text{Zr}/^{90}\text{Zr}$  ratios with equations {6} and {7}, using  $True(^{92}\text{Zr}/^{90}\text{Zr})$  of  
 306 0.333243 (Meija et al., 2016). It was observed by Liu and collaborators that best fit  
 307 occurred between the mass bias affecting  $^{92}\text{Zr}/^{90}\text{Zr}$  and  $^{88}\text{Sr}/^{86}\text{Sr}$  ratios, compared to that  
 308 affecting  $^{91}\text{Zr}/^{90}\text{Zr}$  (Liu et al., 2012). These authors also find a better precision when using  
 309 the  $^{92}\text{Zr}/^{90}\text{Zr}$  ratio. In the present study, both corrections were compared. Measurements  
 310 giving  $\delta^{88}\text{Sr}$  values with differences higher than 0.05 ‰ between the two corrections were  
 311 not considered. The samples  $\delta^{88}\text{Sr}$  values given here with the LGLTPE-2 method are the  
 312  $\delta^{88}\text{Sr}$  values corrected with the  $^{92}\text{Zr}/^{90}\text{Zr}$  ratio. SSB was also applied using equation {8}.  
 313 Specificities of each method are summarized in [Table 3](#).

314

### 315 **2.5. $U$ ( $k=2$ ) Expanded uncertainties**

316 The measurement uncertainties in this work regarding certified reference materials  
 317 are given as expanded uncertainties ( $U$ ) to compare with other studies. The measurement  
 318 uncertainties were calculated by multiplying the combined uncertainty  $u_c(y)$  of isotopic  
 319 ratios by a coverage factor  $k$  such that  $U=ku_c(y)$ . Here  $k=2$ , which corresponds to a level of  
 320 confidence of 95 %. The calculation of the combined uncertainty  $u_c(y)$  of a  $\delta$  value involves  
 321 the uncertainties of the isotopic ratios of the sample and those of the bracketing standards.  
 322 The full description of the calculation is presented in Sullivan et al. (Sullivan et al., 2020),  
 323 and the final equation is given here for a symbolic  $r_{A/a}$  isotope ratio:

$$u^2(r^{A/a}) = \left(\frac{1}{r_{std}^{A/a}}\right)^2 \times u^2(r_{std}^{A/a}) + \left(-\frac{r_{spl}^{A/a}}{(r_{std}^{A/a})^2}\right)^2 \times u^2(r_{spl}^{A/a}) \quad \{10\}$$

324

325 With *std* and *spl* corresponding to the standard and the sample, respectively, and  $u(r)$  the  
326 standard uncertainty for the measured ratio, which can be estimated by using the standard  
327 deviation calculated from the different blocks corresponding to one block of measurement.

328

## 329 **3. Results**

### 330 **3.1. Reference materials**

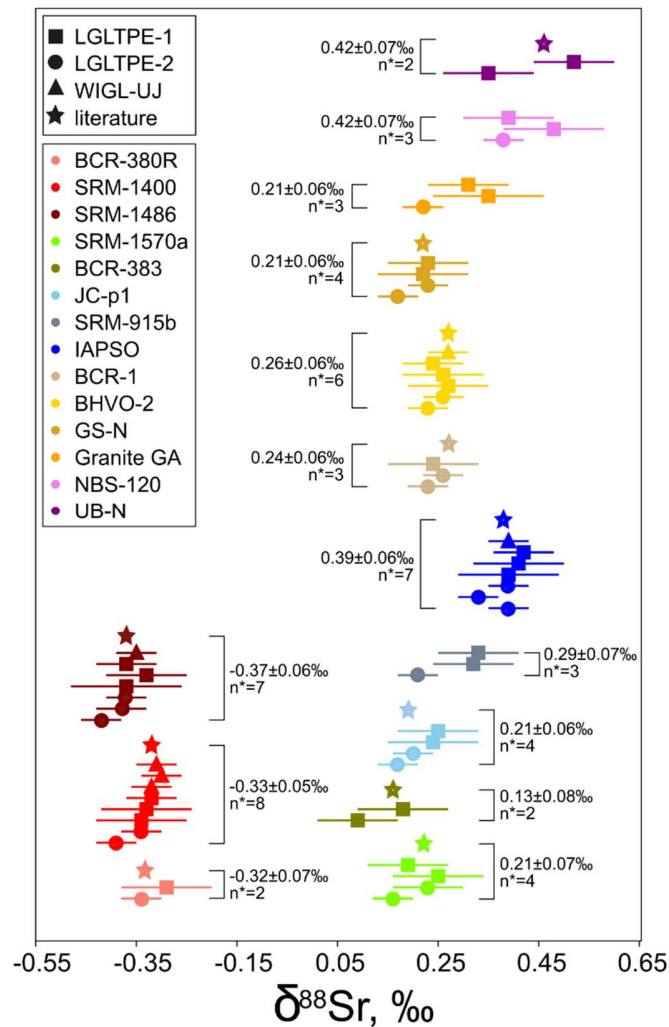
331 Sample-standard bracketing and the Sr correction methods described produced an  
332  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for SRM-987 of  $0.71023 \pm 0.00003$  (U, k=2, n=47) at UJ,  $0.71037 \pm 0.00005$   
333 (U, k=2, n=152) for LGLTPE-1 and  $0.71026 \pm 0.00004$  (U, k=2, n=284) for LGLTPE-2 (note  
334 again that the commonly used  $^{87}\text{Sr}/^{86}\text{Sr}$  value is  $0.71024 \pm 0.00026$  (McArthur et al., 2015;  
335 Weber et al., 2018; Brazier et al., 2019), while the certified value is  $0.71034 \pm 0.00026$ ).  
336 Using the sample-standard bracketing and Zr correction methods, the corresponding SRM-  
337 987  $\delta^{88}\text{Sr}$  values are  $-0.003 \pm 0.039$  ‰ (U, k=2, n=47) at UJ,  $0.001 \pm 0.094$  ‰ (U, k=2,  
338 n=152) for LGLTPE-1 and  $-0.001 \pm 0.039$  ‰ (U, k=2, n=284) for LGLTPE-2. The  $\delta^{88}\text{Sr}$   
339 results for the SRM-987 are summarized in [Figure S4](#). The analytical uncertainties in the  
340 LGLTPE show a clear improvement when using the LGLTPE-2 method. All the uncertainties  
341 are comparable with those measured by TIMS i.e. between 0.026 and 0.074 ‰, U, k=2  
342 (Brazier et al., 2019).

343 The  $\delta^{88}\text{Sr}$  values of the fourteen reference materials are presented in [Figure 1](#) and  
344 compared with the literature values in [Table S3](#). All literature values used for compilation  
345 are presented in [Table S4](#). For the sake of visibility, only some of them are presented in  
346 [Table S3](#).

347 For all standards except UB-N, the results from WIGL-UJ, LGLTPE-1 and LGLTPE-2  
348 are identical within uncertainties. There is a good accuracy with literature values, even for  
349 less studied materials such as SRM-1400, SRM-1486, BCR-380R, BCR-383, SRM-1570a,  
350 BCR-1 and GS-N. The U (k=2) uncertainties calculated in the present study range between  
351 0.04 and 0.09 ‰. The measured values for UB-N are highly variable, and this variability can  
352 be found in the literature, as Brazier et al. (Brazier et al., 2019) and Ma et al. (Ma et al.,  
353 2013) are each finding different  $\delta^{88}\text{Sr}$  values (0.389 ‰ and 0.539 ‰ respectively),  
354 suggesting that UB-N is a heterogeneous material.

355 Radiogenic Sr results for the fourteen reference materials are presented and  
356 compared to literature values in [Table S5](#) and all literature values used for compilation are  
357 presented in [Table S4](#). For all samples, the results of the present study are in good  
358 agreement with referenced values. The expanded uncertainty U (k=2) on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
359 ranges between  $3 \cdot 10^{-5}$  and  $6 \cdot 10^{-5}$ , which is slightly higher than that achieved by TIMS  
360 ( $2 \cdot 10^{-5}$ , (Brazier et al., 2019)).

361



363

364

365 Figure 1:  $\delta^{88}\text{Sr}$  values for the reference materials measured in the WIGL-UJ and in the  
 366 LGLTPE; Error associated to the mean value is the mean of U ( $k = 2$ ) for each aliquot digested  
 367 and processed according to the chromatographic procedure. The  $n^*$  value corresponds to the  
 368 number of these aliquots. A mean of literature values is presented, all references used for the  
 369 compilation are presented in Table S2.

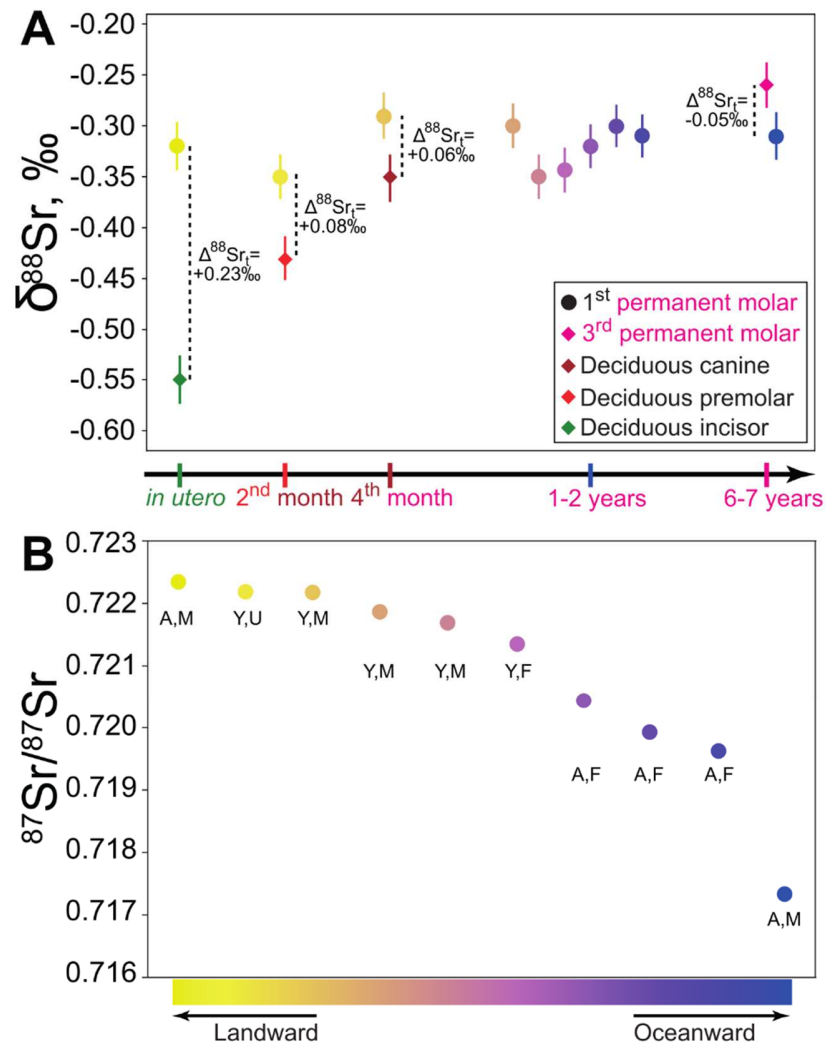
370

### 371 **3.2. Tooth enamel samples**

372 The  $\delta^{88}\text{Sr}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of baboon teeth are given in [Table S1](#). All the  
373 samples from baboon teeth were analyzed only once, using the WIGL-UJ method. The mean  
374  $\delta^{88}\text{Sr}$  value for all first molars of adult baboons is  $-0.31\text{‰}$ . Males ( $-0.30 \pm 0.01\text{‰}$ , 2SD,  
375  $n=2$ ) and females ( $-0.31 \pm 0.02\text{‰}$ , 2SD,  $n=3$ ) have similar  $\delta^{88}\text{Sr}$  values. The mean  $\delta^{88}\text{Sr}$   
376 value of all the first molars (adult and young specimens) is  $-0.32 \pm 0.06\text{‰}$  (2SD,  $n=10$ ).  
377 The three deciduous teeth  $\delta^{88}\text{Sr}$  values are  $-0.55\text{‰}$  (deciduous incisor),  $-0.43\text{‰}$   
378 (deciduous premolar), and  $-0.35\text{‰}$  (deciduous canine). These are significantly lower than  
379 first molars  $\delta^{88}\text{Sr}$  of both adult and young specimens. The third molar has a  $\delta^{88}\text{Sr}$  value of  $-$   
380  $0.26\text{‰}$ , which is significantly higher than first molars and deciduous teeth. These results  
381 are shown in [Figure 2A](#) according to the tooth eruption order in baboon life. The  $^{87}\text{Sr}/^{86}\text{Sr}$   
382 values for the ten baboon specimens are presented in [Figure 2B](#). There appears to be three  
383 significantly different clusters of specimens. Six specimens with high  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.722  
384 to 0.721), three adult females with low values (0.719) and one adult male with a very low  
385 value (0.716).

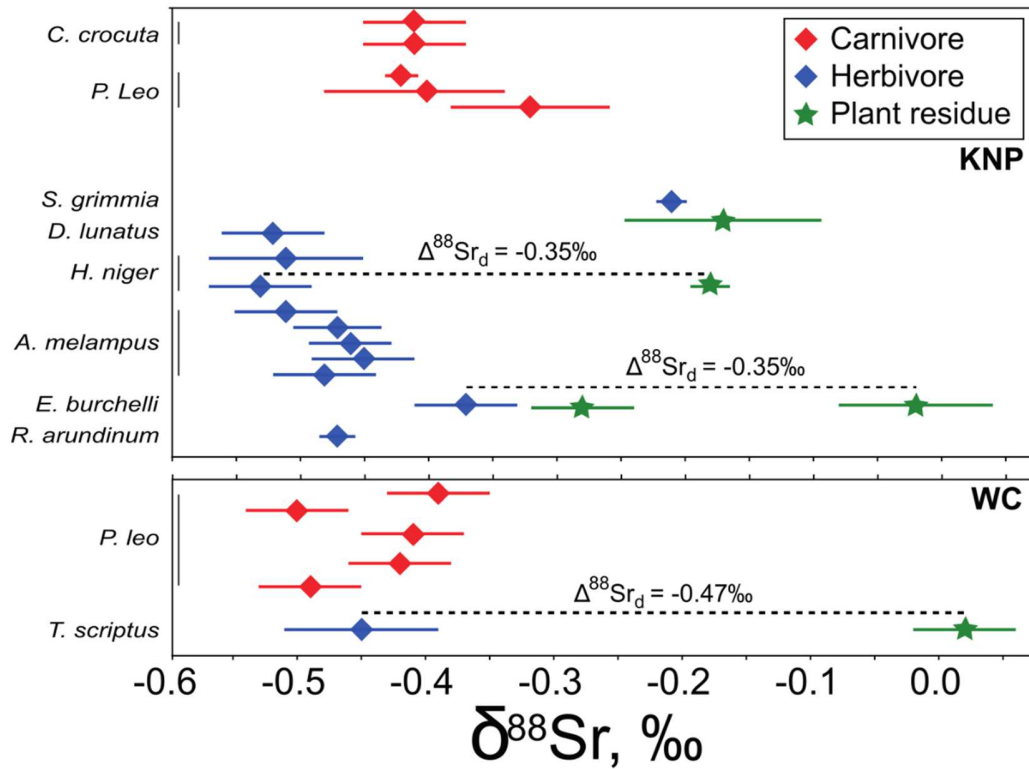
386 The  $\delta^{88}\text{Sr}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of KNP and WC animals are given in [Table S2](#)  
387 and shown in [Figure 3](#) according to species. They were all obtained using the LGLTPE-2  
388 method. The  $\delta^{88}\text{Sr}$  values range from  $-0.52$  to  $-0.21\text{‰}$  in enamel and from  $-0.28$  to  $-0.02\text{‰}$   
389 in plant. At KNP, the mean  $\delta^{88}\text{Sr}$  value for herbivores is  $-0.45 \pm 0.17\text{‰}$  (2SD,  $n=11$ ) and is  $-$   
390  $0.39 \pm 0.07\text{‰}$  (2SD,  $n=5$ ) for carnivores. At WC, there is one herbivorous specimen only  
391 (*Tragelaphus scriptus*) and its  $\delta^{88}\text{Sr}$  value is  $-0.45\text{‰}$ , indistinguishable from the mean  $\delta^{88}\text{Sr}$   
392 value of *Panthera Leo*, which is  $-0.44 \pm 0.10\text{‰}$  (2SD,  $n=5$ ). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios range from

393 0.707 to 0.760 at KNP and from 0.709 to 0.730 at WC and are consistent with previous  
394 results (Balter et al., 2008). This variation range is important and can be explained by the  
395 complex geological context of these regions (Schutte, 1986; Shone and Booth, 2005).  
396



397  
 398 *Figure 2: A  $\delta^{88}\text{Sr}$  results of the set of various teeth from the baboon skulls with their erupting*  
 399 *order (note that for specimen with both deciduous tooth and 1<sup>st</sup> permanent molar analyzed,*  
 400 *the result for the 1<sup>st</sup> permanent molar is not presented according to the timeline). Error bars*  
 401 *are the 2SD calculated from repeated measurements of the SRM1400 during the same*  
 402 *analytical session (0.02 ‰; 2SD; n=4);  $\Delta^{88}\text{Sr}_t$  is defined for a given specimen as the difference*  
 403 *between  $\delta^{88}\text{Sr}$  value in the first molar and  $\delta^{88}\text{Sr}$  value in another tooth. B  $^{87}\text{Sr}/^{86}\text{Sr}$  results for*  
 404 *10 baboon specimens; A = adult, Y = young, F = female, M = male, U = unknown sex; The color*  
 405 *gradient for 1<sup>st</sup> molars identifies individuals in panel 2A and 2B.*





406

407 *Figure 3:  $\delta^{88}\text{Sr}$  values for carnivores, herbivores and plants in KNP and WC; A dashed line links*  
 408 *teeth and associated plant residues; The corresponding Sr isotope fractionation value ( $\Delta^{88}\text{Sr}_d$ )*  
 409 *is given; Errors bars are 2SD calculated on repeated measurements of the same sample*

410

## 411 **4. Discussion**

### 412 **4.1. Strontium isotopes in reference materials**

413 Despite small differences between the WIGL-UJ, LGLTPE-1 and LGLTPE-2 methods,  
414 notably in the chromatographic separation of Sr (Table 2) and the instrumental settings  
415 (Table 3), the  $\delta^{88}\text{Sr}$  values of reference materials show excellent reproducibility between  
416 methods and very good accuracy when compared with literature values. This suggest that  
417 the overall protocol is robust, however several observations can be made for some  
418 analytical procedures. Consistent with the literature (Liu et al., 2012; Xu et al., 2020), the  
419 LGLTPE-2 method using the  $^{92}\text{Zr}/^{90}\text{Zr}$  ratio to correct the instrumental mass bias on  
420  $^{88}\text{Sr}/^{86}\text{Sr}$  shows an enhanced accuracy with literature results (mean accuracy of 0.013 ‰  
421 compared to (Krabbenhöft et al., 2009; Ma et al., 2013; Liu et al., 2017; Brazier et al., 2019)),  
422 than the LGLTPE-1 using  $^{91}\text{Zr}/^{90}\text{Zr}$  ratio (mean accuracy of 0.018 ‰ compared to  
423 (Krabbenhöft et al., 2009; Ma et al., 2013; Liu et al., 2017; Brazier et al., 2019)). The  
424 precision and accuracy at UJ (mean 2SD of 0.02 ‰, and mean accuracy of 0.015 ‰  
425 compared to (Ma et al., 2013; Brazier et al., 2019)) are comparable to those achieved using  
426 LGLTPE-2 (mean 2SD of 0.04 ‰, and mean accuracy of 0.013 ‰), showing the importance  
427 of the on-peak baseline measurement with systematic blank subtraction. This was not done  
428 using LGLTPE-1 and clearly improves the precision of the results and lower the  
429 instrumental uncertainties ( $U(k=2) = 0.09$  ‰ for LGLTPE-1 vs  $U(k=2) = 0.04$  ‰ for  
430 LGLTPE-2 and UJ). The present results agree very well with the literature, which highlights  
431 a clear offset towards  $^{88}\text{Sr}$ -depleted biological materials originating from animals (Brazier  
432 et al., 2019). To the best of our knowledge, three reference materials studied here had not

433 been analyzed for strontium isotopes. The SRM-915b is a calcium carbonate standard used  
434 in analyses of Ca stable isotopes. It has been measured in three different aliquots, and the  
435 mean of its  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is  $0.70800 \pm 0.00005$  (2SD, n=3). The mean  $\delta^{88}\text{Sr}$  value is  $0.33 \pm$   
436  $0.01$  ‰ (2SD, n=2) using the LGLTPE-1 method and  $0.21$  ‰ using the LGLTPE-2 method.  
437 Further measurements are needed to resolve this discrepancy, but we emphasize that the  
438 LGLTPE-2 mean is most probably closer to the true value. The NBS-120c is a phosphorite  
439 rock, which has been measured in three different aliquots yielding a mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  
440  $0.70885 \pm 0.00005$  (2SD, n=3) and a mean  $\delta^{88}\text{Sr}$  value of  $0.41 \pm 0.06$  ‰ (2SD, n=3). Once  
441 again, the dispersion between LGLTPE-1 and LGLTPE-2 is quite high. It must be noted that  
442 this material shows the highest  $\delta^{88}\text{Sr}$  value measured in this study. It may be linked with its  
443 phosphate nature. Granite GA is a geochemical reference sample of granite material. It has  
444 been measured in three different aliquots, yielding a mean  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.71376 \pm$   
445  $0.00005$  (2SD, n=3). The mean  $\delta^{88}\text{Sr}$  value measured using LGLTPE-1 is  $0.33 \pm 0.04$  ‰  
446 (2SD, n=2) and the one measured using LGLTPE-2 is  $0.22 \pm 0.03$  ‰. Further measurements  
447 are needed to choose between these two values, but the LGLTPE-2 mean is most probably  
448 closer to the actual value. As the measurement method is shown to be reliable using  
449 reference materials, it is possible to interpret the results obtained on biological material  
450 such as plant and tooth enamel.

451

#### 452 ***4.2. Intra-individual variations of enamel Sr isotopes***

453 The study of different tooth types in modern baboons allows evaluation of the extent  
454 of intra-individual variations of the  $\delta^{88}\text{Sr}$  value. Of note is that all the baboon teeth have  
455 negative  $\delta^{88}\text{Sr}$  values, in accordance with available data for bone and teeth (Knudson et al.,

456 2010; Romaniello et al., 2015; Lewis et al., 2017; Brazier et al., 2019). Discussion on the  
457 possible use of the  $\delta^{88}\text{Sr}$  value as a dietary proxy is challenging for baboons because there is  
458 a lack of isotopic data for possible dietary sources, which could be numerous as these are  
459 omnivorous animals (Hamilton III et al., 1978; Codron et al., 2006; Johnson et al., 2013). The  
460 most obvious pattern is a clear difference between the  $\delta^{88}\text{Sr}$  value of milk and permanent  
461 teeth, the latter being  $^{88}\text{Sr}$ -enriched compared to the former. This indicates a difference of  
462 diet between baboons older than six years old and baboons younger than four. The most  
463 likely explanation is that young baboons consume breast milk in various but decreasing  
464 amounts during their first years. It is known that the Sr/Ca ratio is much lower in breast  
465 milk than in other non-milk foods (Sillen and Smith, 1984; Mays, 2003; Humphrey et al.,  
466 2008; Nava et al., 2020). This difference between milk and non-milk food is explained by  
467 bio-purification processes, discriminating Sr against Ca in the mother's body. For instance,  
468 Ca is preferentially transferred across the mammary gland during lactation, whereas the  
469 circulation of Sr is passively constrained by the concentration gradient (Tsutaya and  
470 Yoneda, 2015). This process is known to also induce a mass-dependent fractionation of Ca  
471 isotopes, where milk is  $^{44}\text{Ca}$ -depleted. The resulting negative  $\delta^{44/42}\text{Ca}$  signature and lower  
472 Sr/Ca ratio is found in human deciduous teeth and yields information about lactation  
473 period and weaning processes in modern and ancient human population (Tacaïl et al., 2017,  
474 2019; Li et al., 2020).

475 The present  $\delta^{88}\text{Sr}$  results suggest that Sr isotopes may also undergo mass-  
476 fractionation through mammary glands leading to a  $^{88}\text{Sr}$ -depleted breast milk, compared to  
477 non-milk food and can trace the intensity of breast feeding and duration of the weaning  
478 process. Defining  $\Delta^{88}\text{Sr}_t$  for one individual as the difference between the  $\delta^{88}\text{Sr}$  value in the

479 first molar and another tooth, shows decreasing values with increasing age at tooth  
480 eruption (Figure 2A). Providing that milk has a low  $\delta^{88}\text{Sr}$  value, this suggests the declining  
481 contribution of milk in baboon's diet as the animal ages. More precisely, during the first  
482 two-to-three months of life, young baboons are mostly breastfed and start to include non-  
483 milk food after the fourth month, while continuing to consume mother's milk to some  
484 extent. After the first year, baboons seem to shift to a milk-free adult diet. These dietary  
485 histories are consistent with known weaning processes of baboons (Rhine et al., 1985;  
486 Humphrey et al., 2008).

487         The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have been measured in the first molars and are distributed  
488 according to three groups (Figure 2B) that should represent distinct bedrock types of the  
489 WC region. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured in enamel are consistent with the variability of  
490 the bioavailable  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of plants measured in this area. In this region, the plant  
491  $^{87}\text{Sr}/^{86}\text{Sr}$  value gradually increases from 0.7087 to 0.7242 over 100 km between the coast  
492 and the land (Copeland et al., 2016). The baboons  $^{87}\text{Sr}/^{86}\text{Sr}$  values thus indicate that the  
493 specimens were not living altogether at the same place when their first molars were  
494 forming. The baboons analyzed here originated from two different troops that were killed  
495 during hunting for population control in the Calitzdorp area (Brand, 1994). Chacma  
496 baboons are known to form sub-troops seasonally (Anderson, 1981), which are composed  
497 of a majority of adult females and young baboons (Anderson, 1981; Busse, 1984; Henzi et  
498 al., 1999). While it is not possible to reallocate baboon individuals in one or the other troop,  
499 our results however suggest that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in enamel can help to reconstitute sub-  
500 trooping recruitment strategies in living primates.

501

#### 502 4.3. Inter-individual variations of enamel Sr isotopes

503 For individuals found with plant residues, a  $\Delta^{88}\text{Sr}_d$  can be defined as the difference  
504 between  $\delta^{88}\text{Sr}$  value of the animal and that of the plant (Figure 3). TM16661-PR and  
505 TM16690-PR are plant residues from teeth of specimens that were not analyzed in this  
506 study. The  $\Delta^{88}\text{Sr}_d$  is always negative, indicating that the  $\delta^{88}\text{Sr}$  values of herbivores tooth  
507 enamel is  $^{88}\text{Sr}$ -depleted relative to plants, consistent with a feeding study performed on  
508 pigs (Lewis et al., 2017). These authors found a  $\Delta^{88}\text{Sr}_d$  value of  $-0.32 \pm 0.06$  ‰, close to the  
509 average of  $-0.26$  ‰ calculated here. Our results exhibit a much higher dispersion of the  
510  $\Delta^{88}\text{Sr}_d$  values, which can be explained by the natural, and therefore uncontrolled, context of  
511 the study. A Wilcoxon rank test was performed on all the  $\delta^{88}\text{Sr}$  dataset of KNP to compare  
512 results for herbivores and carnivores. The  $P$ -value obtained is 0.03 suggesting that the  
513 differences between herbivores and carnivores can be considered significant. Thus, the  
514  $\Delta^{88}\text{Sr}_d$  values can also be calculated from enamel of carnivores to herbivores, and are,  
515 strikingly, not negative. At KNP, the  $\Delta^{88}\text{Sr}_d$  value is  $0.06$  ‰, but it reaches  $0.08$  ‰ when one  
516 possible herbivore outlier (*Sylvicapra grimmia*) is excluded. Indeed, *Sylvicapra grimmia*  
517 presents the highest  $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  values (respectively  $-0.21$  ‰ and  $0.760$ ) in the KNP  
518 dataset, which suggests a location effect. *Equus burchelli* also presents a higher  $\delta^{88}\text{Sr}$  value  
519 than the other herbivores and represents the only pure grazer in the herbivore set, so  
520 different metabolisms may play a role in  $\delta^{88}\text{Sr}$  differences. In the WC, the  $\Delta^{88}\text{Sr}_d$  value is  
521  $0.01$  ‰, but it is a less robust measure due to the presence of only one herbivore. The  
522 pattern of the Sr stable isotopes fractionation from plants to carnivores resembles that of  
523 Zn, for which the  $\delta^{66}\text{Zn}$  value first strongly increases from plants to herbivores and then  
524 decreases to carnivores (Jaouen et al., 2013). The systematics of Sr stable isotope

525 fractionation up mammal trophic chain thus requires further investigations to understand  
526 the origin of the observed isotopic variability before validating the  $\delta^{88}\text{Sr}$  value as a robust  
527 proxy of past diet and trophic position.

528

#### 529 ***4.4. Further perspectives for combined stable and radiogenic Sr analyses***

530 The present study emphasizes the interest and feasibility of analyzing the  $\delta^{88}\text{Sr}$  and  
531  $^{87}\text{Sr}/^{86}\text{Sr}$  values simultaneously. Cost and duration of measurement is the same as when  
532 analyzing one or the other independently using MC-ICP-MS. The Sr chromatographic  
533 separation for 24 samples takes a day only, and with the whole SSB procedure, one sample  
534 can be analyzed in 45 minutes. The simplicity of the methodology will surely encourage  
535 more studies using stable and radiogenic Sr isotopes for (paleo)ecological and geological  
536 purposes.

537 Other non-traditional stable isotopes are already fulfilling the role of dietary/weaning  
538 tracer, such as  $\delta^{44}/^{42}\text{Ca}$  (Martin et al., 2018; Tacail et al., 2019; Tacail et al., 2020, 2021), and  
539  $\delta^{66}/^{64}\text{Zn}$  (Jaouen et al., 2013, 2016, 2020; Bourgon et al., 2020) measured in the mineral  
540 phase (hydroxyapatite) of bone and teeth. So far, the original  $\delta^{44}/^{42}\text{Ca}$  and  $\delta^{66}/^{64}\text{Zn}$   
541 signatures are shown to be preserved in tooth enamel hydroxyapatite, (Martin et al., 2015;  
542 Hassler et al., 2018; Bourgon et al., 2020). As presented here, the combined  $\delta^{88}\text{Sr}$  and  
543  $^{87}\text{Sr}/^{86}\text{Sr}$  analyses in animal and vegetal tissues provide information about diet and  
544 localization, and thus may enable an extended reconstruction of life history. Further work is  
545 needed to assess the preservation of the biological signature of Sr isotopes in fossil bone  
546 and tooth enamel. More studies are also needed to decipher the behavior of Sr through

547 metabolic processes such as digestion or milk production, because metabolism may  
548 override the Sr dietary isotopic signature. The  $\delta^{88}\text{Sr}$  value could represent a metabolic  
549 signature of the studied taxa. Results of stable Sr isotopes have been recently obtained by  
550 Nitzsche et al. in invertebrates of a stream food web (Nitzsche et al., 2022). The  $\delta^{88}\text{Sr}$  value  
551 seems to discriminate different feeding behaviors and might be a dietary tracer in aquatic  
552 as well as terrestrial ecosystems.

553 The perspectives of  $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  combined analyses are not restricted to  
554 paleo(ecological) studies. A temperature dependent Sr isotope fractionation occurs  
555 between water and biologically mineralized carbonates. A  $0.033\text{‰}/^\circ\text{C}$  thermodependency  
556 is reported for natural coral samples (*Pavona clavus*) (Fietzke and Eisenhauer, 2006) and a  
557 similar value of  $0.026\text{‰}/^\circ\text{C}$  has been determined for another coral species (*Lophelia*  
558 *pertusa*) (Rüggeberg et al., 2008). A preliminary study shows that there might be a similar  
559 thermo-dependent process of fractionation for stable Sr isotopes in coccolithophore species  
560 (Stevenson et al., 2014). These studies suggest that the  $\delta^{88}\text{Sr}$  value in carbonates could be  
561 used as a paleothermometer to reconstruct ancient ocean temperatures along with the  
562  $^{87}\text{Sr}/^{86}\text{Sr}$  value that could be used as a time calibration tool (Veizer et al., 1999).

563 Considering the differences between silicate-dominated (Bulk silicate Earth  $\delta^{88}\text{Sr}$  value  
564 estimated as  $0.29\text{‰}$  (Ma et al., 2013)) and carbonate-dominated systems (Marine  
565 carbonates  $\delta^{88}\text{Sr}$  value between  $0.10$  and  $0.20\text{‰}$  (Krabbenhöft et al., 2010)), the  
566 measurement of  $\delta^{88}\text{Sr}$  could be an added value to that of  $^{87}\text{Sr}/^{86}\text{Sr}$  for studying weathering  
567 processes. There is a preferential leaching of heavy Sr isotopes into the hydrosphere during  
568 silicate weathering, but a preferential leaching of light Sr isotope preferential leaching of



569 heavy strontium during primary formed carbonate weathering (Chao et al., 2015) . The  
570 river  $\delta^{88}\text{Sr}$  value is therefore different whether it is carbonate- or silicate-dominated and  
571 this helps to identify the weathering processes that occurred before the water reached the  
572 river. The concomitant analysis of the  $^{87}\text{Sr}/^{86}\text{Sr}$  value could give additional constrains on  
573 the provenance of the weathered material.

574

## 575 **5. Conclusion**

576 The measurement of Sr stable isotopes by MC-ICPMS using combined sample-  
577 standard bracketing and Zr correction is shown to be a robust and easy method. The  
578 method permits the simultaneous measurement of the stable  $^{88}\text{Sr}/^{86}\text{Sr}$  and radiogenic  
579  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. This method has been implemented and evaluated in different laboratories  
580 and yields accurate and reproducible results on a wide variety of reference materials.  
581 Preliminary results on tooth enamel samples show that the  $\delta^{88}\text{Sr}$  value is a potential  
582 indicator of weaning practices. Encouraging results show that enamel  $\delta^{88}\text{Sr}$  values  
583 potentially discriminate herbivores from carnivores, but this necessitates further studies to  
584 understand the source of isotopic heterogeneity. Generally, more data is necessary to better  
585 understand the effect of physiology on Sr isotopes and to extend the use of the  $\delta^{88}\text{Sr}$  values  
586 as a companion of  $\delta^{44}/^{42}\text{Ca}$  in biomedical studies.

587

## 588 **Conflicts of interest**

589 There are no conflicts of interest to declare.

590

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596

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