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Disentangling diagenetic and biogenic trace elements and Sr radiogenic isotopes in fossil dental enamel using laser ablation analysis

Léonie Rey, Théo Tacail, Frédéric Santos, Stéphane Rottier, Gwenaëlle Goude, Vincent Balter

► To cite this version:

Léonie Rey, Théo Tacail, Frédéric Santos, Stéphane Rottier, Gwenaëlle Goude, et al.. Disentangling diagenetic and biogenic trace elements and Sr radiogenic isotopes in fossil dental enamel using laser ablation analysis. *Chemical Geology*, 2021, pp.120608. 10.1016/j.chemgeo.2021.120608 . hal-03414001

HAL Id: hal-03414001

<https://hal.science/hal-03414001>

Submitted on 5 Jan 2024

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26

27 **Abstract**

28 The reconstruction of life histories traits such as the ontogenic evolution of diet or
29 sequences of mobility can be achieved for fossil mammals thanks to laser ablation analysis of
30 trace elements concentration and radiogenic Sr isotope composition in dental enamel. However,
31 a major limitation for the use of laser ablation to study fossil tooth enamel is that the analysis
32 must be carried out on bulk sample hence prohibiting any *ad hoc* leaching step to remove
33 diagenetic compounds. Biogenic and diagenetic trace elements along with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio
34 must be monitored and *post hoc* correlation tests processed to isolate areas free of diagenesis.
35 The present study combines a unique combination of biogenic (Sr and Ba), diagenetic (Mn and
36 U) trace elements, major elements (Mg and Ca) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio time series obtained by
37 means of laser ablation ICPMS and MC-ICPMS on a large number ($n = 94$) of fossil tooth
38 enamel samples of humans and animals from a set of neighboring Neolithic sites in France.
39 Bone fragments sampled from the same specimens are also analyzed for comparison. Trends
40 between diagenetic and biogenic trace and major elements are first identified using inclusive
41 data analysis. The trends are then validated at the scale of the laser ablation raster, and a protocol
42 of data cleaning is developed to identify areas free of diagenesis. Non-significantly altered
43 Sr/Ca, Ba/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ average values are thus gathered for each cleaned tooth enamel
44 samples and are discussed, along with previously measured bone collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values,
45 in terms of diet and mobility in the context of the Neolithic Revolution.

46

47 **Introduction**

48 The analysis of trace elements and radiogenic strontium isotopes in fossil bone and teeth
49 to reconstruct ancient diet and mobility is nowadays of routine use in bioarchaeology and
50 paleoanthropology. Of particular interest for ancient mammal dietary habits is the analysis of
51 fossil enamel strontium/calcium ratio (Sr/Ca) and barium/calcium ratio (Ba/Ca). Sr and Ba are
52 discriminated against Ca in biochemical pathways, which include Ca as an essential element,
53 resulting in the overall decrease of the Sr/Ca and Ba/Ca ratios up trophic chains and allowing
54 the reconstruction of ancient dietary behaviors (e.g., Austin et al., 2013; Balter et al., 2001;
55 Gilbert et al., 1994; Joannes-Boyau et al., 2019; Sponheimer and Lee-Thorp, 2006). The
56 radiogenic ^{87}Sr isotope abundance is determined after normalization of the stable isotope
57 variations to a reference $^{88}\text{Sr}/^{86}\text{Sr}$ value, therefore the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is immune to biological
58 and any other process up the trophic chain. Consequently, the $^{87}\text{Sr}/^{86}\text{Sr}$ of an animal ultimately
59 reflects that of the bedrock on which it feeds and is used for the reconstruction of ancient
60 mobility (e.g., Sillen et al., 1998; Müller et al., 2003; Balter et al., 2012; Sillen and Balter, 2018;
61 Lugli et al., 2019).

62 Since the very beginnings of this archeometric discipline, diagenesis has been recognized
63 to be a major limitation and two methods have been developed to overcome this problem. The
64 first method is to leach *ad hoc* the bone or enamel sample with dilute acetic acid to remove
65 secondary Ca-carbonates (e.g., Balter et al., 2002; Hopkins et al., 2016; Nelson et al., 1986).
66 However, Ca-carbonates are not the only potential secondary phase, oxy-hydroxides being also
67 frequent diagenetic phases, which are not removed by acetic acid. In addition, bone or enamel
68 can be recrystallized, an extreme case where any leaching technique is helpful. The second
69 method consists to monitor the concentration of an element which is known to be of diagenetic
70 origin and perform *post hoc* correlation tests with the elements (mainly Sr and Ba) supposed to
71 be of biogenic origin. Uranium (U), thorium (Th) and Rare Earth Elements (REE) accumulate

72 in fossil bones and teeth (Kohn et al 1999, Reynard and Balter, 2014), and are good indicators
73 of the intensity of the diagenesis. The influence of oxy-hydroxides on the biogenic elements
74 concentration can easily be assessed by measuring manganese (Mn) concentration (e.g.,
75 Reynard and Balter, 2014). Regarding the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, the existence of a correlation between
76 the concentrations and isotope compositions along a mixing hyperbola will attest of a diagenetic
77 overprinting (Budd et al., 2000, Martin et al., 2016).

78 Thanks to the development of laser ablation, it is now possible to analyze *in situ* the trace
79 elements concentration (Dolphin et al., 2005; Humphrey et al., 2008; Kohn et al., 2013; Müller
80 et al., 2019) and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (e.g., Balter et al., 2008; Lugli et al., 2017; Montgomery et
81 al., 2010). This is of noteworthy interest for enamel because it is less sensible to diagenesis than
82 bone thanks to its less porous structure, and because it grows incrementally, allowing the
83 reconstruction of individual dietary and mobility histories (Austin et al., 2013; Balter et al.,
84 2012; Joannes-Boyau et al., 2019). However, there is a major limitation for the use of laser
85 ablation of fossil tooth enamel, which is that the leaching step is not possible because it needs
86 to be carried out on powdered samples. Biogenic and diagenetic trace elements must be
87 monitored along with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and *post hoc* correlation tests processed to determine
88 the areas free of diagenesis. To the best of our knowledge, this has been done in three studies
89 only (Balter et al., 2012; Simonetti et al., 2008; Willmes et al., 2016), but no trace elements and
90 radiogenic Sr systematics in fossil tooth enamel has been done yet using laser ablation.

91 The present study combines a unique set of biogenic (Sr and Ba), diagenetic (Mn and U)
92 trace elements, major elements (Mg and Ca) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio time series obtained by means
93 of laser ablation ICPMS and MC-ICPMS on a large number of fossil tooth enamel samples (n
94 = 62 and 32 for humans and animals, respectively) from a set of neighboring Neolithic sites in
95 France. Bone samples of same specimen are also analyzed for comparison. In the archaeological
96 context of Neolithic Revolution, which is one of the biggest socio-cultural transitions in human

97 history, dietary behavior and mobility of human groups are central issues because people settled
98 down building villages and hunter-gatherers became farmer-pastoralists. The use of laser
99 ablation in such an archaeological and chrono-cultural context is a crucial methodological step
100 that will pave the way for studies on longitudinal life histories.

101 Laser ablation measurements of trace elements concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
102 produced in the present study a large number of data (> 400,000). Global trends between
103 diagenetic and biogenic trace and major elements are first identified using inclusive data
104 analysis. These trends are then validated at the scale of the laser ablation raster, and a protocol
105 of data cleaning is developed to identify areas free of diagenesis and with reliable $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.
106 Most of the rasters unfortunately exhibit diagenetic portions so that the full time series are not
107 exploitable. Non-significantly altered Sr/Ca, Ba/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ average values are thus
108 gathered for each tooth enamel and bone samples and are discussed, along with previously
109 measured bone collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values.

110

111 **Material**

112 The bone and tooth enamel samples come from seven Neolithic sites within a radius of
113 10 km along the Yonne valley, in the South-East of the Paris basin, at the Northern edge of the
114 Morvan massif, France (Fig.1). The sites with the corresponding material are presented in Table
115 1. They are dated to different and overlapping periods covering the 5th millennium BC and they
116 refer to different and mixed cultural spheres (Table 1). Further archaeological details are
117 available in Rey et al. (2019). The bioavailable Sr local range is determined on the grounds of
118 the geological variability from plants and soil samples given by the iRhum database regionally
119 (within a 15 km radius around the sites, including layers q3, q2, c1, c2 and j3; Fig. 1), and is
120 found to vary from 0.7075 to 0.7145 (Willmes et al., 2013). For humans, all the teeth are second
121 molar (M2) except for 2 individuals for whom the teeth are first molar (M1). This corresponds

122 to a life history between approximately 2.5 and 8.5 years \pm 0.5 for M2 and between
123 approximately 0.5 and 3.5 years \pm 0.5 for M1 (AlQahtani et al., 2010). When it was possible,
124 bone from the same individual was also analyzed to assess dietary and mobility changes
125 between childhood and adulthood because bone records a signal corresponding to the
126 individuals' last years of life (Hedges et al., 2007; Szulc et al., 2000) and to assess potential
127 differential diagenetic sensitivity relative to enamel.

128 All observations (anatomical variations, pathologies, stress indicators, wear, maturation
129 stage) and external metrics were recorded and teeth pictured. In addition, calculus samples,
130 impressions of the crown and μ CT-scans were computed whenever possible for further
131 complementary studies (Le Luyer et al., 2016; Rey et al., 2016). The teeth were cut in two
132 pieces with a diamond saw, along the longitudinal bucco-lingual axis, passing through the top
133 of the mesial cusps and perpendicular to the collar (crown root junction, or crj). The mesial part
134 was embedded, with a bone fragment from the same individual whenever possible. Bone
135 fragments were taken from long bone cortical fragments (the bone type is indicated in table S1).
136 The fragments were surface cleaned with a sandblaster with aluminium oxides, washed by
137 compressed air, embedded with tooth enamel in epoxy resin and finally polished manually
138 (granulometry P4000) to obtain a smooth surface.

139

140 **Method**

141 Laser ablation

142 In tooth enamel, rasters were processed along the enamel dentine junction (edj) to cross
143 the Retzius' striae and the transverse striations. For humans and pigs, the profiles were drawn
144 from the apex (« ocl ») to the crj (« col »). The rasters for concentration and isotopic
145 composition were as close as possible. In bone, one or two small rasters were processed to
146 obtain sufficient data to average. Samples were run according to a fixed sequence procedure

147 according to Tacail et al. (2017). Each sequence was composed of 3 to 6 samples and was
148 bracketed by a sintered international standard SRM1400 "bone ash" (Tacail et al., 2016) at the
149 beginning and the end of the sequence to correct for instrumental biases. Blank was measured
150 during 5 seconds (laser off) before each measurement. The laser ablation device was connected
151 to a quadrupole-ICPMS (Q-ICPMS, X series, ThermoFisher) for the measurement of element
152 concentrations and to a multicollector-ICPMS (MC-ICPMS, Nu500 HR, Nu Instruments) for
153 the measurements of Sr isotopes. The spot size for the acquisition of trace elements and Sr
154 isotopes was respectively 50 and 150 μm , with a frequency of 10 and 20 Hz and a speed of 10
155 $\mu\text{m/s}$ for both. Operating conditions are summarized in Table 2.

156

157 Data processing

158 The laser ablation technique generates a considerable amount of data that must be treated
159 and reduced before being interpreted accurately. Each sequence (two standards bracketing 2-3
160 samples) corresponds to a single block of measurements, either on the Q-ICPMS and MC-
161 ICPMS. These raw data sequences were semi-automatically processed with Spyder Python 2.7
162 software to obtain corrected profiles for each sample. The procedure notably detects and isolates
163 samples and standards measurements using blanks (5 s) that are added between each sample or
164 standard. The procedure for element concentration is fully described in Tacail et al. (2017). For
165 Sr isotopes, the measurements were corrected using the classical ^{85}Rb and ^{83}Kr corrections and
166 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the samples was subsequently normalized by the bracketing SRM1400
167 standards with a factor depending on their position relative to the standards. Because ICPMS
168 and MC-ICPMS have dramatically different data integration time, we use relative position
169 expressed as percent of the raster length to match trace elements concentration and Sr isotope
170 composition at a given location. Elemental ratios are expressed relative to $\text{Ca} \cdot 1000$ otherwise

171 specified. Statistical analyses were performed using the FactoMineR and PerformanceAnalytics
172 packages of the R software.

173

174 **Results and discussion**

175 Quality control of the measurements

176 As previously mentioned, we used a sintered international standard SRM1400 "bone
177 ash" (Tacail et al., 2016) at the beginning and the end of the sequence to correct samples for
178 instrumental biases. A total of 98 and 140 measurements of the SRM1400 standard has been
179 processed for Sr isotopes and trace elements, respectively. Ablation of the SRM1400 standard,
180 certified to contain 250ppm of Sr, produces here a signal for ^{88}Sr of ≈ 0.9 V on the MC-ICPMS
181 and of $\approx 140,000$ cps on the Q-ICPMS. The average value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is $0.71310 \pm$
182 0.00218 (2SD, $n = 98$) very close to the TIMS value of 0.71308 ± 0.00005 (2SD, $n = 25$; Brazier
183 et al., 2020). The average value of the Sr/Ca, Ba/Ca and Mg/Ca ratios are 0.653 ± 0.038 , 0.630
184 ± 0.049 and 17.93 ± 0.73 , respectively, which are always very close to certified values (0.652
185 ± 0.018 , 0.629 ± 0.026 17.91 ± 0.35 , for Sr/Ca, Ba/Ca and Mg/Ca, respectively; Balter and
186 Lécuyer, 2004).

187

188 Bulk radiogenic Sr isotope compositions

189 The standard deviation of standard and sample corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are plotted as a
190 function of the ^{88}Sr voltage in Fig. 2A and show an increase of the variability as the ^{88}Sr voltage
191 decreases, a pattern that has been recognized by Horstwood et al. (2008). Comparing the
192 discrepancy between laser ablation and solution $^{87}\text{Sr}/^{86}\text{Sr}$ measurements, Simonetti et al. (2008)
193 and Copeland et al. (2008) have also observed that the accuracy of the laser ablation
194 measurements decreases with Sr total voltage. The decreasing ^{88}Sr voltage is also accompanied
195 by an increase of the corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios mean values (Fig. 2B). Horstwood et al. (2008)

196 and Simonetti et al. (2008) argued that the increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is due to a $^{40}\text{Ca}-^{31}\text{P}-$
197 ^{16}O polyatomic interference at mass 87. However, using Sr/Rb-free concentrated Ca/P
198 solutions, Müller and Anczkiewicz (2016) recently demonstrated that the $^{40}\text{Ca}-^{31}\text{P}-^{16}\text{O}$
199 polyatomic interference does not occur at the required intensities to explain the observed
200 increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Horstwood et al. (2008) proposed that the complete elimination
201 of this interference should be achieved using rigorous calibration to known reference materials,
202 which is actually not the case given the present results. The increase of the variability of the
203 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is likely due to degraded counting statistics for too low voltage. The concomitant
204 increase of the average value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with decreasing Sr voltage remains
205 unexplained, but must be ultimately linked, at least indirectly, to degraded counting statistics
206 and thus, could not be corrected anyway. We have selected a threshold value at 0.4 V for ^{88}Sr
207 below which the value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is considered inaccurate and thus eliminated for
208 further discussion. This value holds for a Nu Plasma HR MC-ICPMS and should be different
209 for a Neptune instrument. We also note that there is an apparent increase of the variability of
210 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for ^{88}Sr voltage $\geq 1\text{ V}$ (Fig. 2A), but which does not seem to be followed by
211 an increase, or a decrease, of the average value (Fig. 2B). The analysis of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in
212 bone and tooth enamel by laser ablation should be adapted for each sample, by varying the
213 diameter of the spot size and/or the sampling rate of the laser to obtain enough signal that should
214 ideally lie between 0.6 V to 0.9 V for ^{88}Sr .

215

216 Bulk trace elements compositions

217 The dataset has been explored using principal component analysis (PCA). PCA consists
218 at reducing the dimensionality of dataset while preserving most of the information. The basic
219 representation provides eigenvectors of the covariance matrix in two dimensions, the principal
220 components (PCs) which are the new variables. Co-variation of the eigenvectors yields

221 information about correlation of the variables. PCA are particularly useful for large dataset,
222 such as in the present study which considers six independent variables (Mg, Ca, Mn, Sr, Ba and
223 U) representing ~350,000 and 40,000 measurements for enamel and bone, respectively. We
224 have first performed PCA on the whole dataset (Fig. 3A and 3B). For enamel, the first two PCs
225 account for 31.7% and 21.6%, respectively, of the total variation in the dataset, so the two-
226 dimensional scatterplot given by Fig. 3A represents 53.3% of the variance of the original
227 eleven-dimensional space. All eigenvectors except Mg/Ca are positive along PC1, indicating
228 that they are all positively correlated and negatively correlated to Mg/Ca. Along PC2,
229 eigenvectors of biogenic (Mg, Ca, Sr, Ba and related Ca-ratios) and diagenetic (Mn, U and Ca-
230 ratios) variables are clustered indicating that the set of data contains clear biogenic and
231 diagenetic components that intrinsically positively correlated. The direction of the Mg/Ca
232 eigenvector is opposed to that of U/Ca demonstrating that these ratios are strongly anti-
233 correlated. The direction of the Sr/Ca and Ba/Ca eigenvectors is approximately perpendicular
234 to those of Mn/Ca and U/Ca ones, indicating that the biogenic and diagenetic variables are not
235 correlated. To resume, the information carried by the PCA on enamel suggests that the Sr/Ca
236 and Ba/Ca ratios are not correlated with those of Mn/Ca and U/Ca and that the Mg/Ca ratio
237 negatively correlated to the U/Ca and of Mn/Ca ratios. These conclusions apparently hold for
238 bone, except that the Mg/Ca ratio is positively correlated to those of Sr/Ca and Ba/Ca (Fig. 3B).
239 However, inspection of the variance for a given location provides more complex results for
240 enamel (Fig. 3C) and bone (Fig. 3D). Abbreviations of the archaeological sites are given in
241 Table 1. For enamel, the Sr/Ca and Ba/Ca ratios are free of diagenesis at GLN and BMT, while
242 low and high Mg/Ca ratio, respectively, is associated to high Mn/Ca and U/Ca ratios. At NZ,
243 Mon, CHI-ED and CHI-Pat, the enamel Ba/Ca ratio has a diagenetic component because the
244 Ba/Ca, Mn/Ca and U/Ca eigenvectors have closely related directions. In these sites, the enamel
245 Sr/Ca ratio seems to be free of diagenetic influence. For bone, the Sr/Ca and Ba/Ca ratios have

246 most often a diagenetic component, except at Mon, as illustrated by the common direction of
247 the biogenic and diagenetic eigenvectors.

248

249 Cleaning data from diagenesis and too low Sr content

250 PCA indicates that diagenesis occurs on a site-by-site systematics and that the chemical
251 composition of bone and enamel is differently affected by diagenesis. Analysis of the effects of
252 diagenesis at the individual scale reveals even more complicated patterns. An example is
253 provided for the GLN-210 individual (Fig. 4A and 4B). Two diagenetic zones can be identified.
254 In the diagenetic Zone 1, the increase of the Mn/Ca and U/Ca ratios is accompanied by a
255 concomitant increase of the Ba/Ca ratio and of the Ca concentration, and a decrease of the
256 Mg/Ca ratio (Fig. 4A). A simultaneous increase of the Sr/Ca ratio is less evident and is not
257 associated to variations of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio anyway. The most likely explanation is that a Ca-
258 rich, probably calcite, secondary phase precipitated in a crack of the enamel, as recognized
259 earlier by Grün et al (2008) to be a classic process. This secondary calcite was U- and Ba-rich,
260 but Mg-poor, and has a comparable Sr concentration and isotopic composition than enamel.
261 The crack was also filled with Mn-rich oxy-hydroxides. In the diagenetic Zone 2, a small
262 increase of the U/Ca ratio, but not of the Mn/Ca one, is associated to an increase of the Ba/Ca
263 ratio and a decrease of the Mg/Ca ratio, without any change in the Sr/Ca ratio, Sr concentration
264 nor isotopic composition (Fig. 4A). Here, U diffusion only cannot explain the observed
265 diagenetic pattern because it would not take the associated Ba-enrichment and Mg-depletion
266 into account. The observed diagenetic pattern is more likely explained by the presence of a
267 secondary U-enriched phase, which must have been also Ba-enriched. The diagenetic effect on
268 the Mg/Ca ratio is discussed in a subsequent section. The trace elements data were thus cleaned
269 according to the following conditions: increase of the ^{43}Ca concentration or U/Ca or Mn/Ca
270 ratios correlated to an increase of the Sr/Ca or Ba/Ca ratios or a decrease of the Mg/Ca ratio.

271 The efficiency of the removing of the data suspected to be representative of a diagenetic process
272 was globally followed using correlation matrix in which the lower half is filled with bivariate
273 scatterplots (Fig. 4A and 4B). Highlighted are areas exhibiting diagenetic patterns (Fig. 4A)
274 which are absent after the cleaning procedure (Fig. 4B). The procedure was done manually and
275 checked iteratively. The cleaning procedure removed 24% of the original data. We observed
276 that diagenesis occurs very often in the crj area, where the enamel is the thinnest. Regarding
277 the accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, all data with a ^{88}Sr voltage below 0.4 V were removed (Fig.
278 4A and 4B). This procedure removed 76% of the original data. Reduced data are given in Table
279 S1.

280

281 The case of Mg diagenesis

282 Magnesium is a bioessential element and as such, its concentration in the body is
283 metabolically regulated to lie between the deficiency and toxicity thresholds. The concentration
284 of Mg thus cannot be of any interest for tracing the consumption of Mg-enriched or Mg-
285 depleted food items for paleodiet reconstructions (Klepingera, 1990; Reynard and Balter,
286 2014). However, the Mg stable isotope composition ($\delta^{26}\text{Mg}$) of bone and tooth enamel is now
287 recognized to vary according to the position of the animal in the trophic chain (Martin et al.,
288 2014, 2015). It is therefore necessary to know how Mg behaves during diagenetic processes
289 before using the Mg isotope compositions to paleontological applications. Lambert et al. (1985)
290 measured the Mg concentration in a set of excavated bones and found higher values than in a
291 reference set of modern bones. However, no information is available on the initial Mg
292 concentration of the excavated bones. To the best of our knowledge, the results of the present
293 study could be the first robust evidence of Mg diagenesis in enamel. The example of the GLN-210
294 individual provided in Fig. 4 suggests that the Mg/Ca decreases when U/Ca increases, i.e., that
295 Mg is leached out of enamel and bone during diagenesis. The Fig. 5 shows that this is a general

296 pattern for the tooth enamel and bone samples analyzed here. Magnesium, as carbonate groups,
297 represents defects in the hydroxyapatite (HAP) lattice, which decrease crystallinity and increase
298 solubility (e.g., Laurencin et al., 2011; Legeros et al., 1996). Laurencin et al. (2011) also
299 suggested, using Density Functional Theory calculations that a local clustering of Mg within
300 the HAP lattice is likely to occur. A picture of Mg diagenesis in fossil HAP can be emphasized,
301 which posits that Mg clusters, which are poorly crystallized, are likely to preferentially dissolve
302 and react with the diagenetic fluids. The pending question, which requires further experiments,
303 is whether the leaching of Mg is associated with an isotopic fractionation. If the leaching is
304 quantitative, fossil bone and enamel would be Mg-depleted, but without Mg isotopic
305 fractionation, allowing the analysis of accurate $\delta^{26}\text{Mg}$ values for paleontological studies.

306

307 Clean radiogenic Sr isotope and trace elements compositions

308 After cleaning the data, most of the samples exhibited truncated radiogenic Sr and trace
309 elements profiles, so we calculated average and standard deviation for all parameters, which
310 are given in Table S1. Cleaning the data has resulted in the identification of significant
311 correlations among all averaged variables (Fig. 6A). These relationships are first discussed in
312 bone and then in enamel.

313

314 *Bone*

315 Generally, bone $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have local values (Fig. 6B), and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is correlated
316 with the Sr/Ca ratio (Fig. 6A), which would suggest that diagenesis is still overprinting the
317 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Budd et al., 2000). However, a close examination of the scatterplot between the
318 $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca ratios (Fig. 6C) shows that the human (GLN_221B), with the highest
319 $^{87}\text{Sr}/^{86}\text{Sr}$ value and the lowest Sr/Ca ratio contributes to the observed correlation as an outlier.
320 The observed correlation is also due to the higher Sr/Ca ratios of the BMT assemblage, which

321 is composed of livestock remains only, which are known to be enriched relative humans thanks
322 to the Ca biopurification process (Burton et al., 1999; Balter 2004; Peek and Clementz, 2012).
323 However, there is no human remains at BMT so that the Ca biopurification process cannot be
324 validated for this site. At GLN, where human and faunal remains are associated, the Ca
325 biopurification process between human and livestock exists but does not exhibit a typical bone
326 Sr/Ca trophic Sr-enrichment of half a log unit (Fig. 6D, Balter 2004), being closer to ~ 0.1 .
327 While humans have clearly lower bone Ba/Ca than livestock at GLN (Fig. 6D, Wilcoxson, *P*
328 value*** = 0.0004), the typical bone Ba/Ca trophic Ba-enrichment of one log unit is not
329 preserved (it is rather close to ~ 0.5 at GLN, Fig. 6D). The bone biogenic Ba/Ca values seem
330 however to be well-maintained as illustrated by the very good correlation with collagen $\delta^{15}\text{N}$
331 values, where human and livestock samples exhibit a species- and location-specific distribution
332 (Fig. 6E). A distribution of the bone Ba/Ca and collagen $\delta^{13}\text{C}$ values according to species and
333 location is also observed (Fig. 6F).

334 To summarize the results on bone, the overall picture argues for a diagenetic overprinting of
335 Sr, but not Ba, despite the cleaning of the supposed diagenetic data. It is likely that part of the
336 bone Sr burden supposedly cleaned from diagenesis is in fact overprinted by diagenesis in a
337 pervasive way that could not be detectable by local disturbances as identified here with laser
338 ablation in enamel. These results stress the importance of the leaching protocols for eliminating
339 diagenetic compounds in fossil bone and conclude that bone is not a suitable material for laser
340 ablation.

341

342 *Enamel*

343 The variability of the enamel $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6G) is higher than in bone (Fig. 6B). Enamel
344 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are not correlated to Sr/Ca ratios (Fig. 6H) and Sr and Ba are more depleted in
345 enamel (Fig. 6I) than in bone (Fig. 6D). These first observations are in agreement with a lack

346 of significant diagenetic effects on the original Sr and Ba contents (Budd et al., 2000; Peek and
347 Clementz, 2012). In addition, while the Sr/Ca ratio exhibits a slight Sr-enrichment from human
348 to livestock (~ 0.3 log unit), the Ba/Ca ratio has here the expected log unit (>1). These results
349 are in agreement with previous studies (Sponheimer and Lee-Thorp, 2006; Tacail et al., 2019),
350 confirm that the Sr/Ca ratio in enamel is a poor proxy of trophic level and validate that cleaned
351 enamel has not been significantly altered by diagenesis. Noteworthy is the intermediate trophic
352 position of pigs between bovids and humans (Fig. 6I). To summarize the results on enamel, the
353 overall picture to argues for an absence of diagenetic overprinting of the $^{87}\text{Sr}/^{86}\text{Sr}$, Sr/Ca and
354 Ba/Ca ratios, suggesting that the cleaning of the supposed diagenetic data has been efficient.

355

356 The context of the Neolithic revolution

357 Considering the geochemical differences highlighted for human and livestock among locations
358 (Fig. 6E, 6F, 6I), it is likely that the Neolithic society was organized into small communities,
359 managing their resources independently and locally, although probably exchanging people and
360 goods with outside. For instance, the clear distinct bone Ba/Ca signatures between the livestock
361 at BMT and GLN is a strong argument for specific livestock management, as it has already
362 been proposed on the grounds of stable isotopes for these sites (Rey et al., 2019) or for other
363 Neolithic sites (Oelze et al., 2011; Goude et al. 2019). Pending questions regarding livestock
364 management are whether it was free-ranging and to what extent the livestock was allowed to
365 range (e.g., Bickle and Hofmann, 2007). Here, livestock have local enamel $^{87}\text{Sr}/^{86}\text{Sr}$ ratios while
366 humans have generally higher enamel $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6F). This seems to indicate that
367 humans, during the formation of the M2 tooth, i.e., approximately between 2.5 and 8.5 ± 0.5
368 years old, included a non-local diet with high $^{87}\text{Sr}/^{86}\text{Sr}$ value, and were more mobile than the
369 livestock. However, a close examination of the data reveals a more thorough pattern that cannot
370 rule out the existence of micro-regional differences in the bioavailable Sr isotopic baseline.

371 Indeed, some of human Sr isotope values come from MON and CHI-Pat for which there is no
372 associated fauna. The human mobility, as recorded by the enamel $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, is more likely
373 due to practises unrelated to livestock herding.

374 One obvious $^{87}\text{Sr}/^{86}\text{Sr}$ outlier can be identified, i.e., Mon_99-520 (0.7196 ± 0.0018 , $\pm 2\text{SD}$, Fig.
375 6H), who is a female (Table S1). Differences in bone collagen for the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are
376 observed between males and females (Fig. 6J, MANOVA, $p\text{-value}^{**} = 0.0031$, Rey et al.,
377 2019), suggesting dietary sex-related differences (Goude and Fontugne, 2016; Nehlich, 2015).
378 We thus performed histograms on enamel $^{87}\text{Sr}/^{86}\text{Sr}$ ratios according to sex (Fig. 6K). The
379 distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is not statistically different between sexes (Student t test, $p\text{-}$
380 $\text{value} = 0.61$), but that of males seems to have higher $^{87}\text{Sr}/^{86}\text{Sr}$ values than of females in enamel
381 (Fig. 6G). Interestingly, the distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ values for indeterminate is bimodal,
382 suggesting that the sex difference of the $^{87}\text{Sr}/^{86}\text{Sr}$ is real. Despite the small number of samples
383 having provided exploitable results (8 males and 4 females) and that sex differences should be
384 considered in a site-by-site approach, this indicates a differential sex-related mobility pattern.
385 The case of Mon 99-520 is interesting, because it suggests that this girl has grown in a very
386 distinct area with a very high $^{87}\text{Sr}/^{86}\text{Sr}$ value, probably in the neighboring granitic Morvan area.
387 Inclusion of foreign females in Neolithic group is a still debated question (e.g., Bentley et al.,
388 2012; Goude et al., 2019, 2020 ; Rey et al.2021), that could be further assessed by $^{87}\text{Sr}/^{86}\text{Sr}$
389 variation in enamel using laser ablation.

390

391 **Concluding remarks**

392 The laser ablation technique is capable to generate simple profiles of trace elements
393 concentrations and radiogenic Sr isotope compositions in tooth enamel, but not in bone. In
394 enamel, spatial variation not only allows the reconstruction of life traits histories such as diet
395 and mobility, but also the identification of areas where diagenesis has left clues of modifications

396 of the original signatures. Once identified, these areas can be withdrawn from the results. The
397 identification of diagenetic areas in bone is more difficult, probably because the diffusion is
398 higher than in enamel and hence contrasts with normal areas more attenuated. One disadvantage
399 of laser ablation technique is that the sample cannot be cleaned from extraneous components
400 using wet chemistry because the sample needs to be powdered. However, none of this prevents
401 the possibility to soak the chip of fossil bone and tooth enamel in dilute acetic acid to remove
402 surficial calcitic contaminants before laser ablation measurements. The efficiency of such a
403 strategy could be evaluated by performing laser ablation profiles before and after the leaching
404 pretreatment in further studies. Finally, to the best of our knowledge, the Laboratoire de
405 Géologie de Lyon is the only lab that uses solid, homogeneous, matrix-matched, concentration-
406 matched, and certified standard to correct for any interference of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Ca-
407 phosphate samples analyzed by laser ablation. These standards can be shared on demand.

408

409 **Acknowledgement**

410 The authors are very grateful to J.-B. Mallye and P. Magniez who provided anthropological
411 material and related information for this study, G. Devilder for his assistance with the CAD and
412 S. Ciliberto and V. Queste for the financial contribution of the Fonds Recherches of the Ecole
413 Normale Supérieure de Lyon to the laser ablation device. This work was supported by the
414 Institut Danone France/Fondation pour la Recherche Médicale 2015 partnership.

415

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611

612 **Figure captions**

613 **Figure 1: Localization of the sites and regional geological map.** Information is from
614 geoportail.gouv.fr. Scale 1/1,000,000.

615

616 **Figure 2: Quality control of Sr radiogenic isotopes.** A) Scatterplot of the standard deviation
617 of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio a function of the ^{88}Sr voltage showing an increase of the variance with
618 decreasing voltage. B) Scatterplot of the standard deviation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio a function of
619 the ^{88}Sr voltage showing an increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with decreasing voltage.

620

621 **Figure 3: Principal component analysis (PCA) of raw results.** A) PCA of all enamel results.
622 B) PCA of all bone results. C) PCA of enamel results for each locality. D) PCA of bone results
623 for each locality.

624

625 **Figure 4: Effect of cleaning the diagenetic overprinting.** A) Chemical characterization of the
626 raw sample. B) Chemical characterization of the clean sample. Each panel is composed of two
627 parts. The top part is a correlation matrix which gives in the upper part the value of the Pearson
628 correlation coefficient and the associated *P*value annotated with stars (*) as following: *
629 *P*value < 0.05, ** *P*value < 0.001, *** *P*value < 10^{-4} , and in the lower part the scatterplot of the
630 given association. The down part is composed of the rasters expressed in relative position to
631 match elemental and isotopic profiles which had very different integration time, hence length.
632 ^{43}Ca is reported to monitor potential Ca excess due to calcite incorporation. The areas where
633 diagenesis is supposed to have occurred are highlighted in brown, and corresponding values are
634 also highlighted in the scatterplots of the top part. The recognition and the extent of the
635 supposed areas impacted by diagenesis has been done manually, and removed from the dataset,
636 as well as $^{87}\text{Sr}/^{86}\text{Sr}$ values with a corresponding ^{88}Sr below 0.4V.

637

638 **Figure 5: Magnesium is leached during diagenesis.** A) Scatterplot of the Mg/Ca ratio as a
639 function of the U/Ca ratio in enamel. B) Scatterplot of the Mg/Ca ratio as a function of the U/Ca
640 ratio in enamel.

641

642 **Figure 6: Paleoecological and paleobiological significance of clean data.** A) Correlation
643 matrix for all clean results which gives in the lower part the Pearson correlation coefficient and
644 in the upper part the associated *P*value annotated with stars (*) as following: * *P*value < 0.05,
645 ** *P*value < 0.001, *** *P*value < 10⁻⁴. B) Boxplot of all bone ⁸⁷Sr/⁸⁶Sr value for each locality.
646 The gray area represents the local ⁸⁷Sr/⁸⁶Sr range. C) Scatterplot of bone average ⁸⁷Sr/⁸⁶Sr value
647 as a function of bone average Sr/Ca ratio. D) Scatterplot of bone Ba/Ca ratio as a function of
648 bone Sr/Ca ratio. E) Scatterplot of bone average Ba/Ca ratio as a function of bone δ¹⁵N value.
649 F) Scatterplot of bone average Ba/Ca ratio as a function of bone δ¹³C value. G) Boxplot of all
650 enamel ⁸⁷Sr/⁸⁶Sr values for each locality. The gray area represents the local ⁸⁷Sr/⁸⁶Sr range. H)
651 Scatterplot of enamel average ⁸⁷Sr/⁸⁶Sr values as a function of enamel average Sr/Ca ratio. I)
652 Scatterplot of enamel average Ba/Ca ratio as a function of enamel average Sr/Ca ratio. J)
653 Scatterplot of bone δ¹⁵N value as a function of bone δ¹³C value. K) Histogram of the distribution
654 of all cleaned enamel ⁸⁷Sr/⁸⁶Sr values according to sex. The curves represent density distribution
655 for each sex. Ratios are expressed as log (Sr,Ba / Ca * 1000).

656

657 **Table caption**

658 Table 1: Summary of archaeological sites location and samples provenance.

Code site	Name site	Cultural attribution	¹⁴ C date	Spatial organization	Number of humans buried	Animal remains	Enamel samples	Bone samples	Stable isotopes**
NZ	Gurgy "Le Nouzeau"	Cerny (+ local)	5300-4700 cal BC	enclosure with scattered remains + 2 associated burials	2 + scattered remains	yes	2 humans 1 animals	2 humans 2 animals	CNS
GLN	Gurgy "Les Noisats"	local component ?	5200-3800 cal BC	big and dense cemetery	128	yes	34 humans 8 animals	12 humans 6 animals	CNS
Mon	Monéteau "Macherin"	Chassean (+Cerny +local)	5200-3500 cal BC ?	cemetery divided in separated groups	62	no	13 humans	2 humans	CNS
CHI-ED	Chichery "l'Etang David" *	local component ?	5100-4100 cal BC	cemetery partially destroyed	20	no	1 human	1 humans	CN
CHI-Pat	Chichery "Sur les Pâtureaux"	Cerny	4700-4350 cal BC	funerary site with alignments of burials + 1 isolated burial	15	no	6 humans	3 humans	CNS
BMT	Beaumont "Le Crôt aux Moines" *	Chassean	4800-4000 cal BC	enclosure with scattered remains + other structures	scattered remains	yes	2 humans 18 animals	12 animals	CNS
Bon	Bonnard "Le Poirier" *	Chassean	4500-4000 cal BC	2 burials of several inhumations	6	no	1 human	none	CN

*ancient excavation, **Rey et al., 2017; Rey et al., 2019

Laser (Excite 193 nm, Photon Machine)

LA pulse [ns]	< 4
He MFC1 [L.min ⁻¹]	0.8
He MFC2 [L.min ⁻¹]	0.4
Laser Output [%]	100
Rep Rate [Hz]	10
Spot Size [μm]	50/150
Scan speed [μm]	10

ICPMS (X Series, ThermoFisher)

RF-power [W]	1350
Ar gas flow	
Sample [L.min ⁻¹]	1
Coolant [L.min ⁻¹]	13
Auxiliary [L.min ⁻¹]	0.8
Analyzed isotopes	²⁴ Mg, ⁴³ Ca, ⁵⁵ Mn, ⁸⁸ Sr, ¹³⁸ Ba, ²³⁸ U

MC-ICPMS (Nu Plasma HR, Nu Instruments)

RF-power [W]	1400
Cones	Ni
Gas flow	
He Sample [L.min ⁻¹]	1
Ar Coolant [L.min ⁻¹]	13
Ar Auxiliary [L.min ⁻¹]	0.7
Cup configuration	H4(⁸⁸ Sr), H2(⁸⁷ Sr+ ⁸⁷ Rb), Ax(⁸⁶ Sr+ ⁸⁶ Kr), L2(⁸⁵ Rb), L3(⁸⁴ Sr+ ⁸⁴ Kr), L4(⁸³ Kr)