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RESEARCH

Assessing the Utility of Strontium Isotopes in Fossil Dental Calculus

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Abstract

Strontium (Sr) isotopes measured in fossil remains have been a useful tool to assess the geographical origin and even migrations of humans and other animals. In particular, dental enamel generally represents the ideal material, as it is dense and less prone to diagenetic replacement of Sr post-burial. However, fossil teeth can often be precious artefacts and difficult to access for destructive analysis. Here, we assess whether measuring Sr isotopes in fossil dental calculus could be used at least as a rangefinder to determine the geographical origin of an individual. We measured trace element concentrations in modern calculus (from a local dental practice), and trace element concentrations and $^{87}Sr/^{86}Sr$ ratios in human fossil calculus, dentine, and enamel from specimens collected in York, UK. Comparing trace element concentrations between modern and fossil calculus show that metals present in fossil calculus are mostly acquired post-burial, including Sr. The relationship between $^{87}Sr/^{86}Sr$ and Rb/Sr ratios in fossil calculus, dentine, and enamel suggests that the diagenetic end member would have a $^{87}Sr/^{86}Sr$ ratio consistent with the one modelled for the York region, but a low Rb/Sr. Without calculus data, dentine and enamel data would have probably suggested a lower $^{87}Sr/^{86}Sr$ ratio for a diagenetic end member, expecting high Rb/Sr values. Thus, while Sr isotopes in fossil calculus may not be useful to identify the geographical origin of an individual, they may be useful in constraining the composition of the diagenetic end member. Combining Sr isotopes in fossil dental calculus and enamel could be a more robust approach to identify geographical origin than using enamel alone.

Keywords Strontium isotopes · Dental calculus · Fossil teeth · Diagenesis

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Introduction

Strontium (Sr) isotopes are a valuable tool in archaeology for investigating past mobility and migration patterns of humans and animals (Reynard and Balter 2014; Copeland *et al.* 2016; Copeland *et al.* 2011; Copeland *et al.* 2010; Hoppe *et al.* 1999; Stewart *et al.* 2020; Willmes 2015; Wooller *et al.* 2021; Joannes-Boyau *et al.* 2019; Ericson 1985; Leach *et al.* 2009). Strontium isotope ratios in tooth enamel reflect the geological composition of the region where an individual lived during tooth formation. Their measurement can allow for the identification of individuals who migrated to a new region during their lifetime, and to estimate the distances and directions of their migrations. Additionally, Sr isotopes can help distinguish between local residents and non-local individuals buried in the same cemetery, shedding light on social and cultural practices (Price *et al.* 2011; Evans *et al.* 2006). Ericson (1985) discuss the progress and prospects of strontium isotope analysis in archaeology, while Price and Gestsdóttir (2014) and Frei *et al.* (2015) present case studies of its application to Icelandic and Bronze Age contexts, respectively. Such studies have used strontium isotope ratios to identify non-local individuals who likely travelled long distances to a region, providing evidence for long-distance exchange networks and inter-regional interactions.

While Sr isotope measurement in enamel requires only a small amount of material and is of limited destructive nature, it is often not possible to obtain specimens, because of their value in collections. When this is the case, an alternative would be to consider fossil dental calculus, which generally has lesser value to collections. Dental calculus is a calcified deposit that forms on teeth due to the build-up of bacteria and other substances in the mouth (Lang and Bartold 2018). Dental calculus has received increasing attention as a source of information about past diets, health, and behaviour (Power *et al.* 2014). One of the main uses of dental calculus analysis in archaeology is to reconstruct ancient diets, nutritional deficiencies, and other health conditions (*e.g.* Warinner *et al.* 2014; Buckley *et al.* 2014; Hendy *et al.* 2018; Henry *et al.* 2011). Dental calculus has also been studied for DNA and other biomolecules preserved within it. This approach has the potential to reveal information about the genetic makeup of past populations, as well as the presence of pathogens and other microorganisms (Weyrich *et al.* 2017).

In this study, we investigate whether Sr isotopes in dental calculus could be used to assess the origin of an individual. Calculus is much less dense, more porous, and chemically more diverse than enamel. Thus, one potential obvious limitation is that calculus may be prone to diagenesis, thus not providing an accurate record of the individual's Sr isotope signature. In addition to Sr isotopes, trace element ratios were also measured, as Mn/Ca or U/Ca ratios are commonly used as markers of diagenesis (Reynard and Balter 2014). Measurements in fossil calculus were paired and compared with measurements in enamel and dentine of corresponding teeth, since enamel is more dense and commonly less prone to diagenesis (Budd *et al.* 2000). We also measured trace element ratios in modern calculus, to provide a comparison with fossil material and assess further diagenetic uptake of trace elements such as Sr.

Material and Methods

Fossil calculus and teeth samples were previously studied in Adler *et al.* (2013). Specimens are Late Medieval (1200–1300 CE) in age, from Jewbury Cemetery, in York, UK (Lilley *et al.* 1994). Modern (2022 CE) calculus samples were provided by a dentist practice in Wollongong, NSW, Australia. Bulk and *in situ* analysis of trace element concentrations and Sr isotopes were conducted at the Wollongong Isotope Geochronology Laboratory (WIGL). Only calculus samples were processed for bulk analysis.

For bulk analysis of trace element concentrations, 5–12 mg of calculus (fossil or modern) was weighed and dissolved in high-purity HNO_3 and H_2O_2 (Seastar Baseline® grade). Solutions were dried, re-dissolved in 2M HNO_3, and an aliquot was taken for trace element analysis. Analyses were performed on a ThermoFisher iCAP-Q quadrupole inductively coupled plasma mass spectrometer (ICP-MS), with PFA nebuliser, quartz cyclonic spray chamber, nickel sample and skimmer cone, and high matrix insert. Measured analyte intensities were blank corrected, and concentrations were determined using six calibration standards (Inorganic Ventures 71A) with concentrations ranging from 0.1 to 100 ppb. The following elements were measured: calcium (Ca), manganese (Mn), strontium (Sr), lanthanides, and uranium (U). For the fossil calculus, no internal standard was used; for the modern calculus, ^{89}Y was used as internal standard for Ca, Mn, and Sr, ^{159}Tb for lanthanides and ^{209}Bi for U (fossil and modern calculus were analysed three years apart). Internal analytical uncertainties were better than 0.5% for Ca, better than 1% for Mn, Sr, lanthanides, and U. Accuracy during analysis was better than 10%.

For bulk analysis (thereafter termed '*solution analysis*') of Sr isotopes, a fraction of the aliquot dissolved for trace element concentrations was isolated, dried down, re-dissolved in 2M HNO_3, and processed for ion exchange chromatography. Strontium was isolated from the sample matrix using automated, low-pressure chromatographic system Elemental Scientific prepFAST-MC™ and a 1 mL Sr–Ca column (Eichrom™) (Field and Sullivan 2015; Romaniello *et al.* 2015). The Sr elutions were re-dissolved in 0.3 M HNO_3. Strontium isotope analysis was performed on a ThermoFisher Neptune Plus multi-collector inductively coupled plasma mass spectrometry (MC ICP-MS) at WIGL. The sample introduction system consists of an ESI Apex-ST PFA MicroFlow nebulizer with an uptake rate of ~ 0.1 mL/min, a SSI Quartz dual cyclonic spray chamber, jet sample, and X skimmer cones. Measurements were performed in low-resolution mode. The instrument was tuned at the start of each session with a 20 ppb Sr solution, and sensitivity for ^{88}Sr was typically around 4 V. Masses 88, 87, 86, 85, 84, and 83 were collected on Faraday cups. For samples, intensity on mass 88 was typically ~ 4 V, < 0.0005 V on mass 85, and < 0.0001 V on mass 83. Masses 85 and 83 were used to correct the $^{87}Sr/^{86}Sr$ ratio for the isobaric interference of ^{87}Rb and ^{86}Kr, respectively, as well as to calculate the $^{87}Rb/^{86}Sr$ ratio. Instrumental mass bias correction was applied to $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios using measured $^{88}Sr/^{86}Sr$ (and a true value of 8.375209). NIST SRM987 was measured after every five samples to

assess accuracy during analysis. Accuracy of the whole procedure was assessed by processing NIST SRM 1400 and 1486. $^{87}Sr/^{86}Sr$ values for SRM 1400 and SRM 1486 were 0.71309 ± 2 and 0.70930 ± 2 (2SE), respectively; comparable to values published in Brazier *et al.* (2020) (0.71308 ± 2 and 0.70931 ± 2, respectively). Total procedure blank was 35 pg Sr (the typical amount of Sr processed for analysis was ~ 100 ng).

In situ analysis of trace element concentrations was performed on fossil calculus and teeth, by laser ablation ICP-MS at WIGL. Laser ablation was performed using a New Wave Research™ 193 nm ArF excimer laser, equipped with a TV2 cell. Samples were ablated for 60 s with a spot size of 50 µm, a laser pulse rate of 20 Hz, and fluence set to 4 J/cm^2. Pre-ablation was performed 2 s with a spot size of 60 µm, a laser pulse rate of 5 Hz, and fluence set to 1 J/cm^2. Helium (He) was used as a carrier gas at a flow rate of 0.8 L/min. Before entering the ICP-MS, the He carrier gas was mixed with the ICP-MS Ar sample gas in a glass smoothing device. Nickel sample and skimmer cones with a high sensitivity insert were used. At the start of each session, the laser and ICP-MS were tuned using NIST SRM 612 glass for maximum sensitivity and minimum oxide level. USGS MAPS-4 reference material was used as calibration standard, and analysed before and after each sample. The typical analysis sequence consisted of 5 spots on MAPS-4, 10–20 spots on a sample, 5 spots on MAPS-4, and so on, finishing with 5 spots on MAPS-4. On the ICP-MS, the following analytes were collected: ^{43}Ca, ^{48}Ca, ^{55}Mn, ^{88}Sr, ^{137}Ba, lanthanides, and ^{238}U. Dwell time was 0.1 s for each analyte except for ^{43}Ca, ^{48}Ca, and ^{88}Sr (0.01 s). For ^{48}Ca, an interference correction was applied using ^{47}Ti. Data were processed in *Iolite 4*™ (Paton *et al.* 2011) performing a baseline correction, using MAPS-4 as external standard and ^{43}Ca as internal standard (applying values of 33.83 wt. % for MAPS-4, 39.89 wt. % for enamel and 28 wt. % for dentine). Calcium concentrations were then derived using ^{48}Ca (and other element concentrations using their respective analytes).

In situ analysis of Sr isotope ratios was performed on fossil calculus and teeth, by laser ablation MC ICP-MS at WIGL using the same laser ablation system as above and a ThermoFisher Neptune Plus MC ICP-MS. At the start of each session the laser and MC ICP-MS were tuned using NIST SRM 610 glass. Samples were ablated for 50 s with a spot size of 150 µm, a laser pulse rate of 10 Hz, and fluence set to 6 J/cm^2. Pre-ablation was performed 2 s with a spot size of 150 µm, a laser pulse rate of 10 Hz, and fluence set to 1 J/cm^2. Helium and nitrogen were used as carrier gas at a flow rate of 0.9 and 0.01 L/min, respectively. The carrier gas was mixed with the MC ICP-MS argon sample gas before entering the plasma. Jet sample and x skimmer cones were used. A clam shell with modern seawater Sr isotope ratio (0.709182 ± 0.000004 (Ma *et al.* 2013)) was used as primary standard, while a seal tooth enamel was ablated as secondary standard. The typical analysis sequence consisted of 3 spots on the clam, 3 spots on the seal tooth enamel, 10–20 spots on a sample, 3 spots on the clam, 3 spots on the seal tooth enamel, and so on, finishing with 3 spots on the clam. Masses 82 to 88 were collected in Faraday cups in static mode. Typical intensity on mass 88 was 1–2 V and < 0.0003 V on mass 82. Data were processed in *Iolite 4*™ (Paton *et al.* 2011) using the "Sr isotopes" data reduction scheme. A baseline correction was applied. Signal collected at mass 82 was used to correct ^{88}Sr

and ^{86}Sr from isobaric interferences (mainly $CaAr^{2+}$), and signal collected at mass 85 to correct ^{87}Sr from ^{87}Rb isobaric interference. Mass bias was quantified using the interference-corrected $^{88}Sr/^{86}Sr$ ratio and applied to the interference-corrected $^{87}Sr/^{86}Sr$ ratio. Finally, the corrected $^{87}Sr/^{86}Sr$ ratio of samples and seal tooth underwent an additional correction by standard-sample-standard bracketing using the corrected $^{87}Sr/^{86}Sr$ ratio of the clam to improve accuracy. The mean $^{87}Sr/^{86}Sr$ value for seal tooth enamel was 0.709281 ± 0.000004 (2 standard errors, $n = 63$). This differs from the modern seawater value (0.709182 ± 0.000004 (Ma *et al.* 2013)) by 0.0001, which is comparable to quality control results obtained by LA MC ICP-MS in other studies (Boethius *et al.* 2022).

Results

Bulk analysis yields Mn/Ca, Sr/Ca, and U/Ca ratios ranging, respectively, from 5.0 to 52 × 10^{-4}, 12.0 to 15.8, and 0.052 to 0.154 in fossil calculus, and from 0.05 to 0.35 × 10^{-4}, 1.1 to 2.1, and less than 8.3 × 10^{-6} in modern calculus (Table 1). Rare earth element (REE) concentrations determined by bulk analysis range from 0.005 to 4.8 ppm in fossil calculus, and mostly below detection limits (ranging from 0.002 to 0.005 ppm) in modern calculus. *In situ* analysis of fossil tooth enamel and dentine yields Mn/Ca ratios ranging from 0.0035 to 3.2 × 10^{-4} in dentine, 0.0059 to 15 × 10^{-4} in enamel (Supplementary Table 1; Fig. 1) (fossil or modern calculus was not analysed *in situ* for trace element concentrations). Mn/Ca ratios are higher in fossil calculus compared to dentine or enamel, or to modern calculus. In most samples, Mn/Ca is similar between dentine and enamel; although in one sample it is greater in enamel compared to dentine (ACAD8326), and lower in another (ACAD8328).

Bulk analysis yields Sr/Ca ratios ranging from 12 to 25 × 10^{-4} in fossil calculus and from 1.1 to 2.1 × 10^{-4} in modern calculus (Table 1). *In situ* analysis of tooth enamel and dentine yields Sr/Ca ranging from 3.3 to 9.9 × 10^{-4} in dentine, 2.7 to 5.8 × 10^{-4} in enamel (Fig. 2). Bulk analysis of modern calculus yields Ba/Ca ratios ranging from 0.09 to 0.43 × 10^{-4} (Ba was not measured in fossil calculus). *In situ* analysis of tooth enamel and dentine yields Ba/Ca ranging from 0.11 to 2.5 × 10^{-4} in dentine, 0.21 to 4.6 × 10^{-4} in enamel. Ba/Ca values are generally lower in enamel than dentine, except for one enamel analysis (Fig. 3). Bulk analysis of modern calculus yields U/Ca ratios ranging from below detection limit to 0.083 × 10^{-8}. *In situ* analysis of tooth enamel and dentine yields U/Ca ranging from below detection limit to 166 × 10^{-8} in dentine, below detection limit to 381 × 10^{-8} in enamel (not shown).

Solution analysis of $^{87}Sr/^{86}Sr$ ratios in fossil dental calculus yields values between 0.710068 ± 0.000021 and 0.710858 ± 0.000021 (Table 1), while *in situ* analysis yields values between 0.710313 ± 0.000075 and 0.71174 ± 0.00019 (Supplementary Table 2). *In situ* analysis of fossil dentine and enamel yields $^{87}Sr/^{86}Sr$ values between 0.70676 ± 0.00022 and 0.718470 ± 0.000096, and between 0.70637 ± 0.00025 and 0.710783 ± 0.000078, respectively (Supplementary Table 2). Modern calculus was not measured for Sr isotopes, since its origin is unrelated to that of fossil specimens and thus is of little value for comparison of Sr isotope ratios (while

Table 1 Element concentrations and Sr isotope ratios in tooth calculus (bulk analysis)

Sample name	Ca	Mn	Sr	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	U	$^{87}Rb/^{86}Sr$	2SE	$^{87}Sr/^{86}Sr$	2SE
ACAD 8326	30.0	268	444	0.78	0.53	0.22	1.07	0.25	0.08	0.30	0.22	0.04	0.12	0.01	0.09	4.61	0.000258	0.000004	0.710858	0.000021
ACAD 8327	21.0	1086	520	3.19	4.80	0.97	4.66	1.08	0.36	1.29	0.95	0.18	0.50	0.05	0.37	2.81	0.000020	0.000003	0.710732	0.000019
ACAD 8328	17.5	96	291	0.39	0.35	0.12	0.57	0.14	0.04	0.16	0.11	0.02	0.06	0.01	0.04	1.15	0.000084	0.000004	0.710486	0.000020
ACAD 8477	18.7	93	225	0.94	1.12	0.30	1.43	0.35	0.10	0.41	0.30	0.05	0.15	0.01	0.10	0.88	0.000042	0.000005	0.710570	0.000019
ACAD 8817	20.8	219	289	1.80	0.79	0.54	2.78	0.68	0.20	0.86	0.64	0.13	0.35	0.04	0.25	1.12	0.000038	0.000003	0.710068	0.000021
Modern calculus	30.6	1.5	49.9	0.008	0.011	< 0.005	0.003	< 0.003	< 0.003	< 0.004	< 0.005	< 0.003	< 0.003	< 0.003	< 0.004	< 0.002	-	-	-	-
Modern calculus	35.0	2.6	52.6	0.018	0.025	< 0.005	0.007	< 0.003	< 0.003	< 0.004	< 0.005	< 0.003	< 0.003	< 0.003	< 0.004	< 0.002	-	-	-	-
Modern calculus	35.8	3.9	73.5	< 0.002	< 0.004	< 0.005	< 0.005	< 0.003	< 0.003	< 0.004	< 0.005	< 0.003	< 0.003	< 0.003	< 0.004	< 0.002	-	-	-	-
Modern calculus	20.9	1.9	35.1	< 0.002	< 0.004	< 0.005	< 0.005	< 0.003	< 0.003	< 0.004	< 0.005	< 0.003	< 0.003	< 0.003	< 0.004	< 0.002	-	-	-	-
Modern calculus	14.8	3.2	16.1	< 0.002	< 0.004	< 0.005	< 0.005	< 0.003	< 0.003	< 0.004	< 0.005	< 0.003	< 0.003	< 0.003	< 0.004	< 0.002	-	-	-	-
Modern calculus	12.1	4.2	14.2	< 0.002	< 0.004	< 0.005	< 0.005	< 0.003	< 0.003	< 0.004	< 0.005	< 0.003	< 0.003	< 0.003	< 0.004	< 0.002	-	-	-	-

All concentrations are given in ppm except for Ca (wt. %). 2SE denotes 2 standard error (internal analytical uncertainty) on the mean $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ values reported

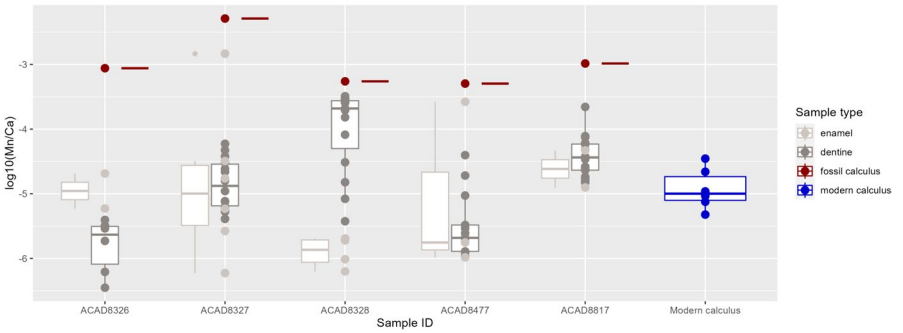

Fig. 1 Boxplot of log10 values of Mn/Ca ratios in fossil enamel, dentine (both measured by *in situ* analysis), fossil, and modern calculus (measured by bulk analysis)

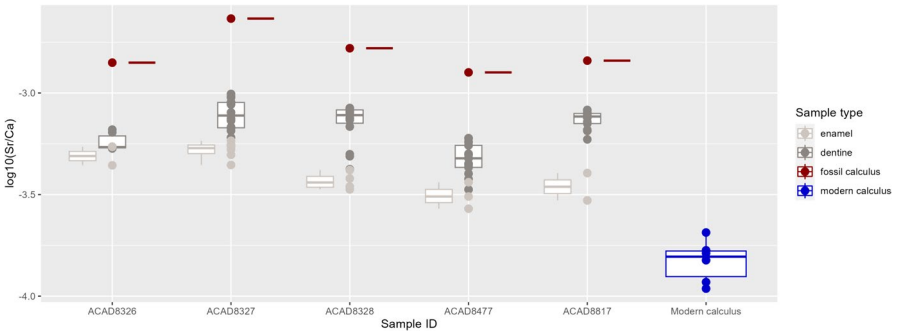

Fig. 2 Boxplot of log10 values of Sr/Ca ratios in fossil enamel, dentine (both measured by *in situ* analysis), fossil, and modern calculus (measured by bulk analysis)

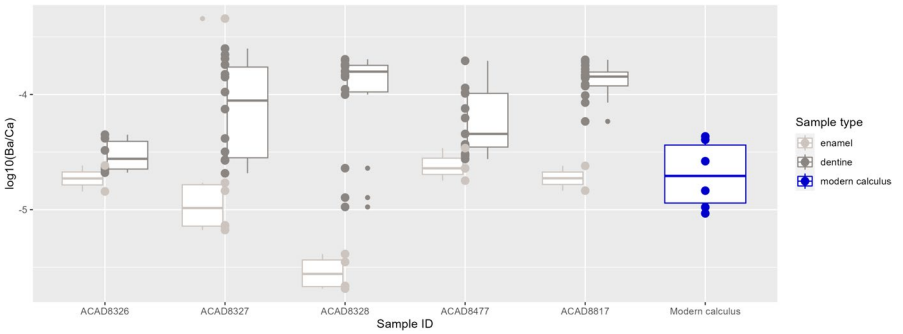

Fig. 3 Boxplot of log10 values of Ba/Ca ratios in fossil enamel and dentine (both measured by *in situ* analysis), and modern calculus (measured by bulk analysis)

comparison of trace element ratios does provide useful insights into diagenetic uptake of such trace elements).

Discussion

Diagenetic Uptake of Trace Elements

In fossil calculus, Mn/Ca ratios are one to three orders of magnitude greater than in dentine or enamel (Fig. 1). Because calculus is much more porous than dentine and enamel, it is more prone to diagenetic uptake of various elements. Alternatively, since the mineralogy of dental calculus is more diverse than that of enamel or dentine (Grøn *et al.* 1967), it is possible that its Mn/Ca is higher than that of dentine and enamel during formation, independent of diagenetic alteration. However, fossil calculus displays Mn/Ca ratios 14 to 1100 times higher than modern calculus (Fig. 1). Similarly, fossil calculus shows Sr/Ca ratios 0.25 to 2 times higher than those of dentine or enamel, and ~ 10 times higher than modern calculus (Fig. 2). Here, too, this likely reflects diagenetic alteration and uptake of Sr. The same is observed for REE, which are enriched by several orders of magnitude in fossil calculus compared to modern calculus (Table 1). Finally, U/Ca in fossil calculus is more than 5000 times greater than in modern calculus (Table 1), illustrating that U uptake occurs within a few centuries of burial. Overall, it is clear that fossil calculus is diagenetically altered, with a significant uptake of Sr and other trace elements such as Mn and U, especially when compared to modern calculus. Below we explore how diagenetic Sr may impact the Sr isotope composition of fossil calculus.

Mn/Ca ratios in dentine are similar, lower, or greater than those in enamel (Fig. 1), suggesting that it is difficult to argue for an unequivocal greater uptake of Mn in dentine compared to enamel, during diagenesis (except perhaps for sample ACAD8328). Conversely, Sr/Ca and Ba/Ca ratios in dentine are systematically greater than in enamel (Figs. 2 and 3), illustrating the diagenetic uptake of Sr and Ba in dentine.

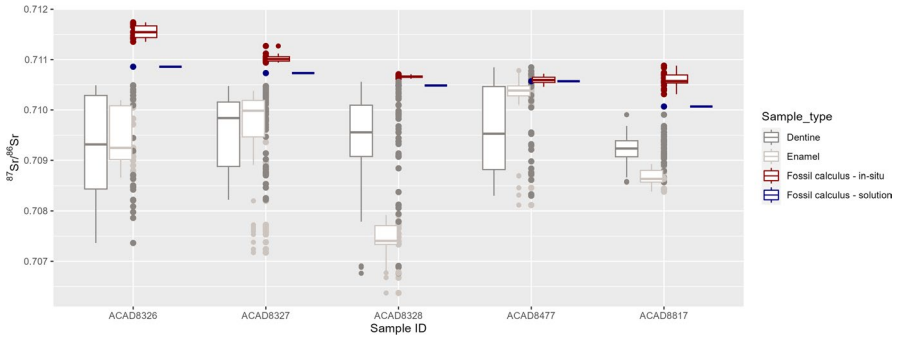

Fig. 4 Boxplot of $^{87}Sr/^{86}Sr$ ratios in fossil enamel, dentine (both measured by *in situ* analysis), and calculus (measured by solution analysis—in navy—or *in situ* analysis—in red)

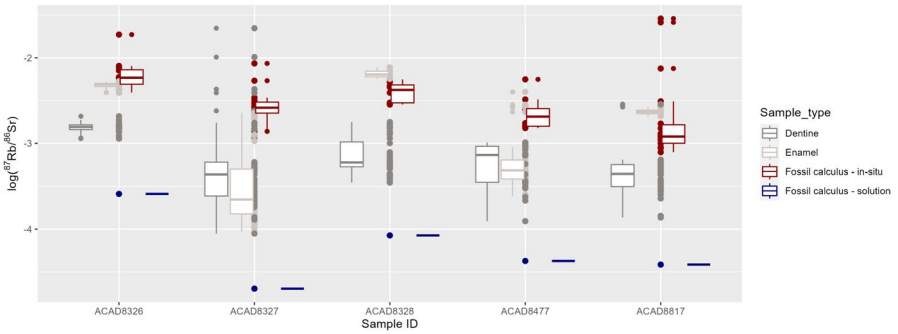

Fig. 5 Boxplot of the log10 values of $^{87}Rb/^{86}Sr$ ratios in fossil enamel, dentine (both measured by *in situ* analysis) and calculus (measured by solution analysis—in navy—or *in situ* analysis—in red)

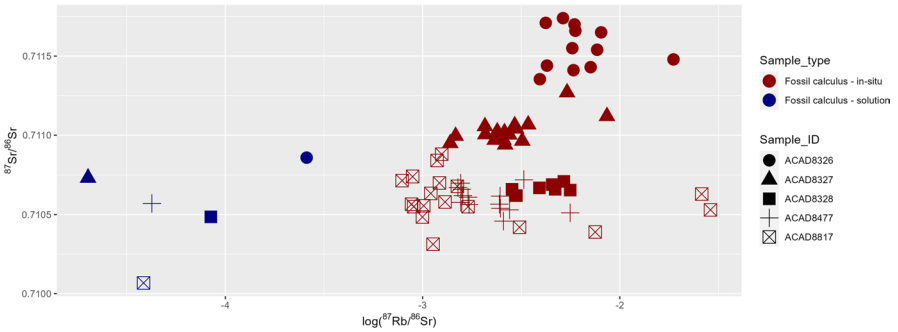

Fig. 6 $^{87}Sr/^{86}Sr$ ratios as a function of the log10 values of $^{87}Rb/^{86}Sr$ ratios for *in situ* and solution calculus analyses

Strontium Isotope Composition of Enamel, Dentine, and Calculus

The Sr isotope values measured in different sample materials are ordered as follows: fossil calculus (*in situ*) > fossil calculus (solution) > dentine ≥ enamel (Fig. 4). The shift between fossil calculus (*in situ*) and enamel ranges from 0.0002 to 0.0016, and between fossil calculus (solution) and enamel ranges from 0.0002 to 0.0014. These ranges are comparable to differences between ratios in enamel determined by *in situ vs.* solution (up to 0.0017; Copeland *et al.* 2010). Note that the difference between fossil calculus determined *in situ vs.* solution (0.00002–0.0007) is less than the difference for enamel analysed *in situ vs.* solution in Copeland *et al.* (2010). Greater $^{87}Sr/^{86}Sr$ values determined *in situ* compared to solution analysis of fossil calculus could potentially result from the isobaric interference of ^{87}Rb onto ^{87}Sr. Rubidium is not removed during *in situ* analysis, while it is removed by chromatography prior to solution analysis. This is illustrated by the $^{87}Rb/^{86}Sr$ ratios in fossil calculus analysed in solution several orders of magnitude lower than during *in situ* analysis (Fig. 5). While there are no

clear positive relationships between $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{87}Sr$ for *in situ* and solution calculus analyses, when each sample is considered separately, *in situ* analyses generally show higher $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{87}Sr$ values than solution analyses (except for sample ACAD8477; Fig. 6).

The shift between dentine and enamel ranges from 0.00004 to 0.001. This is less than what Copeland *et al.* (2010) found in rodents (generally < 0.001 but up to 0.023), suggesting that diagenetic alteration of dentine did not significantly affect its Sr isotope composition. Greater $^{87}Sr/^{86}Sr$ values in dentine compared to enamel could result from the isobaric interference of ^{87}Rb onto ^{87}Sr, since dentine is more porous than enamel and thus more prone to take up metals such as Rb, following burial (and Rb is not removed during *in situ* analysis). However, there is no systematic variation of the Rb/Sr ratio between dentine and enamel. Rb/Sr ratios in dentine are greater, similar, or lower than those in enamel, depending on the sample (Fig. 5). For instance, in samples ACAD8328 and ACAD8817 where $^{87}Sr/^{86}Sr$ values in dentine are greater than in enamel, $^{87}Rb/^{87}Sr$ are lower in dentine compared to enamel. Alternate hypotheses are (i) that primary dentine records a different diet origin than enamel, or (ii) Sr with a high $^{87}Sr/^{86}Sr$ ratio is incorporated post-burial. The former is unlikely since dentine starts mineralising only shortly before enamel (Cate and Richard 1980). For each sample, solution analysis of fossil calculus yields $^{87}Sr/^{86}Sr$ values greater than those in dentine or enamel. This observation would also support to the incorporation of Sr with a high $^{87}Sr/^{86}Sr$ ratio post-burial (since Rb is removed prior to solution analysis and high values cannot be explained by isobaric interference from ^{87}Rb).

For many analyses of enamel and dentine in sample ACAD8327, there is a negative relationship between $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ (Fig. 7). This is interesting as more ^{87}Rb should result in an overestimation of the $^{87}Sr/^{86}Sr$ ratio and thus produce a positive relationship. One of the corollaries of this observation is that correction of *in situ* $^{87}Sr/^{86}Sr$ analyses for the presence of ^{87}Rb seems to be effective. Samples ACAD8328 and ACAD8817 show the same negative relationship but enamel analyses clearly have higher Rb/Sr and lower $^{87}Sr/^{86}Sr$ values than the dentine (Fig. 7). This would imply that enamel is more diagenetically altered than dentine, which is unlikely since it is denser and it is generally accepted that enamel is more resistant to diagenesis (*e.g.* Reynard and Balter 2014). However, while Ba/Ca and Sr/Ca are lower in enamel compared to dentine, this is not systematically the case for Mn/Ca ratios.

Since higher Rb/Sr ratios would generally be interpreted as pointing towards the composition of a diagenetic end member (after ruling out isobaric interference from ^{87}Rb), the negative relationships observed between $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios could hint that the diagenetic end-member has a low $^{87}Sr/^{86}Sr$ value, 0.7085 or lower (Fig. 7). In absence of calculus data, this could be how fossil teeth data would have been interpreted. Nevertheless, this is somewhat lower that the expected modelled value for the York area: 0.7096–0.7117 (IQR) (Evans *et al.* 2018). The closest region with values between 0.708 and 0.7085 would be about 20 km east of York (Evans *et al.* 2018). If the diagenetic end member does have a $^{87}Sr/^{86}Sr$ ratio that low, a possible explanation would be that teeth were buried 20 km east of York for a period of time (during which Sr would be uptaken) before being re-located to York.

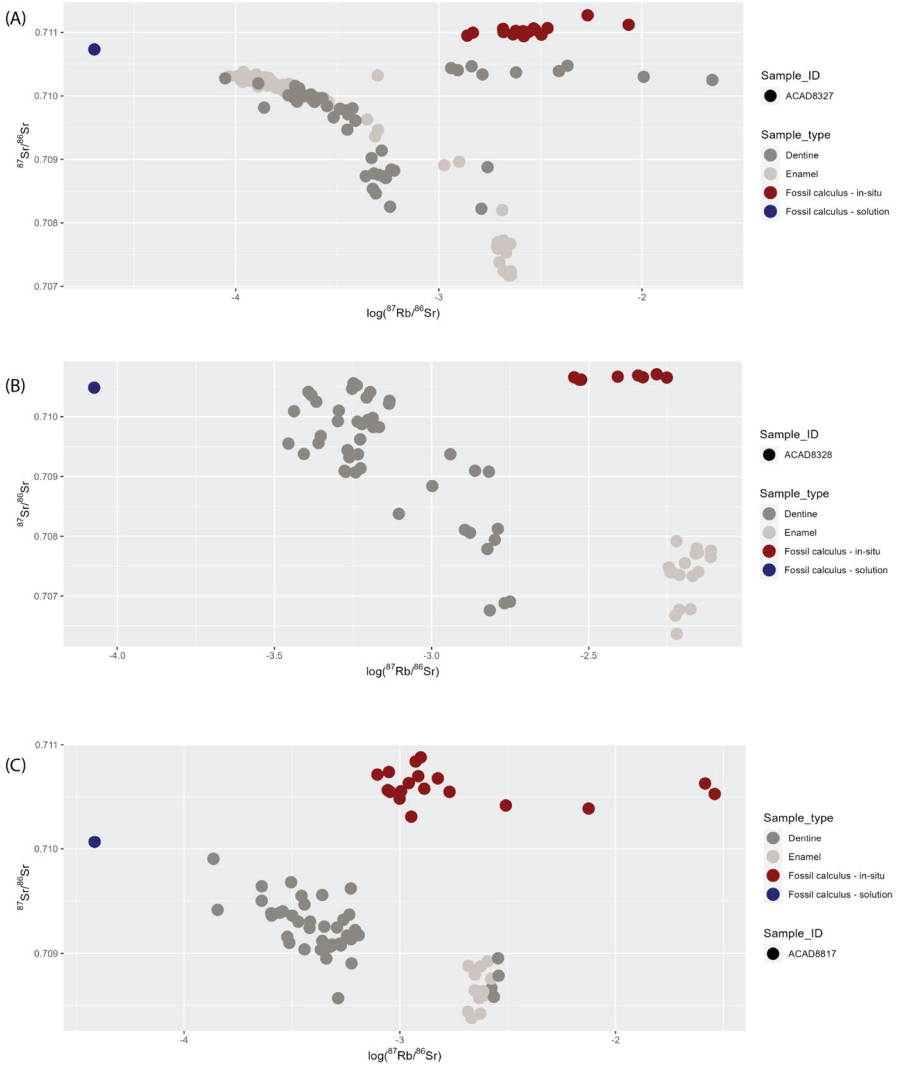

Fig. 7 $^{87}Sr/^{86}Sr$ ratios as a function of the log10 values of $^{87}Rb/^{86}Sr$ ratios in samples **a** ACAD8327, **b** ACAD8328, and **c** ACAD8817, for enamel, dentine, and calculus

Where the negative relationship between $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ is observed, it seems to converge towards that measured in the calculus by solution analysis (~ 0.7100–0.7108) (Fig. 7). Perhaps this indicates that the diagenetic end member has a high $^{87}Sr/^{86}Sr$ ratio and, surprisingly, a low Rb/Sr ratio. Values between 0.7100 and 0.7108 could fall within the range of values expected for bioavailable Sr around York (Evans *et al.* 2018). Overall, the implications are that (i) where only fossil teeth data are available, using the Rb/Sr ratio could be misleading when trying to identify a diagenetic end member; (ii) the $^{87}Sr/^{86}Sr$ ratio of the

fossil calculus is most likely dominated by Sr uptaken post-burial and is unlikely to yield useful information about the past location of an individual (unless it has been relocated post-burial); (iii) fossil calculus can be helpful in determining the Sr isotope composition of the diagenetic end member.

Fig. 8 Possible areas of origin (in orange) for the individuals studied here, using enamel $^{87}Sr/^{86}Sr$ ratios and the UK Biosphere Isotope Domains website (https://mapapps.bgs.ac.uk/biosphereisotopedomains/index.html) (Evans, *et al.* 2018) for samples **A** ACAD8326, **B** ACAD8327, **C** ACAD8328, **D** ACAD8477, and **E** ACAD8817

A corollary from this work is that the Sr isotope composition of fossil enamel for the different samples suggests that the individuals studied were not originally from York. To assess this, we used the range of $^{87}Sr/^{86}Sr$ values measured in enamel for each sample in combination with the Sr isoscape of the UK (using their 90% central data) (Evans *et al.* 2018). For samples ACAD8326, ACAD8477, and ACAD8817, results suggest that these individuals would have most likely originated at a minimum > 20 km east from York, or from southeastern England (Fig. 8). Interestingly, for samples ACAD8327 and ACAD8328, enamel $^{87}Sr/^{86}Sr$ ratios suggest these individuals would have originated from the Glasgow area, at the nearest, 100s of km away from York (Fig. 8).

Conclusions

In this study, we have assessed the potential to use Sr isotope ratios in fossil dental calculus as a way to investigate the geographical origin of individuals. When comparing modern and fossil dental calculus, it is clear that most metals present in fossil calculus were acquired post-burial, including Sr. Sr isotope and Rb/Sr ratios in calculus, dentine, and enamel suggest that the Sr isotope composition of calculus is dominated by that of diagenetic Sr. Combining these results, the Sr isotope composition of calculus seems to reflect that of the soil in which remains were buried, and not that at the time of calculus formation.

Interestingly, measuring Sr isotopes in calculus helped correctly identify the composition of the diagenetic end member. Without those measurements, a low $^{87}Sr/^{86}Sr$ ratio would probably have been assigned to the diagenetic end member, using high Rb/Sr ratios as a guide. This would have resulted in erroneous interpretations on the origin of those individuals and their burial. Thus, while Sr isotopes in fossil dental calculus cannot help constraining the geographical origin of humans and other animals, they could be helpful in correctly defining the composition of the diagenetic component. This could ensure correct interpretation of the Sr isotope composition of enamel, and constraining of geographical origin and migration.

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Data Availability Data are available upon request.

Declarations

Conflict of Interest The authors declare no competing interests.

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