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Critical evaluation of internal and external calibration methods for accurate strontium isotope ratio determination

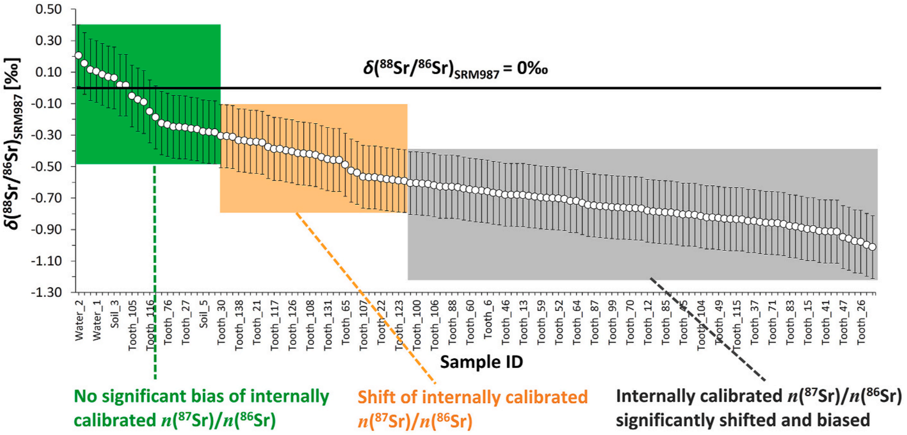
Anastassiya Tchaikovsky [a,*], Bendeguz Tobias [b], Margit Berner [c],
Doris Pany-Kucera [c], Pavlína Ingrová [d], Zuzana Hofmanová [d,e], Theresa Scharl [f],
Walter Pohl [b], Stephan Hann [a]

[a] BOKU University, Institute of Analytical Chemistry, Department of Natural Sciences and Sustainable Resources, Muthgasse 18, Vienna, 1190, Austria
[b] Austrian Academy of Sciences, Institute for Medieval Research, Georg-Coch-Platz 2, Vienna, 1010, Austria
[c] Natural History Museum Vienna, Department of Anthropology, Burgring 7, Vienna, 1010, Austria
[d] Masaryk University, Department of Archaeology and Museology, Arna Nováka 1/1, Brno, 602 00, Czechia
[e] Max Planck Institute for Evolutionary Anthropology, Department of Archaeogenetics, Deutscher Platz 6, Leipzig, 04103, Germany
[f] BOKU University, Institute of Statistics, Department of Natural Sciences and Sustainable Resources, Peter-Jordan-Straße 82/l, Vienna, 1190, Austria

HIGHLIGHTS

- This study confirms that internal calibration can produce biased Sr isotope ratios.
- Internally calibrated data led to wrong conclusions on past human migration.
- External calibration (standard-sample-bracketing) proved to be highly reliable.

GRAPHICAL ABSTRACT



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ABSTRACT

Background: The isotopic composition of strontium $n(^{87}Sr)/n(^{86}Sr)$ provides important information relevant to earth, life, food, archaeological and anthropological sciences. To determine accurate $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios, it is necessary to perform instrumental isotopic fractionation (mass bias) correction, which is a popular metaphor for isotope ratio calibration. Despite the importance of calibration in $n(^{87}Sr)/n(^{86}Sr)$ analysis, experimental studies which critically evaluate the accuracy of conceptually different calibration methods remain scarce. Therefore, this work 1) investigates if $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios differ depending on the calibration

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[*] Corresponding author.
E-mail address: anastassiya.tchaikovsky@boku.ac.at (A. Tchaikovsky).

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method used and 2) discusses whether these differences might impact the outcome of a study on past human mobility.

Results: This work compares $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ results of the same physical sample, which were determined using internal calibration (internal mass bias correction) and external calibration (standard-sample-bracketing) in a large sample set. Reference materials and environmental samples showed consistent results, while 66 % of investigated tooth enamel samples showed significantly different $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios depending on the calibration method used. In-depth evaluation ruled out sample preparation or measurement errors. Instead, internal calibration delivered biased results, because the $\delta(^{88}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}}$ values in the affected samples deviated by more than −0.60 ‰ from the – assumingly constant – reference value. The bias amounted up to 0.00043 and was 2-times larger than theoretically predicted. Ultimately, using internally calibrated $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ data, led to false classification of 6 % of individuals in a provenance study focusing on past human migration. In contrast, external calibration yielded accurate data leading to classification results that were in alignment with existing knowledge on the population under investigation.

Significance: This work empirically confirms theoretical considerations that the traditionally used calibration method in $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio analysis i.e.; internal calibration can produce significantly biased data. Moreover, it shows for the first time that the choice of calibration method has an impact on the outcome of a provenance study. Therefore, future investigations should use a more reliable calibration method in case high accuracy $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios are needed. External calibration via standard-sample-bracketing represents an attractive option.

1. Introduction

The isotopic composition of strontium $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ is of strong interest to many researchers, because it provides information relevant to earth [1,2], life [3], food [4] or archaeological and anthropological sciences [5]. Strontium (Sr) is a natural, non-toxic element, which is mostly present in rocks [6]. It has four stable isotopes (^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr) and the isotope ratio $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ varies significantly in nature as a result of the radioactive decay of ^{87}Rb to ^{87}Sr, while the absolute amount of ^{86}Sr remains stable over time [2]. This process is very slow due to the ^{87}Rb half-life of about 50 billion years, but over geological time it led to different amounts of ^{87}Sr and thus different $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios in rocks depending on the initial amount of rubidium and the geological age of the bedrock material [1]. Weathering releases strontium from rocks and transfers it to soil and water [2]. As strontium is chemically similar to calcium, it is incorporated into plants, animals and further into humans via their diet [7]. This process occurs without significant change of the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio [8]. As a result, soil, water, plants, animals and human tissue reflect the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio of the local geology [5]. This feature rendered the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio an important tracer with applications ranging from determination of the source and mixing of groundwater [9,10], investigation of the migration behaviour of animals [11–14], verification that foodstuffs originate from the declared geographic area [15–19] to studying past human mobility [20–24]. (The International Union of Pure and Applied Chemistry (IUPAC) recommends stating Sr isotope ratios as isotope amount ratios $n(^{87}\text{Sr})/n(^{86}\text{Sr})$. This notation expresses the amount of two isotopes of an element in a sample in the SI unit mole [25,26].)

To determine $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios with high accuracy (i.e., combination of trueness and precision following [27]) it is necessary to use an instrumental technique which facilitates high precision isotope ratio measurements such as thermal ionization mass spectrometry (TIMS) or multi collector inductively coupled plasma mass spectrometry (MC ICP-MS) [28]. In addition, strontium has to be chemically separated from concomitant matrix elements, it is important to monitor and correct for possible isobaric or molecular interferences, and to use a suitable method for instrumental isotopic fractionation (IIF, or mass bias) correction [29–32]. The latter term is a popular metaphor for isotope ratio calibration [31], which is traditionally performed in Sr isotope ratio analysis either by internal calibration or external calibration [33].

The vast majority of studies focusing on the analysis of $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios using TIMS or MC ICP-MS use internal calibration (also termed internal mass bias correction) [31,33]. This method is based on the assumption that only the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio varies in nature, whereas the other isotope ratios of strontium are constant. With this assumption, it is possible to use the $n(^{88}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio in the sample to calibrate the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio within the same physical sample. In practice, the instrument simultaneously acquires the signals of measurand and calibrant in the sample [31] and the instrument's software performs all necessary calculations instantly. These features render internal calibration simple and cost-effective.

The main concern regarding internal calibration is that over the years a considerable number of experimental studies reported that the – assumingly constant – $n(^{88}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio also varies in nature e.g., Refs. [9,34–41]. This variation is expressed in delta values $\delta(^{88}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}}$, which refer to the relative difference between the measured $n(^{88}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio in the sample to that of the certified reference material NIST SRM 987 in per mill [30] and its currently reported range is −3.6 ‰ to +1.7 ‰ [42]. Consequently, the main assumption of internal calibration has been proven to be no longer valid. As a result, if the $\delta(^{88}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}} = n(^{88}\text{Sr})/n(^{86}\text{Sr})$ in the sample is different to the expected – assumingly constant – value, internal calibration will yield biased $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios [33,43,44]. For this reason, numerous researchers argued against using internal calibration for IIF correction of $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios [30–32,43–45].

In contrast, external calibration uses the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio of the certified reference material NIST SRM 987 to calibrate the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio in the sample of interest [30–33]. The standard is measured before and after each sample giving this method the synonym standard-sample-bracketing (SSB). The calculations used are very simple. Furthermore, this calibration method is considered to be more robust than internal calibration because it does not rely on any theoretical assumptions about certain isotope ratios in nature [33]. In addition, it fosters comparability of measurement results, because they are metrologically traceable to the same reference. The main disadvantages of external calibration are the need to match the Sr concentration of the standard and the sample and to measure two standards in addition to the sample. Thus, the improvement in robustness and traceability comes at the cost of an increased workload and measurement time.

Despite the importance of calibration in TIMS and MC ICP-MS, experimental studies that critically evaluate $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ results, which were obtained using conceptually different calibration methods remain scarce. Neymark et al. [39] determined the $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratio in eighteen samples of abiogenic and biogenic origin using internal calibration and ^{87}Sr–^{84}Sr double spike TIMS, but did not compare the results, because the publication concentrated on $\delta(^{88}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}}$ analysis. Horsky et al. [33] reported $n(^{87}\text{Sr})/n(^{86}\text{Sr})$

isotope ratios in the same physical sample, which were determined using internal and external calibration. However, the data relate to two wood samples only, which were presented as proof-of-concept, since the main focus of the work was on calculation of measurement uncertainty of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in MC ICP-MS. Therefore, this work attempts to 1) explore the influence of conceptually different calibration methods on the accuracy of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in a large dataset and to 2) discuss if different calibration methods can have an impact on the outcome of a provenance study, with a focus on past human mobility.

2. Methods

2.1. Reagents and consumables

Water was purified using a Milli-Q® system (18.2 MΩ cm; SG Water GmbH, Barsbüttel, Germany) and subsequent single stage sub-boiling (MLS LabSystems GmbH, Leutkirch, Germany) to obtain ultrapure water. High-purity nitric acid (HNO_3, $\omega = 65$ % of p.a. grade, Merck, Darmstadt, Germany) was prepared by single sub-boiling (MLS LabSystems GmbH). High-purity hydrochloric acid (HCl, $\omega = 37$ % of p.a. grade, Merck) was prepared by double sub-boiling (MLS LabSystems GmbH). Hydrogen peroxide (H_2O_2, $\omega = 30$ %, Merck) was of suprapur quality.

The reference materials SRM 987 (highly purified $SrCO_3$), SRM 1400 (bone ash) and SRM 1486 (bone meal) were obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, USA). Single element standards of phosphorous (P), calcium (Ca), rubidium (Rb), Sr, zirconium (Zr) and indium (In) were purchased from Merck (CertiPur). Multi-elemental ICP-MS standards were obtained from Inorganic ventures (ICP-MS calibration standard 6, Inorganic ventures, Christiansburg, USA) or Merck (ICP-MS multi-element standard solution VI).

All laboratory consumables such as polyethylene (PE) bottles, tubes, pipette tips, etc. were pre-cleaned in a two-step washing procedure using HNO_3 ($\omega = 10$ % followed by $\omega = 1$ %) before use. PFA (perfluoroalkoxy) vials were cleaned by 2-times boiling in HNO_3 ($\omega = 10$ %) for 1 h.

Sample preparation and analysis were performed in cleanroom laboratories of class ISO 8 (ISO norm 14644-1 [46]).

2.2. Natural samples

The $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio is an important tracer for the investigation of past human mobility [5,20–24]. Identification of local or migratory individuals can be performed by comparison of the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio of human skeletal remains against environmental samples from the assumed geographic area of origin [22,24,47,48].

This study focused on skeletal remains from individuals that were excavated at an Avar-age cemetery (7th-9th ct. CE) in Leobersdorf-Ziegelei Polsterer, Austria [49]. The sample set consisted of 125 tooth enamel samples from predominantly first molar teeth. The enamel of this type of teeth develops between the ages 0–3 [50]. It can be expected that the investigated Avar-age population subsisted on agriculture and animal husbandry and that their young children obtained food and water predominantly from sources in the immediate vicinity of the excavated cemetery. Thus, it can be assumed that the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio in tooth enamel of the investigated individuals reflects the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio of their local environment.

To determine the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio of the local environment, 10 environmental samples (soil and water) in the area around the excavation site were collected in December 2023. The sampling sites were chosen based on existing archaeological knowledge and likelihood of being former food production areas as well as drinking water sources for humans and animals living at the presumed Avar-age area of life. Soil was sampled using a Pückhauer sampler from a depth of 0–20 cm. At each sampling site approximately 250 g of soil were obtained from three different spots within an area of 3 m^2. Soil was collected in clean PE bags and allowed to dry on air. Dried soil samples were homogenized and sieved using a 2 mm mesh width sieve (Retsch, Haan, Germany). One water sample was taken at each site at about 10 cm below the water surface in pre-cleaned PE bottles (100 mL). Supplementary Material Table 1 summarizes the details on the environmental sampling sites.

2.3. Sample pretreatment

The enamel samples were drilled following [51]. About 50 mg of the obtained enamel were digested via closed-vessel hot plate digestion. Enamel was weighted into pre-cleaned PFA vials, mixed with 1.5 mL HNO_3 ($\omega = 65$ %) and 0.5 mL H_2O_2 ($\omega = 30$ %) and digested at 120 °C for 8 h. The reference materials SRM 1400 bone ash and SRM 1486 bone meal were used as quality control materials and treated in the same way as the samples. Soil extraction followed the protocol described in DIN ISO 19730 [52] to obtain the labile fraction. Briefly, 10 g of dried and sieved soil was mixed with 25 mL ammonium nitrate ($c = 1$ mol L^{-1}) and extracted by 2 h shaking at 20 rpm in an overhead shaker (GFL Gesellschaft für Labortechnik GmbH, Burgwedel, Germany). The slurry was filtered (Grade 14/N, 150 mm, 84 g m^{-2}; Munktell Filter AB, Ahlstrom, Falun, Sweden). Water was filtered using 0.45 μm pore size filter (Sartorius, Göttingen, Germany) to obtain the dissolved elemental fraction. For stabilization soil extracts and water filtrates were acidified to a HNO_3 mass fraction of 2 %.

2.4. Multielement analysis

Tooth enamel digests, soil extracts, water filtrates and QC samples were diluted using HNO_3 ($\omega = 2$ %) to fit the working range of an external 10-point calibration curve (ICP-MS calibration standard 6 by Inorganic ventures diluted using HNO_3, $\omega = 2$ %). The element content of P, Ca, Rb and Sr was determined using an inductively coupled plasma quadrupole mass spectrometer (ICP-QMS, either NexION 2000, PerkinElmer, Waltham, USA or iCAP Q, Thermo Fisher Scientific, Bremen, Germany) following standard protocols. Indium (Merck) was used as internal standard to correct for potential instrument drifts, matrix effects or sample introduction variability, which can occur during ICP-MS analysis. Therefore, In was added to all sample aliquots in a way that the final measurement solution contained 1 ng g^{-1} of In. The limit of detection (LOQ) was determined following EURACHEM guidelines [53] as 10-times the standard deviation of the method blank and taking into account the dilution factor of the samples, respectively. A multielement standard (ICP-MS multi-element standard solution VI, Merck) spiked with P, Ca, Rb, and Sr single element standard solutions was used as in-house QC. The measured and expected values of the in-house QC were in excellent agreement (Supplementary Material Table 2).

2.5. Separation of strontium from matrix elements prior to MC ICP-MS analysis

The separation of strontium from concomitant elements was performed following the protocol by Zimmermann et al. [54] using a commercially available fully automated low pressure chromatographic sample handling system (prepFAST-MC™, Elemental Scientific, Omaha, USA) with a 3 mL-bed volume column (Elemental Scientific) packed with DGA resin (100–150 μm particle size, TrisKem International, Bruz, France). For optimal separation the samples need to have a HNO_3 concentration of 2 mol L^{-1} [54]. Therefore, tooth enamel digests were diluted by sub-boiled water to a HNO_3 concentration of 2 mol L^{-1}, while soil and water samples were acidified to a HNO_3 concentration of 2 mol L^{-1} using conc. HNO_3 ($\omega = 65$ %). In addition, tooth enamel samples were diluted using HNO_3 ($c = 2$ mol L^{-1}) to a Ca mass fraction of 600 μg g^{-1}, because the DGA resin cannot handle large on-column Ca loads [54]. Subsequently, all samples were subjected to automated matrix separation using the separation scheme in Supplementary Material Table 3.

After separation, a sample aliquot was diluted 10-fold using HNO_3 (ω = 2 %) and screened with ICP-QMS (either NexION 2000, PerkinElmer or iCAP Q, Thermo Fisher Scientific) following standard protocols. The LOQ was determined as 10-times the standard deviation of the instrument blank and taking into account the dilution factor of the samples. The screening showed that the procedure allowed for a nearly quantitative Sr recovery, Sr in separation blanks < LOQ and removal of the major interfering elements Rb and P to levels < LOQ after separation. The removal of Ca to a mass fraction ratio of Ca/Sr < 10 was considered fit-for-purpose as experimental tests [54–56] showed that Ca/Sr levels of <10 had no significant impact on the trueness of $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios.

The reference material SRM 987, which is certified for Sr isotopic composition, was used as quality control standard to monitor for on-column fractionation. A detailed description of the general principle of the prepFAST-MC™ system is given in Retzmann et al. [57].

2.6. Sr isotope ratio analysis

The analysis of Sr isotope ratios was performed on a MC ICP-MS (Neptune Plus, Thermo Fisher Scientific, Bremen, Germany) equipped with 9 Faraday cups, which were connected to 10^{11} Ω or 10^{13} Ω amplifiers. Supplementary Material Table 4 shows the used cup and amplifier configuration. Samples were introduced into the MC ICP-MS via a PFA self-aspirating nebulizer (100 μL flow rate, Elemental Scientific, Omaha, USA) and a desolvation unit (Aridus 3, Teledyne, Thousand Oaks, USA).

A preliminary test showed that an integration time of 2.097 s over 100 data points for a signal intensity of approximately 20 V for ^{88}Sr allowed to obtain a measurement precision of approximately 0.00005 for the $I(^{87}\text{Sr})/I(^{86}\text{Sr})$ signal ratio (1 *SD*, $n = 100$, Supplementary Material Table 5). This measurement precision was considered fit-for-purpose for the targeted expanded measurement uncertainty of $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios of <0.00020 (U, $k = 2$; see below). Therefore, all further measurements were performed using these parameters. Table 1 details the typical instrumental and data acquisition conditions.

Separated samples were diluted using HNO_3 (ω = 2 %) to a Sr elemental content of approximately 10 ng g^{-1} Sr, which allowed for a signal intensity of 20 V for ^{88}Sr. A solution of the certified reference material SRM 987 in HNO_3 (ω = 2 %) was used as external calibration standard. A Zr single element solution (Merck) was added to all samples and standards prior to measurement for combined internal standardization and standard-sample-bracketing [58]. The Sr and Zr content in the samples and standards was matched within ±10 %. The HNO_3 (ω = 2 %), which was used for sample and standard dilution and measured before and after every block of four standards and three samples was used for blank correction. Samples and the SRM 987 were measured in standard-sample-bracketing (SSB) mode.

Table 1
Used MC ICP-MS operating conditions.

Instrument settings	
RF power	1200 W
Plasma gas	16 L min^{-1}
Auxiliary gas	0.8 L min^{-1}
Sampler cone	Nickel, Jet-type
Skimmer cone	Nickel, X-type
Sample introduction	Aridus 3 with 100 μL self-aspirating PFA nebulizer
Aridus Ar	4.0–4.8 L min^{-1}
Aridus N_2	2.0–3.5 mL min^{-1}
Spray chamber temperature	110 °C
Desolvator temperature	140 °C
Sample uptake rate	100 μL min^{-1}
Sample uptake time	90 s
Wash time	150 s
Data acquisition parameters	
Scan type	Static
Cup configuration	see Supplementary Material Table 4
Mass resolution	low
Sensitivity	20 V for^{88}Sr/10 ng g^{-1} Sr
Integration time	2.097 s
Number of blocks	1
Number of cycles/block	100
Data acquisition time	210 s

2.7. Data processing

Data processing for Sr isotope ratio determination was performed following the protocol described in Horsky et al. [33]. In brief, raw signals were outlier corrected applying the 2 *SD* criterion. Blank correction was performed by on-peak zeros i.e., subtraction of measured signals at all relevant m/z in the blank solution from all measured signals in the standards and samples. Residual ^{87}Rb was corrected for by peak-stripping. Furthermore, three frequently used calibration methods for instrumental isotopic fractionation (IIF) correction were used and compared:

a) Internal calibration: The $I(^{88}\text{Sr})/I(^{86}\text{Sr})$ signal ratio was measured in the sample and used to correct the $I(^{87}\text{Sr})/I(^{86}\text{Sr})$ signal ratio for IIF via Russell's law [59] and the $n(^{88}\text{Sr})/n(^{86}\text{Sr}) = 8.37861$ from the SRM 987 certificate as reference. The $n(^{88}\text{Sr})/n(^{86}\text{Sr}) = 8.375209$, which is sometimes referred to as 'accepted' value was not used. This value originates from Nier's 1938 publication [60], which reported a $n(^{86}\text{Sr})/n(^{88}\text{Sr}) = 0.1194$ — equivalent to $n(^{88}\text{Sr})/n(^{86}\text{Sr}) = 8.375$ considering the number of significant digits. As instrumental precision improved, the number of significant digits in the calculated $n(^{88}\text{Sr})/n(^{86}\text{Sr})$ value was increased from 8.375 to 8.375209 without considering that the applied denominator of $n(^{88}\text{Sr})/n(^{86}\text{Sr}) = 1/0.1194$ has only 4 significant digits. This inaccuracy has a negative influence on the outcome of the IIF correction: Using the 8.375209 ratio to correct $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ via Russell's law in the certified reference material SRM 987 results in a value of $n(^{87}\text{Sr})/n(^{86}\text{Sr}) = 0.710245$ [61], which deviates from the certified value of 0.71034 [62]. In contrast, using the certified ratio $n(^{88}\text{Sr})/n(^{86}\text{Sr}) = 8.37861$ – equivalent to $n(^{86}\text{Sr})/n(^{88}\text{Sr}) = 0.119351$ – as reference, yields the certified $n(^{87}\text{Sr})/n(^{86}\text{Sr}) = 0.71034$. Thus, applying $n(^{86}\text{Sr})/n(^{88}\text{Sr}) = 0.1194$ as reference leads to systematically biased $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ isotope ratios.
b) External calibration (standard-sample-bracketing, SSB): The SRM 987 was measured before and after each sample. Subsequently, the average $I(^{87}\text{Sr})/I(^{86}\text{Sr})$ signal ratio of the two measured SRM 987 and the certified $n(^{87}\text{Sr})/n(^{86}\text{Sr}) = 0.71034$ as reference were used to correct the $I(^{87}\text{Sr})/I(^{86}\text{Sr})$ signal ratio in the sample for IIF.
c) External calibration using Zr as internal standard (SSB–Zr): This method combines the advantages of external and internal calibration [58]. In the first step, the average $I(^{87}\text{Sr})/I(^{86}\text{Sr})$ signal ratio in the bracketing standards and the certified value $n(^{87}\text{Sr})/n(^{86}\text{Sr}) = 0.71034$ of the SRM 987 were used to determine an estimate of the $n(^{91}\text{Zr})/n(^{90}\text{Zr})$ isotope ratio of the Zr standard (which does not necessarily need to be certified for Zr isotope ratios) applying the Russell's law. Subsequently, the estimated $n(^{91}\text{Zr})/n(^{90}\text{Zr})$ isotope ratio and the measured $I(^{91}\text{Zr})/I(^{90}\text{Zr})$ signal ratio in the sample were used to correct the $I(^{87}\text{Sr})/I(^{86}\text{Sr})$ signal ratio in the sample for IIF via the Russell's law.

All formulas and constants, which are necessary for performing the calculation using internal and external calibration (SSB, SSB-Zr) are described in detail in the supplementary material sub-chapter 'Isotope ratio calibration'. All calculations in this work were performed using a template, which is provided as a spreadsheet file (Microsoft Excel®) in the electronic supplementary material of the publication by Horsky et al. [33].

The intermediate precision of internally and externally (SSB, SSB-Zr) calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios was determined using the SRM 987 under the same measurement conditions by the same operator on the same MC ICP-MS over a period of one year and amounted to 0.710387 ± 0.000020 (internal calibration, $n = 16$, 1 *SD*), 0.710329 ± 0.000026 (SSB, $n = 16$, 1 *SD*) and 0.710334 ± 0.000031 (SSB–Zr, $n = 16$, 1 *SD*). The SRM 987 was measured at the beginning of each measurement session in the same way as samples.

2.8. *Measurement uncertainty*

Traditionally, $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios are stated together with a standard deviation [29], which typically indicates how close results obtained during the measurement of the same sample solution are to one another. However, this does not reflect the contribution of all sources of error, which influence the result of an analytical measurement. Therefore, according to the *International Vocabulary of Metrology*, each measurement result should be reported together with an associated measurement uncertainty [27]. The latter is the combination of all sources of error, which contribute to the result of an analytical measurement. Thus, the measurement uncertainty is a realistic estimation of the quality of an analytical result and allows the comparison of results, which were obtained under different conditions and in different laboratories [63].

In this study, the measurement uncertainty of Sr isotope ratios was calculated using a Kragten approach according to Horsky et al. [33]. Therefore, the errors and probability distributions associated with the instrumental measurement precision, blank correction, $^{87}\mathrm{Rb}$ correction and IIF correction were determined and used as input variables for the uncertainty calculation. The error of the IIF correction was determined for each of the three investigated calibration methods in order to compare their influence to the overall measurement uncertainty. The spreadsheet file (Microsoft Excel®), which was used for the calculation of measurement uncertainties can be found in the electronic supplementary material of [33]. The measurement uncertainty was determined for each matrix individually i.e., water, soil and tooth enamel samples, respectively. The measurement uncertainty of the elemental mass fraction of P, Ca, Rb and Sr amounted to 10 % including the uncertainty contribution of the blank, measurement precision, slope of the calibration curve and analytical balance.

In this work the measurement uncertainty is stated as expanded uncertainty (U, $k = 2$). It is calculated using a coverage factor k of 2, which corresponds to a level of confidence of approximately 95 % [63].

2.9. *Statistical data analysis*

To compare single measurement results among themselves or to a reference value this work used the concept of measurement uncertainty [63]. In particular, according to the EURACHEM guideline *Quantifying Uncertainty in Analytical Measurement* values which overlap within limits of uncertainty cannot be considered significantly different [63]. For example, the values $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr}) = 0.71034 \pm 0.00026$ (U, $k = 2$) and $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr}) = 0.71050 \pm 0.00016$ (U, $k = 2$) overlap within limits of uncertainty and thus, can be considered equal.

To assess correlations between data, this work applied a linear correlation analysis after Pearson.

3. Results and discussion

3.1. *Comparison of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ results for different calibration methods*

To ascertain the validity of internal and external (SSB, SSB-Zr) calibration we compared the observed and expected $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of three reference materials, which were treated in the same way as samples. Fig. 1 shows that the $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of the SRM 987, SRM 1400 and SRM 1486 agreed with the certified value of 0.71034 ± 0.00026 (U, $k = 2$; Fig. 1A) as well as the published values of 0.71310 ± 0.00016 (U, $k = 2$ following [54]; Fig. 1B) and 0.70931 ± 0.00012 (2 *SD* following [64]; Fig. 1C) within limits of uncertainty. According to EURACHEM guidelines values which overlap within limits of uncertainty can be considered equal [63]. In addition, typical expanded uncertainties of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios amounted to 0.00011 (U, $k = 2$; internal calibration), 0.00014 (U, $k = 2$; external calibration SSB) and 0.00016 (U, $k = 2$; external calibration SSB-Zr). Internal calibration yielded marginally smaller uncertainties than external calibration (SSB, SSB-Zr) mainly because the latter requires the analysis of bracketing standards before and after the samples. Notably, all $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ uncertainties determined in this work were below the targeted uncertainty of 0.00020 (U, $k = 2$) and aligned well with $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ uncertainties in similar experimental studies [9,16,33,41,54,57].

These results demonstrated the accuracy of the investigated calibration methods.

Comparison of internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in the investigated soil and water samples showed excellent agreement within the limits of uncertainty (Supplementary Material Table 6). In contrast, $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in tooth enamel samples did not differ significantly depending on the applied calibration

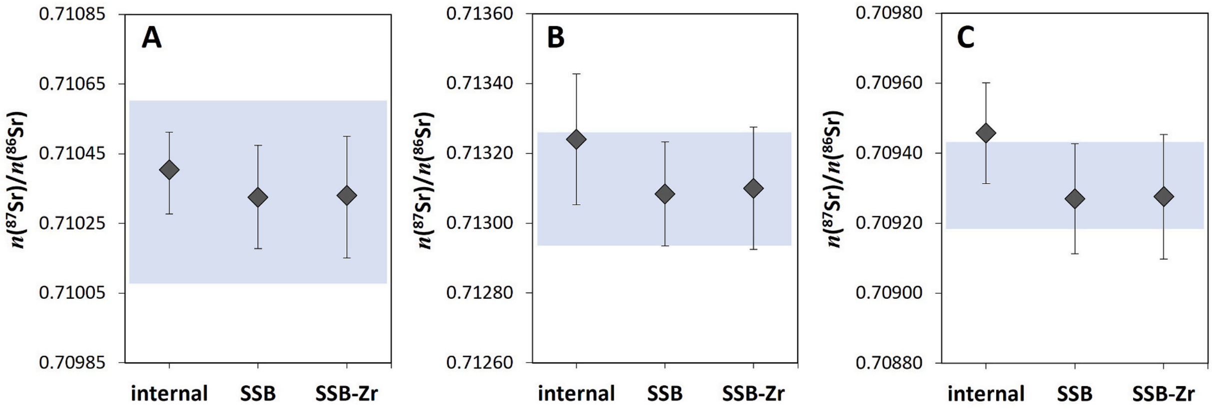

Fig. 1. Comparison of the average $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of the A) SRM 987 ($n = 36$), B) SRM 1400 ($n = 6$) and C) SRM 1486 ($n = 4$) after internal and external (SSB, SSB-Zr) calibration. The blue bar represents the reported reference range according to the certificate and [54,64], respectively. Error bars correspond to the combination of the standard deviation of repeated measurements and the combined measurement uncertainty (u_c) to obtain the expanded uncertainty (U, $k = 2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

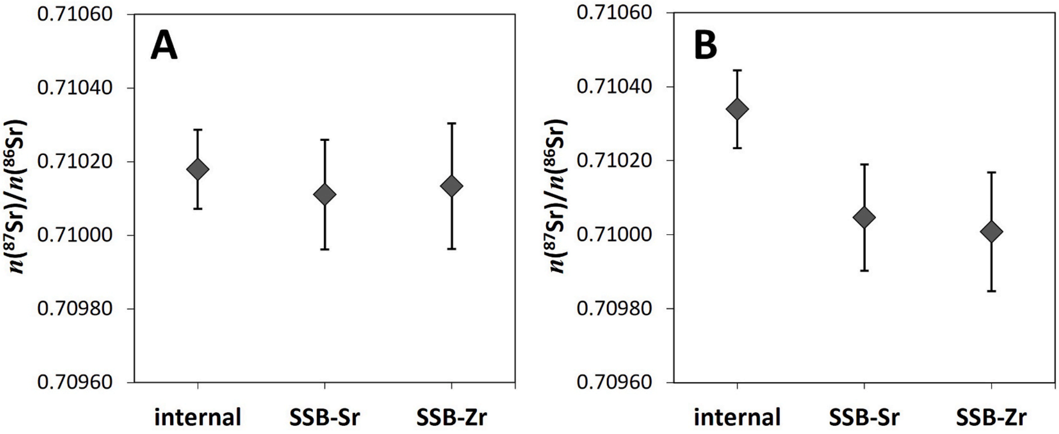

Fig. 2. Comparison of internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in two different tooth enamel samples (A, B). Error bars correspond to the expanded uncertainty (U, $k = 2$).

method in one third of the investigated samples only when considering expanded uncertainties, according to sample A in Fig. 2. In two third of the investigated tooth enamel samples the internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ result was significantly higher in comparison to the externally calibrated data, as on the example of sample B in Fig. 2. The difference between internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios amounted up to $\Delta n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})_{\text{internal-SSB-Zr}} = 0.00043$, while there was no significant difference between SSB and SSB-Zr calibrated data. Accordingly, these findings imply that reference materials and environmental samples show consistent results, whereas tooth enamel shows significantly different $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios depending on the calibration method used in 66 % of all investigated samples. (Please note that the entire $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ dataset will be presented in a separate publication focusing on past human migration.)

On-column fractionation during Sr/matrix separation could be a potential source of error leading to biased $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in tooth enamel. However, the applied protocol allowed a nearly quantitative extraction of Sr from tooth enamel with an average recovery of 98 % ± 7 % (1 *SD*, $n = 125$). Furthermore, observed $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in the SRM 987, which was separated as QC in each batch and in two matrix matched reference materials, were in agreement to their reference values (Fig. 1), respectively. In addition, Supplementary Material Table 7 provides evidence against on-column fractionation of $n(^{88}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios, which are traditionally expressed is the delta notation as $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ [30]. Of interest, there was no significant relationship of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios or $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values in tooth enamel and the recovery in case the Sr recovery was above 80 % ($R^2_{\text{Pearson}} < 0.003$, Supplementary Material Fig. 1), respectively. These findings speak against a significant on-column fractionation during Sr/matrix separation and cannot explain the observed discrepancy of internal and external calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in tooth enamel.

Potential Kr interferences were corrected for by on-peak zero. Moreover, elemental Rb and P content was <LOQ after Sr/matrix separation and traces of residual Rb in all samples were below a $I(\mathrm{Rb})_{\text{total}}/I(\mathrm{Sr})_{\text{total}}$ signal ratio of 0.35 %, which allows mathematical correction without significant bias [33]. The Ca/Sr mass fraction ratio complied with the specified benchmark of Ca/Sr < 10 following [54–56] in 90 % of tooth enamel samples. 10 % of tooth enamel samples showed Ca/Sr mass fraction ratios ranging from 10 to 90, because they were separated at the end of the resin's lifetime. This stage began typically after 100-130 separations and was characterized by a decreased ability to retain Ca, which resulted in an increase of the Ca content in the samples after separation. Ramos et al. [55] showed that a Ca/Sr mass fraction ratio of up to 550 had no significant effect on the trueness of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios determined by internal calibration. To investigate if this finding could be reproduced for our setup and evaluate if increased Ca levels had an effect on the trueness of externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ results, a test experiment was conducted. Therefore, a SRM 987 with Ca/Sr mass fraction ratios ranging from 1 to 120 was prepared and measured (a Ca/Sr mass fraction ratio of 120 corresponds to approximately 1200 ng g^{-1} Ca and 10 ng g^{-1} Sr in the test sample solution). Fig. 3 shows agreement of internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios to the certified isotope ratio within levels of uncertainty even in case the measured solution had a Ca/Sr mass fraction ratio of 120. This result aligned with experimental work by Ramos et al. [55] and suggested no significant effect of Ca on the trueness of $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in tooth enamel for Ca/Sr < 120.

Mass-independent fractionation (MIF) within the MC ICP-MS system can be a further potential cause for differences between internal and external calibrated results, since external calibration can correct for this effect, while internal calibration cannot [29]. To test if MIF was present within the used MC ICP-MS setup, we followed the recommendations described by Yang et al. [29]. Therefore, we performed an 11 point measurement of the SRM 987 at different RF power settings ranging from 1150 to 1250 W and obtained blank corrected intensity ratios of $I(^{88}\mathrm{Sr})/I(^{86}\mathrm{Sr})$ and $I(^{87}\mathrm{Sr})/I(^{86}\mathrm{Sr})$. The determined slope of the $\ln(I(^{88}\mathrm{Sr})/I(^{86}\mathrm{Sr}))$ and $\ln(I(^{87}\mathrm{Sr})/I(^{86}\mathrm{Sr}))$ plot amounted to 0.490 ± 0.040 (1 *SD*; Supplementary Material Table 8 and Supplementary Material Fig. 2). The experimental value did not differ significantly from the theoretical value of 0.504 [42,56] based on Russell's law considering the limits of uncertainty. This result indicated no significant MIF for $^{87}\mathrm{Sr}$ within our MC ICP-MS system.

Accordingly, these findings implied that the observed discrepancy between internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in tooth enamel did not result from sample preparation nor measurement. Ultimately, calculations using an alternative calibration method, the revised exponential model following Baxter et al. [65], confirmed the trueness of externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ results in six tooth enamel samples, which were measured in different MC ICP-MS sessions in the course of approximately one year, respectively (Supplementary Material Table 9). This finding provided additional evidence for the accuracy of external calibration. (Since there was no significant difference between SSB and SSB-Zr calibrated isotope ratios, the following text will refer to SSB-Zr IIF corrected data when discussing external calibration.) In turn, this result challenged the trueness of internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in tooth enamel. This calibration method yields accurate data under the condition that the $n(^{88}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio in the sample is identical to the – assumingly constant – $n(^{88}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio [30,31,33] i.e., the certified value of 8.37861. This prerequisite was fulfilled for the SRM 987. Thus, internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of the SRM 987

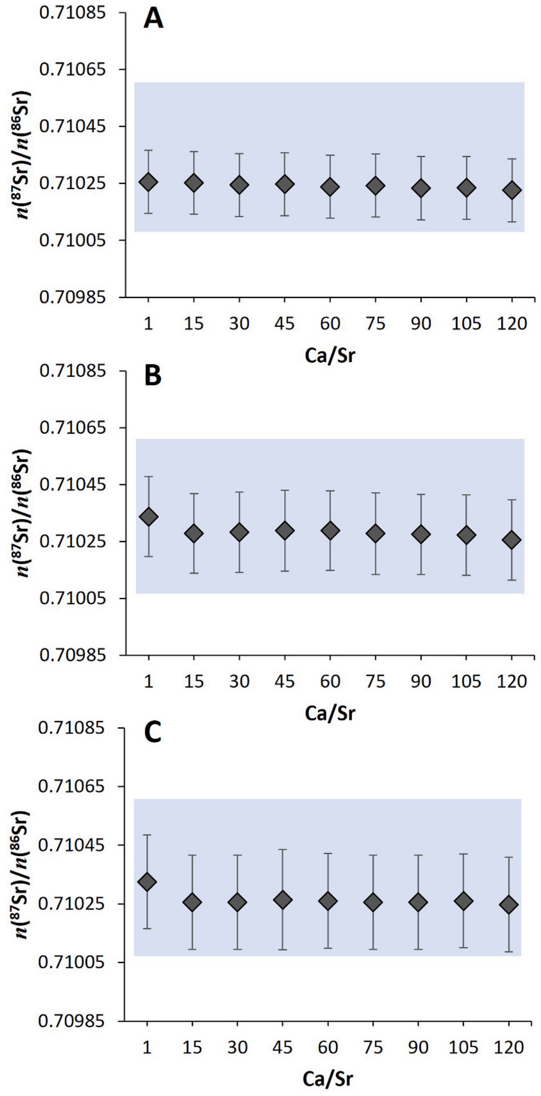

Fig. 3. $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios determined in test solutions of the SRM 987 spiked with increasing levels of Ca. The Ca/Sr (mass fraction ratio) ranged from 1 to 120. Isotope ratios were determined using A) internal, B) SSB and C) SSB-Zr calibration. The blue bar represents the reported reference range according to the certificate. Each test solution was measured 3-times. Error bars correspond to the combination of the *SD* of repeated measurements and u_c to obtain U, $k = 2$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

were in agreement to the certified value (compare Fig. 1A). Yet, a considerable number of experimental studies reported significant variation of $n(^{88}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ - expressed as $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values - in natural samples [9,33–41,54]. Therefore, we hypothesize that the discrepancy between internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ data arise from $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values in tooth enamel that deviate from the – assumingly constant – value of 0 ‰ (corresponding to $n(^{88}\mathrm{Sr})/n(^{86}\mathrm{Sr}) = 8.37861$, as certified in the SRM 987).

3.2. $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ and its influence on internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$

Indeed, the majority of the investigated samples showed significantly different $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values to 0 ‰ considering the limits of uncertainty (Fig. 4; Data are sorted from highest to lowest value. A discussion on the variation of the $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values in natural samples is subject of active research and beyond the scope of this analytical work. For more information on each data point see Supplementary Material Table 10.).

This result provides evidence that the main methodological prerequisite of internal calibration was not fulfilled for the majority of the investigated tooth enamel samples. Thus, internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ data of samples, which show a $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value that is significantly different to the – assumingly constant – reference value, cannot be considered accurate. In practice, further investigations showed that in case the $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value in the sample differed by less than ±0.30 ‰ from 0 ‰, the resulting internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios showed no significant bias. This observation explained the good agreement of internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of sample A in Fig. 2, which displayed a $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value of −0.05 ‰ ± 0.20 ‰ (U, $k = 2$; SSB-Zr) as well as all investigated environmental samples (compare green circles in Fig. 4 and data in Supplementary Material Table 6). In case the $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value ranged between −0.30 ‰ and −0.60 ‰, the internally calibrated results shifted towards higher $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios. Though considering the measurement uncertainty this bias was not significant as in the example of the SRM 1400 and SRM 1486 in Fig. 1B and C (the respective $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values are in Supplementary Material Table 7). However, internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ results of samples, which displayed a $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ lower −0.60 ‰ were significantly biased considering the measurement uncertainty as on the example of sample B in Fig. 2. The $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value in this sample amounted to −0.76 ‰ ± 0.20 ‰ (U, $k = 2$; SSB-Zr).

In this dataset, the largest bias in internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios was 0.00043, which was observed in a tooth enamel sample with a $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value of −1.01 ‰ ± 0.20 ‰ (U, $k = 2$; SSB-Zr). This bias was 2-times larger than assumed by theoretical calculations [43,44] and by 0.00013 larger than empirically observed so far [33]. To investigate if the extent of bias could be predicted based on the observed $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value in a sample, we plotted the $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values against the calculated difference between internally and externally (SSB–Zr) calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of environmental and tooth enamel samples ($n = 135$), respectively. Fig. 5 shows a linear relationship between these variables with a R^2_{Pearson} of 0.98. The obtained linear equation allowed to predict that a $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value of e.g., −0.60 ‰ biased the internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio in the sample by 0.00028 ± 0.00011 (U, $k = 2$). This value was in agreement to the experimentally determined bias of a sample with $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}} = -0.60$ ‰ in this study and verified a preliminary observation based on two data points [33]. The uncertainty or the predicted value resulted from the propagation of the uncertainty of the input variables.

These findings speak in favor of our hypothesis and provide empirical evidence that internal calibration is a simple and cost-effective method, but this comes with the risk of producing significantly biased data. Furthermore, it is important to note that the prediction of the bias of internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios requires knowledge of the $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value in the sample. However, due to methodological reasons this variable cannot be determined by internal calibration [31]. Thus, when using only internal calibration for IIF correction, it is not possible to determine if a bias exists nor to estimate its extent.

3.3. Differently calibrated Sr isotope ratios in the context of a provenance study

Building on the results above, this work aspired to investigate if $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios, which were determined by conceptually different calibration methods, can lead to different conclusions on the provenance of a sample. For this purpose, we used an exemplary dataset comprising of sixteen selected samples from a study on past human mobility. (Note that the entire $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ dataset will be presented

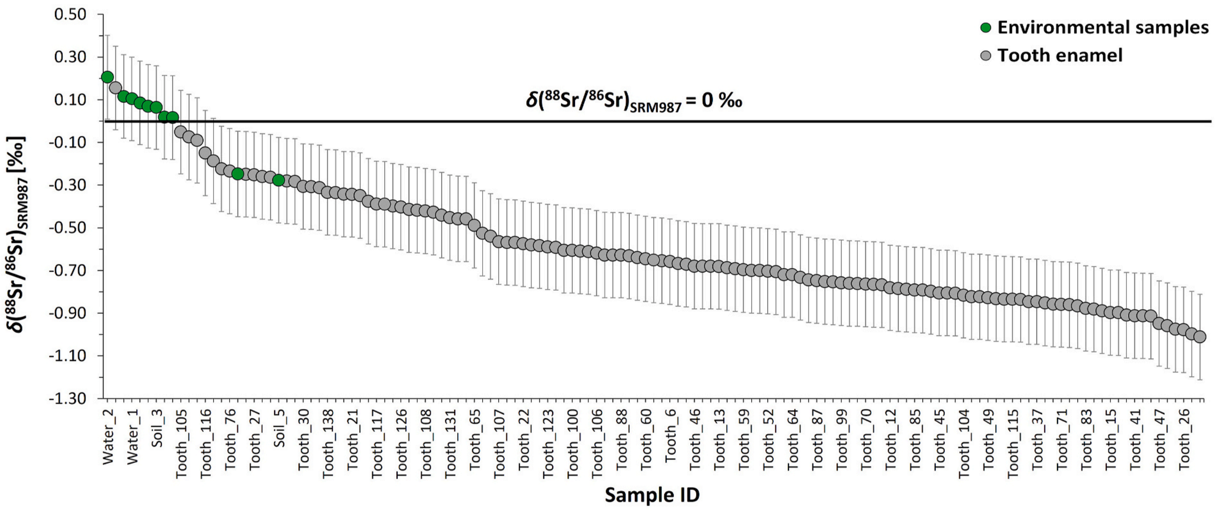

Fig. 4. The $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values in the investigated environmental (n = 10, green circles) and tooth enamel (n = 125, grey circles) samples determined using SSB-Zr. Data are sorted from highest to lowest value. Error bars correspond to the expanded uncertainty (U, k = 2). For information on each data point see Supplementary Material Table 10. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

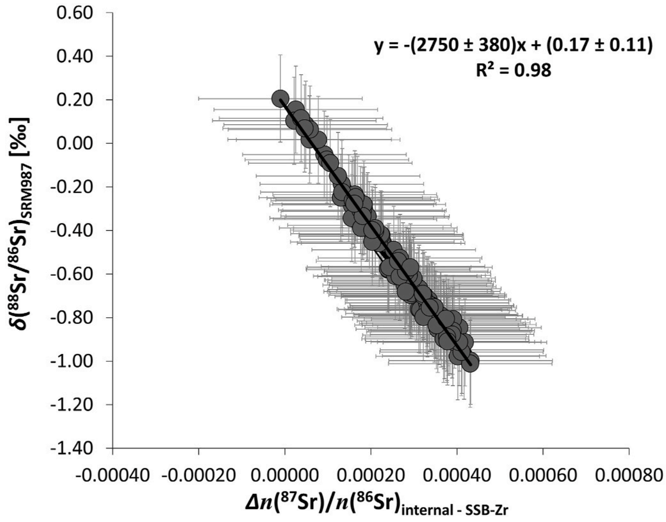

Fig. 5. Observed $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ values plotted against the difference between internally and externally (SSB–Zr) calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of n = 135 samples. Error bars of $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ and $\Delta n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})_{\mathrm{internal\text{-}SSB\text{-}Zr}}$ correspond to 0.20 ‰ (U, k = 2) and 0.00019 (U, k = 2). The linear equation is stated with the SD of the slope and the intercept.

in a different publication.)

In the first step, we determined the environmental range, which corresponds to the local $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ signal of the investigated site using the average $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratio of environmental samples ± 2 standard deviation. There was no significant difference between internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in the investigated environmental samples within limits of uncertainty (compare Fig. 6A and 6B). This is because the $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ of these environmental samples did not deviate to more than ±0.30 ‰ from the – assumingly constant – value of 0 ‰ (see sub-chapter 3.2). Therefore, the environmental ranges, which were determined using different calibration methods are basically the same i.e., the environmental range based on internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ data corresponded to 0.7085–0.7101 and 0.7084–0.7100, respectively (green bars in Fig. 6).

In the second step, we plotted internally and externally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of six tooth enamel samples against the environmental range, respectively. To allow comparability, these tooth enamel samples displayed a $\delta(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SRM987}}$ value of approximately −0.85 ‰. Thus, internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in these tooth enamel samples were biased by approximately 0.00037 (see sub-chapter 3.2). Fig. 6 shows that $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios of tooth enamel samples 24, 58 and 75 plotted within the environmental range independent of the calibration method used. This result suggests that these individuals could be of local origin. Consequently, although different calibration methods yielded significantly different $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ results, the overall conclusion regarding the provenance of these three individuals was the same. In comparison, internally calibrated $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in the remaining tooth enamel samples suggested two non-local (sample 33 and 72) and one local (sample 115) individual. Data obtained through external calibration indicated the exact opposite. This example showed that different calibration methods can lead to different conclusions on past human mobility in case the observed $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios plot close to the upper or lower border of the environmental range.

In this study, internal calibration yielded significantly biased $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ isotope ratios in two thirds of the investigated tooth enamel samples. Nonetheless, the majority of these data plotted within the environmental range. Thus, the interpretation of these results in context of human provenance led to the same conclusion as for data determined by external calibration. Ultimately, only 6 % of the investigated individuals were wrongly assigned. This raised the question if this low number of false-positive or false-negative results has a meaningful impact on the overall conclusion on past human mobility of the investigated society. In this regard, it is important to consider that for an analytical result to be fit-for-its-intended-use it must be sufficiently reliable so that any decision based on it can be taken with confidence [53]. Furthermore, modern archaeological research integrates multiple lines of evidence. For the present dataset, a previous study [66] reported – among other information – the sex and genetic relationship of most individuals under investigation. The genetic analyses identified approximately three larger biological pedigree lines with subgroups residing in the settlement over a period of roughly 150 years. Notably, there was little evidence of intermarriage within the community; instead, women appear to have entered the Leobersdorf community through exogamous marriage practices [21,66]. Tooth enamel sample 115 in Fig. 6 belongs to a woman, who exhibited no direct genetic relationship to any member of the investigated community. The $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$ data obtained by external calibration suggests that she was of non-local origin, because her tooth enamel $n(^{87}\mathrm{Sr})/n(^{86}\mathrm{Sr})$

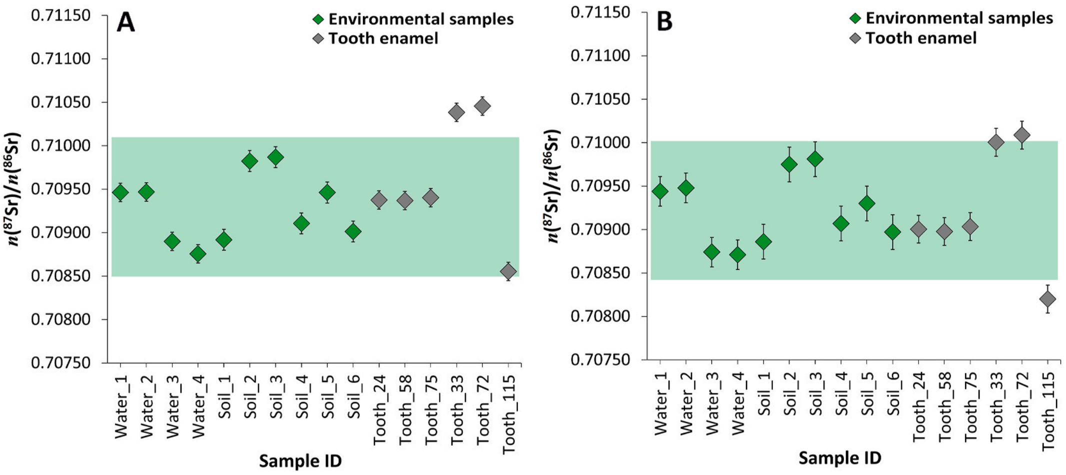

Fig. 6. Comparison of $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios determined by A) internal and B) external calibration in environmental samples (green diamonds) and tooth enamel (grey diamonds). Error bars correspond to the expanded uncertainty (U, $k = 2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

isotope ratio was significantly different to the environmental range of the investigated settlement within limits of uncertainty (Fig. 6B). This result is consistent with the proposed pattern of female exogamy in Avar society [21,66]. In contrast, when using internal calibration, the resulting $n(^{87}Sr)/n(^{86}Sr)$ isotope ratio overlapped with the environmental range within limits of uncertainty (Fig. 6A). As a result, this woman should be classified as most likely local. This raises a critical question: How can an individual with no relatives within the community be of presumably local origin? This example highlights that already a single analytical artefact can open the door to speculations, which distort efforts to elucidate social dynamics in ancient societies.

3.4. Broader implication of these findings

The $\delta(^{88}Sr/^{86}Sr)_{SRM987}$ values observed in this study align with literature e.g. Refs. [35,37–39,67], nonetheless several studies reported significantly different $\delta(^{88}Sr/^{86}Sr)_{SRM987}$ values in tooth enamel [38] or water [39,68] (Fig. 7). Thus, the bias of internally corrected $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios in the same type of samples from another site can be different to observations reported in this work. In the best case, there is no bias. In the worst case, $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios in environmental samples bias towards lower and in tooth enamel towards higher values, which would result in a high number of false-negative classified individuals.

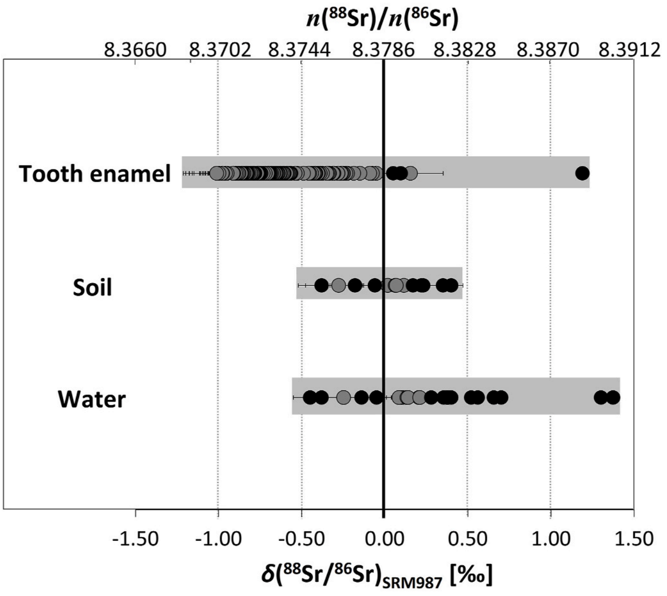

Fig. 7. Comparison of observed (grey circles) to selected published (black circles) $\delta(^{88}Sr/^{86}Sr)_{SRM987}$ values in tooth enamel [38,39], soil [35,37,67–69] and water [9,34,37,39,68,70,71]. The grey bar highlights the displayed range. Error bars correspond to U, $k = 2$ or reported uncertainty. The $n(^{88}Sr)/n(^{86}Sr)$ isotope ratio scale is plotted for comparison.

It can be expected that the same issue could influence conclusions on the provenance of samples in context of geological, ecological or food forensic studies. Moreover, Di et al. [42] performed a theoretical calculation and showed that variation of $\delta(^{88}Sr/^{86}Sr)_{SRM987}$ values and high $^{87}Rb/^{86}Sr$ ratios in geologic material can in some cases generate a significant bias in internally corrected $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios, which can potentially lead to wrong results using the $^{87}Rb–^{87}Sr$ 'chronometer'. This underlines the importance of using a reliable calibration method in order to prevent potentially wrong conclusions not only in provenance studies but also beyond.

4. Conclusion

This work critically evaluated the accuracy of two conceptually different calibration methods, which are frequently used in TIMS and MC ICP-MS analysis of $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios. The presented experimental data confirmed theoretical considerations that the most widely used calibration method in $n(^{87}Sr)/n(^{86}Sr)$ isotope ratio analysis i.e.; internal calibration (internal correction) can produce significantly biased data. Moreover, due to the inherent mechanism of this method, it is not possible to determine if a bias exists nor to estimate its extent. This had a far-reaching impact on the outcome of a provenance study. In particular, this work showed that biased data stimulated wrong conclusions on past human migration. In contrast, external calibration (standard-sample-bracketing) proved to be highly reliable delivering accurate results for all investigated matrices in the analysed sample set. Therefore, we conclude that internal calibration is not a reliable calibration method in case high accuracy $n(^{87}Sr)/n(^{86}Sr)$ isotope ratios are required and recommend using other calibration methods instead. External calibration proved to be an attractive option.

CRediT authorship contribution statement

Anastassiya Tchaikovsky: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Bendeguz Tobias:** Writing – review & editing, Resources, Methodology, Investigation. **Margit Berner:** Writing – review & editing, Resources, Methodology, Investigation. **Doris Pany-Kucera:** Writing – review & editing, Resources, Methodology, Investigation. **Pavlína Ingrová:** Writing – review & editing, Resources. **Zuzana Hofmanová:** Writing – review & editing, Resources. **Theresa Scharl:** Writing – review & editing, Formal analysis. **Walter Pohl:** Writing – review & editing, Validation, Funding acquisition. **Stephan Hann:** Writing – review & editing, Validation, Resources, Methodology.

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Declaration of competing interest

There is nothing to declare.

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Glossary

n	amount-of-substance (of an isotope) in the SI unit mole
ω	mass fraction
c	concentration
m/z	mass-to-charge ratio
$I(^{i}X)$	measured voltage corresponding to nuclide ^{i}X
u_c	combined measurement uncertainty
U	expanded uncertainty
k	coverage factor

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2025.344783.

Data availability

Data will be made available on request.

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