Science and Justice 55 (2015) 34–42

Contents lists available at ScienceDirect

Science and Justice

journal homepage: www.elsevier.com/locate/scijus

Identification of the geographical place of origin of an unidentified individual by multi-isotope analysis

Laura Font [a,*], Gerard van der Peijl [b], Carina van Leuwen [c], Isis van Wetten [a], Gareth R. Davies [a]

[a] Deep Earth Cluster, Faculty of Earth and Life Science (FALW), Vrije Universiteit Amsterdam, 1085 De Boelelaan, 1081 HV Amsterdam, The Netherlands
[b] Netherlands Forensic Institute, Laan van Ypenburg 6, 2497 GB The Hague, The Netherlands
[c] Bureau Bijzondere Recherche Expertise, Jan van den Oevergebouw, Kabelweg 25, Amsterdam, The Netherlands

ARTICLE INFO

Article history:
Received 19 December 2013
Received in revised form 13 June 2014
Accepted 27 June 2014

Keywords:
Multi-isotope
Provenancing
Enamel
Bone

ABSTRACT

A multi-isotope investigation (Sr and Pb isotopes and $\delta^{18}O$, $\delta^{13}C$ and $\delta^{15}N$) was applied to bone and teeth from an unidentified male found drowned in the"IJ" Ruyterkade in Amsterdam, The Netherlands in March of 1999. The individual remained unidentified until mid 2013, after the isotope study was completed. Coupled $\delta^{13}C$ and $\delta^{15}N$ values in bone collagen recovered from rib and femur are consistent with an omnivore living in a region where C3-type diet dominates (i.e. Europe). Integrated Sr and Pb isotopes and $\delta^{18}O$ values in canine and third molar teeth and femur and rib bone data exclude extended residence in north-west Europe and particularly The Netherlands. Characteristic Pb isotope ratios coupled with inferred $\delta^{18}O$ values of drinking water argue for a most probable place of origin for the unidentified individual in west and south Poland, south-east Slovakia and the region of Ukraine–Romania–Bulgaria, specifically the region associated with the Carpathian Mountains. Independent of the isotope study, the Cold Case Team made a positive identification with an individual from south-west Poland, validating the results of the multiple-isotopic approach.

1. Introduction

The use of multi-stable isotope analysis for the determination of the geographical place of origin of unidentified living or deceased individuals in forensic police investigations has rapidly expanded during the last decade [1–3]. The multi-isotope method is also being more frequently applied in archaeological research for human provenancing and cultural studies [4–6]. This analytical approach is, however, still in its early stages and further validation and development of laboratory methods, databases and predictive models are required [2,1]. Nevertheless, this method is an important tool in providing forensic intelligence in ongoing police investigations. Successful examples of the application of the multi-isotope methods in police investigations, including one example using both stable and radiogenic isotope systems, are "the Adam torso" [7], the "Scissors sisters" [1], "Salt Lake Sally" [2,8] and the "lady of Mammoth lake" cases [9].

The multi-isotope method integrates the analysis of human tissues (i.e., tooth enamel, bone, hair) from up to seven isotope systems; hydrogen ($\delta^{2}H$), oxygen ($\delta^{18}O$), carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), sulphur ($\delta^{34}S$), strontium ($^{87}Sr/^{86}Sr$) and lead ($^{207}Pb/^{206}Pb$) and compares data with the isotope signatures of the bio-available elements in the local environment. The underlying principle is that the isotope signatures recorded in human tissues are transferred into the human body through diet and ingested water. Furthermore, different types of tissues grow at various stages of an individual's life. For example, tooth enamel is fully mineralised during childhood and adolescence [10], depending on the specific tooth element. Thus, tooth enamel will record the isotope signatures of the environment where the individual resided during early life. In contrast, hair keratin, because of its general rapid growth, records the isotope signatures of the environment where the individual lived during the last weeks/months of an individual's life. Isotope signatures recorded in bone bio-apatite record the isotopic composition of time period of an individual's life integrated over a time period depending on bone turnover rate. Estimated turnover rates for cortical (compact) bone are in the order of ~3% per year and ~26% per year for trabecular (spongy) bone [11,12]. Therefore, bones such as the central part of the femur shaft have a slow turnover time of ~25–30 years and ribs have fast turnover time of ~4–6 years. Moreover, the turnover time of an individual bone will vary depending on the degree to which it is put under stress with joints having faster turnover times than the centre of a bone. Consequently, different bones and parts of bones will provide an isotopic signature integrated over a few years to several decades. Any major geographic movement in the lifetime of an individual is therefore expected to be recorded as isotopic variations, if the individual moved to locations with contrasting isotope compositions in the environment. The main aim of the multi-isotope methodology is to provide information on the geographical regions of origin and recent movements of unidentified individuals.

* Corresponding author.
E-mail address: l.fontmorales@vu.nl (L. Font).

http://dx.doi.org/10.1016/j.scijus.2014.06.011
1355-0306/

In this paper, we present a comprehensive methodology that integrates stable and radiogenic isotope analyses on teeth and bone samples of an unidentified individual that was part of a forensic human identification project lead by the Cold Case and Review Team of the Amsterdam-Amstelland Police in The Netherlands. The aim of this project was to apply newly available forensic techniques, including multi-isotope analysis, to determine the place of origin and last place of residence to a number of unidentified individuals found deceased in the Amsterdam area between 10 and 20 years ago. A number of exhumations were carried out in the Sint Barbara cemetery in Amsterdam between September of 2010 and July of 2011. Teeth, bone, hair and nail samples were obtained from the individual remains for multi-isotope analysis and other forensic investigations. The case discussed here was from a number of cases (n = 12) where the multi-isotope method was applied as part of the large identification project. This case is examined in detail because the individual was identified after the isotope study was completed. Therefore this case can potentially be used as validation of the multi-isotope method.

2. Information about the case

A deceased male was found in the water at the "IJ" Ruyterkade in Amsterdam, The Netherlands, in March of 1999. Drowning was established to be the cause of death. The estimated age of the victim was between 39 and 42 years of age, according to the information provided when the case request was submitted for human provenancing investigations. The individual was identified at the beginning of 2013, however his identity remained undisclosed to the isotope investigators until the isotope study was completed and reported. Then, the real age of the individual was found to be 23 years at the time of death. The interpretations of the isotope signatures in the individual's teeth and bone were based, however, on the estimated age provided to the isotope investigators when the study was requested.

3. Samples

3.1. Samples from the victim

The samples available for this study were a mandibular canine and third molar teeth, a ~4 cm piece of femur bone sampled from the middle part of the shaft and a ~5 cm central piece of rib bone (Table 1).

3.2. Sample from The Netherlands: third molars, scalp hair, tap water, soil/street dust

To characterise the isotope signatures of the environment in The Netherlands we have carried out multi-isotope analyses of third molar crown enamel from individuals (n = 30) born and living in The Netherlands. These data are presented here for the first time (Table 2). We have also included average isotope values of scalp hair from non-travelling individuals, tap water and street dust/soil from around The Netherlands (Table 2). These average isotope compositions were initially presented in Font et al. [13]. However, the number of samples of our database has increased and updated average values are reported in this study (Table 2).

4. Analytical methods

4.1. Sample preparation and chemistry procedures for Sr and Pb isotope analysis

4.1.1. Teeth

The crown was cut from the root using a diamond coated disc attached to a drilling tool (Dremel). The crown was rinsed with ultrapure water (Milli-Q water) and immersed in ultrapure H_2O_2 31% (Merck) in a pre-cleaned 50 mL centrifuge tube for 12 h to remove organics and impurities. Subsequently the crown was rinsed and sonicated with Milli-Q water three times and dried down on a hot plate at 80 °C. Enamel powder was extracted from the clean crown by drilling, using a diamond coated drill bit. The most external surface of the enamel was first mechanically removed with a diamond coated drill and discarded. Tooth enamel powder (14 mg canine and 58 mg third molar) was weighed into pre-cleaned Teflon beakers and left to dissolve in 2 mL of 14 N HNO_3 for 12 h on the hot plate at 110 °C. The sample solutions were dried down on the hot plate at 100 °C. After complete dryness, the samples were dissolved with 1 mL 3 N HNO_3. This solution was used to separate the Sr and Pb fractions for isotope ratio analysis following a low-blank chromatographic column chemistry procedure using Sr spec resin [13]. The acids used during the chemistry procedures were purified by sub-boiling distillation (HNO_3 in Teflon; HCl in quartz) from initial pro analysis grade acids (Sigma-Aldrich and Romil). The water used throughout this study for sample treatment and acid dilution is ultrapure water obtained from a Milli-Q Element system (Millipore; resistivity >18 MΩ at 25 °C).

4.1.2. Bone

The pieces of bone samples were initially rinsed with Milli-Q water and ethanol and were sonicated several times until the Milli-Q water remained clear. The femur bone sample from the compact section was extracted by drilling with a diamond coated drill bit. Rib bone was also drilled in the same manner, but the most external layer of the bone was mechanically removed with a diamond coated drill and subsequently discarded to obtain a clean sample. Approximately 50 mg of drilled bone powder was weighed and placed into a centrifuge tube. A total amount of 4 mL of chloroform:methanol (2:1) mixture was added and the mixture placed onto a rocker bed for 30 min to de-fat the bone sample. After incubation the samples were centrifuged and rinsed in Milli-Q water three times in three separate steps with centrifugation in between. The de-fatted bone sample was then transferred into a pre-cleaned Teflon beaker for dissolution. The bone samples were dissolved in 4 mL of 14 N HNO_3 on the hot plate at 110 °C. After dissolution the samples were dried down on the hot plate at 110 °C and subsequently dissolved in 3 N HNO_3. The same low-blank chromatographic column chemistry procedure for Sr and Pb separation was followed as described in Section 4.1.1.

4.2. $^{87}Sr/^{86}Sr$ isotope analysis

Sr isotopes were measured on the Triton-plus Thermo Finnigan Thermal Ionisation Mass Spectrometer (TIMS) instrument at the Vrije Universiteit Amsterdam. The Sr fractions were loaded onto Re filaments using a TaF_5 activator to enhance ionisation. The $^{87}Sr/^{86}Sr$ were

Table 1
Sr and Pb isotope ratios and $\delta^{18}O_{VPDB}$ values (‰) in tooth enamel and bone bio-apatite from the victim. Errors are (2SE).

Sample	$\delta^{18}O$ (±1σ)	$^{87}Sr/^{86}Sr$ (2SE)	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Mandibular canine	−6.64 ± 0.04	0.708865 ± 6	38.093 ± 2	15.606 ± 1	18.1339 ± 6	1.16200 ± 5	2.44097 ± 2
Mandibular third molar	−6.87 ± 0.08	0.708913 ± 5	38.109 ± 2	15.600 ± 1	18.1827 ± 5	1.16566 ± 4	2.44285 ± 2
Femur bone (external part)	n.a.	0.709194 ± 6	38.1673 ± 8	15.6098 ± 8	18.2503 ± 3	1.16916 ± 3	2.44509 ± 2
Femur bone (internal part)	n.a.	0.709212 ± 5	38.1696 ± 8	15.6085 ± 6	18.2495 ± 3	1.16920 ± 3	2.44543 ± 2
Rib bone	n.a.	0.709454 ± 6	38.1142 ± 9	15.6099 ± 6	18.1886 ± 4	1.16519 ± 3	2.44166 ± 2

n.a., not analysed.

Table 2
Average Sr and Pb isotope ratios and $\delta^{18}O_{VPDB}$ values (‰) of third molar enamel (3M) from individuals born and living in The Netherlands (collected in 2010), scalp hair, tap water and soils/street dust (collected 2008–2012) from The Netherlands. Errors are 2 SE. Gender: male (M), female (F) and age in years.

Sample	Gender/age	City	$\delta^{18}O$ (±1σ)	$^{87}Sr/^{86}Sr$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
3M enamel									
1	M/24	Dordrecht	−5.31 ± 0.03	0.709611 ± 9	37.9626 ± 13	15.6094 ± 8	18.0329 ± 5	1.1553 ± 1	2.43201 ± 3
2	F/28	Nootdorp	−4.65 ± 0.02	0.709340 ± 6	37.9029 ± 10	15.6037 ± 10	18.0182 ± 4	1.1547 ± 1	2.42906 ± 2
3	F/20	Maarssen	−5.06 ± 0.07	0.708951 ± 6	38.0090 ± 15	15.6172 ± 10	18.1328 ± 6	1.1611 ± 1	2.43375 ± 3
4	F/23	Dordrecht	−4.99 ± 0.15	0.709644 ± 5	37.9190 ± 10	15.6029 ± 8	18.0329 ± 4	1.1557 ± 1	2.43023 ± 2
5	M/27	Heerlen	−4.85 ± 0.38	0.708469 ± 6	37.9227 ± 11	15.6038 ± 6	18.0516 ± 4	1.1569 ± 1	2.43032 ± 2
6	M/32	Amsterdam	−5.51 ± 0.08	0.709322 ± 5	37.8416 ± 9	15.5953 ± 9	17.9398 ± 4	1.1503 ± 1	2.42643 ± 2
7	F/30	Maastricht	−4.78 ± 0.01	0.709382 ± 6	–	–	–	1.1561 ± 1	2.43240 ± 6
8	F/25	Bunnik	−4.93 ± 0.05	0.709570 ± 5	–	–	–	–	–
9	F/23	Amstelveen	−4.83 ± 0.15	0.709231 ± 4	–	–	–	–	–
10	M/34	Hoorn	−5.13 ± 0.02	0.709315 ± 6	–	–	–	–	–
11	F/20	Hoofddorp	−5.06 ± 0.05	0.709317 ± 4	37.9529 ± 24	15.6091 ± 25	18.0977 ± 7	1.1594 ± 1	2.43130 ± 7
12	M/30	Alkemade	−6.40 ± 0.71	0.709267 ± 5	37.8348 ± 8	15.5958 ± 5	17.9329 ± 3	1.1499 ± 1	2.42593 ± 2
13	M/33	Amsterdam	−4.71 ± 0.08	0.709402 ± 5	37.8161 ± 8	15.5905 ± 6	17.9241 ± 3	1.1497 ± 1	2.42551 ± 2
14	M/27	Zwijndrecht	−5.88 ± 0.22	0.709153 ± 6	–	–	–	–	–
15	F/18	Amsterdam	−5.85 ± 0.15	0.709441 ± 4	37.7724 ± 11	15.5797 ± 6	17.8547 ± 4	1.1460 ± 1	2.42443 ± 2
16	F/26	Almelo	−5.21 ± 0.22	0.709674 ± 8	37.9606 ± 13	15.6104 ± 8	18.0527 ± 5	1.1565 ± 1	2.43175 ± 3
17	M/56	Amsterdam	−5.01 ± 0.07	0.709135 ± 6	37.8517 ± 9	15.5856 ± 6	17.9139 ± 3	1.1494 ± 1	2.42859 ± 2
18	F/21	Amsterdam	−5.70 ± 0.02	0.709584 ± 6	37.9177 ± 11	15.6049 ± 5	18.0381 ± 4	1.1559 ± 1	2.42982 ± 2
19	M/21	Utrecht	−5.09 ± 0.06	0.709273 ± 6	37.9519 ± 13	15.6108 ± 9	18.0596 ± 5	1.1569 ± 1	2.43110 ± 3
20	F/38	Amsterdam	−5.17 ± 0.09	0.709267 ± 7	–	–	–		
21	F/25	Amsterdam	−5.46 ± 0.07	0.708991 ± 7	–	–	–		
22	F/19	Amsterdam	−5.92 ± 0.08	0.709214 ± 6	37.9830 ± 20	15.6099 ± 13	18.0619 ± 6	1.1573 ± 1	2.43371 ± 4
23	F18	Amsterdam	−4.81 ± 0.01	0.709301 ± 8	37.9924 ± 12	15.6141 ± 8	18.0745 ± 5	1.1576 ± 1	2.43323 ± 2
24	F/32	Amsterdam	−5.11 ± 0.07	0.709378 ± 7	37.9755 ± 11	15.6089 ± 6	18.0813 ± 5	1.1584 ± 1	2.43290 ± 3
25	F/18	Amsterdam	−5.35 ± 0.12	0.709430 ± 5	37.9952 ± 16	15.6132 ± 15	18.0888 ± 6	1.1586 ± 1	2.43357 ± 4
26	F/28	Leeuwarden	−5.03 ± 0.11	0.709678 ± 7	38.0339 ± 11	15.6098 ± 7	18.1188 ± 5	1.1607 ± 1	2.43650 ± 2
27	F/27	Zaandam	−4.58 ± 0.33	0.709409 ± 8	37.9963 ± 34	15.6039 ± 33	18.1062 ± 12	1.1604 ± 1	2.43529 ± 4
28	M/27	Amsterdam	−4.86 ± 0.08	0.709279 ± 5	37.9423 ± 11	15.6056 ± 8	18.0437 ± 4	1.1562 ± 1	2.43131 ± 2
29	F/28	Amsterdam	−5.11 ± 0.30	0.709083 ± 6	37.9691 ± 12	15.6007 ± 7	18.0324 ± 4	1.1559 ± 1	2.43377 ± 3
30	F/28	Edam	−5.18 ± 0.15	0.709145 ± 7	37.9421 ± 12	15.6032 ± 6	18.0579 ± 4	1.1573 ± 1	2.43166 ± 3
Average scalp hair (n = 30), (2σ)			n.a.	0.708899 ± 232	37.7877 ± 0.3917	15.5961 ± 0.0792	17.9062 ± 0.3138	1.1484 ± 0.0173	2.4229 ± 0.0183
Average tap water (n = 17), (2σ)			−6.98 ± 2.23	0.709068 ± 913	37.7684 ± 0.3022	15.5581 ± 0.0507	17.9174 ± 0.2365	1.1517 ± 0.0114	2.4174 ± 0.0109
Average soils/street dust (n = 9),(2σ)			n.a.	0.708961 ± 489	37.9790 ± 0.1871	15.6044 ± 0.0165	18.0540 ± 0.2079	1.1568 ± 0.0090	2.4339 ± 0.0143

(–) Analysis failed; (n.a) not analysed.

measured using a static multi-collection routine. An analysis consisted of 15 blocks of 10 cycles with an integration time of 8.1 s per cycle. The $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ were corrected for mass fractionation using an exponential law and $^{86}Sr/^{88}S$ ratio of 0.1194. Analyses of international standard NBS987 on load sizes of 100 ng were carried out to monitor the system's performance. The long term 100 ng average $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ for the NBS987 measurements were 0.710242 ± 0.000008 (2 SD) (n = 36) and 0.0564919 ± 0.000004 (n = 36). The analytical uncertainty of the standards is 0.0010% (2σ). See more details about the analytical method in Font et al. [13].

4.3. Pb isotope analysis

Pb isotope ratios were analysed on a Neptune Thermo Finnigan Multicollector ICP-MS (MC-ICPMS) instrument at the Vrije Universiteit Amsterdam. The samples were measured using a standard-sample bracketing method [14,15] in a static multi-collection routine. NBS SRM-981 standard was used for bracketing and an in-house standard Pb solution (100 ppb CPI International) was used to check instrument performance during Pb isotope analysis. Standards were measured in 100 ppb solutions and the NBS SRM-981 standard values used are after Baker et al. [16]. Sample Pb concentrations typically were ≤100 ppb. The long term average ratios (2011–2012) and precision of the in-house Pb standards analysed during this study are: $^{208}Pb/^{204}Pb$ = 16.38950 ± 0.008 (2σ), $^{207}Pb/^{204}Pb$ = 15.48775 ± 0.004 (2σ), $^{206}Pb/^{204}Pb$ = 36.14369 ± 0.004 (2σ), $^{206}Pb/^{207}Pb$ = 1.05821 ± 0.0001 (2σ), $^{208}Pb/^{206}Pb$ = 2.20527 ± 0.0002 (2σ). Instrument blanks were analysed before and after each standard and sample and the average of these two measurements was subtracted from each cycle before calculation of the Pb isotope ratios. Instrumental blanks were always <5 mV for ^{208}Pb. Samples were introduced into the MC–ICP-MS using a Cetac Aridus I desolvating nebuliser. The wash out time between analyses was 3 min and the uptake time was 1 min. A total of 5 blocks of 20 cycles was measured with an integration time of 4 s per cycle. Levels of ^{201}Hg were monitored during each analysis but the signal was always <0.003 mV and therefore no corrections for ^{204}Hg on ^{204}Pb were applied. A session of Pb isotope measurements consisted typically of 10 samples and 2 in-house standards, 14 NBS SRM-981 standards and 27 blank measurements (≤50 pg Pb). Instrument settings and data acquisition parameters are as in Font et al. [13].

4.4. Oxygen ($\delta^{18}O$) isotope analysis in structural carbonate

Oxygen isotope analyses were carried out on tooth enamel structural carbonate. Tooth enamel powder (1 mg), pre-leached in ultrapure H_2O_2 31% (Merck) to remove organics, was weighed into glass vials sealed with a septum. Each sample was prepared in triplicate. Oxygen isotope analyses were carried out using a Delta plus IRMS with GasBench in the Stable Isotope laboratory at Vrije Universiteit Amsterdam. The samples were placed in a hot block at 45 °C for 24 h after adding 100% H_3PO_4. The measured isotope values are reported as a δ (delta) values in units of per mil (δ [‰] = [($^{18}O/^{16}O_{sample}$) − ($^{18}O/^{16}O_{standard}$) / ($^{18}O/^{16}O_{standard}$)] * 1000) normalised to the PDB scale using an in-house carbonate reference material (VICS) calibrated against NBS19 and LSVEC certified reference materials. The $\delta^{18}O$ values are then converted into the SMOW scale using the published conversion equation of Coplen [17] (SMOW = 1.03091 * $\delta^{18}O_{PDB}$ + 30.91). International standard IAEA-CO1 was used as a control standard to check instrument performance. The

reproducibility of IAEA-CO1 analysed during the analytical session was ±0.16‰ (1σ) for $\delta^{18}O$.

4.5. Carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope analysis of bone collagen

4.5.1. Bone collagen extraction

Femur and rib bone sample powder (~50 mg) was weighed into 2 mL centrifuge tubes. The tubes were filled with a chloroform:methanol (2:1) mixture to de-fat the bone and were subsequently placed onto a rocker bed for 30 min. The sample was then centrifuged and the supernatant removed. The residue was rinsed three times with Milli-Q water and centrifuged between rinses. To remove non-protein base soluble contaminants, 2 mL of 0.1 M NaOH was added to the sample and it was placed on the rocker bed for 20 hour incubation. The supernatant was then decanted and the sample was rinsed three times with Milli-Q water and centrifuged between rinses.

The bio-apatite mineral fraction of the de-fatted bone samples was dissolved by adding 0.6 M HCl at room temperature for one day. When the dissolution was complete, the sample was rinsed three times in Milli-Q water and centrifuged between rinses. To keep the collagen in solution pH = 3 HCl acid was added to each sample. The samples were incubated at 80 °C overnight to gelatinise the collagen fraction. Then, the samples were freeze dried and stored in a desiccator prior to analysis.

4.5.2. $\delta^{13}C$ and $\delta^{15}N$ isotope analysis

The $\delta^{13}C$ and $\delta^{15}N$ isotopes in bone collagen were analysed using an IRMS Delta XP plus mass spectrometer. The collagen samples (~0.5 mg) were placed into tin capsules and loaded into a zero-blank auto-sampler interfaced with a Flash elemental analyser where they were combusted to produce CO_2 and N_2 gases for $\delta^{13}C$ and $\delta^{15}N$ isotope analysis. The resulting gases were chromatographically purified through a GC column and carried to the mass spectrometer with He gas. International standards used for sample calibration for $\delta^{13}C$ isotope analyses were USGS 40 and USGS 41 (L-glutamic acid standards). The analytical uncertainty for the standards was better than 0.15‰. For $\delta^{15}N$ isotope analysis the standards used were N1, IAEA-310(A) and IAEA-NO3. The analytical uncertainty was better than 0.32‰.

5. Results

5.1. Tooth enamel

The tooth enamel $\delta^{18}O_{VPDB}$ values of the canine and third molar samples of the victim are within analytical error (Table 1). The $\delta^{18}O_{VPDB}$ values of the tooth enamel from the victim were compared with $\delta^{18}O_{VPDB}$ values of tooth enamel of third molars from individuals born and currently living in The Netherlands. The samples from the victim have more negative $\delta^{18}O$ values and plot outside the range of third molars from Dutch individuals (Fig. 1a). The $\delta^{18}O_{DW}$ values of drinking water ingested by the individual can be derived from the $\delta^{18}O$ values of tooth enamel based on the direct relationship between the oxygen isotope composition in human body tissues and oxygen isotope composition of ingested water [18–20]. The $\delta^{18}O_{DW}$ values have been calculated using the equation presented by Chenery et al. [21] derived from the Daux et al. [20] equations. The calculated $\delta^{18}O_{DW}$ values for the canine and third molar tooth enamel are −10.35‰ and −10.73‰ respectively. These values are also more negative compared to $\delta^{18}O_{DW}$ values derived from the third molars enamel from Dutch individuals (Fig. 1b, Table 2).

The $^{87}Sr/^{86}Sr$ isotope ratios of tooth enamel from both, canine and third molar are within error and both samples plot within the $^{87}Sr/^{86}Sr$ isotope range of bio-available Sr in The Netherlands (Fig. 2 and Tables 1 and 2). The $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of the mandibular canine from the victim are comparable to the most radiogenic values recorded by third molars from Dutch individuals (Fig. 3 and Tables 1 and 2). However, the third molar from the victim

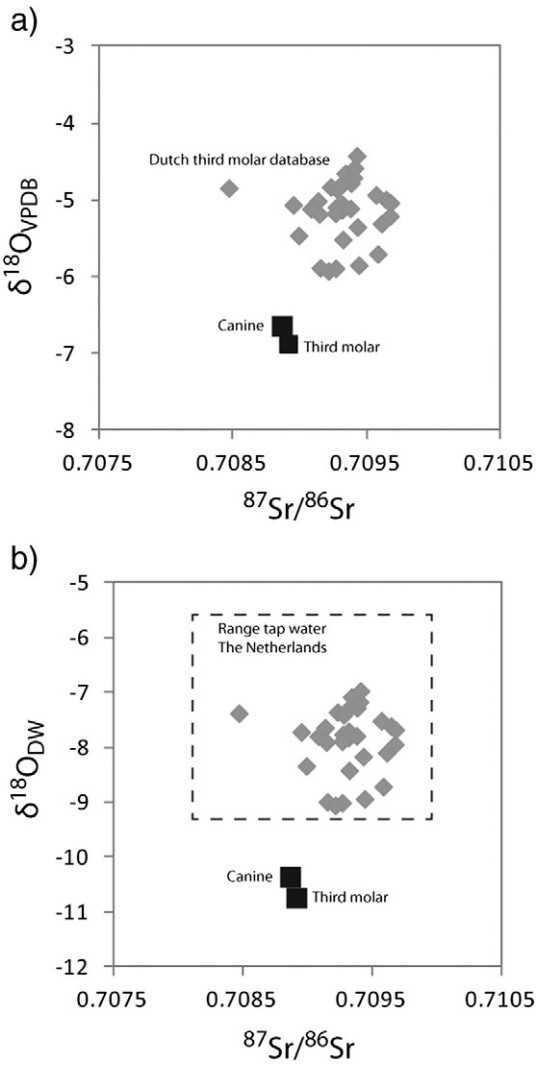

Fig. 1. a) $\delta^{18}O_{VPDB}$ (‰) vs $^{87}Sr/^{86}Sr$ in canine and third molar enamel carbonate from the victim and from third molars of Dutch individuals born and living in The Netherlands (n = 30). b) Inferred $\delta^{18}O_{DW}$ drinking water values vs $^{87}Sr/^{86}Sr$ in canine and third molar enamel carbonate from the victim and from third molars of Dutch individuals as for figure a). The $\delta^{18}O_W$ (‰) and $^{87}Sr/^{86}Sr$ range of tap water in The Netherlands is marked by a dashed line box. The error bars are the analytical uncertainty which for $^{87}Sr/^{86}Sr$ is 0.0010% (2σ) and for $\delta^{18}O_{DW}$ is 1‰ (1σ).

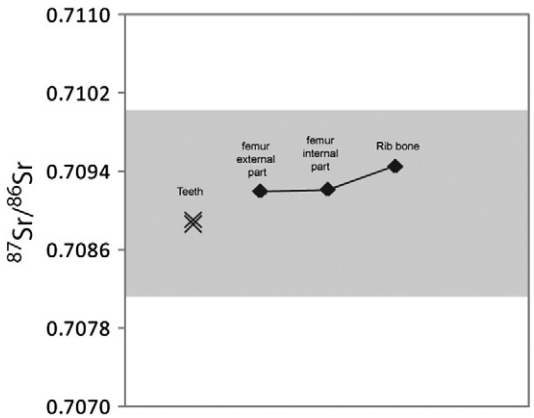

Fig. 2. $^{87}Sr/^{86}Sr$ isotope ratios of canine and third molar tooth enamel and of rib and femur (external and internal parts) bone bio-apatite. The grey box represents the $^{87}Sr/^{86}Sr$ isotope range of the bio-available Sr in The Netherlands determined by human scalp hair and third molar tooth enamel from modern Dutch individuals born and living in The Netherlands, tap water and soils/street dust.

plot outside the range defined by Dutch individuals in our database and overlap with the $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of teeth from Bulgaria and Poland [22,23] (Fig. 3). The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios of the canine and third molar of the victim plot along a possible mixing line between Pb ore deposits from Poland, Bulgaria and Romania and Pb ore deposits from Siberia, Australia and Canada [24–28]. These Pb isotope ratios also overlap with the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ field of Pb ore deposits in west-central Europe and east Russia and Kazakhstan (Fig. 4).

5.2. Bone bio-apatite

The $^{87}Sr/^{86}Sr$ ratios of femur and rib bone from the victim are within the Sr isotope range of the environment in The Netherlands (Fig. 2). They are, however, outside analytical error compared to the $^{87}Sr/^{86}Sr$ ratios recorded in tooth enamel from the victim, for both, canine and third molar. The $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of rib bone overlap with the $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of the third molar from the victim (Fig. 3). The $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of the compact femur bone are outside error of the range defined by the canine and third molar and rib bone (Fig. 3). The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios of femur and rib bone overlap with the canine and third molar $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios and plot along the same mixing line in Fig. 4.

5.3. Bone collagen

The C/N ratios in femur and rib bone collagen samples are ~3.2. The $\delta^{13}C$ and $\delta^{15}N$ values analysed in femur and rib bone collagen of the victim yielded $\delta^{13}C$ values between ~−20.5‰ and −22.5‰ respectively and $\delta^{15}N$ values between 10.4‰ and 10.6‰ (Table 3 and Fig. 5).

6. Interpretation

In this section we discuss the isotopic data for the different tissue types on the basis of the different isotope systems.

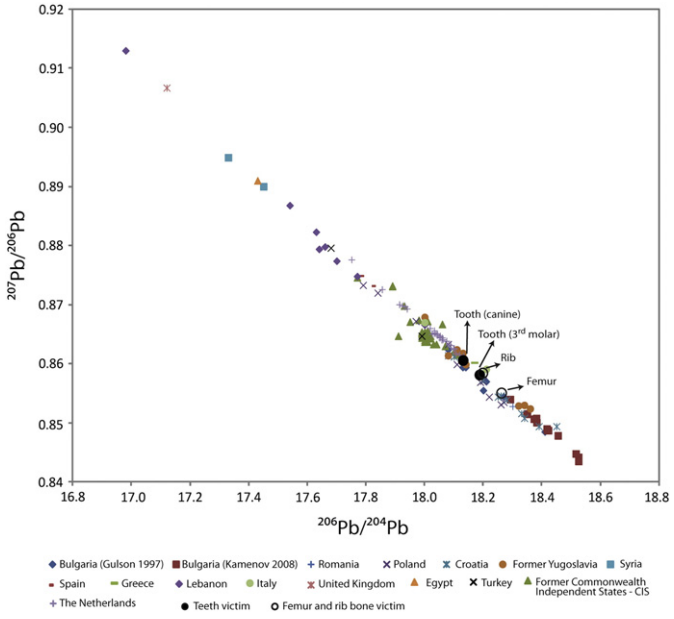

Fig. 3. $^{207}Pb/^{206}Pb$ vs $^{206}Pb/^{204}Pb$ isotope ratios of canine and third molar tooth enamel from the victim. The error of the measurements and external reproducibility are smaller than the symbols. $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of crown tooth enamel of modern individuals from Europe, parts of Asia and Africa from Gulson et al. [22]. $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios from crown tooth enamel of modern individuals from Bulgaria from Kamenov [23]; and $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios of third molar crown tooth enamel of modern individuals from The Netherlands part of this study.

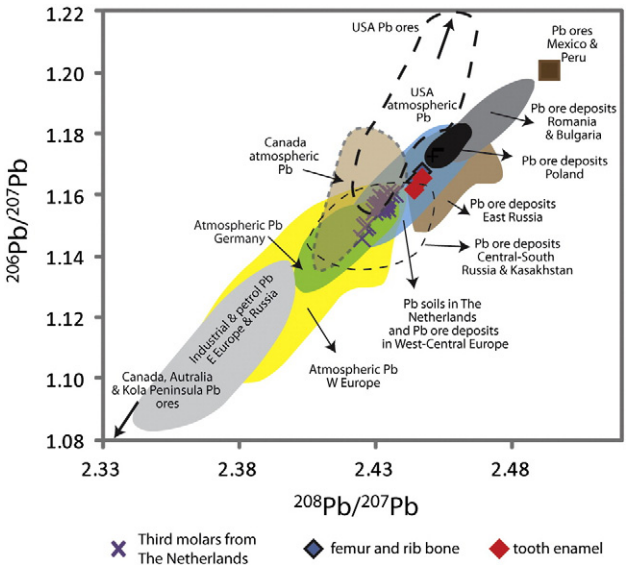

Fig. 4. $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ ratios of canine and third molar tooth enamel and rib and femur bone from the victim. The error of the measurements and external reproducibility are smaller than the symbols. $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ ratios of atmospheric Pb, industrial and petrol Pb and Pb ore deposits from Mukai et al. [24], Tomassini et al. [26], Sangster et al. [25], Large et al. [27], Zartman et al. [28] Bollhofer and Rosman [58,65]. $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ ratios from soils in The Netherlands from Hagens et al. [73]. $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ isotope ratios from third molars from Dutch individuals are from this study.

6.1. $\delta^{13}C$ and $\delta^{15}N$ values

The $\delta^{13}C$ and $\delta^{15}N$ values in bone collagen provide information about the integrated dietary habits of an individual over time periods ranging from recent years to throughout their lifetime depending on the bone turnover time. The C/N ratios of bone collagen are determined along with $\delta^{13}C$ and $\delta^{15}N$ values as this ratio provides an indication of the state of preservation of bone collagen. The accepted C/N range of well-preserved bone collagen is 2.9–3.6 [29]. In this case, the C/N ratios of femur and rib bone collagen of the individual are ~3.2, indicating good preservation of the bone. The $\delta^{13}C$ values of both, femur and rib bone collagen suggests the individual ingested a diet dominated by C3 plants and the $\delta^{15}N$ values suggests ingestion of an omnivore diet rich in animal protein [30–34]. The collagen $\delta^{13}C$ and $\delta^{15}N$ values are compared to $\delta^{13}C$ and $\delta^{15}N$ values of modern hair from Europe and USA in Fig. 5 [36]. An offset of ~1‰ has to be considered when comparing collagen $\delta^{13}C$ and $\delta^{15}N$ values with hair $\delta^{13}C$ and $\delta^{15}N$ values due to fractionation effects occurring in the human body between food protein source and human tissues [32,35]. A C3 plant diet consumer is typical for example in Europe in contrast with most of North and South America and parts of Africa where diet is influenced by C4 plants (i.e., wheat vs. corn) [32,36–39]. These data suggest that the individual did not originate from a region where C4 plant rich diet dominates. Therefore, we decided to initially focus the investigation in Europe and adjacent regions. If additional intelligence information were to become available suggesting a non European origin, then we would have to consider other regions in the world (e.g. Asia).

Table 3
$\delta^{13}C_{VPDB}$ and $\delta^{15}N_{AIR}$ values of bone collagen samples.

Sample	$\delta^{13}C_{VPDB}$	$\delta^{15}N_{AIR}$
Rib bone	−22.52 ± 0.89	10.46 ± 0.05
Femur bone (external part)	−20.48 ± 0.03	10.54 ± 0.17
Femur bone (internal part)	−21.98 ± 0.66	10.79 ± 0.10

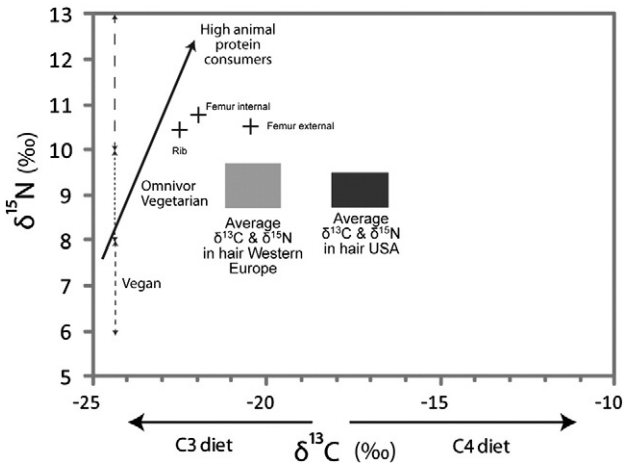

Fig. 5. $\delta^{13}C$ and $\delta^{15}N$ values of femur (external and internal part) and rib bone collagen of the victim. The grey and black box show the $\delta^{13}C$ and $\delta^{15}N$ range of modern human scalp hair in western Europe and USA for comparison [33-36]. An offset of ~1‰ in $\delta^{13}C$ between bone collagen and hair needs to be taken into account when comparing the $\delta^{13}C$ values.

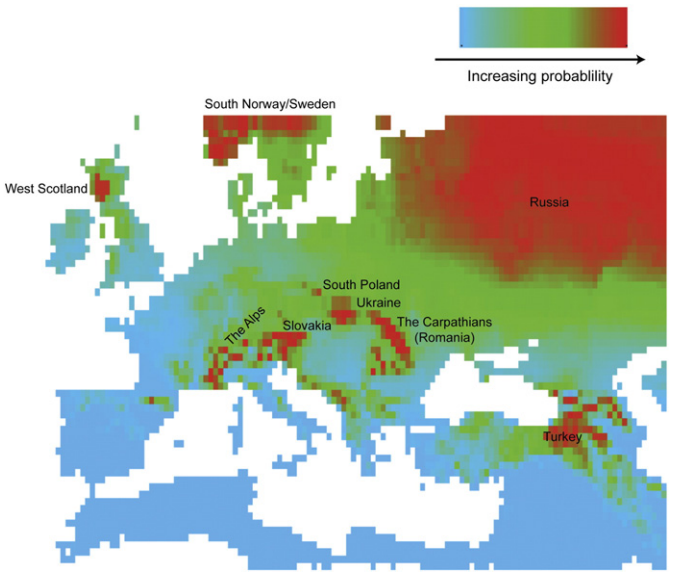

Fig. 6. Assignment map of most probable regions of provenance (red) in the larger Europe. This map is based on the $\delta^{18}O$ values in the canine tooth of the victim and derived $\delta^{18}O_{Dw}$ values of ingested water. The $\delta^{18}O_{Dw}$ calculated value is used to model the most likely regions of provenance [44] using a precipitation $\delta^{18}O$ model [42,43] taking into account precipitation data between 1960 and 2000 with a standard deviation of 1‰. The colour scale varies from regions where the isotopic values are indistinguishable from measured values (red) to regions that have progressively more distinct isotopic values (green to blue). This map is calculated using Isomap.org program [40].

6.2. $\delta^{18}O$ values

Generally, isotope analysis in crown tooth enamel provides information on the isotope composition of the diet and the environment that the individual was exposed to during early childhood and adolescence. For this study, crowns of the mandibular canine and third molar were available, which are fully mineralised at the age of 6–7 years and 12–16 years respectively. The $\delta^{18}O$ values in teeth are interpreted to reflect the $\delta^{18}O_{DW}$ of ingested water. It is commonly assumed that ingested water is dominated by meteoric input [18–20]. Following this approach it is possible to assess which parts of the world are compatible with the $\delta^{18}O_{DW}$ calculated values derived from the $\delta^{18}O$ values of the teeth of the victim (Fig. 6). The meteoric water from the teeth has more negative $\delta^{18}O$ values than precipitation in the Netherlands and is consistent with a less maritime and colder climate. Fig. 6 is an illustration of the most probable regions of origin in Europe and includes: the south of Poland in the border region with Slovakia, the Carpathian Mountains (Romania, Slovakia and Ukraine), the Alps (Italy, Switzerland and Austria), Russia, Turkey, south of Norway and south Sweden and east Scotland. This assessment has been carried out using the Isomap program (http://isomap.org) [40,41] by developing an $\delta^{18}O_W$ isoscape map of the larger Europe [42] based on a precipitation model [43] and an assignment model based on the inferred $\delta^{18}O_{DW}$ values of the canine tooth [44]. Assuming that $\delta^{18}O_{DW}$ of ingested water is mostly dominated by meteoric input is a relatively simplistic approach and does not take into account the large scale movement of water in rivers and ancient underground reservoirs [2]. However, it gives an indication that the victim was highly unlikely to have lived in The Netherlands during his childhood and adolescence years and he probably lived in a region dominated by a colder climate less influenced by proximity to the sea.

6.3. $^{87}Sr/^{86}Sr$ isotope ratios

Sr isotope ratios undergo no isotopic fractionation within the body [45] unlike light stable isotopes. The $^{87}Sr/^{86}Sr$ ratios of the teeth are interpreted to reflect the integrated composition of the bio-available Sr in the environment during the period of tooth mineralisation. The Sr isotope ratios recorded in the tooth enamel of the individual suggest, however, similarities with the Sr isotope signatures of the bio-available Sr in The Netherlands (~0.709). The fact that the Sr isotope ratios of the canine and third molar tooth enamel are within error, suggests that the individual did not move during his childhood and adolescence. The Sr isotope ratios in femur bone and rib are more radiogenic (0.7091–0.7094) compared to tooth enamel. The Sr isotope ratios of the teeth (~0.7089) are typical of environments dominated by coastal and deltaic sediments, such as found in The Netherlands, south of the UK and other parts of north west Europe (i.e., mixed river derived sands, clays and old marine limestone). Similar Sr isotope ratios are recorded in many parts of the Earth. The more radiogenic Sr isotope ratios in bones suggest that the individual moved to a region that is compatible with an environment characterised by aeolian sands and loess, and mixed sandstone, shale and conglomerate successions that formed as terrestrial or shallow marine deposits. This type of geology is found in many parts of Earth, as well as in the east and south of the Netherlands and in the foothills of rising mountain chains like, for instance, the Alps. This geology, however, contrasts markedly with the marine sediments found in the west of The Netherlands. The Sr isotope ratios from the tooth enamel and femur–rib of the victim are within the Sr isotope range of third molars from Dutch individuals and the Sr isotope range of the bio-available Sr in The Netherlands. However, these ratios are not particularly diagnostic and Sr isotope ratios used as a single system, without the combination of another isotope system, are not sensitive enough indicators of provenance in this case. However, they can be used to exclude provenance from three geological environments dominated by: a) volcanic regions (~0.703–0.705); b) pre-Cambrian basement rocks or derived sediments (>0.715) and c) purely limestone regions (~0.708). The Sr isotope data therefore helps to exclude some of the areas suggested based only on the inferred drinking water $\delta^{18}O_{DW}$ values, such as: west Scotland (Tertiary volcanic flood basalt region; [46–48]); south of Norway and south Sweden (Pre-Cambrian basement; [49]) and the Alps (metamorphic > 0.710–0.720 [50,51] and calcareous Alps < 0.7089; [52]).

6.4. Pb isotope ratios

In contrast to Sr, bio-available Pb in the environment represents a mixture of Pb derived from both geological and anthropogenic sources. An indication of the present day Pb contribution to European agricultural soil from underlying geology is provided by the study of Reimann et al. [53]. This study demonstrates a clear E–W variation in Pb isotope

ratios in the bulk soils that is predominantly controlled by the variation in the age of the underlying geology. As with Sr, the isotopic composition of the bio-available Pb derived from the bulk soil will not be equal to that of the bulk soil due to preferential breakdown of specific minerals by weathering processes. The exact isotopic compositions of bio-available Pb derived from soils will depend on the mineralogy and maturity of the soil and the prevailing climatic conditions [53–57]. Bio-available Pb in soils, particularly the top soils, will also contain an anthropogenic component ultimately derived from fertilisers and Pb ores from around the world [57]. The ores have specific Pb isotopic signatures determined by the geological age and initial U/Pb and Th/Pb ratios of the source rocks from which ore forming fluids are derived. The effect of mining Pb ores and related smelting and the use of such Pb in industry, combustions of fossil fuels (former use of gasoline, coal) and Pb containing products such as batteries and plastics, has introduced anthropogenic Pb worldwide into the environment [58–60]. Thus, the Pb isotopic signatures of bio-available Pb in the environment record a mixed signal of all Pb sources dominated by pollution related Pb (anthropogenic) and Pb in soils (mostly geological).

Pb isotope analyses in human tissues have been successfully used to study the exposure of humans to particular Pb polluted environments since Pb isotope composition is linked to Pb ore sources [22,61–63]. The use of Pb isotopes as a provenance indicator is successful when isotopic differences between regions are resolvable [63]. Due to globalisation and gradual change of the Pb isotope composition in the environment, the identification of possible geographical areas of human origin are not always possible. Currently, atmospheric Pb is mostly produced by industry, but several decades ago leaded gasoline was a large contributor to atmospheric Pb in Europe and other countries in the world [26,64,65]. Consequently, the Pb isotope ratios of atmospheric pollution vary through time [66]. However, in Europe, there has been east–west variation of atmospheric Pb isotope ratios (Fig. 4). For example, ratios such as $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ were higher in atmospheric Pb in the west than in eastern European countries [26,65]. However, there is an overlap in $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of Pb ores in central Europe and Russia, except for Pb ores in the Koala Peninsula, Russia and Pb ores in Poland, Bulgaria and Romania that are lower and higher respectively compared to most of Pb ores in Central Europe and Russia [24–28]. These regional isotopic differences are due to the different Pb sources used by industry and former use of gasoline.

The Pb isotope ratios from teeth and bones of the victim are compared with Pb isotope signatures from the environment in the 1980s–1990s and more recent times in Figs. 3 and 4. Temporal variations in Pb isotope ratios have been determined in a limited number of isolated locations worldwide [66–73] but regional coverage of Pb isotope variation across Europe over the last 4–5 decades is not known. According to the initial age estimation provided to us, the subject was calculated to be most probably born around 1957–1960. The Pb isotope data in the atmosphere and soils during his childhood (1960s) are not available and, therefore, we based our interpretations on more modern data (1980s–1990s) and the tooth databases that include a limited number of samples from people born in the 1950–1960s. The individual, however, was found to be 23 years of age when he died and therefore, was born in the 1970s. Then, the Pb data used in this study was relevant for the childhood and adolescent time period of the individual. The Pb isotope variations observed in the geology and atmospheric Pb are recorded in human teeth (bio-available Pb) sampled across Europe, but also in parts of Asia and Africa (Fig. 3) [22,23]. These data represents the best currently available record of the bio-available Pb in Europe and other countries several decades ago (between 1940s and 1980s). The databases are of direct use in making comparisons with Pb isotope signatures in femur and rib bone bio-apatite, which provides an integrated signal of environmental Pb isotope composition during the last ~25–30 years of his life for femur bone and the last 4–6 years for rib.

The Pb isotope data from the subject's teeth and bones are comparable with Pb ore deposits from north-west and Central Europe and soils in The Netherlands and also with Pb ores from eastern Russia and parts of central-south Russia and Kazakhstan (Fig. 4). But as explained above Pb isotope ratios of ores and soils are predicted not to be the isotopic ratios of the bio-available Pb. Both teeth and bone samples plot along a mixing line between the Pb isotope ratios of ore deposits in Poland, Bulgaria, Romania (east Europe) and east Russia and atmospheric Pb in Europe and Russia (Fig. 4). This suggests an incorporation of eastern European Pb in the victim's tooth enamel and bone bio-apatite. The teeth and bone of the victim overlap with the range of Pb isotope ratios of teeth from Poland, Romania, former Yugoslavia and Bulgaria (Fig. 3) [22]. The canine teeth have combined $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ ratios at the edge of the Pb isotope range defined by third molar from Dutch individuals (Fig. 3). However, when the data are plotted on a $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ (Fig. 4), the data can be seen to be distinct from that of the Netherlands tooth database. The tooth Pb data therefore, imply that the subject was not born and raised in The Netherlands. The similarity in the combined Sr and Pb isotope ratios and $\delta^{18}O$ values of teeth and bone suggest that the subject was not very mobile during the majority of his lifetime. Initially, this conclusion was based considering the estimated age of 39–42 years. However, this also applies for the real age of the individual.

7. Conclusions: integration of all isotopic systems

Based on the combination of $\delta^{18}O$ values and Sr isotope ratios, it is possible to eliminate regions with extreme isotopic values such as The Netherlands, west Scotland, south of Norway and Sweden, the Alps, Russia and Turkey as the possible area of birth and childhood. The Pb isotope signatures of teeth rule out childhood in regions such as Belarus and south-west Russia (former Commonwealth of Independent States — CIS) and east of Turkey and Georgia (if we assume a similar Pb isotope composition as for CIS states). The Pb isotope composition of tooth enamel from the Balkan regions, such as former Yugoslavia and Bulgaria are compatible with the victim's teeth and bone, but can be excluded since the $\delta^{18}O_{DW}$ values derived from the teeth of the victim which are incompatible with the $\delta^{18}O$ values of meteoric water from these regions. The Pb isotopes suggest the influence of Pb isotope signals in the individual typical from east Europe and the Balkan region. Therefore, we conclude that the region including south Poland, south-east Slovakia and the region of Ukraine–Romania–Bulgaria, specifically the region associated with the Carpathian Mountains is the most probable place of origin for the unidentified individual. However, due to the complexity of the geology of these areas we are currently unable to pinpoint the precise locations within this region. A detailed study of local drinking water and geology is required to give our conclusion better spatial resolution.

After the multi-isotope study was initiated, the Cold Case and Review Team from the Amsterdam-Amstelland Police informed the isotope investigators that they had made a positive identification of the individual. The identification had been confirmed by DNA analysis. Details of the individual's birth place and mobility were withheld until completion of the multi-isotope study and submission of a detailed report to the Cold Case Team to ensure that the interpretation of the isotopic data could not be influenced by foreknowledge. The individual originated from south-west Poland, where he spent most of his life. The region lies within the area proposed by this study and consequently provides strong validation of the potential power of the combined multi-isotope methodology.

This study illustrates the importance of using multi-isotope systems for human provenance investigations. In many cases the use of single systems, such as Sr isotope ratios in tooth enamel and bone apatite, appear to be insensitive indicator of provenance. However, the combination of $\delta^{18}O$ values and Sr isotope ratios and the combination of different Pb isotope ratios appear to be the most useful parameters for determining the provenance of victims. A major conclusion is that it is essential to have isotope databases available of different environmental

and human tissue samples for comparative purposes as well as the use of existing isotope precipitation data and geological maps.

Acknowledgements

We would like to thank the Cold Case Team from the Amsterdam-Amstelland Police (The Netherlands) for partially funding this study. This research was also partially funded by the Marie Curie Reintegration Grant "IDIS" (FP7-PEOPLE-2009-RG) awarded to Dr. Laura Font. We are very grateful to Jacques A. Baart M.D. and Tymour Forouzanfar M.D. from the Vrije University Amsterdam Medical Center for facilitating the acquisition of third molar samples from Dutch patients for this study. Finally, we would like to thank Anouk Borst for helping with the sample preparation for this study.

References

[1] W. Meier-Augenstein, I. Fraser, Forensic isotope analysis leads to identification of a mutilated murder victim, Sci. Justice 48 (2008) 153–159.
[2] J.R. Ehleringer, A.H. Thompson, D.W. Podlesak, G.J. Bowen, L.A. Chesson, T.E. Cerling, T. Park, P. Dostie, H. Schwarcz, A framework for incorporation of isotopes and isoscapes in geospatial forensic investigations, in: J.B. West, G.J. Bowen, T.E. Dawson, K.P. Tu (Eds.), Isoscapes: Understanding Movement, Pattern and Process on Earth Through Mapping, Springer, New York, 2010, pp. 357–387.
[3] P. Degryse, D. De Muynck, S. Delporte, S. Boven, L. Jadoul, J. De Winne, T. Ivaneanu, F. Vanhaecke, Strontium isotopic analysis as an experimental auxiliary technique in forensic identification of human remains, Anal. Methods 4 (2012) 2674–2679.
[4] G. Eriksson, L. Papmehl-Dufay, K. Lidén, Cultural interaction and change: a multi-isotopic approach to the Neolithization in coastal areas, World Archaeol. 45 (2013) 430–446.
[5] G. Müldner, C. Chenery, H. Eckardt, The 'Headless Romans': multi-isotope investigations of an unusual burial ground from Roman Britain, J. Archaeol. Sci. 38 (2011) 280–290.
[6] W. Müller, H. Fricke, A.N. Halliday, M.T. McCulloch, J. Wartho, Origin and migration of the Alpine Iceman, Science 302 (2003) 862–866.
[7] W. O'Reilly, The 'Adam case', London, in: T. Thompson, S. Black (Eds.), Forensic Human Identification: An Introduction, Taylor & Francis Group, Boca Raton, 2007, pp. 473–484.
[8] C.D. Kennedy, G.J. Bowen, J.R. Ehleringer, Temporal variation of oxygen isotope ratios ($\delta^{18}O$) in drinking water: implications for specifying location of origin with human scalp hair, Forensic Sci. Int. 208 (2011) 156–166.
[9] H.P. Schwarcz, Tracing unidentified skeletons using stable isotopes, Forensic Mag. 4 (2007).
[10] S. Hillson, Dental Antropology, Cambridge University Press, Cambridge, 1996. 373.
[11] A.M. Parfitt, The physiologic and clinical significances of bone histomorphometric data, in: R.R. Recker (Ed.), Bone Histomorphometry: Techniques and Interpretation, CRC Press, Boca Raton, Florida, 1983, pp. 143–223.
[12] T.D. Price, L. Manzanilla, W.D. Middleton, Immigration and the ancient city of Teotihuacan in Mexico: a study using strontium isotope ratios in human bone and teeth, J. Archaeol. Sci. 27 (2000) 903–913.
[13] L. Font, G. van der Peijl, I. van Wetten, P. Vroon, B. van der Wagt, G.R. Davies, Strontium and lead isotope ratios in human hair: investigating a potential tool for determining recent human geographical movements, J. Anal. At. Spectrom. 27 (2012) 719–732.
[14] M. Elburg, P. Vroon, B. van der Wagt, A. Tchalikian, Sr and Pb isotopic composition of five USGS glasses (BHVO-2G, BIR-1G, BCR-2G, TB-1G, NKT-1G), Chem. Geol. 223 (2005) 196–207.
[15] M.F. Thirlwall, Multicollector ICP-MS analysis of Pb isotopes using a ^{207}pb–^{204}pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization, Chem. Geol. 184 (2002) 255–279.
[16] J. Baker, Waight, D. Peate, T. Waight, C. Meyzen, Pb isotopic analysis of standards and samples using a ^{207}Pb–^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC–ICP-MS, Chem. Geol. 211 (2004) 275–303.
[17] T.B. Coplen, Normalization of oxygen and hydrogen isotope data, Chem. Geol. 72 (1988) 293.
[18] A. Longinelli, Oxygen isotopes in mammal bone phosphate: anew tool for paleohydrological and paleoclimatological research? Geochim. Cosmochim. Acta 48 (1984) 385–390.
[19] B. Luz, Y. Kolodny, M. Horowitz, Fractionation of oxygen isotopes between mammalian bone-phosphate and environmental drinking water, Geochim. Cosmochim. Acta 48 (1984) 1689.
[20] V. Daux, C. Le'cuyer, M.A. He'ran, R. Amiot, L. Simon, F. Fourel, F. Martineau, N. Lynnerup, H. Reychler, G. Escarguel, Oxygen isotope fractionation between human phosphate and water revisited, J. Hum. Evol. 55 (2008) 1138–1147.
[21] C.A. Chenery, V. Pashley, A.L. Lamb, H.J. Sloane, J.A. Evans, The oxygen isotope relationship between the phosphate and structural carbonate fractions of human bioapatite, Rapid Commun. Mass Spectrom. 26 (2012) 309–319.
[22] B.L. Gulson, C.W. Jameson, B.R. Gillings, Stable lead isotopes in teeth as indicators of past domicile: a potential new tool in forensics science? J. Forensic Sci. 42 (1997) 787–791.
[23] G.D. Kamenov, High-precision Pb isotopic measurements of teeth and environmental samples from Sofia (Bulgaria): insights for regional lead sources and possible pathways to the human body, Environ. Geol. 55 (2008) 669–680.
[24] H. Mukai, T. Machida, A. Tanaka, Y. Pavel Vera, M. Uematsu, Lead isotope ratios in the urban air of eastern and central Russia, Atmos. Environ. 35 (2001) 2783–2793.
[25] D.F. Sangster, P.M. Outridge, W.J. Davis, Stable lead isotope characteristics of lead ore deposits of environmental significance, Environ. Rev. 8 (2000) 115–147.
[26] S. Tommasini, G.R. Gavies, T. Elliott, Lead isotope composition of tree rings as biogeochemical tracers of heavy metal pollution: a reconnaissance study from Firenze, Italy, Appl. Geochem. 15 (2000) 891–900.
[27] D. Large, R. Schaeffer, A. Hohndorf, Lead isotope data from selected galena occurrences in the North Eifel and North Sauerland, Germany, Miner. Deposita 18 (1983) 235–243.
[28] R.E. Zartman, J. Pawlowska, Z. Rubinowski, Lead isotopic composition of ore deposits from the Silesia–Cracow mining district, Research on the Genesis of Zinc–Lead Deposits of Upper Silesia, Prace Instytutu Geologiczigo, Poland, 1979, pp. 133–151, (TOM XCV).
[29] S.H. Ambrose, Preparation and characterization of bone and tooth collagen for isotopic analysis, J. Archaeol. Sci. 17 (1990) 431–451.
[30] N.J. van der Merwe, J.C. Vogel, 13C content of human collagen as a measure of prehistoric diet in woodland North America, Nature 276 (1978) 815–816.
[31] M.J. De Niro, Postmortem preservation and alteration of in vivo of bone collagen isotope ratios in relation to paleodietary reconstruction, Nature 317 (1985) 806–809.
[32] T.C. O'connell, R.E.M. Hedges, Isotopic comparison of hair and bone: archaeological analysis, J. Archaeol. Sci. 26 (1999) 661–665.
[33] K.J. Petzke, B.T. Fuller, Stable isotopes ratio analysis in human hair, Handbook of Hair in Health and Disease, Human Health Handbooks, no. 1, Wageningen Academic Publishers, 2012, pp. 333–351.
[34] F. Huelsemann, K. Koehler, H. Braun, W. Schaenzer, U. Flenker, Human dietary $\delta^{15}N$ intake: representative data for principal food items, Am. J. Phys. Anthropol. 152 (2013) 58–66.
[35] K.J. Petzke, H. Boeing, C.C. Metges, Choice of dietary protein of vegetarians and omnivores is reflected in their hair protein ^{13}C and ^{15}N abundance, Rapid Commun. Mass Spectrom. 19 (2005) 1392–1400.
[36] L.O. Valenzuela, L.A. Chesson, G.J. Bowen, T.E. Cerling, J.R. Ehleinger, Dietary heterogeneity among western industrialised countries reflected in the stable isotope ratios of human hair, PLoS One 7 (2012) 1–8.
[37] D.A. Schoeller, M. Minagawa, R. Slater, I.R. Kaplan, Stable isotopes of carbon, nitrogen and hydrogen in the contemporary North American human food web, Ecol. Food Nutr. 18 (1986) 159–170.
[38] S.H. Ambrose, M.J. DeNiro, Reconstruction of African human diet using bone collagen carbon and nitrogen isotope ratios, Nature 319 (1986) 321–324.
[39] T.C. O'connell, R.E.M. Hedges, Investigations into the effect of diet on modern human hair isotopic values, Am. J. Phys. Anthropol. 108 (1999) 409–425.
[40] G.J. Bowen, J.B. West, C.C. Miller, L. Zhao, T. Zhang, IsoMAP: Isoscapes Modelling, Analysis and Prediction (version 1.0) The IsoMAP Project, http://isomap.org 2013.
[41] IAEA/WMO, Global network of isotopes in precipitation. The GNIP database, http://www.iaea.org/water 2011.
[42] L. Font, IsoMAP job 20502, isoscapes modelling, analysis and prediction (version 1.0). The IsoMAP Project, http://isomap.org 2013.
[43] L. Font, IsoMAP job 20500, isoscapes modelling, analysis and prediction (version 1.0). The IsoMAP Project, http://isomap.org 2013.
[44] L. Font, IsoMAP job 20506, isoscapes modelling, analysis and prediction (version 1.0). The IsoMAP Project, http://isomap.org 2013.
[45] R.A. Bentley, Strontium isotopes from the Earth to the archaeological skeleton: a review, J. Archaeol. Method Theory 13 (2006) 135–187.
[46] C.H. Emeleus, M.C. Gyopari, British Tertiary Volcanic Province, Geological Conservation Review, Chapman & Hall, London, 1992.
[47] R.N. Thompson, Magmatism of the British Tertiary Volcanic Province, Scot. J. Geol. 18 (1982) 49–107.
[48] L. Font, J.P. Davidson, D.G. Pearson, G.M. Nowell, D. Jerram, C.J. Ottley, J. Petrol. 49 (2008) 1449–1471.
[49] H.K. Brueckner, Interpretation of Rb–Sr ages from the Precambrian and Paleozoic rocks of southern Norway, Am. J. Sci. 272 (1972) 334–358.
[50] J.C. Hunziker, J. Desmons, A.J. Hurford, Thirty-two years of geochronological work in the Central and Western Alps: a review on seven maps, Mém. Géol. (Lausanne) 13 (1992) 1–59.
[51] S. Inger, W. Ramsbotham, Syn-convergent exhumation implied by progressive deformation an metamorphism in the Valle dellÓrco transect, NW Italian Alps, J. Geol. Soc. 154 (1997) 667–677.
[52] G. Faure, R. Assereto, E.L. Tremba, Strontium isotope composition of marine carbonates of Middle Triassic to Early Jurassic age, Lombardic Alps, Italy, Sedimentology 25 (1978) 523–543.
[53] C. Reimann, B. Flem, K. Fabian, M. Birke, A. Ladenberger, P. Négrel, A. Demetriades, J. Hoogewerff, Lead and lead isotopes in agricultural soils of Europe — the continental perspective, Appl. Geochem. 27 (2012) 532–542.
[54] Y. Erel, Y. Harlavan, J.D. Blum, Lead isotope systematics of granitoid weathering, Geochim. Cosmochim. Acta 58 (1994) 5299–5306.
[55] A. Taylor, J.D. Blum, Relation between soil age and silicate weathering rates determined from chemical evolution of a glacial chronosequence, Geology 23 (1995) 979–982.
[56] Y. Harlavan, Y. Erel, J.D. Blum, The coupled release of REE and Pb to the soil labile pool with time by weathering of accessory phases, Wind River Mountains, WY, Geochim. Cosmochim. Acta 73 (2009) 320–336.

[57] S.J.A. Jung, G.R. Davies, G.M. Ganssen, D. Kroon, Stepwise Holocene aridification in NE Africa deduced from dust-borne radiogenic isotope records, Earth Planet. Sci. Lett. 221 (2004) 27–37.
[58] N. Walraven, P.F.M. van Gaans, G. van der Veer, B.J.H. van Os, G. Th. Klaver, S.P. Vriend, J.J. Middelburg, G.R. Davies, Lithologically inherited variation in Pb isotope ratios in sedimentary soils in The Netherlands, Appl. Geochem 37 (2013) 228–241.
[59] M. Komárek, V. Ettler, V. Chrastný, M. Mihaljevič, Lead isotopes in environmental sciences: a review, Environ. Int. 34 (2008) 562–577.
[60] N. Walraven, P.F.M. van Gaans, G. van der Veer, B.J.H. van Os, G. Th. Klaver, S.P. Vriend, J.J. Middelburg, G.R. Davies, Tracing diffuse anthropogenic Pb sources in rural soils by means of Pb isotope analysis, 37 (2013) 242–257.
[61] B. Gulson, Tooth analyses of sources and intensity of lead exposure in children, Environ. Health Perspect. 104 (1996) 306–312.
[62] B. Gulson, K.J. Mizon, J.D. Davis, J.M. Palmer, G. Vimpani, Identification of sources of lead in children in a primary zinc–lead smelter environment, Environ. Health Perspect. 112 (2004) 52–60.
[63] B. Gulson, Stable lead isotopes in environmental health with emphasis on human investigations, Sci. Total Environ. 400 (2008) 75–92.
[64] B. Gulson, K. Mizon, M. Korsch, A. Taylor, Changes in the lead isotopic composition of blood, diet and air in Australia over a decade: globalization and implications for future isotopic studies, Environ. Res. 100 (2006) 130–138.
[65] A. Bollhofer, K.J.R. Rosman, Lead isotopic ratios in European atmospheric aerosols, Phys. Chem. Earth 26 (2001) 835–838.
[66] W. Shotyk, D. Weiss, P.G. Appleby, A.K. Cheburkin, R. Frei, M. Gloor, J.D. Kramers, S. Reese, W.O. Van der Knaap, History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland, Science 281 (1998) 1635–1640.
[67] L.J. Eades, J.G. Farmer, A.B. MacKenzie, A. Kirika, A.E. Bailey-Watts, Stable lead isotopic characterization of the historical record of environmental lead contamination in dated freshwater lake sediment cores from northern and central Scotland, Sci. Total Environ. 292 (2002) 55–67.
[68] K.J.R. Rosman, W. Chisholm, C.F. Boutron, J.P. Candelone, U. Gorlach, Isotopic evidence for the source of lead in Greenland snows since the late 1960s, Nature 362 (1993) 333–335.
[69] H. Shiharata, W. Elias, C.C. Patterson, Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond, Geochim. Cosmochim. Acta 44 (1980) 149–162.
[70] M.A. Vile, R. Kelman Wieder, M. Novák, 200 years of Pb deposition throughout then Czech Republic: patterns and sources, Environ. Sci. Technol. 34 (2000) 12–21.
[71] D. Weiss, W. Shotyk, P.G. Appleby, J.D. Kramers, A.K. Cheburkin, Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources, Environ. Sci. Technol. 33 (1999) 1340–1352.
[72] E.W. Wolff, E.D. Suttie, Antarctic snow record of southern hemisphere lead pollution, Geophys. Res. Lett. 21 (1994) 781–784.
[73] W.I. Hagens, N. Walraven, M. Minekus, R. Havenaar, J.P.A. Lijzen, A.G. Oomen, Relative oral bioavailability of lead from Dutch made grounds, RIVM Report, 2009. (711701086).