Unlocking Teeth

Development and application of isotopic methods for human provenance studies

Esther Plomp-Peterson

Cover: The open access logo (front) and a map of the Netherlands (back), decorated with the schematic image of a human molar.

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VRIJE UNIVERSITEIT

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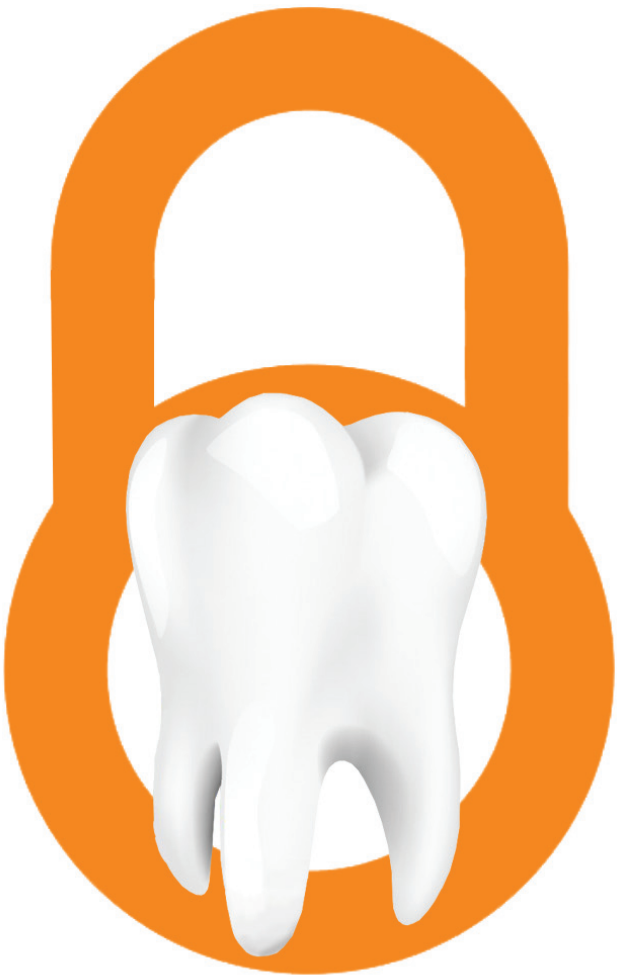

Chapter 1

Scope and Aim

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1.1 Scope of project

This research was conducted as part of the international research project NEXUS1492 (ERC-Synergy) which studied the impacts of the colonial encounters in the Caribbean. NEXUS1492 aimed to characterise the interactions between Amerindians, Europeans and Africans across the Caribbean, after 1492 following the first interactions between the Old and New World. By incorporating techniques from multiple disciplines, across three universities (Leiden University, Vrije Universiteit Amsterdam and University of Konstanz), NEXUS 1492 aimed to evaluate current theoretical frameworks in order to investigate this period in history. The team consisted of scholars from the fields of archaeology, anthropology, bioarchaeology, genetics, physical geography, computer sciences, bio- and geochemistry, and heritage studies. Perhaps more so than in other regions, the Caribbean archaeological record is under threat from natural disasters such as climate change and rising sea levels, earthquakes, volcanic eruptions and hurricanes. Moreover, the archaeological record needs to be protected from looters who illegally trade ancient artefacts as well as from construction development. To prevent further destruction of the archaeological record, the Caribbean's past needs to be put on the heritage agenda in order to increase awareness of the rich Caribbean heritage. Sustainable heritage management strategies were set up by NEXUS1492 in cooperation with local Caribbean experts to create a future for the Caribbean past.

The NEXUS1492 project is divided into four projects:

(1) Transformations of Indigenous Caribbean Cultures and societies across the historical divide *(Leiden University, Principal Investigator: Corinne L. Hofman)*
Project 1 aimed to examine the transformations of indigenous societies in the Caribbean from the pre-colonial to colonial era (AD 1000-1800), through examination of the archaeological record (*Antczak et al. 2018; Hofman et al. 2018; Hofman & Antczak 2019; Hofman & Hoogland 2016, 2018; Hofman & Keehnen 2019; Valcárcel Rojas 2016; Valcárcel Rojas, Laffoon et al. 2019; Valcárcel Rojas, Pérez Iglesias et al. 2019; Weston & Valcárcel Rojas 2016*). The impacts of the arrival of the Europeans on Caribbean populations were poorly studied as it was believed that the Amerindians rapidly declined after the first encounters. This simplistic vision was addressed by analysing the burial practises of the indigenous population (*Mickleburgh et al. 2019*), exchange relationships between Amerindians and Europeans (*Hofman et al. 2014; Laffoon et al. 2014*), and the Amerindian material culture and changing native landscapes (*Castilla-Beltrán et al. 2018; Hooghiemstra et al. 2018; Malatesta & Hofman 2019; Sonnemann et al. 2016; Stancioff et al. 2018*).

By analysing the human skeletal remains and the indigenous burial practices information could be obtained on health and disease patterns, biological and social identities, diet, and physical activity during the contact period (*Ciofalo et al. 2019; Mann et al. 2018; Mickleburgh 2015; Mickleburgh et al. 2019; Mickleburgh & Wescott 2018; Schroeder et al. 2015, 2018; Ziesemer et al. 2015, 2019*). Through the analysis of material culture of the Amerindians, such as ceramics, the impact of European and African contact on Amerindian identity could be studied (*Antczak et al. 2015; Antczak & Antczak 2015; Degryse et al. 2018; Ernst & Hofman 2015; Falci et al. 2019; Schertl et al. 2019; Ting et al. 2016, 2018*). The process of colonisation transformed the native landscapes, which resulted in forced depopulation, dispersal and reformation of Amerindian communities, and the imposition of land use and labour regimes. To study these processes, NEXUS1492 examined Amerindian settlement organisation and patterns, land use and landscape transformations and documented present-day landscape transformations which destroy sites.

(2) Human mobility and the circulation of materials and objects *(Vrije Universiteit Amsterdam, Principal investigator: Gareth R. Davies)*

The research carried out in project 2 focused on the development and application of biogeochemical methods to address human mobility patterns and the circulation of materials and objects across the historical divide. The development of biochemical methods focused on the extraction of strontium, neodymium and lead isotopes in small samples (*Koornneef et al. 2014*) and aimed to test whether provenance information from bone material, usually affected by diagenetic effects, could be obtained (see **Section 3.1**) (*Laffoon, Sonnemann et al. 2018*). Human mobility and diet was studied using a multi-isotope approach employing carbon, nitrogen, oxygen and strontium isotope analysis (*Bataille et al. 2018; Hrnčíř & Laffoon 2019; Laffoon 2016; Laffoon et al. 2016, 2017; Laffoon, Espersen et al. 2018; Mickleburgh & Laffoon 2018; Pestle & Laffoon 2018*) (see **Chapters 6** and **7**). This isotopic repertoire was extended by assessing the application of neodymium isotopes in human dental enamel (*Plomp et al. 2017; Plomp, von Holstein et al. 2019*) (**Chapters 4** and **5**). Human isotopic variation in dental enamel was assessed for established isotopic techniques (oxygen, carbon, and strontium: **Chapter 6**). Pottery, lithic and metal artefacts of both Amerindian and European origin were analysed to study their provenance with the aim to investigate if the utilisation of source areas and materials changed through time. A portable laser sampling system was developed to permit the analysis of rare artefacts in museums that were previously not considered to be suitable for sampling. The optimisation of sampling methods and the decrease of sample sizes opened up new opportunities to study the past.

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(3) Reconstructing archaeological networks and their transformations across the historical divide *(University of Konstanz, Principal Investigator: Ulrik Brandes)*

Project 3 aimed to reconstruct the transformations of archaeological networks of objects, peoples and ideas across the Caribbean in the period AD 1000-1800. This network approach allowed the modelling of relations between past cultures, communities and individuals (*Amati, Lomi et al. 2018; Amati, Munson et al. 2019; Amati, Schönenberger et al. 2019; Brandes 2016; Frank & Shafie 2016; Hart et al. 2016; Mol et al. 2015; Shafie 2016*). New graphical methods were developed to make these relationships more visible (*Amati et al. 2015; Brughmans et al. 2018; Lhuillier et al. 2019; Mumtaz et al. 2019; van Garderen et al. 2017; Weidele et al. 2016*). The archaeological record is difficult to reconstruct using models as it consists of fragmentary data (*Amati, Mol et al. 2019; Amati, Shafie et al. 2018; Habiba et al. 2018*). The Amerindian regional networks in which peoples, goods and ideas were circulated were altered by the interactions with the Europeans and Africans. The project aimed to document how these networks adapted and integrated new networks, using material culture as a proxy. This material culture was related to the production, distribution and consumption of goods and services which were exchanged across the Caribbean. By reconstructing these changing networks NEXUS1492 provided a more nuanced view on dynamics influencing European, African and Amerindian interactions.

(4) A future for diverse Caribbean heritages *(Leiden University, Principal Investigator: Corinne L. Hofman, formerly by the late Willem J.H. Willems)*

Project 4 analysed the uses of the Caribbean past in the present cultural heritage sector and aimed to construct inclusive policies in order to connect indigenous heritage with present-day Caribbean society (*Haviser & Hofman 2015; Hofman et al. 2015; Hofman & Hoogland 2015; Hoogland & Hofman 2015; Jean & Hofman 2018; Strecker 2016; van der Linde & Mans 2015; van Dries et al. 2015*). The project developed practical tools for inclusive heritage management, to address the relationship between local communities and museum collections, and to engage communities through outreach projects, public education and active community participation (*Aguilar et al. 2018; Sankatsing Nava & Hofman 2018*). This approach also addressed issues of cultural ownership and identity of Caribbean communities in order to raise local awareness and understanding of the importance of heritage resources and their protection. To protect the indigenous heritage, the natural and human threats to the archaeological records were addressed in heritage policies. Currently, Caribbean museums often have insufficient financial and legislative support due to the lack of local awareness of the indigenous heritage. The scholars of project 4 and local heritage institutions and communities increased this awareness

by creating a travelling exhibition, Caribbean Ties, that incorporates the indigenous Amerindian past in the Caribbean.

1.2 Isotopic applications to human teeth

As part of NEXUS1492, project 2, this research focused on the development and application of biogeochemical methods, or isotopic analyses, to address past human mobility. Isotopic analysis of human tissues can provide information on three aspects of human behaviour: (1) what the individual consumed; (2) mobility patterns during tissue formation and; (3) how old the remains are. Within archaeology, these applications are used to answer questions on subsistence and mobility strategies (*Laffoon et al. 2014; Liu et al. 2016*), weaning and breastfeeding (*Beaumont et al. 2015; Jay et al. 2008; Jenkins et al. 2001; King et al. 2018; Waters-Rist & Katzenberg 2010*), cultural identity (*Craig-Atkins et al. 2018*), environmental reconstructions (*Beaumont et al. 2013; Montgomery & Jay 2013*), and life history (*Beaumont & Montgomery 2016*). Isotopic analysis can be used for studies at both individual and population level (*Britton 2017*) and is an unique tool in studying individual human behaviour in archaeological populations. In forensic cases, isotopic analyses can be used as a screening tool that may contribute to the identification of an individual (*Bartelink et al. 2016, 2018; Ehleringer et al. 2010; Font et al. 2015; Kramer et al. 2020; Meier-Augenstein 2017*). Forensic isotopic analyses provide information on potential regions of origin (*Chesson, Barnette et al. 2018; Kramer et al. 2020*), diet (*Hatch et al. 2006; Mekota et al. 2006, 2009*), years of birth and death of individuals (thus allowing reconstruction of a post-mortem interval (PMI)) (*Alkass et al. 2013; Cook & MacKenzie 2014; Ubelaker et al. 2006; Wild et al. 2000*), or diagnoses of death in drowning cases (*Azparren et al. 2007*). Forensic application of isotopic analysis is therefore increasingly applied on human tissues (*Bartelink & Chesson 2019; Bell 2009; Font et al. 2015; Hoffmann & Jackson 2015; Matos & Jackson 2019*).

In addressing these questions there are some uncertainties in the interpretations of isotopic results due to several parameters.

(1) Isotopic analyses are limited by sample availability, as not all human tissues can always be used; either these are unavailable or they may be affected by diagenesis (changes in the physical and/or chemical composition of the material). This is particularly problematic in archaeological studies, but can also become ambiguous in forensic studies when remains have been exposed to the environment for years.

(2) Similar isotopic compositions may be the result of multiple causal pathways (equifinality), such as different diets with the same isotopic compositions or different geographic environments that have a similar isotopic signature. In case of mobility studies, the geological

and/or climatic environment has to differ significantly in order to discern that movement took place, which is not always the case (*Bentley 2006; Bowen 2010b; Pederzani & Britton 2019; Slovak & Paytan 2011*). As a result, it is likely that the degree of mobility within a population is underestimated as it is impossible to detect movement between geologically and/or climatically similar regions.

(3) Import of food can affect the isotopic values of humans as the imported food could be grown in isotopically different environments compared to the local environment of an individual (*Bentley 2006; Burton & Wright 1995; Haverkort et al. 2010; Price & Gestsdóttir 2006; Wright 2005*). This could lead to an overestimation of migration as it was the food that moved, rather than humans moving towards the food (*Bowen et al. 2009; Ehleringer et al. 2008; Thompson et al. 2010, 2014*). The import of food may have a limited effect in most archaeological societies, but in the global society we are living in today this likely alters the isotopic signal of individuals living in countries that are heavily reliant on the import of food.

(4) Various socio-political factors play a role in local and global networks and can influence dietary patterns, access to water and the degree of human migration (*Bartelink et al. 2018; Mbeki et al. 2017*), which may not become evident from solely looking at the isotopic results.

(5) Dietary reconstruction from bulk isotopic data can only estimate the type of food that has been consumed (marine versus terrestrial, plant versus animal protein and C3 vs C4 plants) (*Fernandes et al. 2015; Kohn & Cerling 2002; Montgomery & Jay 2013; Roberts et al. 2018*). The application of Bayesian models may allow for a better distinction better between contributions of various types of foods (*Fernandes 2016; Fernandes et al. 2012, 2014, 2015*).

(6) The interpretation of isotopic data requires sufficient background data, or a bioavailable baseline, of the individual or population under study to compare the isotopic values and establish whether an individual derived from the local environment. This baseline may not always be possible to establish due to limited resources available. Furthermore, environmental samples such as soil and water may not directly reflect the biologically available elements consumed by humans (*Maurer et al. 2012; Montgomery & Jay 2013; Snoeck et al. 2020*). Currently, archaeological animal teeth are preferably used as a way to establish the bioavailable baseline (*Kootker, van Lanen et al. 2016*), but this material is not always available. Comparing datasets based on archaeological and modern sample materials may also induce errors, as modern samples are influenced by other factors such as globalisation, fertilisers and changes in precipitation patterns. Only a limited number of isoscapes, graphical displays of spatial variations in isotope landscapes (*West et al. 2006*), have currently been established using human isotopic values (*Keller et al. 2016; Laffoon et al. 2017*), as isoscapes are generally based on water, soil, dust, plants and faunal isotopic values (*Adams et al. 2019; Bataille et al. 2012, 2018;*

Bataille & Bowen 2012; Beard & Johnson 2000; Bentley & Knipper 2005; Bowen 2010a; Bowen & Revenaugh 2003; Bowen & Wilkinson 2002; Brems et al. 2013; Ehleringer et al. 2008, 2010; Evans et al. 2009, 2010, 2012; Giustini et al. 2016; Hoogewerff et al. 2019; Kootker, Mbeki et al. 2016; Ryan et al. 2018; Snoeck et al. 2020; Terzer et al. 2013; Voerkelius et al. 2010; Warner et al. 2018; Wassenaar et al. 2009; West et al. 2014; West et al. 2006; Willmes, Bataille et al. 2018).

(7) The effect of human variation on the isotopic composition of human tissues is not properly addressed (*Wright 2013*). Most isotopic analyses focus on single sample loci isotopic data and assume that the isotopic variation within the dental element is homogeneously enough that the isotopic results are not influenced by the selected sample locations. The isotopic homogeneity of dental elements has therefore not been addressed, which can impact interpretations on changes in the diet and location. Particularly for oxygen, large intra- and inter-individual isotopic variation has been demonstrated (2-3 ‰, *Hakenbeck 2013; Lightfoot & O'Connell 2016; Wright 2013*), which can result in overestimation of migration when a limited amount of individuals of a population are analysed. As isotopic variation is likely to vary between populations, it is crucial that it is better quantified before proposing off-sets for dietary change or migration. The analysis of single loci samples from multiple teeth of the same individual is becoming increasingly more common for strontium isotope analysis, where a minimal offset of ~0.00100 is often applied to indicate migration (*Hrnčíř & Laffoon 2019; Knipper et al. 2014, 2018; Kootker, Mbeki et al. 2016; Price et al. 1998; Scheeres et al. 2013, 2014; Slater et al. 2014*). Nevertheless, it remains unclear how much of this variation is resulting from migration, how much can be attributed to human variation and how this isotopic variation varies in different contexts.

(8) The discipline is further affected by a lack of standardised protocols for terminology, sampling strategies, pre-treatment and quality control, and standardised statistical treatment and graphical presentation (*Pestle et al. 2014; Roberts et al. 2018; Slovak & Paytan 2011; Szpak et al. 2017*). This lack of standardisation complicates the comparison of datasets generated in different labs.

1.3 Aim of the thesis

This thesis developed an isotopic analytical technique to provide additional information to constrain the geographic origin of individuals and critically assessed established techniques to improve the robustness of their application. The work in this thesis focused on the isotopic investigation of dental enamel of third molars from individuals that were born and raised primarily in the Netherlands.

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New Developments

This thesis addressed the potential use of neodymium isotope ratios for human provenancing. The addition of another isotopic system could improve the spatial resolution derived from combined isotopic interpretations, as the information of an additional system provides complementary information to other isotopic systems. The combination of different isotope systems may overcome the limitations that the use of single isotopic systems have and strengthen the confidence in the interpretations (*Bartelink et al. 2016; Font et al. 2015; Knipper et al. 2014; Laffoon et al. 2017; Laffoon, Espersen et al. 2018; Moore et al. 2020; Pederzani & Britton 2019; Royer et al. 2017*). The aim was to assess whether neodymium could be used as a complementary isotopic provenancing system and to gain insights into the mechanisms (e.g., geology) that control the neodymium isotope composition in human tissues. The goal of this thesis was therefore to (1) develop a technique to analyse the low elemental abundance of neodymium in human enamel, (2) assess the geological control in neodymium isotope composition in human enamel, as well as to (3) provide an assessment of the practical use its application in human provenance studies.

Quantifying limitations of current isotopic applications

Existing isotopic techniques are increasingly applied to human remains from archaeological and forensic cases. Fundamental research on the isotopic variability and the impact of sample location in human dental enamel is still lacking, despite considerable geochemical variability in enamel demonstrated by previous studies (*Hare et al. 2011; Smith et al. 2018; Willmes et al. 2016*). As this isotopic variability affects archaeological and forensic interpretations, quantification of the amount of variation that can be expected within a dental element is needed for robust interpretations of changes in geographical location or diet.

This research therefore aims to (1) quantify the degree of isotopic variation within modern human enamel of a third molar; (2) compare this variation to that seen in other third molars of the same individual, (3) establish if there is any spatial control within individual dental elements on the isotopic composition, (4) whether isotopic values of single sample locations are comparable with total bulk isotopic analysis of the same dental element; (5) to establish the effect of an individual's life history (year and region of birth) on their isotopic variation in their teeth; (6) to assess the effects of enamel defects such as caries on the isotopic composition of a dental element. The resulting data can be used to (7) recommend sampling protocols and establish an estimation of the isotopic variation in modern human dental enamel.

1.4 Organisation of the thesis

In **Chapter 2**, a general introduction to isotopic analyses is given. It provides an overview of the current state of the isotopic applications to human dental enamel, with particular attention paid to the isotopic systems employed in this thesis (strontium – Sr, carbon – C, and oxygen – O).

Chapter 3 provides a more detailed overview of the formation and composition of dental enamel, the tissue under study in this thesis. The chapter touches briefly upon bone, and osteocalcin, to address one of the original research questions of the project.

Chapter 4, *TIMS analyses of neodymium isotopes in human tooth enamel using 10^{13} Ω amplifiers*, presents the first application of neodymium isotope composition in human dental enamel. The addition of neodymium isotopes to the human provenancing repertoire would improve our estimations of the geographical location an individual was in when their tissues formed. Neodymium isotope composition analysis was not yet applied to human remains as it is only present in human tissues in very low concentrations (<0.1 ppm), complicating its analysis. This chapter provides an overview of the previous neodymium isotope concentration analyses of human tissues. It includes a detailed description of the method employed to analyse the enamel of the Dutch individuals and serves as a first demonstration of the potential of neodymium isotope composition to provide improved spatial resolution in isotopic interpretations of human provenance.

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Chapter 5, *Evaluation of neodymium isotope analysis of human dental enamel as a provenance indicator using 10^{13} Ω amplifiers (TIMS)*, presents an evaluation of the potential of neodymium isotope analysis to infer human provenance. The study reports results from individuals born and raised in the Netherlands that were analysed for their neodymium concentration and isotope ratios. To infer the geological control on the neodymium isotope composition, coupled neodymium-strontium isotope analysis of the same third molar was employed. To complement the Dutch results, teeth from individuals that grew up in other geological environments were also analysed (Caribbean, Columbia and Iceland). The majority of the individuals (n = 25) had neodymium and strontium isotope composition that was isotopically indistinguishable from

the geological environment in which they grew up while their third molars were formed. The results of five individuals indicated that the neodymium composition of enamel is not solely influenced by the geological environment. In order for neodymium isotopes to be applied to archaeological and forensic case studies, more data is needed from individuals from various geographical areas, with well-defined dietary neodymium isotope data. For now, the technique is only applicable in specific cases where sufficient sample material is present. Ongoing technical developments may enable the analyses of smaller sample sizes and make the technique applicable in forensic and archaeological studies.

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Protocol: dx.doi.org/10.17504/protocols.io.xzmfp46

Chapter 6, *Strontium, oxygen and carbon isotope variation in modern human dental enamel*, provides the first quantified overview of intraindividual isotopic variation in human enamel using thermal ionisation mass spectrometry (TIMS) and isotope ratio mass spectrometry (IRMS) analysis. It furthermore describes the first results of caries and their effect on the isotopic composition of enamel. The strontium, oxygen and carbon isotope analysis from 47 individuals from the Netherlands, the Caribbean, South America, Somalia, and South Africa demonstrated significant variation that exceeded the variation introduced by the analytical error. Dental elements affected by caries showed even more variable results, but there was no indication that the caries incorporated the isotopic composition of the geographical environment in which they developed. This chapter illustrates that quantifying the degree of isotopic variation within individuals of a particular population is essential before interpretations are made on the geographical location or diet of individuals.

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Protocol: dx.doi.org/10.17504/protocols.io.37dgri6

Chapter 7, *Strontium isotopes in modern human dental enamel and tap water from the Netherlands: implications for forensic provenancing*, provides an extensive overview of the modern strontium isotope ratios from Dutch tap water (n = 143) and dental enamel (n = 153). The $^{87}Sr/^{86}Sr$ ratios of tap water were found to be predominantly determined by the underlying bedrock geology. There was no correlation found between Sr ratios of tap water and human enamel $^{87}Sr/^{86}Sr$ ratios. This makes tap water an unsuitable proxy for human strontium values in the Netherlands. A reference dataset consisting preferably of modern human enamel data

from individuals with known provenance must therefore be established before Sr isotope analysis can be successfully applied as a provenance tool in forensic contexts.

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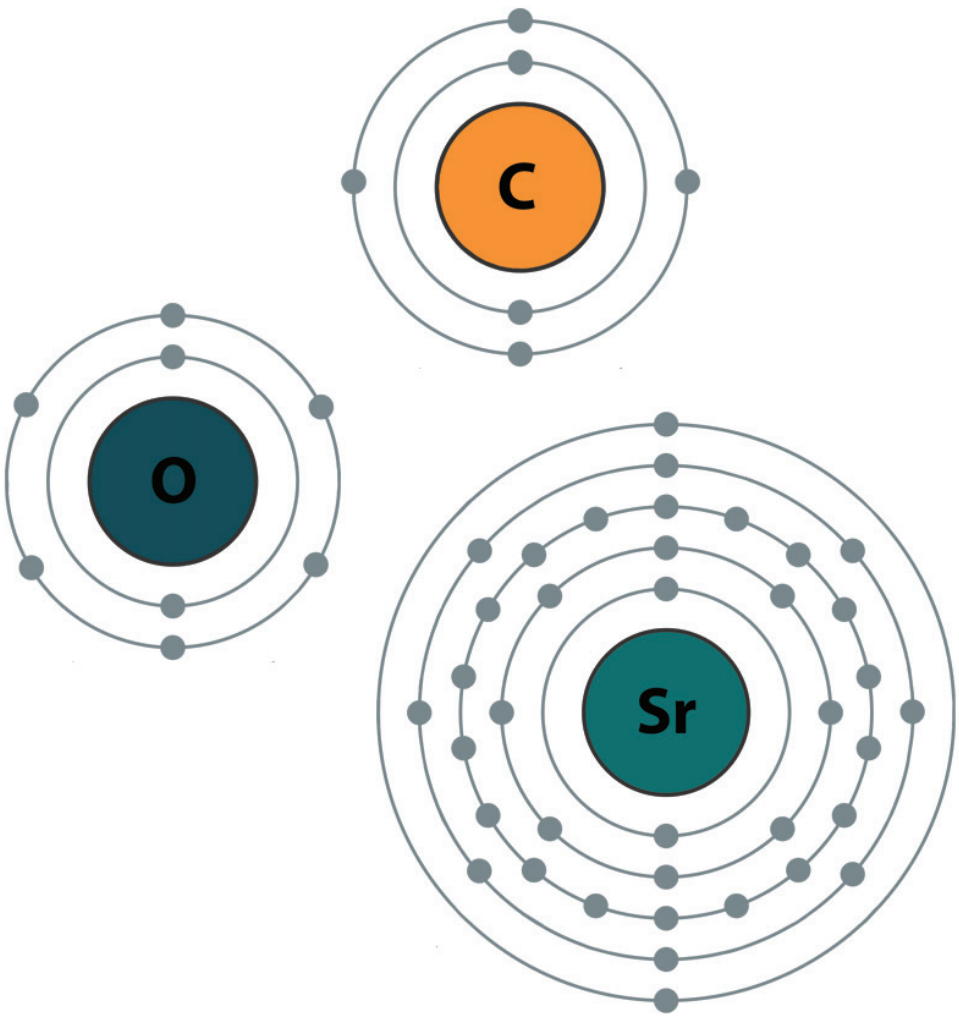
In **Chapter 8** a critical evaluation of the previous chapters is presented. This critical evaluation is extended to the broader field of isotopic analyses of human tissues, where there is a need for standardisation of isotopic research. It concludes with recommendations and considerations for future isotopic research in forensic and archaeological studies.


C
O
Sr

Chapter 2

Introduction to isotopic analyses

2.1 Isotopes

Isotope, consisting of the Greek words *isos* (same) and *topos* (place), is a word that was coined by Margaret Todd in 1912 (*Britton 2017; Meier-Augenstein 2019a*). Isotopes consist of neutrons and protons which are the building blocks of atoms, the smallest constituent unit of a chemical element. Isotopes have the same number of protons (Z) and hence belong to the same chemical element, but may have different number of neutrons (N) in their nuclei. For example, the strontium (Sr) isotopes ^{87}Sr and ^{86}Sr both have 38 protons (and all atoms with 38 protons are always Sr atoms), but 49 and 48 neutrons, respectively. The variation caused by different amounts of neutrons determines the different atomic mass (A) (*Dickin 2005; Fry 2006; Sharp 2017*).

This mass difference result in tiny variations in their thermodynamic properties that leads to different reaction rates in chemical reactions (*Dickin 2005; Pate 1994; Peterson & Fry 1987; Urey 1947*). Heavier isotopes are slower to react, whereas lighter elements react faster. The predictable variability in mass leads to preferential incorporation of some isotopes in reaction products compared to reactants (e.g., weathering water compared to geological solids, animal tissue compared to dietary tissue). This change in isotopic ratios is called fractionation: the enrichment or depletion of the isotopic composition relative to the atmospheric, water or dietary ratios (*Dickin 2005; Fry 2006; Hoefs 2015; Pate 1994; Sharp 2017*). Isotopic fractionation is particularly evident in lighter elements, such as carbon (C), nitrogen (N), hydrogen (H), and sulphur (S) (*DeNiro & Epstein 1978, 1981; Dickin 2005; Jaouen & Pons 2017; Schoeninger 1995; Schoeninger & DeNiro 1984; Urey 1947*). Metabolic fractionation is seen in these lighter elements as they diffuse and react faster than heavier isotopes when incorporated in human and plant tissues through metabolic processes (*Sharp 2017*), resulting in preferential uptake and excretion of lighter isotopes (*Schwarcz 2000*). As atomic weight increases, the differences in mass between the isotopes become smaller, resulting in less isotopic fractionation (*Urey 1947*). Therefore, heavier isotopes, such as strontium (Sr), lead (Pb) and neodymium (Nd), are not as easily fractionated during biological processes (*Beard & Johnson 2000; Flockhart et al. 2015; Jaouen & Pons 2017*). For example, ^{13}C is 7.7 % heavier than ^{12}C, whereas ^{87}Sr is only 1.2 % heavier than ^{86}Sr and ^{144}Nd is only 0.7 % heavier than ^{143}Nd.

Isotopes can be stable ($^{16,18}O$, $^{12,13}C$, $^{14,15}N$, H, ^{86}Sr, ^{144}Nd), radiogenic (^{87}Sr, ^{143}Nd) or radioactive (^{14}C, ^{90}Sr) (*Faure & Mensing 2005*). Proportions of stable isotopes do not change over time unless involved in chemical reactions while radiogenic and radioactive isotopes decrease or

decay over predictable periods. The abundances of isotopes are generally analysed using mass spectrometers. The radiogenic isotopes, such as Sr and Pb, are typically expressed as ratios (*Dickin 2005; Hoefs 2015*). In stable isotopic research (O, H, C, N and S), the *δ*-notation is used to express differences in parts per thousand (‰) relative to a standard reference point (*Hoefs 2015; Sharpe et al. 2018*) (**Equation 2.1**, **Sections 2.3**, **2.4**). A positive *δ* indicates that the ratio of heavy to light isotopes is higher in the sample than in the standard (and vice versa).

$$\delta = \left(\frac{Rx}{Rstd} - 1\right) x\ 1000 \qquad \textbf{Equation 2.1}$$

The isotopic composition of plants is derived from the soil in which they grow, the CO_2 that they process and their water uptake. The isotopic composition of plants is passed onto animals through their diet and influence by the water consumed and air respired by the animal. In turn, these isotopes are incorporated in the human body by incorporating the bioavailable isotopic values through eating the plants, animals and drinking water/respiration (*Bentley 2006; Schwarcz 2000; Sharp 2017*). The isotopic variation in an individual's teeth is thus derived from the diet, water and air they consume and hence representative of the chemical composition of their geographical and climatic environment. Isotopic variation in human tissues can therefore provide information about the place of residence, migration and dietary patterns (*Bentley 2006; Katzenberg 2008; Lee-Thorp 2008*).

The various isotopic systems incorporated in human tissues represent different aspects of the environment where individuals lived. Oxygen isotope composition is primarily controlled by the water consumed by an individual and can therefore be used as a provenance indicator as isotopic ratios in drinking water vary in different geographical environments (**Section 2.3**). Strontium isotopes also provide information on the location of an individual, as they are primarily controlled by the geology in which the food consumed was grown (**Section 2.2**). Carbon isotopes provide information on the type of plants and animals consumed by an individual, and are therefore primarily used as a dietary indicator (**Section 2.4**). The combined analysis of multiple isotopic systems therefore provides more reliable data, as each isotopic system reflects different aspects of human behaviour (**Table 2.1**). The multi-isotopic approach is accordingly the recommended approach in archaeological and forensic studies (*Bartelink et al. 2016; Font et al. 2015; Knipper et al. 2014; Laffoon et al. 2017; Laffoon, Espersen et al. 2018; Moore et al. 2020; Pederzani & Britton 2019; Royer et al. 2017*).

Table 2.1 *Simplified overview of isotope systems analysed in human tissues (after Montgomery & Jay 2013).*

Element	Abundance	Notation	Tissue	Use
Barium	^{130}Ba (0.1 %), ^{132}Ba (0.1 %), ^{134}Ba (2.4 %), ^{135}Ba (6.6 %), ^{136}Ba (7.9 %), ^{137}Ba (11.2 %), ^{138}Ba (71.7 %)	Ba/Ca	Enamel	Diet (weaning)
Calcium	^{40}Ca (96.9 %), ^{42}Ca (0.6 %), ^{43}Ca (0.1 %), ^{44}Ca (2.1 %), ^{46}Ca (trace), ^{48}Ca (0.2 %)	$\delta^{44/42}$Ca, $\delta^{44/40}$Ca	Enamel	Diet (trophic level)
Copper	^{63}Cu (69.2 %), ^{65}Cu (30.9 %)	δ^{65}Cu	Enamel	Sex, diet
Iron	^{54}Fe (5.8 %), ^{56}Fe (91.7 %), ^{57}Fe (2.2 %), ^{58}Fe (0.3 %)	δ^{56}Fe, δ^{57}Fe	Enamel	Sex, diet (trophic level)
Magnesium	^{24}Mg (79.0 %), ^{25}Mg (10.0 %), ^{26}Mg (11.0 %)	δ^{25}Mg, δ^{26}Mg	Enamel	Diet (trophic level)
Strontium	^{84}Sr (0.6 %), ^{86}Sr (9.9 %), ^{87}Sr (7.0 %), ^{88}Sr (82.6 %)	δ^{88}Sr, ^{87}Sr/^{86}Sr, ^{90}Sr	Enamel	Diet, origin (geology), dating
Zinc	^{64}Zn (49.2 %) ^{66}Zn (27.7 %),^{67}Zn (4.0 %), ^{68}Zn (18.5 %), ^{70}Zn (0.6 %)	δ^{66}Zn, δ^{67}Zn, δ^{68}Zn, $^{66/64}$Zn	Enamel	Trophic level
Nitrogen	^{14}N (99.6 %), ^{15}N (0.4 %)	δ^{15}N	Bone (collagen)	Diet (trophic level, marine vs terrestrial)
Carbon	^{11}C (synthetic), ^{12}C (98.9 %), ^{13}C (1.1 %), ^{14}C (trace)	^{14}C, δ^{13}C	Bone (collagen), enamel (carbonate)	Diet (marine vs. terrestrial, C3 vs. C4), origin, dating (up to 55.000 years old)
Oxygen	^{16}O (99.8 %), ^{17}O (0.1 %), ^{18}O (0.2 %)	δ^{18}O	Enamel (carbonate, phosphate)	Climate, origin (hydrology)
Hydrogen	^{1}H (99.9 %), ^{2}H (0.1 %), ^{3}H (trace)	δ^{2}H	Bone (collagen)	Climate, origin (hydrology), diet (trophic level)
Iron	^{54}Fe (5.9 %), ^{56}Fe (91.8 %), ^{57}Fe (2.1 %), ^{58}Fe (0.3 %), ^{60}Fe (trace)	δ^{56}Fe, δ^{57}Fe	Blood, bone, enamel	Trophic level
Lead	^{202}Pb (synthetic), ^{204}Pb (1.4 %), ^{205}Pb (trace), ^{206}Pb (24.1 %), ^{207}Pb (22.1 %), ^{208}Pb (52.4 %), ^{209}Pb (trace), ^{210}Pb (trace), ^{211}Pb (trace), ^{212}Pb (trace), ^{214}Pb (trace)	$^{204/206}$Pb,$^{204/207}$Pb, $^{204/208}$Pb,$^{206/207}$Pb, $^{206/208}$Pb, $^{207/208}$Pb	Enamel	Origin (geology and pollution), dating
Neodymium	^{142Nd} (27.2 %), ^{143}Nd (12.2 %), ^{144}Nd (23.8 %), ^{145}Nd (8.3 %), ^{146}Nd (17.2 %), ^{148}Nd (5.8 %), ^{150}Nd (5.6 %)	$^{143/144}$Nd, εNd	Enamel	Origin (geology and possibly pollution)
Sulphur	^{32}S (94.9 %), ^{33}S (0.8 %), ^{34}S (4.3 %), ^{35}S (trace), ^{36}S (0.1 %)	δ^{34}S	Bone (collagen)	Diet (marine vs terrestrial), origin (geology), coastal proximity due to sea spray effect
Mercury	^{196}Hg (0.2 %), ^{198}Hg (10 %), ^{199}Hg (17 %), ^{200}Hg (23.1 %), ^{201}Hg (13.2 %), ^{202}Hg (29.7 %), ^{204}Hg (6.8 %)	δ^{202}Hg, Δ^{199}Hg, Δ^{201}Hg	Hair	Fish consumed (freshwater, coastal or ocean)

Table 2.2 *A list of reference materials used in isotopic analyses applied in this work (after Chesson, Tipple et al. 2018; Elburg et al. 2005; Koornneef et al. 2017; Tanaka et al. 2000).*

Abbreviation	Full name	Isotope	Ratio
VSMOW	Vienna Standard Mean Ocean Water	$^{2}H/^{1}H$	0.00015576
VSMOW	Vienna Standard Mean Ocean Water	$^{18}O/^{16}O$	0.0020052
VPDB	Vienna Pee Dee Belemnite	$^{13}C/^{12}C$	0.0112372
VPDB	Vienna Pee Dee Belemnite	$^{18}O/^{16}O$	0.0020671
SRM-987	Strontium carbonate NIST SRM	$^{87}Sr/^{86}Sr$	0.710244/0.710338
JNdi-1	JNdi-1	$^{143}Nd/^{144}Nd$	0.512120
CIGO	Centrum Isotopen Geologisch Onderzoek, In-house standard	$^{143}Nd/^{144}Nd$	0.511332
La Jolla	La Jolla	$^{143}Nd/^{144}Nd$	0.511834
TSTD	Tooth Standard, In-house standard	$^{143}Nd/^{144}Nd$	0.512134
TSTD	Tooth Standard, In-house standard	$^{87}Sr/^{86}Sr$	0.707854

During any analytical procedure reference materials or standards (see **Table 2.2)** are used to assure the quality of the data collected and allow for comparison of internationally created results (*Chesson, Barnette et al. 2018; Hoefs 2015; Sharp 2017; Szpak et al. 2017*). These reference materials should be composed of materials with similar chemical compositions to the samples that are processed (matrix matching) (*Carter & Barwick 2011; Chesson, Barnette et al. 2018; Irrgeher & Prohaska 2016; Roberts et al. 2018; Szpak et al. 2017*).

Isotopic analyses have been employed since the 1970s to study past human mobility and diet (*Ericson 1985; Vogel & Van Der Merwe 1977*). The application of isotopic analysis to forensic cases started in the 2000s (*Aggarwal et al. 2008; Juarez 2008; Meier-Augenstein & Fraser 2008*). Isotopic studies are increasingly applied since then, and many reviews have been written on the topic (see **Table 2.3)**. A general overview of the current state of the established isotopic systems in this research is provided on strontium (**Section 2.2**), oxygen (**Section 2.3**) and carbon (**Section 2.4**).

Table 2.3 *Incomplete table containing reviews discussing isotope systems and their application to human tissues.*

Study	Modern/Archaeology	Topic	Sr	O	C	Other
Aggarwal et al. 2008	Modern	Review	X			Pb
Ambrose & Katzenberg 2002	Archaeology	Overview	X	X	X	N
Ambrose & Krigbaum 2003	Archaeology	Review	X		X	
Bartelink & Chesson 2019	Modern	Review		X	X	H, N, S
Bartelink et al. 2014	Modern	Review			X	N
Bartelink et al. 2016	Modern	Overview	X	X	X	H, N, S, Pb
Baskaran 2011	Modern/Archaeology	Review	X	X	X	N, H, Pb
Benson et al. 2006	Modern/Archaeology	Review		X	X	H, N, S
Bentley 2006	Archaeology	Review	X			
Britton 2017	Archaeology	Review	X	X	X	
Carter & Fry 2013	Modern/Archaeology	Review, sample prep.		X	X	
Cerling et al. 2016	Ecology	Overview		X	X	H
Chesson et al. 2013	Modern	Overview		X	X	S, N
Chesson, Barnette et al. 2018	Modern	Review, ecology		X		S, N, H
Chesson, Tipple et al. 2018	Modern	Review, case study		X		
Chesson et al. 2020	Modern	Overview	X	X	X	N, Pb
Coelho et al. 2017	Modern/Archaeology	Review	X			
Cook & MacKenzie 2014	Modern	Review, method	X			Pb, Th
Ehleringer et al. 2008	Modern	Review		X		H
Ehleringer et al. 2010	Modern	Review		X		H
Gentile et al. 2011	Modern	Review, standardisation		X	X	
Gentile et al. 2015	Modern	Review	X	X	X	
Gulson 2008	Modern	Review				Pb
Gulson 2011	Modern	Review				Pb
Hakenbeck 2013	Archaeology	Review		X	X	N
Harrison & Katzenberg 2003	Archaeology	Review			X	
Hedges et al. 2005	Archaeology	Review	X	X	X	N
Jaouen & Pons 2017	Modern/Archaeology	Review	X			Ca, Cu, Fe, Mg, Sr, Zn
Katzenberg 2008	Archaeology	Review	X	X	X	N, H, S
Kramer et al. 2020	Modern	Review, case study	X	X		
Koch 1998	Archaeology	Review		X	X	N

Kohn & Cerling 2002	Archaeology	Overview, diagenesis	X	X	X	
Lee-Thorp 2008	Archaeology	Review		X	X	N
Lightfoot & O'Connell 2016	Archaeology	Review		X		
Nixon 1969	Modern/Archaeology	Review				Trace elements
Matos & Jackson 2019	Modern	Review		X	X	H, N
Meier-Augenstein 2017	Modern	Review		X	X	
Meier-Augenstein 2019b	Modern	Review		X	X	H, N
Meier-Augenstein & Schimmelmann 2019	Modern/Archaeology	Method, ref. materials		X	X	
Oulhote et al. 2011	Modern/Archaeology	Review, statistics	X	X	X	H, N, S, Pb,
Pate 1994	Archaeology	Review	X	X		N, Mg, Ca, Zn
Paul et al. 2007	Modern/Archaeology	Review, normalisation		X	X	
Pederzani & Britton 2019	Archaeology	Review		X		
Pestle et al. 2014	Modern/Archaeology	Review, lab variability		X	X	
Pollard 2011	Modern/Archaeology	Review	X			Pb
Price 2014	Archaeology	Review	X	X	X	Pb, N
Pye 2004	Modern/Archaeology	Review	X	X	X	Pb, H, S, Nd
Reitsema 2013	Modern/Archaeology	Review, pathology			X	N, H, O, Ca
Richards & Montgomery 2012	Archaeology	Review, pathology	X	X	X	N, Pb
Roberts et al. 2018	Modern/Archaeology	Review, standardisation		X	X	
Schoeninger 1995	Archaeology	Review	X	X	X	N, H
Schoeninger 2010	Archaeology	Review	X	X	X	N, H
Schoeninger & Moore 1992	Archaeology	Review			X	N
Schwarcz & Schoeninger 1991	Archaeology	Review			X	N
Slovak & Paytan 2011	Archaeology	Review	X			
Szpak et al. 2017	Archaeology	Review, standardisation		X	X	
Thompson et al. 2014	Modern	Review		X	X	H, S, N
Tsutaya & Yoneda 2015	Archaeology	Review, breastfeeding	X	X	X	N

2.2 Strontium

The first application of strontium isotope analysis in human tissues by *Ericson* (*1985*) demonstrated that strontium can be used to study mobility in ancient human populations. The ratio between ^{87}Sr and ^{86}Sr ($^{87}Sr/^{86}Sr$) serves as a geochemical signature that can be used as a proxy to identify non-locally born or raised people, as $^{87}Sr/^{86}Sr$ varies spatially due to the differences in the amount of ^{87}Sr in the geological bedrock. This variation is the result of the decay from ^{87}Rb to ^{87}Sr. Over time, older geological bedrocks (or bedrock deposits with high initial ^{87}Rb concentrations) have higher $^{87}Sr/^{86}Sr$ ratios compared to younger deposits or bedrock containing lower concentrations of ^{87}Rb (*Beard & Johnson 2000; Bentley 2006; Hoefs 2015; Sharp 2017*).

The strontium isotope values from the geological bedrock enter the human food chain through consumption of plant and animal tissue, as well as water (*Bentley 2006*). These isotope ratios are also influenced by strontium derived from rainfall, atmospheric input such as dust (*Aarons et al. 2013; Burton & Hann 2016*), sea spray (which has a relatively constant value of 0.7092 throughout oceans in the world (*Bentley 2006; Pye 2004; Veizer 1989*)) and fertilisers (*Bentley 2006*). Weathering processes, climate and seasonality may also have an impact on strontium in water due to differential weathering (*Maurer et al. 2012*). These different strontium sources contribute to the biologically available strontium in the environment that are reflected in human tissues. The $^{87}Sr/^{86}Sr$ value in the human body will correspond to the biological available strontium as the mass-dependent fractionation is negligible because of the small mass differences of Sr (^{87}Sr is only 1.16 % heavier than ^{86}Sr, *Bentley 2006; Schoeninger 1995*). Furthermore, any mass dependent fractionation is corrected during measurement by routine normalisation using a fixed $^{86}Sr/^{88}Sr$ ratio of 0.1194 (*Beard & Johnson 2000; Nier 1938*). Strontium (Sr^{2+}) incorporated in the human body substitutes for calcium (Ca^{2+}) in hydroxyapatite, as they have a similar atomic radius (215 and 197 pm respectively (*Eanes 1979*)) and chemical properties (*Bentley 2006; Pate 1994; Schroeder et al. 1972; Zapanta LeGeros 1981*). Strontium is therefore found in bones and teeth. Strontium is primarily controlled by the consumption of plants (*Bentley 2006; Pate 1994; Schroeder et al. 1972*), as Sr is most concentrated within plants and decreases in quantity higher up the food chain (*Burton & Hann 2016; Pate 1994; Schroeder et al. 1972; Snoeck et al. 2020*). It is estimated that less than 10 % of dietary strontium is obtained through drinking water (*Pate 1994; Schroeder et al. 1972*), depending on dietary preferences and Sr levels of consumed water (see *Montgomery et al.* (*2006*) for higher estimated contributions of Sr from drinking water).
Only after a local isotopic baseline signature has been established will it be possible to establish

when strontium values are deviant from this local signature, and thus derive from a different place of origin (non-local). Due to the multiple influences that affect the bioavailable strontium (*Bentley 2006; Price et al. 2002*), it is best to establish a baseline of the expected strontium values in an environment using strontium ratios obtained from human samples where possible (*Burton & Hann 2016; Wright 2005*). Animal samples can be used when human material is limited. River water, soils, plants, and snails should only be used with caution as they do not yield consistent or comparative values for human values (*Burton & Hann 2016; Maurer et al. 2012; Poszwa et al. 2004; Price et al. 2002; Snoeck et al. 2020*). Plant and animal samples should be selected with care (*Price et al. 2002*), using archaeozoological and archaeobotanical information to establish dietary preference to select relevant materials for isotopic analysis.

Diagenesis

In archaeological studies only the enamel of the teeth should be used for Sr isotope analysis. Enamel, the hardest tissue of the human body, is more resistant than other human tissues to diagenesis (changes in the physical and/or chemical composition) (*Budd et al. 2000; Hoppe et al. 2003; Koch et al. 1997; Quade et al. 1992; Trickett et al. 2003; Wang & Cerling 1994*). Bone and dentine are more porous and hence subjected to diagenesis (*Ambrose & Norr 1993; Bell et al. 1991; Budd et al. 2000; Hoppe et al. 2003; Kohn et al. 1999; Nelson et al. 1986; Trickett et al. 2003*). Due to diagenesis, the $^{87}Sr/^{86}Sr$ ratio of buried bones does not reflect the biogenic strontium ratio of archaeological individuals, but is instead a reflection of the soil it is retrieved from. Forensic cases may be less influenced (*Degryse et al. 2012*). Nevertheless, as no data is available yet on the time scale of incorporation of diagenetic Sr in buried bone, dental enamel is the preferred tissue for analysis.

Analysis

Strontium isotopes in enamel are analysed using mass spectrometry. This can be done by drilling the sample material followed by sample dissolution (*Slovak & Paytan 2011*). The sample is then digested in acid and Sr is separated from the rest of the matrix using ion exchange chromatography. This chemical separation is necessary as the high-calcium matrix suppresses the ionisation of Sr (*Dickin 2005; Montgomery 2002*). By separating the elements using column chromatography, isobaric interferences with other elements are also avoided, as the interfering elements are discarded (*Dickin 2005; Jaouen & Pons 2017*). After column chromatography the solution is analysed using either thermal ionisation mass spectrometry (TIMS) or multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). These two mass spectrometry

methods differ in how the sample is taken up and ionised, but otherwise they are similar in separating the ions and counting these ions on the basis of the mass to charge ratio of the ions (*Dickin 2005; Hoefs 2015; Irrgeher & Prohaska 2016*). In situ analysis is performed using laser ablation (LA)-MC-ICP-MS (*Dickin 2005; Hoefs 2015*). Using LA-MC-ICP-MS, the sample is directly analysed instead of undergoing chemical separation. The preferred method of analysis is TIMS, as these analyses are generally more precise and reproducible, and they require less sample material for analysis (*Hoefs 2015; Irrgeher & Prohaska 2016; Jaouen & Pons 2017; Montgomery 2002; Slovak & Paytan 2011; Vroon et al. 2008*). The analyses presented in this work are performed using a Thermo Scientific Triton *Plus* TIMS. Contamination during laboratory procedures is monitored using "blanks" that are analysed in the same manner as the samples so that background contributions to analytical procedures can be quantified (*Dickin 2005; Irrgeher & Prohaska 2016*). Elemental concentrations can also be analysed by using the isotope dilution (ID) technique. This involves the addition of a small, quantified amount of a "spike" that is enriched in one isotope (e.g., ^{84}Sr or ^{150}Nd) to the sample prior to chemical separation (*Dickin 2005; Hoefs 2015; Irrgeher & Prohaska 2016*). The concentration can then be calculated based on the sample analysis results and the added spike values (see **Chapters 5** (Nd) and **6** (Sr)).

Considerations

The use of Sr isotope analysis for provenance studies has some limitations that should be assessed on a case by case basis:

(1) Sr isotope analysis is dependent on the variation of the geology in an area: if the geology is similar it is impossible to distinguish areas isotopically (*Bentley 2006; Slovak & Paytan 2011*). This is likely to underestimate migration rates.

(2) Sr isotope compositions in soils and plants may be influenced by sea spray (*Bentley 2006; Hoogewerff et al. 2019; Slovak & Paytan 2011; Snoeck et al. 2020*). In coastal areas where marine food consumption takes place, individuals Sr values will partly reflect the marine signature (0.7092, *Veizer 1989*) rather than the terrestrial Sr values. This may lead to an underestimation of migration, as areas dominated by sea spray are isotopically indistinguishable (*Bentley 2006; Whipkey et al. 2000*).

(3) The consumption of non-local foods, particularly products that have high Ca and Sr concentrations such as dairy products, vegetables and sea salt (*Wright 2005*), and marine products (*Haverkort et al. 2010; Price & Gestsdóttir 2006*) can alter the local Sr isotope ratios (*Bentley 2006; Burton & Wright 1995*). When there is no isotopic, archaeobotanical or archaeozoological information available about the dietary patterns of a population, the consumption of non-

local foods can result in overestimation of migration.

(4) The natural variation in Sr ratios in human populations has not yet been characterised (*Price et al. 2002; Wright 2013*), making it difficult to determine what ratios should be considered as outliers and indicative of migration. The degree of natural variation is likely to vary between populations, as the range of Sr isotopic values in diets will also vary. Previous studies have used an offset of ~0.00100 for strontium to indicate migration (*Hrnčíř & Laffoon 2019; Knipper et al. 2014, 2018; Kootker, Mbeki et al. 2016; Price et al. 1998; Scheeres et al. 2013, 2014; Slater et al. 2014*). Without data on individual Sr isotope variation, this remains an estimation that will have to be verified in different populations and contexts.

(5) Modern agricultural practices can influence Sr isotope composition of a region and may thus have an effect on the isotopic composition of human tissues (*Maurer et al. 2012; Thomsen & Andreasen 2019*).

2.3 Oxygen

Oxygen isotopes in human tissues can be related to the oxygen values of water consumed by an individual. The technique was first applied by *Fricke et al.* (*1995*) to human dental enamel. Oxygen isotopes are incorporated into human tissues through drinking water, food and respiration (*Bryant & Froelich 1995; Kohn 1996; O'Grady et al. 2012; Pederzani & Britton 2019; Podlesak et al. 2008, 2012; Pye 2004*). Oxygen values of water vary geographically due to the Rayleigh processes in the hydrosphere (**Figure 2.1**) (*Bowen 2010b; Craig 1961; Dansgaard 1964; Gat 1996; Gat & Gonfiantini 1981; Pederzani & Britton 2019; Pye 2004; Rozanski et al. 1993*) and are influenced by:

(1) Mass differentiation effects during evaporation and condensation. When water evaporates from the ocean surface, the vapour is enriched in ^{16}O as it is easier to evaporate due to its lighter mass compared to ^{18}O, resulting in negative $\delta^{18}O$ values. As $\delta^{18}O$ is also first removed during condensation due to its mass difference, increasingly negative $\delta^{18}O$ values are found further inland.

(2) Altitude effect, with decreasing $\delta^{18}O$ values at higher altitudes.

(3) Variations in climate and season, with more negative $\delta^{18}O$ in colder areas or seasons.

(4) Latitudinal effect, with lower $\delta^{18}O$ found at increasing latitudes.

Due to these geographic differences in oxygen values, it is possible to infer where an individual resided when their tissues were formed when local water is ingested (*Chenery et al. 2012; Podlesak et al. 2012*). To establish the local isotopic signature, (1) human values can be compared to local

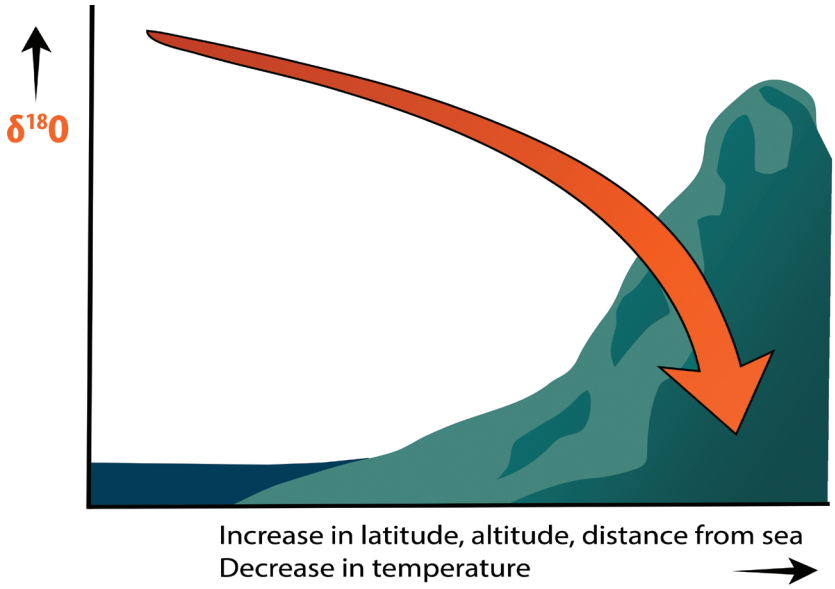


Figure 2.1 *Visualisation in changes in $\delta^{18}O$ as a result from an increase in latitude, altitude and distance from see, as well as a decrease in temperature.*

drinking water (a method which is prone to uncertainties as results differ depending on the conversion formulae used and which should only be used as a guide (*Chenery et al. 2012; Daux et al. 2008; Longinelli 1984; Pederzani & Britton 2019; Pollard et al. 2011*)) ; or (2) the distribution of the isotopic ratios of humans can be used to exclude outliers using statistical approaches where sample sizes are large enough for statistical analyses (e.g., *Eckardt et al. 2009; Kendall et al. 2013; Pederzani & Britton 2019; Stark et al. 2020*). Using oxygen in combination with other migratory indicators such as strontium isotope analysis provides more reliable information.

Because the isotopic differences between oxygen isotopes are small, they are usually reported as delta values in per mil notation relative to a standard (**Equation 2.2**):

$$\delta^{18}O(‰) = \left(\frac{18_O/16_O\ x}{18_O/16_O\ std} - 1\right)\ x\ 1000 \qquad \textbf{Equation 2.2}$$

Relative oxygen values should be normalised using the VSMOW (Vienna Standard Mean Ocean Water) or VPDB (Vienna Pee Dee Belemnite) (see **Table 2.2**).

Diagenesis

Oxygen isotopes should be analysed in bioapatite of enamel, as it is more closely related to environmental water compared to collagen in bone and dentine (*Kirsanow & Tuross 2011; Pederzani & Britton 2019*). Moreover, enamel is resistant to diagenesis (*Chenery et al. 2012; Kohn & Cerling 2002*). There are no reliable quality controls for the analysis of diagenetic alteration of oxygen in collagen (*Pederzani & Britton 2019*) and diagenesis has been observed in previous studies (*Koch et al. 1997; Pederzani & Britton 2019; Sharp et al. 2000; von Holstein et al. 2018; Wright & Schwarcz 1996*). Furthermore, results from collagen yield unreliable inter-lab results (*Demény et al. 2019; Koch et al. 1997*). Hence, oxygen isotope analysis should not be applied to bone and dentine.

Analysis

Two analytical techniques using isotope ratio mass spectrometry (IRMS) are employed to analyse oxygen in enamel: (1) analysing oxygen from the structural carbonate group (CO_3) or (2) analysing the phosphate oxygen (PO_4) (*Chenery et al. 2012; Pederzani & Britton 2019; Pellegrini et al. 2011*). Analysing the carbonate involves less sample preparation, requires smaller sample sizes, and gives greater measurement precision (*Balasse 2002; Bryant et al. 1996; Chenery et al. 2012; Pederzani & Britton 2019; Pellegrini & Snoeck 2016; Snoeck & Pellegrini 2015; Wright & Schwarcz 1998*). Analysing the phosphate oxygen provides a more stable oxygen value as phosphate constitutes the predominant source of oxygen within enamel (*Chenery et al. 2012*). Moreover, it is argued that the P-O bond is more resistant to chemical alterations (*Koch et al. 1997; Kohn & Cerling 2002; Lee-Thorp 2002; Pederzani & Britton 2019; Sharp et al. 2000*) and the relationship between phosphate oxygen and drinking water oxygen values is better established (*Bryant et al. 1996; Daux et al. 2008; Kirsanow & Tuross 2011; Levinson et al. 1987; Longinelli 1984; Luz et al. 1984*). Nevertheless, oxygen data reported in this work (**Chapter 6**) are from carbonate oxygen, as diagenesis is less relevant to the modern samples analysed.

The majority of oxygen isotope analyses performed today are made using continuous flow–IRMS (*Chesson, Barnette et al. 2018; Muccio & Jackson 2009*). The oxygen and carbon values reported in this work were analysed using a Thermo Finnigan Delta plus IRMS with a GasBench II. The values were normalised to the international standard IAEA-603 and reported relative to the VPDB standard (see **Table 2.2** and **Chapter 6**).

Considerations

Due to the predictable influence of factors influencing the oxygen isotope composition, it is possible to construct models that allow the creation of isoscapes (*Bowen 2010a; Bowen & Revenaugh 2003; Bowen & Wilkinson 2002; West et al. 2014*). These predictions have their limitations, however:

(1) The range of global $\delta^{18}O$ is small compared to the range of variability seen in the human body. Many parts of the world, particularly temperate and tropical regions, have similar $\delta^{18}O$ values (-2.0 ‰ to -8.0 ‰; *Bowen et al. 2005; Warner et al. 2018*), making regional distinction difficult.

(2) Oxygen isotope composition can be influenced by non-local water (*Dutton et al. 2005; Bowen et al. 2007; Kennedy et al. 2011*) and evaporative $\delta^{18}O$ enrichment in surface waters (particularly in tropical and arid regions; *Mook 2001; Smith et al. 1992; Warner et al. 2018*).

(3) Isoscapes based on plant data can give variable results as oxygen isotope composition of plants is species dependent (*Kohn & Cerling 2002; Pederzani & Britton 2019*).

(4) Oxygen isotope fractionation is driven by physiology and metabolism (*Kohn & Cerling 2002; Pederzani & Britton 2019*), which may result in variation within and between species and human individuals (*Bryant et al. 1996; Fricke & O'Neil 1996; Wright 2013; Wright & Schwarcz 1998*).

(5) Large intra- (2-4 %; *Neil et al. 2016; Smith et al. 2018; Wright 2013; Wright & Schwarcz 1998*), and inter- (3 ‰; *Hakenbeck 2013; Lightfoot & O'Connell 2016*) archaeological site variations in human $\delta^{18}O$ values have been demonstrated, with a high degree of overlap in oxygen isotope values in Europe (*Lightfoot & O'Connell 2016*).

(6) Cooking practices, such as boiling or brewing water can enrich $\delta^{18}O$ values in food and thus in human tissues (*Brettell et al. 2012; Daux et al. 2008; Royer et al. 2017*).

(7) Weaning practices can result in enriched $\delta^{18}O$ (by ~ 0.7 ‰) when dental elements are mineralised during breastfeeding (such as the first molar) (*Wright 2013; Wright & Schwarcz 1998, 1999*), as the body water of the mother is ^{18}O enriched relative to drinking water due to respiration (*Bryant & Froelich 1995; Kohn 1996*).

(8) The consumption of particular drinks, such as milk, wine and juice are enriched relative to local water (*Chesson et al. 2010; Hakenbeck 2013*) and their consumption may alter the local signature.

2.4 Carbon

Carbon isotopes in human tissues are related to an individual's consumption of plants and animals. Carbon isotopes were first used by *Vogel and van der Merwe* (*1977*) to interpret dietary practices of humans. The application of carbon isotope analysis to human tissues is now an established tool for the reconstruction of diet (*Ambrose & DeNiro 1986; Fernandes et al. 2012; Fernandes 2016*), breastfeeding and weaning age patterns (*Wright 2013; Wright & Schwarcz 1998, 1999*), and migration (*Cox et al. 2001; Hülsemann et al. 2015; Kamenov & Curtis 2017*).

Similar to oxygen isotopes, carbon data are reported as delta values in per mil notation relative to a standard of known composition (*Werner & Brand 2001*) (**Equation 2.3**):

$$\delta^{13}\mathrm{C}(‰) = \left(\frac{{}^{13}C/{}^{12}Cx}{{}^{13}C/{}^{12}Cstd} - 1\right) x\ 1000 \qquad \textbf{Equation 2.3}$$

The majority of δ^{13}C in human tissues is derived from the consumption of C3 or C4 plants. These plants have different photosynthetic pathways (*Bender 1968; Farquhar et al. 1989; Koch 1998; Lee-Thorp 1989; O'Leary 1981, 1988; Smith & Epstein 1971*). As a result, C3 based plants, primarily temperate grasses and trees, have lower δ^{13}C values (~20 ‰) than C4 plants (~10 ‰), primarily subtropical grasses such as maize, sugar cane, and millet (*Ambrose & Norr 1993; Fernandes 2016; Schoeninger 1995; Smith & Epstein 1971; Tieszen 1991*). Plants that employ CAM photosynthesis and marine plants show variable δ^{13}C values, generally intermediate between those of C3 and C4 plants (*Farquhar et al. 1989; Lee-Thorp 2002, 2008; Mays & Beavan 2012; Osmond et al. 1973; Schoeninger 1995; Schoeninger & DeNiro 1984*). CAM plants in hot and arid regions, however, exhibit δ^{13}C values indistinguishable from those of C4 plants (*Koch 1998; Smith & Epstein 1971; Warinner et al. 2013*). All plants are ^{13}C depleted relative to the atmospheric CO_2, due to the preferential incorporation of the lighter isotope ^{12}C during photosynthesis (*Ambrose & Norr 1993; Koch 1998; Lee-Thorp 2008*).

An isotopic enrichment of ~5-7 ‰ takes place in herbivores (*Ambrose & Norr 1993; Fernandes et al. 2012; Kohn & Cerling 2002; Krueger & Sullivan 1984; Lee-Thorp 1989, 2008; Tieszen 1991; Tieszen & Fagre 1993*), with considerable degree of variation within species demonstrated in previous studies (*Bocherens et al. 2000*). Additional fractionation, ~1-4 ‰, takes place between successive trophic levels, including carnivores and humans (*Ambrose & Norr 1993; Fernandes et al. 2012; Lee-Thorp 2008; Schoeninger 1985; Schoeninger & DeNiro 1984; van Klinken et al. 2002*). Physiology and health (*Lee-Thorp 2008; Schoeninger & DeNiro 1984; Schwarcz 2000*), age (*Hare et*

al. 1991; Tieszen & Fagre 1993), sex, and dietary preferences may also affect $\delta^{13}C$ values in human tissues. Other influences that have an effect are breastfeeding, as human milk is depleted in ^{13}C (*Wright & Schwarcz 1998*).

Analysis

Carbon isotopes can be analysed in bone and enamel mineral hydroxyapatite and collagen using IRMS (see **Section 2.3**). Carbon values in collagen represents the protein portion of the diet, and $\delta^{13}C$ in mineral apatite in bone and teeth represents the whole diet (*Ambrose & Norr 1993; Fernandes et al. 2012; Krueger & Sullivan 1984; Lee-Thorp 1989; Schoeninger 2010; Tieszen & Fagre 1993*). The $\delta^{13}C$ in mineral apatite of humans is isotopically enriched by ~5-7 ‰ compared to collagen (*Harrison & Katzenberg 2003; Krueger & Sullivan 1984; Lee-Thorp 1989*).

Diagenesis

While bones can be analysed for $\delta^{13}C$ values, the high susceptibility of bone and dentine to diagenesis may compromise their isotopic integrity (*Berna et al. 2004; Collins et al. 2002; Koch et al. 1997; Lee-Thorp 2002; Wright & Schwarcz 1996*). The collagen yield and elemental data (weight percentages and C:N atomic ratios) are most widely used to assess the quality of the extracted bone collagen (*Ambrose 1990; van Klinken 1999*). This is beyond the scope of this work, as only the mineral apatite of modern human enamel is analysed in **Chapter 6**. Enamel apatite is more resistant to diagenesis than bone collagen (*Koch et al. 1997; Lee-Thorp 2002; Wright & Schwarcz 1998*) but it should be notated that there is no generally accepted method for assessing carbon diagenesis in enamel (*Schoeninger 2010*).

Considerations

Carbon isotope composition can improve our understanding of dietary practices and migrations, but does not provide specific information:

(1) Only a general distinction can be made between consumption of C3, C4 and possible CAM and marine resources due to the variation seen in $\delta^{13}C$ in plants (*Fernandes et al. 2015; Kohn & Cerling 2002; Montgomery & Jay 2013; Roberts et al. 2018*). Particularly C3 plant $\delta^{13}C$ can vary widely in different environments (*Koch 1998*), depending on light intensity (*Bonafini et al. 2013; Ehleringer & Monson 1993; Farquhar et al. 1989; Kohn & Cerling 2002; O'Leary 1981; van Klinken et al. 2002*), re-cycling of plant-fractionated C in dense vegetation ('canopy effect') (*Bonafini et al. 2013; Schoeninger 2010; van der Merwe & Medina 1991; van Klinken et al. 2002*), temperature

and humidity (*Ambrose & Norr 1993; Ehleringer & Monson 1993; Farquhar et al. 1989; Lee-Thorp 2008; Smith & Epstein 1971; Tieszen 1991; van Klinken et al. 2002*), as well as intra-plant variation between separate parts and biological fractions of plants (*Ambrose & Norr 1993; Farquhar et al. 1989; Tieszen 1991*).

(2) Considerable variation in the $\delta^{13}C$ within populations has been demonstrated (*Hülsemann et al. 2015; Kamenov & Curtis 2017; van Klinken et al. 2002*), requiring a context specific baseline to interpret dietary practices that are dependent on the carbon isotope composition in plants and animals.

(3) In establishing baselines, modern and archaeological values may not be directly comparable due to changes in the CO_2 in the atmosphere as a result of burning of fossil fuels (also known as the Suess effect), causing a shift of -1.5 ‰ (*Bocherens et al. 2000; Lee-Thorp 2002; Schoeninger 1995; Tieszen 1991; van Klinken et al. 2002*).

(4) Migration estimations are dependent on the types of food available to populations, with similarities in diets resulting in overlapping $\delta^{13}C$ values (*van Klinken et al. 2002*). In modern human population a distinction is seen between (1) Europe, Asia, Australia and northern and western Africa with low $\delta^{13}C$ values due to their dependence on primarily C3 plants; (2) USA with moderate $\delta^{13}C$, due to more C4 plant based diets (maize) and (3) Mexico, Central America, South America and Southern and Eastern Africa with high $\delta^{13}C$ values, where C4 plants are more common (*Hülsemann et al. 2015; Kamenov & Curtis 2017*). Carbon should therefore only be used as a provenance indicator to complement other provenance indicators such as oxygen, hydrogen, lead and strontium.

2.5 Conclusion

Considering the many factors that have to be taken into account when interpreting the results of isotopic analyses, it would be beneficial to have additional isotopic systems that can provide supplementary information and address some of these limitations. Therefore, the potential of the neodymium isotope system for human provenancing is explored in **Chapters 4** and **5**. The isotopic variation seen in human tissues is a factor of consideration for all isotopic systems. To assess the impact that isotopic variability may have on interpretations of diet and mobility, multiple sample locations from the same dental element were analysed for strontium, oxygen and carbon, and discussed in **Chapter 6**. Before the Sr-O-C and Nd isotope systems are examined in more detail, an introduction on the sample material used is provided in the next chapter.

Chapter 3

Human tissues used for isotopic analyses

Analysing multiple skeletal elements can provide information on the life history of an individual, by incorporating information from different components of their diet or from different time periods of their life (*Fahy et al. 2017; Pollard et al. 2012; Scharlotta et al. 2018*). Through the analysis of the enamel of the teeth information can be retrieved from their childhood (**Section 3.2**). By analysing the bone, an averaged signal of a number of years before their death can be obtained, the period depending on the bone element analysed (**Section 3.1**). The isotopic analysis of the hair provides information of their last months or years. While hair is an important tissue in isotopic analysis used in forensic case studies (*Bartelink et al. 2016; Bartelink & Chesson 2019; Matos & Jackson 2019; Meier-Augenstein 2019b*), it is beyond the scope of this work. Instead, the main focus of this chapter will be on the enamel of the teeth, as this was the tissue analysed in the following **Chapters** (**4-7**). First, however, the isotopic metabolism of bone will be discussed, as one of the original aims of NEXUS1492 was to test whether provenance information could be extracted from buried bone.

3.1 Bone

The human skeleton consists of bone, a living tissue that is continuously regenerated and remodelled (**Section 3.2**, *Martin et al. 2015; Pearson & Lieberman 2004; Teitelbaum 2000; Toppets et al. 2004; Walsh et al. 2003; White et al. 2011*). Bone consists of two components: (1) an organic matrix composed mostly of protein collagen (~90 %), noncollagenous proteins (~5 %), and <5 % lipids and carbohydrates (*Kendall et al. 2018; Pate 1994; Teitelbaum 2000; Toppets et al. 2004; White et al. 2011*) that provide the bone with elasticity and (2) the principal inorganic component (65 %) consisting largely of calcium phosphate (hydroxyapatite) which provides the bone with strength (*Betts et al. 1981; Pearson & Lieberman 2004; Zapanta LeGeros 1981*). A distinction in bone density can be made between cortical and trabecular bone (*Martin et al. 2015; Toppets et al. 2004; Walsh et al. 2003*): (1) Cortical bone is loadbearing and therefore much more dense and located on the exterior part of bones than (2) trabecular or cancellous bone which is more porous and located in the interior of the bone.

Bone is organic-rich, poorly crystalline and very porous (*Zapanta LeGeros 1981*). As a result, bone is susceptible to post-mortem alterations and diagenetic processes (*Collins et al. 2002; Kendall et al. 2018*). Some studies have suggested that proteins such as osteocalcin are more robust to archaeological degradation compared to collagen (*Nielsen-Marsh et al. 2002, 2005*), and potentially could be of use for provenance studies.

Osteocalcin

Osteocalcin (OC) or BGLAP (bone gamma-carboxyglutamic acid-containing protein) is a hormone protein in human bone and dentine (*Hauschka et al. 1989; Mera et al. 2017*). Osteocalcin is the most abundant non-collagenous protein (consisting of 1-20 % of the noncollagenous bone proteins), contributing less than 1 % of the total bone protein (*Ajie et al. 1992; Hauschka et al. 1989*). Osteocalcin binds to bone mineral (Ca^{2+}) due to the presence of gamma-carboxyglutamic acid residues (*Buckley et al. 2008*). Osteocalcin is secreted by osteoblasts and plays a role in the body's metabolic regulation, bone deposition and mineralisation (*Ajie et al. 1992; Hauschka et al. 1989*). Osteocalcin also regulates insulin sensitivity (*Fernández-Real et al. 2009; Levinger et al. 2011; Mera et al. 2017; Rochefort et al. 2011*), affects male reproductive functions by stimulating testosterone production (*Karsenty & Oury 2014*) and may influence vitamin D levels (*Lorentzon et al. 2001*). Osteocalcin content within the bone is higher when the bone is more mineralised and has been shown to increase with exercise (*Fernández-Real et al. 2009; Hauschka et al. 1989; Mera et al. 2017*).

The ability of osteocalcin to bind to hydroxyapatite, which is normally more resistant to diagenesis (*Hauschka et al. 1989; Nielsen-Marsh et al. 2002, 2005*), made it a potential candidate for isotopic analyses. While fossil bones have similar levels of gamma-carboxyglutamic acids to modern bones (*Ajie et al. 1992; Nielsen-Marsh et al. 2002*), the extracted osteocalcin consists primarily of broken polypeptide fragments rather than intact protein (*Ajie et al. 1992*). This complicates the analysis of osteocalcin in fossils (*Ajie et al. 1992; Cleland et al. 2016; Humpula et al. 2007*). Furthermore, archaeological samples show similar states of degradation of osteocalcin, collagen, crystallinity and histological alteration (*Buckley et al. 2008; Nielsen-Marsh et al. 2005; Smith et al. 2005*), demonstrating that osteocalcin in archaeological bone is not as stable as initially thought (*Buckley et al. 2008; Smith et al. 2005*). The similar patterns of preservation seen in osteocalcin of fossils compared to collagen suggests that osteocalcin is unlikely to produce isotopic results that are unaffected by diagenetic processes. Lastly, unlike carbon to nitrogen atomic ratios that can be used to identify diagenetically altered collagen samples (**Section 2.4**), there is no control to assess the preservation of osteocalcin. In conclusion, the difficulty of determining the effect of diagenesis and the complicated extraction of osteocalcin make it an unfavourable tissue for isotopic analysis.

Remodelling

Bone constantly renews itself through bone remodelling after its initial formation. Remodelling

is the biological mechanism that destroys pre-existing bone (bone resorption through osteoclasts cells) followed by the formation of new bone (osteoblasts cells) (*Frost 1969; Gosman & Stout 2010; Harada & Rodan 2003; Karsenty & Oury 2014; Katsimbri 2017; Manolagas 2000; Martin et al. 2015; Robling et al. 2006*). This process is slow, and results in a mixture of bone material formed over several years. The time taken for a bone to be completely remodelled or replaced is called the turnover time.

Remodelling is a complex process, with time frames of destruction and new growth not properly quantified (*Katsimbri 2017; Mahoney et al. 2018; Martin & Seeman 2008; Neuman & Neuman 1958; Robling et al. 2006*). An important factor in bone remodelling is the age of an individual (*Britz et al. 2009; Hedges et al. 2007; Jowsey 1961; Katzenberg 1993; Manolagas & Jilka 1995; Martin et al. 2015; Martin & Seeman 2008; Mulhern 2000; Pate 1994; Pearson & Lieberman 2004; Pitfield et al. 2017; Rabinowitz 1991; Ubelaker et al. 2006*). It is estimated that, at age 20, the skeleton has already been remodelled by at least 95% (*Pate 1994*). This remodelling process slows with advancing age (*Manolagas & Jilka 1995; Neuman & Neuman 1958*), with the range in annual replacement percentages from ~85 % in the first few years of childhood, to ~7 % in individuals in their twenties and >3 % in individuals in their thirties (*Hedges et al. 2007; Jowsey 1961; Martin et al. 2015; Rabinowitz 1991*). After the age of 50-60 the rates increase again to ~4 % (*Frost 1969; Pearson & Lieberman 2004; Rabinowitz 1991*). Bone remodelling also varies by skeletal element (*Fahy et al. 2017; Hill & Orth 1998; Miszkiewicz & Mahoney 2019*). The cortical turnover rate in adults is ~8 % for vertebrae, ~5 % for ribs and 2-3 % for the leg bones (femurs, tibiae and fibulas, but see *Fahy et al. 2017* for contrasting results), with lowest remodelling rates found in the skull >1 % (*Fahy et al. 2017; Marshall et al. 1973; Parfitt 2002; Pate 1994; Rabinowitz 1991*). This does not mean that the skeletal elements are remodelling homogeneously, as various regions within the skeletal element are known to have different turnover times (*Hedges et al. 2007; Manolagas & Jilka 1995; Martin et al. 2015; Matsubayashi & Tayasu 2019; Parfitt 2002; Ubelaker et al. 2006*), depending on the size of the surface areas where bone remodelling occurs (*Frost 1969; Hill & Orth 1998; Martin & Seeman 2008; Matsubayashi & Tayasu 2019; Parfitt 2002*). Average estimates for annual replacement percentages for adult human cortical bone are 2-8 % (*Frost 1969; Gulson et al. 1997; Katsimbri 2017; Neuman & Neuman 1958; Pate 1994; Pearson & Lieberman 2004; Rabinowitz 1991; Young Shin et al. 2004*), with trabecular bone remodelling faster at a rate of 10-30 % (*Hill & Orth 1998; Manolagas & Jilka 1995; Martin et al. 2015; Mulhern 2000; Pate 1994; Pearson & Lieberman 2004; Ubelaker et al. 2006*).

Other factors influencing bone remodelling are physiological factors such as sex and hormones

(*Harada & Rodan 2003; Hedges et al. 2007; Hill & Orth 1998; Karsenty & Oury 2014; Katsimbri 2017; Martin & Seeman 2008; Mera et al. 2017; Mulhern & Van Gerven 1997; Pearson & Lieberman 2004; Toppets et al. 2004*), genes (*Harada & Rodan 2003; Martin & Seeman 2008; Pearson & Lieberman 2004*), mechanical load and physical activity (*Britz et al. 2009; Gosman & Stout 2010; Harada & Rodan 2003; Hedges et al. 2007; Hill & Orth 1998; Katsimbri 2017; Martin et al. 2015; McNamara & Prendergast 2007; Pearson & Lieberman 2004; Robling et al. 2008, 2006; Schlecht et al. 2012*), health and vitamin deficiencies (*Gage et al. 1989; Martin & Armelagos 1979; Martin & Seeman 2008; Mulhern & Van Gerven 1997; Paine & Brenton 2006*), and energy metabolism (*Betts et al. 1981; Mera et al. 2017*). In periods of low-calorie intake (such as anorexia nervosa), bone formation may be arrested and osteoporosis can occur (*Beaumont et al. 2015; Legroux-Gerot et al. 2005; Mera et al. 2017; Misra & Klibanski 2011*). Different skeletal elements from various individuals therefore record different periods of formation due to these various processes. The significance of this variation on the isotopic values in bone is difficult to determine and is not the only process that should be taken into account. Additionally, the isotopic composition of bone depends on whether new isotopic input is only incorporated in the bone through bone formation and remodelling, or whether isotopic input is continuously exchanged and recycled in the human body (*Ubelaker et al. 2006*). As the turnover time (full tissue renewal) is estimated to be in the order of years to decades (*Gulson et al. 1997; Hedges et al. 2007; Katzenberg 1993; Libby et al. 1964; Manolagas 2000; Meier-Augenstein & Fraser 2008; Pate 1994; Robling & Stout 2008; Ubelaker et al. 2006; Wild et al. 2000*), bone samples reflect an individual's dietary intake for a period longer than 10 years. In adults, bone isotopic composition may still be dominated by input during childhood and adolescence, the period of skeletal growth (*Hedges et al. 2007; Matsubayashi & Tayasu 2019*). Isotopic analyses on bone will therefore not provide information on a short time period, and instead represent an average ratio of a significant portion of the life span of an individual. Ribs, with relatively fast turnover rates, will record dietary intake from shorter periods prior to death than will femurs that have a relatively slow turnover rate (*Cox & Sealy 1997; Fahy et al. 2017*). Furthermore, different components of the bone will reflect different inputs of the diet, with bioapatite reflecting the whole diet and collagen only recording the dietary protein (*Ambrose & Norr 1993; Fernandes et al. 2012; Krueger & Sullivan 1984; Lee-Thorp 1989; Tieszen & Fagre 1993*).

The type of bone and type of tissue selected for isotopic analysis therefore has a significant impact on the interpretation of their isotopic ratios (*Fahy et al. 2017; Matsubayashi & Tayasu 2019*). Combining isotopic analysis of multiple skeletal elements of the same individual can provide more insights in the remodelling process, the isotopic heterogeneity in bone, and

information about the life histories of individuals (*Brady et al. 2008; Chenery et al. 2012; Fahy et al. 2017; Jørkov et al. 2007*). Consistent sampling of skeletal elements is required for comparison of isotopic studies. Using both inner and outer parts of bones with faster and slower turnover times, respectively, is recommended for life history studies (*Matsubayashi & Tayasu 2019*).

3.2 Teeth

The human dentition can provide information on sex, age, health, diet, mobility, ancestry and identification through a wide range of methods applied in biological anthropology and forensics (*Hillson 1996, 2005; Katzenberg & Saunders 2008; Kelley & Larsen 1991; Mickleburgh 2006; Smith 2018; Teaford et al. 2006; White et al. 2011*).

Humans are diphyodont: they have two sets of dentition: (1) the deciduous (primary or milk) dentition that begins development in the first trimester of pregnancy, with enamel formed between 14 weeks in utero and completed a year after birth (*ElNesr & Avery 2002; Gustafson & Koch 1974; Massler et al. 1941; Moorrees et al. 1963; Nanci 2012; Scheuer & Black 2004; White et al. 2011*), which is replaced after the first years of life with (2) the permanent dentition that is formed during childhood and not replaced or remodelled.

The tooth type (incisor, canine, premolar or molar, see **Figure 3.1**) and the dental development is determined by the mesenchyme (see *Piesco & Avery* (*2002*) and *Fincham et al.* (*2000*) for a review on the molecular control of tooth development). Individual teeth are described in this work using the FDI World Dental Federation notation (ISO 3950, **Figure 3.1**). The directional terms used to describe specific tooth sites are visualised in **Figure 3.1** and outlined in **Table 3.1.**

Table 3.1 *Directional terms for teeth and major cusp names (after White et al. 2011).*

Direction name	Direction
Mesial	Portion of the tooth closest to the central incisors
Distal	Portion of the tooth away from the central incisors
Lingual	Portion of the tooth towards the tongue
Labial	Portion of the incisor/canine towards the chin
Buccal	Portion of the (pre)molar towards the cheek
Occlusal	Chewing surface of teeth
Interproximal tooth surface	Contact point of adjacent teeth

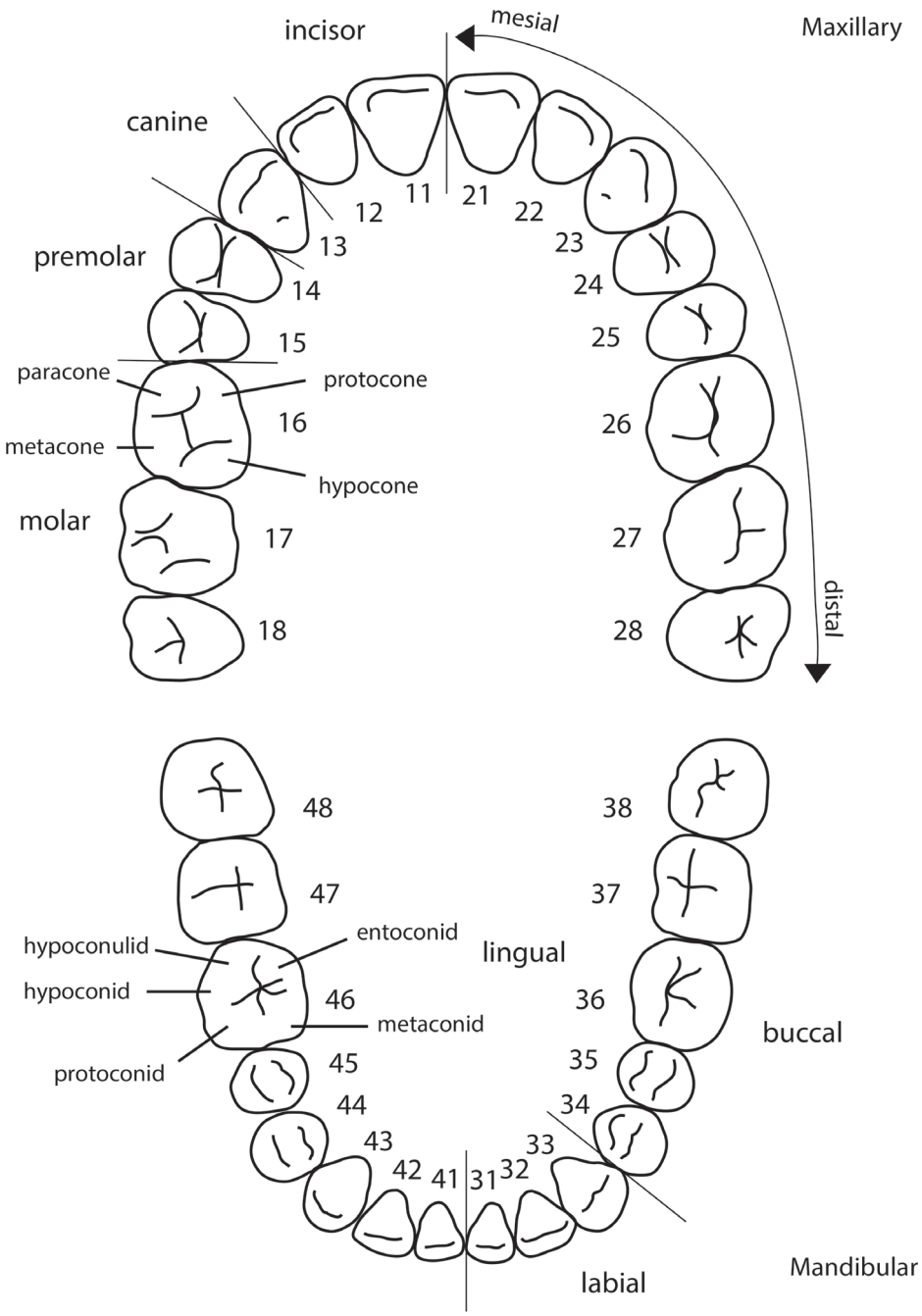


Figure 3.1 *Schematic of the permanent dentition, highlighting tooth types, individual tooth FDI notation, directional terms and molar cusp names (after White et al. 2011).*

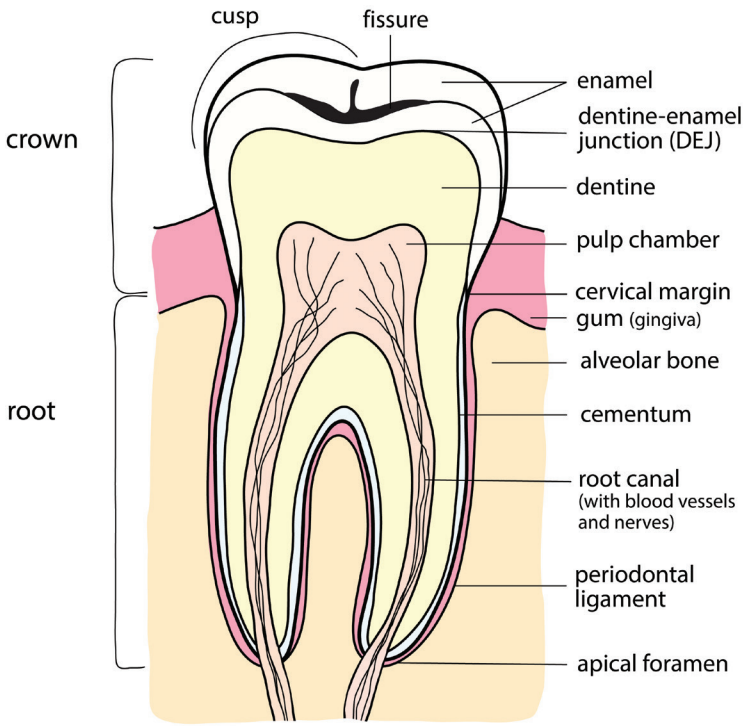


Figure 3.2 *Schematic of a molar, highlighting the different components of a tooth (Plomp 2020).*

All teeth have a crown and a root (**Figure 3.2**). The crown consists of an outer layer, the enamel, that covers the inner layer, the dentin, and the pulp chamber within the dentin**.** The line that separates the enamel from the dentine is termed the Dentine-Enamel Junction (DEJ). The pulp chamber contains the ends of the blood vessels and nerves that enter the tooth through the root. The root of the tooth is held into its alveolar bone socket by the collagen fibres of the periodontal ligament (*Bartlett 2013; Le Cabec et al. 2018; White et al. 2011; Williams & Elliott 1989*). The root is covered by a thin layer of cementum which is similar in many respects, particularly in chemical composition, to bone (*White et al. 2011; Williams & Elliott 1989*).

The development, eruption and size of teeth can vary based on sex, with the degree of sexual dimorphism varying between populations (*Hunt & Gleiser 1955; White et al. 2011*). Girls are generally ahead of boys in dental development (*Esan & Schepartz 2019; Nolla 1960; Nyström et al. 2007; Scheuer & Black 2004*). The greatest dimorphism is found in (deciduous) canines (*Bailit & Hunt 1964; Beyer-Olsen & Alexandersen 1995; Cardoso 2008; De Vito & Saunders 1990; Dean 2000; Ditch & Rose 1972; Garn et al. 1967; Hattab et al. 1996; İşcan & Kedici 2003; Viciano et al. 2011*).

Accuracy of sexing based on dental metrics varies usually lies between 58 % and 90 % (*Bailit & Hunt 1964; Cardoso 2008; De Vito & Saunders 1990; Ditch & Rose 1972; Hunt & Gleiser 1955; İşcan & Kedici 2003; Rösing 1983*). More recent methods use a minimally destructive surface etching of tooth enamel and identify the sex based on chromosome-linked isoforms of amelogenin, using nanoflow liquid chromatography mass spectrometry (*Stewart et al. 2017*).

Due to the lack of remodelling of teeth, their isotopic composition is not changed once they are formed (*Montgomery 2002; Ubelaker et al. 2006; Weatherell 1975; Zazzo et al. 2010*). Teeth form during childhood and thus provide isotopic information from an individual's diet and environment during that time period. Due to the different formation times of teeth it becomes possible to compare isotopic values for different time periods of an individual, containing information from birth up until 16 years of age (**Table 3.2**, **Figures 3.3** and **3.4**) (*AlQahtani et al. 2010; ElNesr & Avery 2002; Gustafson & Koch 1974; Massler et al. 1941; Moorrees et al. 1963; Nanci 2012; Reid & Dean 2006; Schour & Massler 1941; Smith 1991; White et al. 2011*).

The formation times of teeth are genetically constrained and as they are the most resistant tissue to external variables, such as diagenesis, malnutrition and disease, they are considered to be a reliable age indicator (*Liversidge 2003, 2015; Nolla 1960; Šešelj et al. 2019; Smith 1991*). Crown and root growth (*Fitzgerald & Rose 2008; Li & Risnes 2004; Risnes 1998; Smith 2006*), as well as maturation stages and eruption phases (*AlQahtani et al. 2010; Gustafson & Koch 1974; Massler et al. 1941; Schour & Massler 1941; Smith 1991*), cementum (*Le Cabec et al. 2018*), dentine development and composition (*Cameriere et al. 2013; Karkhanis et al. 2014; Kvaal et al. 1995; Marroquin et al. 2017; Meinl et al. 2007*), can therefore be used to estimate dental age. Tooth development remains the most reliable technique used for aging subadults (*AlQahtani 2019; Esan & Schepartz 2019; Scheuer & Black 2004; White et al. 2011*), with the exception of methods using the third molar (see below). Overviews and reviews of dental estimation methods and applications are extensively described elsewhere (*Drusini et al. 1997; Fitzgerald & Rose 2008; Griffin et al. 2009; Hillson 2005; Jayaraman et al. 2013; Liversidge 2003, 2015; Marroquin et al. 2017; Scheuer & Black 2004; Šešelj et al. 2019; Smith 1991; Soomer et al. 2003; Wang et al. 2017; Yan et al. 2013*).

There is idiosyncratic, sex, socio-economic, environmental and population variation in tooth development and eruption (*Blankenship et al. 2007; Chaillet et al. 2005; ElNesr & Avery 2002; Esan & Schepartz 2019; Guatelli-Steinberg et al. 2012; Harris 2007; Hillson 1996; Huda & Bowman 1994; Kasper et al. 2009; Liversidge 2008, 2015, 2003; Martin-de las Heras et al. 2008; McKenna et*

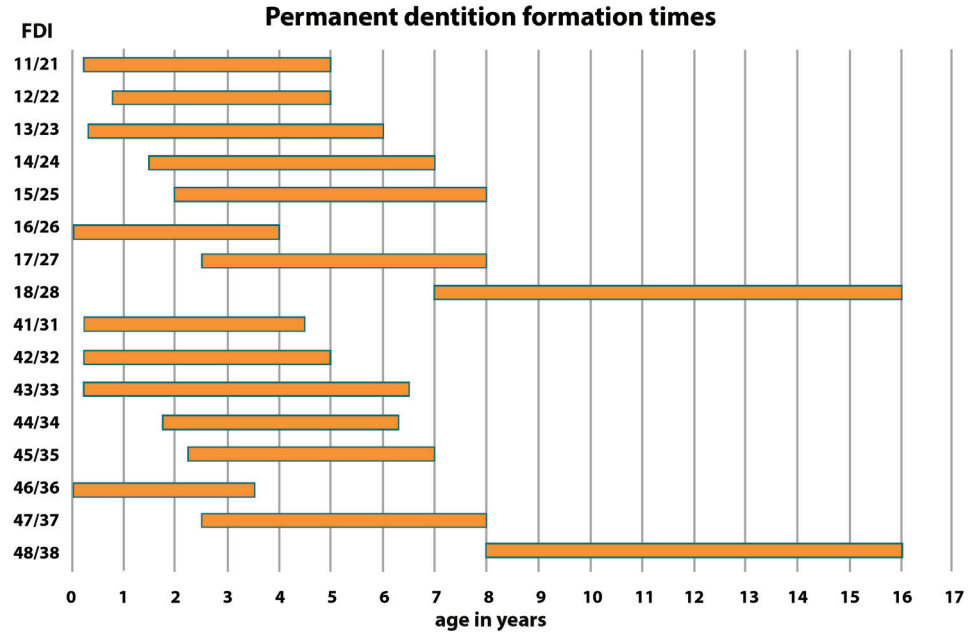


Figure 3.3 *Initial enamel formation until enamel crown completion ages (in years), based on previous studies (AlQahtani et al. 2010; ElNesr & Avery 2002; Gustafson & Koch 1974; Massler et al. 1941; Moorrees et al. 1963; Nanci 2012; Reid & Dean 2006; Schour & Massler 1941; Smith 1991; White et al. 2011). In general, the mandibular teeth precede the maxillary teeth in the permanent dentition.*

Table 3.2 *Enamel initiation and completion indicated per tooth (using FDI notation) in years. Information compiled from previous studies (AlQahtani et al. 2010; ElNesr & Avery 2002; Gustafson & Koch 1974; Massler et al. 1941; Moorrees et al. 1963; Nanci 2012; Reid & Dean 2006; Schour & Massler 1941; Smith 1991; White et al. 2011).*

Tooth	FDI Right	FDI Left	Initiation	Completion
Central Incisor	11	21	0.25	5
Lateral Incisor	12	22	0.8	5
Canine	13	23	0.3	6
First premolar	14	24	1.5	7
Second premolar	15	25	2	8
First molar	16	26	0	4
Second molar	17	27	2.5	8
Third molar	18	28	7	16
Central Incisor	41	31	0.25	4.5
Lateral Incisor	42	32	0.25	5
Canine	43	33	0.25	6.5
First premolar	44	34	1.75	6.3
Second premolar	45	35	2.25	7
First molar	46	36	0	3.5
Second molar	47	37	2.5	8
Third molar	48	38	8	16

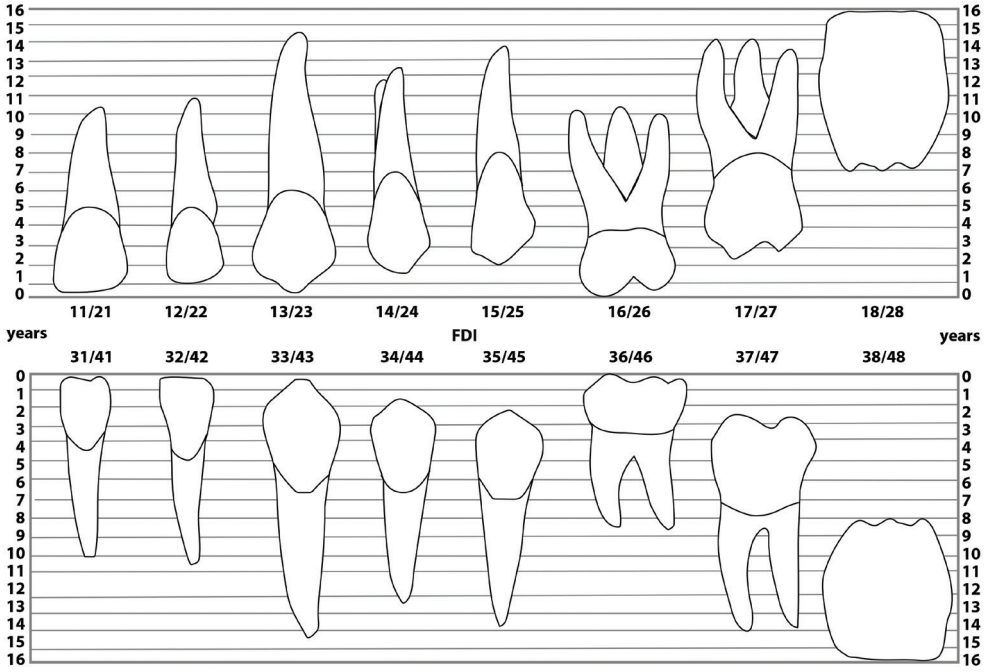


Figure 3.4 *Schematic representation of the growth time of the enamel of the permanent dentition. FDI notation is used to indicate the individual teeth (left and right side combined). The growth time is indicated in years. The data are derived from* **Table 3.1** *and the visual representation is based on a figure by Massler et al. (1941). Note the relative constricted time period in which the enamel of the first molars (16, 26, 36, 46) is formed (3-4 years), especially relative to the third molars (18, 28, 38, 48) where the enamel can take 7-8 years to develop.*

al. 2002; Nanci 2012; Nanda & Chawla 1966; Odusanya & Abayomi 1991; Olze et al. 2004; Prieto et al. 2005; Scheuer & Black 2004; Smith 2004; Thevissen et al. 2010). These factors have a greater impact on bone modelling than the dentition, however (*Antoine et al. 2009; Beaumont et al. 2015; Demirjian et al. 1985; Elamin & Liversidge 2013; Esan & Schepartz 2019; Garn et al. 1965; Jayaraman et al. 2013; Liversidge 2015; McKenna et al. 2002; Smith 1991; Smith 2004; Wang et al. 2017; Yan et al. 2013*), and several scholars argue that population-specific standards for age estimation based on the dentition are therefore not required (*Braga et al. 2005; Liversidge 2015; Liversidge & Marsden 2010; Marroquin et al. 2017; Thevissen et al. 2010*). Nevertheless, the enamel formation times in **Table 3.2** are broad estimates and not all world regions are represented (*Esan & Schepartz 2019; Smith 1991*).

The third molar, the tooth under study in this work, is the most variable tooth in size, formation and eruption (*Blankenship et al. 2007; Dean 2000; Garn et al. 1962; Harris 2007; Liversidge 2008; Martin-de las Heras et al. 2008; Massler et al. 1941; Mincer et al. 1993*), see **Figures 3.3** and **3.4**. Third molars are not always developed and may be malformed and impacted (*Levesque et al. 1981; Liversidge 2008; Thevissen et al. 2010*). Maxillary third molars tend to develop faster than their mandibular counterparts (*Arany & Yoshioka 2004; Jung & Cho 2014; Kasper et al. 2009; Mincer et al. 1993; Solari & Abramovitch 2002*; but see *Martin-de las Heras et al. 2008; Odusanya & Abayomi 1991*). Differences between left- and right-side molars are random (*Arany & Yoshioka 2004; Blankenship et al. 2007; Daito et al. 1992; Demisch & Wartmann 1956; Levesque et al. 1981; Mincer et al. 1993; Prieto et al. 2005*; but see *Kasper et al. 2009*). Sex differences are noted, with third molar development occurring earlier in males (*Arany & Yoshioka 2004; Blankenship et al. 2007; Garn et al. 1962; Harris 2007; Jung & Cho 2014; Kasper et al. 2009; Martin-de las Heras et al. 2008; Mincer et al. 1993; Nyström et al. 2007; Šešelj et al. 2019; Solari & Abramovitch 2002*; but see *Daito et al. 1992; Demisch & Wartmann 1956; Levesque et al. 1981; Nolla 1960*), a pattern opposite to the rest for the dentition (*Nyström et al. 2007; Scheuer & Black 2004*).

Once a tooth erupts, it begins to progressively wear during an individual's lifetime. This wear is the loss of the occlusal (chewing) surface of the tooth crown. Wear rate and patterns are governed by tooth developmental sequences, tooth morphology and size, internal crown structure, tooth angulation, non-dietary tooth use, the biomechanics of chewing, and diet which are population-specific (*Hillson 1996; Walker et al. 1991*). Several studies have quantified the rate of tooth wear to estimate age (*Bartholdy et al. 2019; Brothwell 1989; Kvaal et al. 1994; Mays 2002; Miles 2001; Walker et al. 1991*). Dental wear, as well as dental modifications, can also be analysed to study an individual's life history (*Mickleburgh 2008; Milner & Larsen 1991*). As dental wear and dental modification damage the tooth and expose the dentine this affects sample availability for isotopic analyses.

3.2.1 Dentine

Dentine is the second hardest tissue in the body, consisting primarily of hydroxyapatite and collagen (**Table 3.3**, *Gage et al. 1989; Piesco & Simmelink 2002; Williams & Elliott 1989*). Due to its elastic nature, dentine serves as a shock absorber for the overlying enamel (*Bartlett 2013; Moradian-Oldak 2012; Pashley 1996; Piesco & Simmelink 2002*). Mineralised dentine is present before the enamel formation begins and dentine formation follows a separate formation processes from enamel (Ars*enault & Robinson 1989; Diekwisch et al. 1995; Fincham & Simmer*

1997; Kallistová et al. 2017; Sasaki et al. 2007). Like bone, dentine is a living tissue (*Williams & Elliott 1989*). Unlike bone, however, it does not contain blood vessels and does not continuously remodel (*Rowles 1967*). The formation of dentine (dentinogenesis) can be subdivided into primary, secondary, and tertiary dentine:

(1) Primary dentine comprises the bulk of the dentine (*Rowles 1967*). Primary dentine is formed before and during eruption of the tooth (*Nanci 2012; Piesco & Avery 2002*). Primary dentine does not remodel during life (*Beaumont et al. 2014; Hillson 2005; Piesco & Avery 2002*) and therefore contains isotopic values representing the childhood period, like enamel. Human primary dentine begins to form in what later becomes the crown and moves away from the dentinal enamel junction towards the pulp chamber (**Figure 3.2**). The dentine is laid down in incremental layers around the pulp chamber (**Figure 3.5**, *Dean & Scandrett 1995; Hillson 1996, 2005; Piesco & Avery 2002; Simmer et al. 2010*). This makes sampling the actual increments difficult as the increments curve around the pulp chamber and down the root (*Pederzani & Britton 2019*). As such, horizontal sampling will always result in the average isotopic value of multiple sequentially ordered "sleeves" (*Balasse 2003; Beaumont et al. 2013; van der Sluis et al. 2015*).

Table 3.3 *The enamel and dentine composition, density and crystal size of teeth, based on Brudevold & Söremark 1967; Hillson 2005; Pashley 1996; Piesco & Simmelink 2002; Williams & Elliott 1989.*

Characteristics	Enamel	Dentine
Weight	96 % inorganic >1 % organic 3 % water	70 % inorganic 20 % organic (primarily collagen) 10 % water
Volume	89 % inorganic 2 % organic 9 % water	47 % inorganic 32 % organic 21 % water
Organic	Amelogenins (removed during development) Enamelins (tightly bound to the enamel crystals)	Collagen types I and II Phosphoproteins Carboxyglutamate-containing (GLA) proteins (osteocalcin and matrix gla) Acidic glycoproteins Plasma proteins Lipids Growth-related factors
Knoop Hardness	343	68
Crystal size	30 nm in width and 90 nm in thickness. lengths of at least 100 pm	Crystals of dentine and bone are only 3-6 nm thick and up to 60 nm long

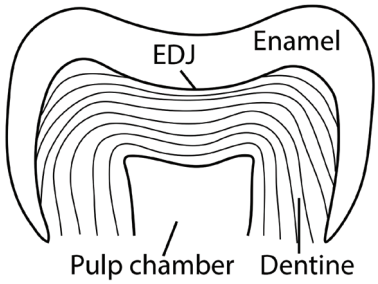


Figure 3.5 *Schematic of incremental deposition of dentine (after Fitzgerald & Rose 2008).*

(2) After completion, primary dentine remains in connection with the pulp chamber. In contrast to enamel, this allows for the deposition of secondary dentine inside the pulp chamber during life (*Drusini et al. 1997; Gage et al. 1989; Rowles 1967*). As secondary dentine is connected to the blood supply, isotopic concentrations can accumulate in dentine over life (*Montgomery 2002; Rowles 1967*), with lead turnover estimations of 1 % per year (*Gulson et al. 1997; Kamenov & Curtis 2017*). The regular deposition of secondary dentine can be used to estimate age of adults over the age of 25 years (*Cameriere et al. 2013; Karkhanis et al. 2014; Kvaal et al. 1995; Marroquin et al. 2017; Meinl et al. 2007*).

(3) Tertiary (or reparative) dentine is formed in response to caries, attrition, and trauma (*Drusini et al. 1997; Gage et al. 1989; Hillson 2005; Pashley 1996; Piesco & Avery 2002*). The degree of secondary and tertiary dentine formation depends on physiological and pathological stimuli (*Nanci 2012*).

Incremental isotopic analysis of dentine is based on the principle that this tissue forms at a known rate, and once formed does not remodel (*Hillson 1996; Nanci 2012*). This means that the dentine can be sectioned into increments that represent a specific period of time during development (*Beaumont et al. 2013; Beaumont & Montgomery 2015; Eerkens et al. 2011; Henderson et al. 2014; King et al. 2018*). Incremental isotopic analysis of dentine has been applied to study weaning and dietary patterns in archaeological populations (*Beaumont et al. 2013; Beaumont & Montgomery 2016; Burt 2015; Eerkens et al. 2011; Eerkens, Sullivan et al. 2016; Eerkens & Bartelink 2013; Scharlotta et al. 2018*).

3.2.2 Enamel

Enamel, the crown covering teeth, is the hardest tissue in the human body and the archaeological diamond of human tissues (**Figures 3.2** and **3.5**). Enamel is highly mineralised and has a low degree of porosity which generally allows it to preserve well in archaeological contexts (*Bell et*

al. 1991; Chiaradia et al. 2003; Hoppe et al. 2003; Lee-Thorp 1989; Lee-Thorp & Sponheimer 2003; Lee-Thorp & van der Merwe 1991; Schoeninger et al. 2003; Trickett et al. 2003; Wang & Cerling 1994). Enamel is, however, not always unaffected by diagenesis, and particular the surface of enamel can be chemically altered, depending on the integrity of the structure of the tooth itself, the age and environmental context of the sample (*de Winter et al. 2019; Kohn et al. 1999; Schoeninger et al. 2003*). In mature mineralised enamel the pore size is accessible to univalent ions, but higher charge and larger sized polyvalent ions (such as Pb^{2+}, Sr^{2+} and Nd^{3+}) cannot enter the pore space (*Simmer & Fincham 1995; Smith 1998; Sollner 1955*). After the formation of enamel is complete, it does not remodel like bone, as it is avascular (not regulated by blood vessels) and acellular (not containing cells) (*Fitzgerald & Rose 2008; Hillson 2005; Lacruz et al. 2017; Simmer et al. 2010; Simmer & Fincham 1995; Simmer & Snead 1995; White et al. 2011*). This means that enamel can only be changed by physical processes (wear, cultural modifications, trauma) or chemical processes (caries). The isotopic composition of human tooth enamel is therefore representative of the diet at time of tooth formation (*Montgomery 2002; Ubelaker et al. 2006; Weatherell 1975; Zazzo et al. 2010*).

Enamel is an heterogenous material which consists primarily (~95-97 %) of inorganic material, with less than 2 % organic material and ~2-4 % water (**Table 3.3**, *Deakins & Volker 1941; Eanes 1979; He & Swain 2009; LeFevre & Manly 1938; Nanci 2012; Piesco & Simmelink 2002; Simmer & Fincham 1995; Weatherell 1975; White et al. 2011; Williams & Elliott 1989*). Most of the inorganic material is hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$ (*Aoba 1996; Elliott 2002; Hillson 2005; Lacruz et al. 2013, 2017; Nurbaeva et al. 2017; Piesco & Simmelink 2002; Robinson, Kirkham et al. 1995; Sakae et al. 1997; Smith 1998; Weatherell 1975; Zapanta LeGeros 1981*). The (OH) in $Ca_{10}(PO_4)_6(OH)_2$ can be a variety of ions (usually hydroxyl (OH^-) and fluoride (F^-) (*Hillson 2005; Lacruz et al. 2017; Piesco & Avery 2002; Simmer et al. 2010*). Calcium (Ca^{2+}) and phosphate (PO_4^{3-}) may also be replaced by other ions, such as Sr^{2+}, Zn^{2+}, Pb^{2+} etc. There is continuous variation in this general formula, with substitution, partial or complete, of any of the ions (*Betts et al. 1981; Brudevold & Söremark 1967; Eanes 1979; He & Swain 2009; Hillson 2005; Lacruz et al. 2017; Lee-Thorp 1989; Sakae et al. 1997; Simmer & Fincham 1995; Zapanta LeGeros 1981*).

Enamel consists of large hydroxyapatite crystals (30 nm in thickness and 60-90 nm in height; *Brudevold & Söremark 1967; Eanes 1979; Hillson 2005; Nanci 2012; Piesco & Simmelink 2002; Rönnholm 1962b; Sakae et al. 1997; Zapanta LeGeros 1981*), which are highly orientated to provide them with a certain degree of flexibility (*Boyde 1997; Piesco & Simmelink 2002; Rönnholm 1962b*). This flexibility is enhanced by the organic fraction of the enamel, primarily

protein, that functions as a binding material (*Piesco & Simmelink 2002; Simmer & Fincham 1995*). The orientation of the crystals and proteins that bind them allows enamel to resist fracture and load-bearing wear (*An et al. 2012; Castiblanco et al. 2015; Ge et al. 2005; He & Swain 2009; White et al. 2001; Xu et al. 1998*). The proteins consist of two classes: amelogenin (AMELX) and non-amelogenins (enamelin (ENAM), tuftelin, ameloblastin (AMBN), enamelysin (MMP20)) (*Bartlett 2013; Castiblanco et al. 2015; Deutsch 1989; Moradian-Oldak 2012*). Higher protein concentrations are found close to the EDJ, in cuspal enamel (**Figure 3.6**), in fissures on the occlusal surface, and in the cusp enamel immediately beneath the occlusal surface (*He et al. 2010; He & Swain 2009; Hillson 2005; Montgomery 2002; Robinson, Kirkham et al. 1995; Simmons et al. 2013; Weatherell 1975*). These areas are therefore slightly less mineralised than the lateral enamel and inner enamel (*Akkus et al. 2016; Montgomery 2002; Robinson, Weatherell et al. 1995; Simmons et al. 2013; Weatherell 1975*). The surface and occlusal enamel is more mineralised and provides the tooth surface with resistance to external chemical and physical influences (*Al-Mosawi et al. 2018; Brudevold & Söremark 1967; Crabb 1959; Cuy et al. 2002; He et al. 2010; He & Swain 2009; Meredith et al. 1996; Park et al. 2008; Piesco & Avery 2002; Piesco & Simmelink 2002; Simmons et al. 2013; Weidmann et al. 1967; Williams & Elliott 1989; Zazzo et al. 2005*). Differences in rates of mineralisation of enamel have, however, been reported between individuals and for different sites of the same tooth of humans, including more mineralised inner enamel at the DEJ (*Akkus et al. 2016; Al-Mosawi et al. 2018; Brudevold & Söremark 1967; Cuy et al. 2002; Deakins & Volker 1941; Gustafson & Gustafson 1967; Humphrey et al. 2007; LeFevre & Manly 1938; Weatherell et al. 1966; Weidmann et al. 1967*). Lower degrees of mineralisation have been reported for carious teeth (*Akkus et al. 2016; Eanes 1979; He et al. 2010; LeFevre & Manly 1938*).

The enamel proteins play an important role in the organisation and formation of the enamel crystals (*Bartlett 2013; Simmer et al. 2010; Simmer & Fincham 1995; Simmer & Snead 1995; Smith 1998*). The most abundant protein in enamel is amelogenin (90 %) (*Castiblanco et al. 2015; Fincham & Moradian-Oldak 1995; Moradian-Oldak 2012; Robinson et al. 1998; Simmer & Fincham 1995; Simmer & Snead 1995*). Amelogenin, enamelin and ameloblastin are suggested to promote and/or control crystal organisation, crystal morphology and growth (*Aoba et al. 1987; Bartlett 2013; Carneiro et al. 2016; Diekwisch et al. 1995; Du et al. 2005; Fincham et al. 1995, 2000; Kwak et al. 2014; Moradian-Oldak 2012; Piesco & Avery 2002; Robinson et al. 1998; Simmer & Fincham 1995; Tarasevich et al. 2007; Wang et al. 2008; Wright et al. 2009*). Less information is available on non-amelogenin matrix proteins and lipids (*Castiblanco et al. 2015; Fincham et al. 2000; Robinson, Kirkham et al. 1995; Smith 1998*). Enamelin and tuftelin, expressed prior to crystal formation and persistent at the DEJ (*Fincham et al. 2000*), have been suggested as potential candidates

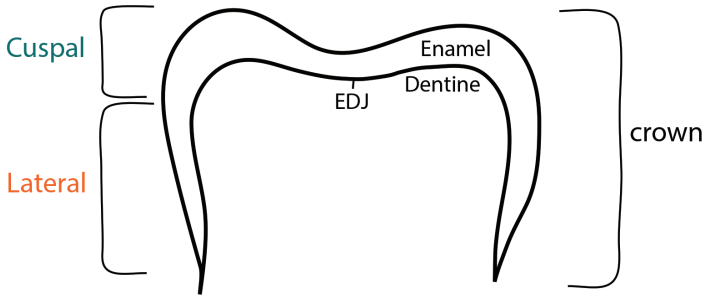


Figure 3.6 *Schematic of outer layer of the tooth crown, the enamel. A distinction can be made between the occlusal surface (cuspal enamel) and the sides of the dental element (lateral enamel), where lateral enamel is secreted in a lateral direction and does not contribute to increase the tooth height (Dean 2000).*

to start the enamel formation (enamel nucleator) (*Aoba et al. 1987; Bartlett 2013; Deutsch 1989; Moradian-Oldak 2012*).

Enamel formation

Enamel is formed (in a process named dentinogenesis) by cells called odontoblasts (*Berkovitz et al. 1989; Nanci 2012; Piesco & Avery 2002*). Limited information is available on the timing and the mechanisms of the enamel mineralisation process, as this is a complex process and human samples are scarce (*Al-Mosawi et al. 2018; Balasse 2002; Bartlett & Simmer 1999; Carneiro et al. 2016; Fincham et al. 1999; Kallistová et al. 2017; Montgomery 2002; Park et al. 2008; Robinson et al. 1981; Simmer & Fincham 1995; Simmons et al. 2013*). Several studies have reviewed enamel development and structure in detail (*Bartlett 2013; Bartlett & Simmer 1999; Berkovitz et al. 1989; Guatelli-Steinberg 2010; Gustafson & Gustafson 1967; Nanci 2012; Piesco & Avery 2002; Simmer & Fincham 1995; Smith 1998; Smith 2004*), using a number of development stages. Here enamel development is described in three stages:

(1) Pre-secretion

Once the shape of the crown of the tooth is established by the internal enamel epithelium it differentiates into a closely linked chain of cells called ameloblasts, the cells that secrete the organic enamel matrix (**Figure 3.7**, *Nanci 2012; Rönnholm 1962a; Sasaki et al. 2007*). Enamel crystals form on the previously calcified dentine surface, at the EDJ (*Simmer et al. 2010*). The EDJ connects the enamel and dentine, with dentinal components projecting into the enamel

(*Boyde 1997; Montgomery 2002; Shore et al. 1995*). The initial enamel layer is aprismatic as the Tomes' processes did not form yet (**Figure 3.7**, *Risnes 1998; Smith 2004*). The Tomes' process (**Figure 3.7**) is a distal/apical extension of the ameloblasts which secretes enamel (amelogenins) and is present throughout the secretion phase (*Hillson 2005; Piesco & Avery 2002; Risnes 1998; Rönnholm 1962a*).

(2) Secretion

In the secretory stage the ameloblasts elongate and develop the Tomes' process**,** which provides the sites of matrix secretion, matrix removal and mineral transport (*Lacruz et al. 2017; Sasaki et al. 2007; Smith 1998*). Tomes' processes vary in size and shape between different stages in amelogenesis, and in different areas of the crown. The movement of the ameloblasts in relation to one another allows for the deposition of complex patterns of enamel that make the enamel resistant to grinding and cutting processes (*Bartlett 2013; Hillson 2005*). This pattern is more complex in the cusps of molars (also known as gnarled enamel) (*Piesco & Simmelink 2002*) and further strengthens the enamel (*Piesco & Simmelink 2002; Skobe & Stern 1980*).

Each ameloblast secretes hydroxyapatite crystals from its Tomes' process to create a layer of enamel (**Figure 3.7**). Crystals secreted from the proximal portion of the Tomes' process (interrod enamel) are orientated perpendicular to those secreted from the distal portion of the Tomes' process (enamel rods) (**Figure 3.7**, *Avery et al. 1961; Piesco & Simmelink 2002; Risnes 1998; Rönnholm 1962b; Sasaki et al. 2007; Simmer & Fincham 1995; White et al. 2001*).

The initial layer of enamel is formed by the Tomes' processes, which secrete proteins that are laid down on the dentine and mineralised immediately, thus not containing enamel rods (**Figure 3.7**, *Piesco & Avery 2002*). As more enamel is formed the ameloblasts move away from this initial layer at the EDJ and secrete a protein rich matrix (30 %), seeding ribbon-like crystallites into the space they leave behind (*Bartlett 2013; Boyde 1997; Hillson 2005; Robinson, Weatherell et al. 1995; Sasaki & Shimokawa 1995*). The enamel crystallites are organised into bundles known as prisms that vary in orientation and are 3-12 µm in size (**Figure 3.8**, *Al-Mosawi et al. 2018; Bartlett 2013; Hillson 2005; Shore et al. 1995; Simmer & Fincham 1995*). At the border between the rod and inter-rod enamel (**Figure 3.7**), a prism sheath (also known as enamel or rod sheath) is formed that has a more concentrated organic matrix (corresponding to the non-secretory surfaces of the Tomes' process) (*Bartlett 2013; Gustafson & Gustafson 1967; Hillson 2005; Piesco & Avery 2002; Robinson, Kirkham et al. 1995; Sasaki et al. 2007; White et al. 2001*).

The ameloblasts continue to secrete the hydroxyapatite crystal layer by layer, building up the enamel incrementally (successive apposition of different layers), leaving growth lines called Retzius Lines (**Figure 3.8**, *Gustafson & Gustafson 1967; Li & Risnes 2004; Risnes 1998*). Retzius lines are a result of differential deposition of rod and interrod enamel and vary in their width and darkness throughout the enamel (*Fitzgerald 1998; Fitzgerald & Rose 2008; Newman & Poole 1974; Piesco & Simmelink 2002; Risnes 1998*). Retzius lines reach the outer surface of the enamel, where they are known as perikymata (**Figure 3.8**, *Fitzgerald & Rose 2008; Gustafson & Gustafson 1967; Piesco & Simmelink 2002; Risnes 1998; Tafforeau et al. 2007*).

Retzius lines represent a time period that can vary from 6 to 14 days between individuals (*Dean 2000; Dean et al. 2001; Dean 1987, 1989; Fitzgerald & Rose 2008; Guatelli-Steinberg 2010; Huda & Bowman 1994, 1995; Mahoney et al. 2018; Newman & Poole 1974; Piesco & Simmelink 2002; Reid & Dean 2006; Risnes 1998; Smith & Tafforeau 2008; Tafforeau et al. 2007*). Their sequence in one tooth can be matched with other teeth formed at the same time in the same individual (*Fitzgerald 1998; Fitzgerald & Rose 2008; Gustafson & Gustafson 1967*). This suggest that the secretory ameloblast may be under circadian control (daily rhythms that regulate the activity of cells) (*Antoine et al. 2009; Dean 1989; Fitzgerald & Rose 2008; Lacruz et al. 2012; Mahoney et al. 2018; Newman & Poole 1974; Schour 1936; Schour & Poncher 1937; Zheng et al. 2013*). It should be noted that the cuspal enamel of the crown grows more slowly than the lateral enamel, resulting in thinner layers in lateral enamel (**Figure 3.8**, *Fitzgerald & Rose 2008; Huda & Bowman 1995; Smith 2004*).

The neonatal line is the most prominent Retzius line (*Antoine et al. 2009; Piesco & Simmelink 2002*) found in teeth that are formed at the time of birth (deciduous teeth and first molars), and marks the boundary between prenatal enamel and postnatal enamel (*Dean et al. 2019;*

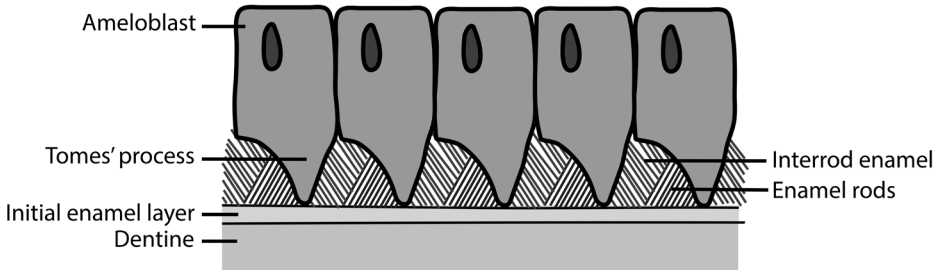


Figure 3.7 *Schematic drawing of the Tomes' process of ameloblasts secreting interrod and rod enamel.*

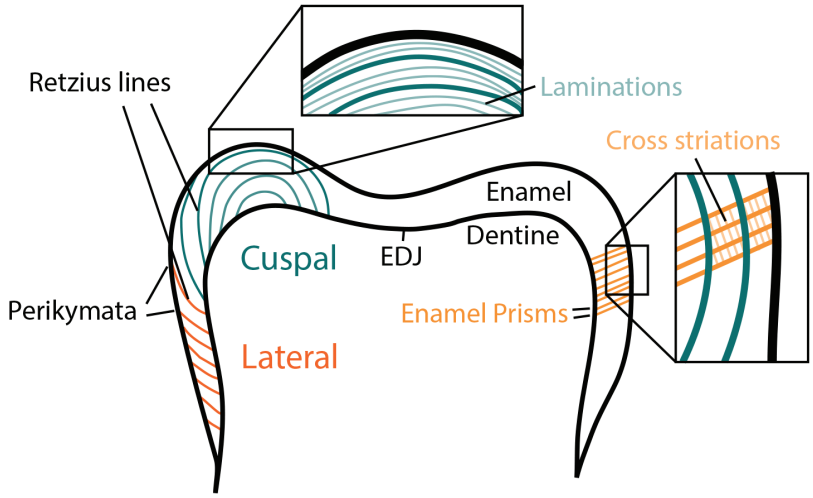


Figure 3.8 *Schematic representation of enamel formation, after Dean (2000) and Smith (2006). The Retzius lines are growth lines in the inner enamel that reach the surface where they are called perikymata. In between the Retzius lines smaller growth lines are found: laminations. Both Retzius lines and laminations are crossed by the enamel prisms, which contain cross-striations within them.*

Fitzgerald & Rose 2008; Huda & Bowman 1995; Humphrey et al. 2007, 2008; Schour 1936). It is thought that the neonatal line is more pronounced due to the nutritional and hormonal changes occurring at birth (*Piesco & Avery 2002; Simmer et al. 2010*). Diseases or deficiencies may also result in more pronounced lines (also known as Wilson's bands) (*Fitzgerald & Rose 2008; Gustafson & Gustafson 1967; Piesco & Simmelink 2002; Risnes 1998; Simmer et al. 2010*).

Laminations, regularly spaced and parallel to Retzius lines also represent regular (or daily, *Smith 2006; Smith & Tafforeau 2008*) enamel deposition in aprismatic enamel (**Figure 3.8**, *Allan 1959; Crabb 1959; Smith 2004, 2006; Tafforeau et al. 2007*).

Prism cross-striations are incremental enamel markings consisting of light and dark bands across the prisms (**Figure 3.8**), formed within a day (*Antoine et al. 2009; Crabb 1959; Dean 2000; Dean 1989; Fitzgerald 1998; Fitzgerald & Rose 2008; Hillson 2005; Lacruz et al. 2012; Li & Risnes 2004; Mahoney et al. 2018; Newman & Poole 1974; Piesco & Avery 2002; Piesco & Simmelink 2002; Risnes 1998; Simmer et al. 2010; Smith 2004, 2006; Smith & Tafforeau 2008; Zheng et al. 2013*). Cross-striations vary in size within the enamel, being smaller due to slower formation rate in the inner enamel compared to the outer/occlusal enamel (*Huda & Bowman 1995; Risnes 1998*).

As Retzius lines, perikymata, laminations and cross-striations are believed to be under circadian

control (*Antoine et al. 2009; Lacruz et al. 2012; Smith 2004, 2006; Tafforeau et al. 2007; Zheng et al. 2013*), they can be used to establish a chronology of enamel formation (*Dean 2000a; Dean et al. 2001; Hillson 2005; Smith 2004, 2006*), and thus can be used to estimate the age of an individual (*Fitzgerald & Rose 2008; Hillson 1996, 2005; Huda & Bowman 1994, 1995; Li & Risnes 2004; Risnes 1998; Smith 2006*).

(3) Maturation

Once the enamel layer reaches its full height, the ameloblasts enter the maturation stage. The maturation stage is the longest stage in enamel formation, lasting for years, where the enamel crystals expand in thickness (*Daculsi & Kerebel 1978; Robinson 2014; Simmons et al. 2013; Smith 1998*). The majority of the mineral is added to the enamel matrix in the maturation phase (*Green et al. 2018; Simmer et al. 2010*). The ameloblasts stop movement and retract their Tomes' processes (*Nanci 2012; Piesco & Avery 2002*). There are two types of maturation ameloblasts: ruffled- and smooth-ended, which ameloblasts may switch between (*Lacruz et al. 2017; Smith 2004*). The ruffled-ended ameloblast incorporate the calcium and phosphate into the enamel. The smooth-ended ameloblasts remove the protein and water (*Lacruz et al. 2017; Smith 2004; Zheng et al. 2013*). The ameloblasts degrade and are eventually shed (*Fitzgerald & Rose 2008*).

The ameloblasts and proteins degrade and are replaced by hydroxyapatite (*Bartlett & Simmer 1999; Crabb & Darling 1960; Hillson 2005; Nanci 2012; Piesco & Avery 2002; Piesco & Simmelink 2002; Sasaki et al. 2007; Simmer & Fincham 1995; Smith 1998; Suga 1982*). Small fragmented peptides are left from the original protein-rich matrix. Proteinases play a role in the removal of the structural proteins and facilitate crystal maturation (*Aoba et al. 1987; Simmer & Hu 2002; Smith 1998*): Matrix metalloproteinase-20 (MMP20) during secretion and kalikrein-4 (KLK-4) during the maturation stage (*Bartlett 2013; Lu et al. 2008; Moradian-Oldak 2012*). By removing the proteins, the crystallites can gradually expand in volume and form mature enamel (*Bartlett 2013; Brudevold & Söremark 1967; Diekwisch et al. 1995; Green et al. 2017; Kallistová et al. 2017; Nanci 2012; Robinson 2014; Robinson et al. 1997; Simmons et al. 2013*). Prolongation of tooth development is associated with an increase of crystallinity in molars (*Kallistová et al. 2018*).

The enamel surface is smoothed off with a final layer of aprismatic enamel (*Bartlett 2013; Hillson 2005; Piesco & Avery 2002; Risnes 1998; Shore et al. 1995; Simmer et al. 2010; Smith 1998; Smith 2004*). The final thickness of the enamel is the result of the growth rate and duration (*Guatelli-Steinberg et al. 2012; Risnes 1998; Simmer et al. 2010*), as well as the active number of ameloblasts present (*Mahoney et al. 2018; Simmer et al. 2010*).

The exact mechanisms underlying the mineralisation process of human enamel are debated (*Simmer & Fincham 1995*). Most scholars think mineralisation is a single continuous process in which the entire cusp is involved, where the innermost portion of the enamel mineralises first (*Allan 1959; Avery et al. 1961; Balasse 2003; Crabb 1959; Crabb & Darling 1960; Engfeldt & Hammarlund-Essler 1956; Fincham et al. 1995; Humphrey et al. 2007; Kallistová et al. 2017; Montgomery 2002; Reade et al. 2015; Smith 1998; Wilson & Beynon 1989*). Other studies (*Al-Mosawi et al. 2018; Aoba & Moreno 1990; Applebaum 1943; Dean 2000; Passey & Cerling 2002; Piesco & Avery 2002; Reade et al. 2015; Suga 1982*) describe the mineralisation process as starting from the occlusal surface and moving downwards to the EDJ and cervical part of the crown. These conflicting interpretations illustrate that the process of mineralisation is complex and consists of multiple processes of which the mechanics and interrelationships are not yet fully understood.

Enamel defects

Enamel can show defects resulting from disturbances during enamel secretion (defects in the amount of enamel such as hypoplasia, grooves and pits) or maturation (deficiencies in the mineral content such as hypocalcifications and opaque patches) (*Goodman & Rose 1991; Guatelli-Steinberg 2010; Hillson 2005, 2008; Hu et al. 2007; Lacruz et al. 2017; Smith & Tafforeau 2008*). These defects are non-specific, as the growth of enamel can be affected by various factors including diet, disease, exposure to heavy metals or excessive fluoride, vitamin or iron deficiencies, nutritional and physiological factors (*Avery 2002; Garn et al. 1965; Goodman & Rose 1991; Hillson 2008; Lacruz et al. 2017; Schour & Poncher 1937; Smith 2004*). Mutations in structural proteins can also affect enamel formation (*Bartlett 2013; Bartlett & Simmer 1999; Castiblanco et al. 2015; Lacruz et al. 2017; Moradian-Oldak 2012; Robinson et al. 1998; Simmer et al. 2010*). The extent of the defect is dependent on the nature of the causal substance, the degree of excess or deficiency, and the developmental time frame (*Avery 2002*). It is currently unknown what the effect of these defects are on the isotopic composition of the enamel.

3.3 Dental caries

Dental caries cause progressive demineralisation of the enamel, dentine and cement (*Akkus et al. 2016; Arends & Ten Cate 1981; Hillson 2005, 2008; White et al. 2011*). The demineralisation of dental caries is caused by organic acids which are formed during the fermentation of carbohydrates, primarily sugars, by bacteria in dental plaque (*Arends & Ten Cate 1981; García-*

Godoy & Hicks 2008; Hillson 2005, 2008; Mundorff-Shrestha et al. 1994; Robinson, Weatherell et al. 1995; Selwitz et al. 2007). Dental plaque is a soft adherent coating, or biofilm, consisting primarily of bacteria (*Selwitz et al. 2007*). Plaque accumulates in areas that are not cleaned effectively (molar fissures, interproximal spaces, etc.). The bacteria that make up dental plaque produce acids that attack the enamel which responds by releasing calcium in defence, thereby decreasing its mineral content (*Akkus et al. 2016; He et al. 2010; Selwitz et al. 2007; Sui et al. 2018*). If the plaque is not removed it can become calcified, forming dental calculus (*Hillson 2005, 2008; Piesco & Simmelink 2002; Williams & Elliott 1989*). The falling pH (5.5) as a result from the acids produced by bacteria in the plaque and calculus causes the enamel to dissolve and become porous (*García-Godoy & Hicks 2008; Robinson, Weatherell et al. 1995; Selwitz et al. 2007; Williams & Elliott 1989*). Initially, the porosity appears as a white or brown spot in the otherwise translucent enamel (*Bell et al. 1991; Brudevold & Söremark 1967; Ismail 1997; Lacruz et al. 2017; Piesco & Simmelink 2002; Selwitz et al. 2007*). Demineralisation progresses beneath an intact enamel surface (*Brudevold & Söremark 1967; Ismail 1997*). Collapsing of the surface structure or cavitation occurs with progressive demineralisation. However, the removal of plaque and saliva can prevent the demineralisation process (*García-Godoy & Hicks 2008; Selwitz et al. 2007*). Additionally, reversal of the demineralisation process or remineralisation can occur (*Cross et al. 2018; García-Godoy & Hicks 2008; Ismail 1997; Li et al. 2014; Piesco & Simmelink 2002; Robinson, Weatherell et al. 1995; Selwitz et al. 2007; Sui et al. 2018*). Remineralisation may take place as minerals from oral secretions return to the partially demineralised enamel (*Arends & Ten Cate 1981; Featherstone et al. 1981; García-Godoy & Hicks 2008; Li et al. 2014; Selwitz et al. 2007*). The frequency and length of the respective stages in this cycle (demineralisation vs remineralisation) and the complex interactions (bacterial metabolism, salivary composition, diet, hygiene, etc.) will determine whether or not a carious lesion develops (see *Figure 3 in García-Godoy & Hicks 2008; Piesco & Simmelink 2002; Selwitz et al. 2007*). Fluoride also plays an important role in the remineralisation process and is exchanged within surface enamel, the outer layer of enamel of approximately ~200 µm (*Arends & Ten Cate 1981; Brudevold & Söremark 1967; García-Godoy & Hicks 2008; Humphrey et al. 2007; Ismail 1997; Piesco & Simmelink 2002; Robinson, Weatherell et al. 1995*). The rate at which the enamel crystals demineralise may also be governed by the enamel crystal size or enamel mineral concentration (*Akkus et al. 2016; Shellis 1984; Targino et al. 2011*), and defects or impurities in the enamel (*Eanes 1979; Piesco & Avery 2002*). Remineralised enamel is discontinuous in structure compared to the highly-ordered structure originally produced in mineralisation processes (*Arends & Ten Cate 1981*). The effects of caries on the isotopic composition of enamel are currently unquantified.

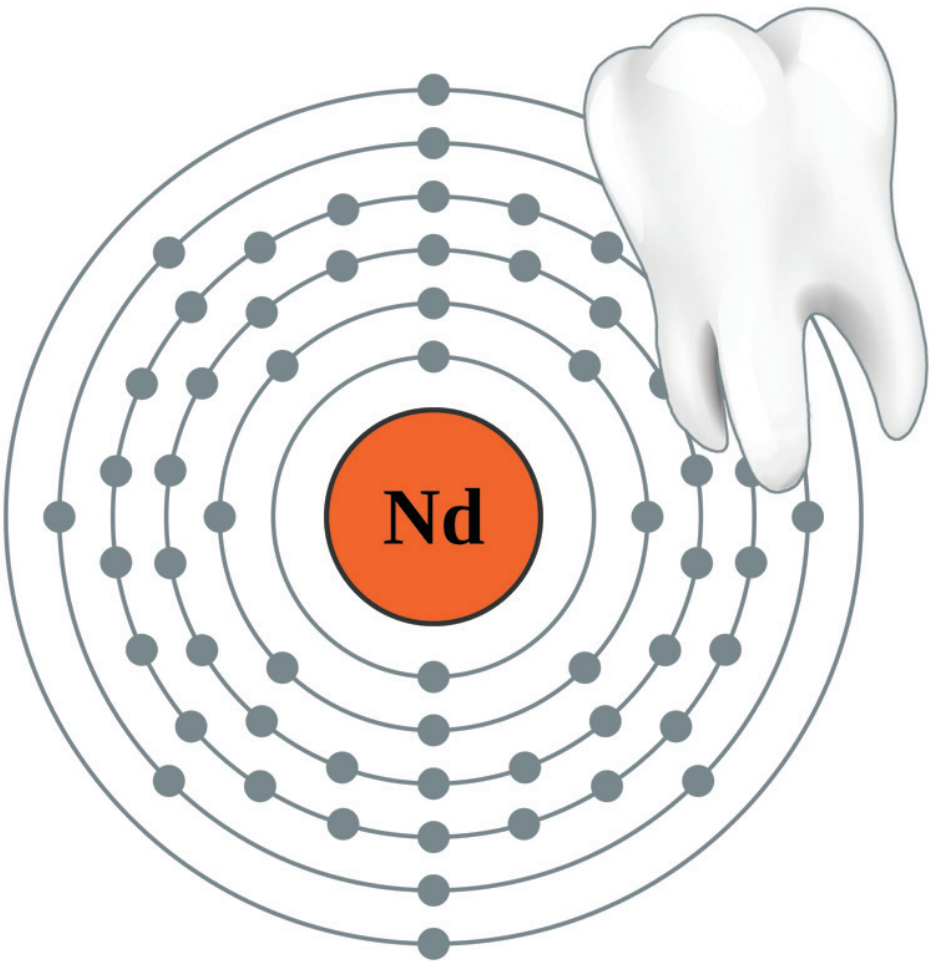
Dental calculus

Calculus, calcified dental plaque, has been used in isotopic studies to provide additional information on the diet of individuals (*Eerkens et al. 2014; Poulson et al. 2013; Salazar-García et al. 2014; Scott & Poulson 2012*). Dental calculus has been analysed for DNA in the context of the NEXUS1492 project by Kirsten Ziesemer (*Mann et al. 2018; Ziesemer et al. 2015, 2019*). As the time involved in dental calculus formation is unclear and the potential for calculus to preserve the isotopic signatures during life has not been confirmed, calculus is currently not widely used for isotopic analyses.

3.4 Implications for isotopic analyses

There is currently no consensus on the precise timing and duration of the isotopic input in human tooth enamel (*Balasse 2003; Bentley 2006; Humphrey et al. 2007; Lacruz et al. 2017; Montgomery & Evans 2006; Pederzani & Britton 2019; Simmons et al. 2013; Smith 2004; Smith & Tafforeau 2008; Trayler & Kohn 2017*). There are uncertainties about what time frame single loci samples represent (**Chapter 6**, *Balasse et al. 2012; Zazzo et al. 2010*). It is also unclear whether or not the isotopic signal is homogenised during mineralisation (*Dean et al. 2019; Green et al. 2017, 2018; Trayler & Kohn 2017*) and to what degree this homogenisation of the isotopic composition takes place (*Balasse 2002; Trayler & Kohn 2017*). Nor is it established whether there is any spatial pattern preserved in the isotopic averaging during enamel mineralisation (*Green et al. 2017, 2018; Trayler & Kohn 2017*). Some studies suggest that the isotopic composition from the incremental secretion stage may be preserved (*Balasse 2002; Dean et al. 2019; Humphrey et al. 2007, 2008; Smith & Tafforeau 2008*). Most studies assume that some degree of homogenisation of the isotopic composition takes place during the mineralisation phase of enamel formation (*Balasse 2003; Dolphin et al. 2005; Hoppe et al. 2004; Tafforeau et al. 2007; Trayler & Kohn 2017*). Thus, while theoretically tooth enamel can be sampled incrementally along its formation lines using laser ablation or microdrilling, if the isotopic composition is averaged during the mineralisation phase it will represent the averaged signature instead of the incremental signature (*Balasse 2002; Bendrey et al. 2015; Bentley 2006; Blaise & Balasse 2011; Blumenthal et al. 2014; Green et al. 2017; Hoppe et al. 2004; Montgomery et al. 2010; Montgomery & Evans 2006; Passey & Cerling 2002; Pederzani & Britton 2019; Tafforeau et al. 2007; Zazzo et al. 2005, 2012*). Hence, single loci bulk sampling approaches (usually taken from the lateral enamel), indiscriminate of enamel growth, are currently recommended instead of attempting incremental sampling (*Balasse*

2003; Bentley 2006; Montgomery & Evans 2006; Pederzani & Britton 2019; Slovak & Paytan 2011; Zazzo et al. 2005, 2006).


Nd

Chapter 4

TIMS analysis of neodymium isotopes in human tooth enamel using 10^{13} Ω amplifiers

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Abstract

Human provenance studies employing isotope analysis are essential in archaeological and forensic sciences but current applications provide limited spatial resolution. This study reports on the potential of neodymium isotope composition ($^{143}Nd/^{144}Nd$) to improve human provenancing capabilities. Human tissues contain very low (<0.1 ppm) neodymium concentrations, such that previous composition analysis was not possible. Additionally, Nd composition analysis in human enamel is hindered by Ca in the sample matrix. A modified Nd chromatographic separation technique is reported here, which removes large Ca quantities and accommodates large sample sizes (300-1000 mg). Verification of the modified chromatographic procedure was achieved using an internal synthetic tooth standard. These advancements allow for high precision Nd isotope composition analysis on ~500 mg of tooth enamel, or >100 pg of Nd, by thermal ionisation mass spectrometry (TIMS) using 10^{13} Ω resistors. Neodymium concentrations in enamel from third molars of modern Dutch residents range between 0.1-21.0 ppb (n = 23). The $^{143}Nd/^{144}Nd$ values for Amsterdam (0.51204-0.51259, n = 12) and Rotterdam (0.51187-0.51239, n = 8) are significantly different (P value = 0.02), demonstrating the potential of neodymium isotope composition to provide improved spatial resolution. Further assessment of Nd composition in enamel of residents from other geological contexts is required to better understand the human provenance capabilities of neodymium.

4.1 Introduction

Isotope analysis of human remains is used in the investigation of human mobility in forensic (*Font et al. 2015; Lehn et al. 2015*) and archaeological contexts (*Kamenov & Gulson 2014; Kootker, Mbeki et al. 2016; Laffoon et al. 2017; Schroeder et al. 2013*). These analyses centre on the principle that the isotopic values of the environment are reflected in the hair, skeletal and dental tissues of an individual. Tooth enamel is preferentially used for analysis as it is resistant to post-mortem alteration, in contrast to bone (*Trickett et al. 2003*). Tooth enamel mineralises during childhood and adolescence (*AlQahtani et al. 2010*) and thereby preserves the isotope signatures of an individual's early years. The most commonly used isotopic systems for human provenancing are strontium ($^{87}Sr/^{86}Sr$), oxygen ($\delta^{18}O$) and, less often, lead ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$). Isoscapes, maps that predict the bioavailable isotopic abundance ratios, have been constructed for O and H (*Bowen 2010a*), Sr (*Bataille et al. 2012; Evans et al. 2010*), and Pb (*Keller et al. 2016; Reimann et al. 2014*) for several countries in order to pinpoint the origins of humans.

There are still limitations that restrict the interpretation of mobility patterns, despite the widespread application of these isotopic systems. The primary source of radiogenic isotope abundance ratios is assumed to be of geological origin, however, non-geological sources can also contribute to the isotopic composition of bones and teeth. In the Pb system, anthropogenic sources (such as exposure from mining and smelting, battery manufacture, and lead based paints) may overwrite geological signatures (*Montgomery et al. 2010*), while bioavailable Sr can be affected by marine-derived aerosols (*Bentley 2006*). Furthermore, distinguishing between similar geological environments using a single isotopic system remains impossible (*Bentley 2006*). These complications affect the interpretation of the isotopic results and it has previously been stressed that a multi-isotope approach is required to better constrain provenance (*Font et al. 2015; Kootker, Mbeki et al. 2016; Laffoon et al. 2017; Moore et al. 2020*).

The power of a multi-isotope approach can be extended with the addition of a new isotope system. One such candidate is neodymium ($^{143}Nd/^{144}Nd$). The ^{147}Sm-^{143}Nd decay system has been widely applied in the Earth and Planetary Sciences for geochronology and has proved particularly successful in determining the provenance of igneous and sedimentary rocks (see *Dickin* (*2005*) for an overview), and paleoseawater (*Dera et al. 2009; Jeandel et al. 2007; Pearce et al. 2013*). Furthermore, neodymium has been used to investigate changing climatic conditions related to differential erosion rates and mechanisms (*Jung et al. 2004; Meyer et al. 2013; Pye*

2004) and to assess diagenesis in fossils (*Kohn et al. 2013; Tütken et al. 2011*). The potential of Nd as a provenance indicator was demonstrated by Nd isotope composition found in modern animal bones, which was in accordance to underlying bedrock or ambient water (*Tütken et al. 2011*). Moreover, neodymium isotope composition has been successfully used to provenance archaeological artefacts (*Boschetti et al. 2017; Brems et al. 2016; Gallo et al. 2015*).

Despite its potential for provenance studies, neodymium isotope analyses are yet to be applied to human remains due to: (1) problems caused by diagenesis following long term burial of bones (*Kohn et al. 2013; Tütken et al. 2011*), and (2) low concentrations (<1 ppm) of Nd in human (*Pye 2004*) and animal teeth (*Kohn et al. 2013; Tütken et al. 2011*). Nevertheless, Nd isotopes could provide valuable complementary provenance information because of their different geochemical characteristics compared to other isotopes used for provenance purposes. In contrast to the Rb-Sr isotope system, which experiences elemental fractionation during mineral break down, neodymium has limited mobility during weathering processes and, therefore, bioavailable $^{143}Nd/^{144}Nd$ provides a better representation of the bedrock compositions than Sr (*Jung et al. 2004; Tütken et al. 2011*). Additionally, the Nd of oceanic basins provides a greater reflection of surrounding geology, due to the shorter residence time of Nd in the ocean than Sr (*Jeandel et al. 2007; Tachikawa et al. 2017*). This observation may prove advantageous in coastal regions due to the reduced sea spray effect of the Nd isotope system. The goal of this study was therefore to: (1) develop a technique to reliably analyse Nd isotopes in human tooth enamel despite low elemental abundance; (2) provide a preliminary assessment of the practicality of its use for human provenance studies.

4.2 Neodymium isotopes

Neodymium is a light rare earth element (LREE) of the lanthanide series. Variations in Nd isotope composition of rocks are dependent on the time of formation, and the Sm/Nd ratio which is dependent on the rock type and tectonic setting in which they formed (*Banner 2004; Pye 2004*). The surface of the Earth has $^{143}Nd/^{144}Nd$ abundance ratios between 0.510 for Archaean continental crust and 0.514 for mid-ocean ridge basalts (*Dickin 2005*). Conventionally, Nd isotope composition is expressed in the epsilon notation (εNd) where $^{143}Nd/^{144}Nd$ ratios are compared to the chondritic uniform reservoir (CHUR), which represents the bulk Earth Nd isotope composition based on an assessment of chondritic meteorites. The accepted present day chondritic value is 0.512638 (*Jacobsen & Wasserburg 1980*) and εNd is calculated according to **Equation 4.1**:

$$\varepsilon\mathrm{Nd} = \left(\frac{\frac{^{143}Nd}{^{144}Nd}sample}{\frac{^{143}Nd}{^{144}Nd}CHUR} - 1 \right) x\ 10^4 \qquad \textbf{Equation 4.1}$$

εNd values can be as low as –56 in old crustal rocks, while young magmatic rocks have high εNd values up to +15 (*Dickin 2005*). Detailed mapping of variation in geological Nd isotope composition is, however, limited (but see *Jeandel et al.* (*2007*) and *Brems et al.* (*2016*)).

Neodymium is transferred from the geology to bodies of water and vegetation, and enters the human body through diet, where Nd substitutes Ca in the enamel of human teeth *(Evans 1990*). Due to its relatively heavy mass, it is assumed that Nd isotopes do not undergo any significant mass-dependent isotopic fractionation within the environment and human body (*Pye 2004; Tütken et al. 2011*). Coupled with the conservative behaviour of REE during weathering (*White et al. 1986*), this means that dietary Nd isotope composition within teeth is unaltered along the food chain or during biomineralisation, and should therefore reflect the values of the diet of an individual, and in turn also the local bioavailable Nd. The biological and physiological functions of Nd are, however, not fully understood because studies on Nd in biological systems are very limited due to low Nd concentrations in human tissues (<0.7 ppm, **Table 4.1**). Neodymium, similar to other REE, has no physiological function in humans (*Evans 1990*) and large quantities of Nd can be toxic to the human body (*Evans 1990; Rim et al. 2013*). Elevated Nd concentrations in lung tissues (>50 ppb), urine (>4 ppb) and hair (>160 ppb), are found in individuals with occupations that involved contact with REEs (*Pietra et al. 1985; Wei et al. 2013*), which suggests that Nd is additionally accumulated within the human body by inhalation of dust or through dermal contact.

4.3 Material

Neodymium isotope analysis was performed on third molars (M3) donated by native Dutch inhabitants of the Netherlands (**Figure 4.1**). The Netherlands is a low-lying (predominantly <100 m) mostly flat country in the northwest of Europe, with the south-western parts of the country formed by the estuary of three river systems: the Rhine, the Meuse, and the Scheldt (**Figure 4.1**). The geology consists of Holocene deposits in the northwest, and Pleistocene areas in the south where there is more relief (*Vos 2015*). The surface deposits comprise marine, fluvial and glacial sediments Quaternary of age (2.6 Ma-present). Locally these regions include loess and peat layers (*van der Veer 2006*). Currently no regional Nd isoscape is available for this

Table 4.1 *Nd concentrations in tissues from healthy human individuals that were not directly associated with mining areas or professions involving contact with REEs.*

Tissue Type	Range (ppb)	Mean Nd content (ppb)	± SD	n	Country	Reference
Hair	41-789	134	30	41	Baotou city, China (N)	*Wei et al. 2013*
Hair	0.0-0.3	0.1		30	Dong and Ping Village, China (S)	*Tong et al. 2004*
Hair	7.8-9.4	8.7	0.5	3	China	*Ming & Bing 1998*
Hair	60-890	480	590	12	Hetian town, China (SE)	*Li et al. 2013*
Nail	35-500	275	233	4	Italy (N)	*Pietra et al. 1985*
Bone (rib)	1-62	11	9	80	Obninsk, Russia	*Zaichick et al. 2011*
Lung	11-88	46	31	11	Italy (N)	*Pietra et al. 1985*
Lymph nodes		118		7	Italy (N)	*Vocaturo et al. 1983*
Laryngeal tissues		96	9	15	Italy	*Collecchi et al. 1987*
Blood	<1-<8	<1.5		4	Italy (N)	*Pietra et al. 1985*
Blood	2840-3980	3370	420	5	Nagoya City, Japan	*Inagaki & Haraguchi 2000*
Blood	425-1275	690	254	12	Hetian town, China (SE)	*Li et al. 2013*
Plasma		28	1	5	Italy (N)	*Esposito et al. 1986*
Plasma		46	3	30	Italy	*Collecchi et al. 1987*
Urine	1.8-3.4	2.7	1.6	4	Italy (N)	*Pietra et al. 1985*
Kidney stone	60-<3000	<112		10	Vienna, Austria	*Koeberl & Bayer 1992*
Brain	<80-<100	<100		1	Vienna, Austria	*Koeberl & Bayer 1992*

region and very limited background sampling has been performed in the Netherlands (see **Table 4.2**). For the purposes of this study, the total range of $^{143}Nd/^{144}Nd$ expected in human teeth is defined by the Rhine River sediment data range ($^{143}Nd/^{144}Nd$ = 0.511983 to 0.512166, n = 18; *Bayon et al. 2015; Kuhlmann et al. 2004*), which is a general proxy for the total range of the Quaternary deposits in the Netherlands.

The Dutch residents lived in the area of Amsterdam (n = 22) and Rotterdam (n = 13) at the time of formation of their M3's. Amsterdam and Rotterdam are situated in locations that were formed by different parts of the greater Rhine river system, potentially leading to local Nd isotope variations (as demonstrated for Sr by *Kootker, van Lanen et al.* (*2016*)). Individuals

Figure 4.1 *A map of the Netherlands and localities where the individuals lived during formation of their third molars (modified from Kootker, van Lanen et al. 2016).*
1 = Warmenhuizen
2 = Alkmaar
3 = Purmerend
4 = Zaandam
5 = Amsterdam
6 = Rotterdam
7 = Dordrecht

Table 4.2 *Background dataset for the Netherlands and surrounding areas.*

Sample	n	Location	$^{143}Nd/^{144}Nd$	Age	±2 σ	εNd	Reference
Enamel (Mammoth)	1	Rhine River, Germany	0.512288	Late Pleistocene	10	-6.8	*Tütken et al. 2011*
Enamel (Mammoth)	1	North Sea	0.512408	Late Pleistocene	8	-4.2	*Tütken et al. 2011*
Sediment	35	North Sea	0.511579 to 0.512028	Pliocene		-20.7 to -11.9	*Kuhlmann et al. 2004*
Sediment	16	Rhine River, Netherlands	0,511983 to 0.512101	Pliocene		-12.8 to -10.5	*Kuhlmann et al. 2004*
Sediment	2	Rhine River, Netherlands	0.512159 to 0.512166	Holocene		-9.3 to -9.1	*Bayon et al. 2015*
Bone (fossil)	10	North Sea	0.512077 to 0512196	Pleistocene		-10.9 to -4.2	*Tütken et al. 2011*
Bone (*Plesiocetus* sp.)	1	North Sea	0.512034	Modern	23	-11.8	*Tütken et al. 2011*
Clay	1	North Sea	0.512126	Pleistocene	10	-10.0	*Tütken et al. 2011*

residing in Warmenhuizen (n = 1), Alkmaar (n = 1), Purmerend (n = 1) and Zaandam (n = 2) were included in the Amsterdam population as these cities are located in similar geological substrates. The individuals from Dordrecht (n = 2) were similarly combined with those from Rotterdam. Analysis was performed on the hard mineralised outer surface of the teeth, the enamel. The enamel of third molars is formed between the age of 8-16 years (*AlQahtani et al. 2010*) and isotopic results are representative of the origin of the individual during this time period. This study was approved by the Medical Ethics Review Committee of the VU University Medical Center. Anonymous questionnaires were filled in by donors, covering general background information, including their geographical origin, diet, health, smoking and exercise habits. Teeth from Amsterdam were previously analysed for Sr, O, and Pb (*Font et al. 2015*). In this study the enamel was analysed for both Nd concentration and composition.

4.4 Methodology

4.4.1 Sample preparation

All teeth were sampled, chemically processed and analysed at the Faculty of Science, Vrije Universiteit Amsterdam. The teeth were leached overnight in 30 % H_20_2 (Sigma-Aldrich Company Ltd) followed by a rinsing step in ultrapure water (Milli-Q) and air dried on a hotplate at 50 °C prior to sampling. The enamel was sampled using a dental micro-drill fitted with a diamond-tipped rotary burr and blade (Minilor Perceuse). The burr and blade were cleaned between sampling with 3 N HNO_3 in an ultrasonic bath for 3 minutes to remove any residual particles and then rinsed with Milli-Q and dried. The innermost layer of enamel (at the enamel-dentine junction) was mechanically removed to ensure optimal enamel-dentine separation. Sample weight ranged from 273-1233 mg, average 515 mg. If a M3 pair was available from a single donor, the enamel from both teeth was combined to increase available sample size.

4.4.2 Chemical separation

Sample dissolution and Nd chromatographic separation was performed in a class 100 clean laboratory. All PFA laboratory equipment was sub-boiled in pro-analysis quality 7 N HNO_3 and 6 N HCl for two hours each, followed by two leaching steps at 125 °C with (1) double distilled 6.5 N HCl (>5 days) and (2) 7 N HNO_3/12 N HF (>2 days).

Thorough removal of organic matter was essential due to large sample size required to obtain enough Nd for analysis. The enamel was dissolved in 3-6 mL 6.5 N HCl, dried, nitrated, and

re-dissolved in 3-6 mL 6.5 N HCl and 0.75-1.5 mL 14.0 N HNO_3, depending on the sample weight. The solution was dried and nitrated before it was dissolved in 10 mL 2.0 N HNO_3 for the extraction of the LREE with TRU-resin using an adapted protocol described below. After LREE extraction Nd was separated from the other LREE using Ln-resin (Eichrom Technologies) following standard procedure (*Koornneef et al. 2015*).

Neodymium isotope concentration

In order to determine the range of Nd concentrations in human teeth, isotope dilution using a ^{150}Nd enriched spike ($^{150}Nd/^{144}Nd$ = 142.93) was performed on a 10 % aliquot of a subset of the samples (n = 23). Sample aliquots were chromatographically separated following standard TRU-resin column extraction (Eichrom, 150 µL resin, 100–150 µm) and standard Ln-resin columns (Eichrom, 740 µL, 50-100 µm) (*Koornneef et al. 2015*).

Neodymium isotope composition

The calcium-rich enamel samples of >250 mg required the development of a new Nd separation protocol, to prevent overloading of conventional chromatographic columns and to achieve removal of Ca in the purified Nd fraction, while minimizing the procedural blank because of low Nd concentrations in the samples (<0.1 ppm). Excessive Ca in the tooth enamel samples initially caused poor Nd column yields and low ionisation efficiency in the mass spectrometer. Removal of Ca was accomplished with a novel TRU-resin protocol using a modified column made from Pasteur pipettes (**Figure 4.2**). The TRU-resin volume used depended on the sample size: 0.75 mL resin for samples up to 550 mg and 1.3 mL resin for samples >550 mg.

Column extraction followed the procedure described in **Figure 4.2**. Samples were ultrasonicated for 30 minutes and centrifuged for 4 minutes at 4000 rpm before loaded onto the column. After the first extraction in 8 mL (samples <550 mg) or 14 mL (samples >550 mg) Milli-Q, the REE fraction was collected and reloaded onto the column for further purification. The REE fraction was then dried overnight on a hotplate at 120 °C, followed by dissolution in 2 mL 0.165 N HCl for Nd separation using Ln columns. Standard Ln-resin procedure (*Koornneef et al. 2015*) was followed after LREE extraction, as the tooth enamel matrix is removed during TRU-resin purification. After Nd extraction, samples were dried down and nitrated with ten drops of concentrated HNO_3, fluxed for two hours at 120 °C, before a final drying step prior to TIMS analysis.

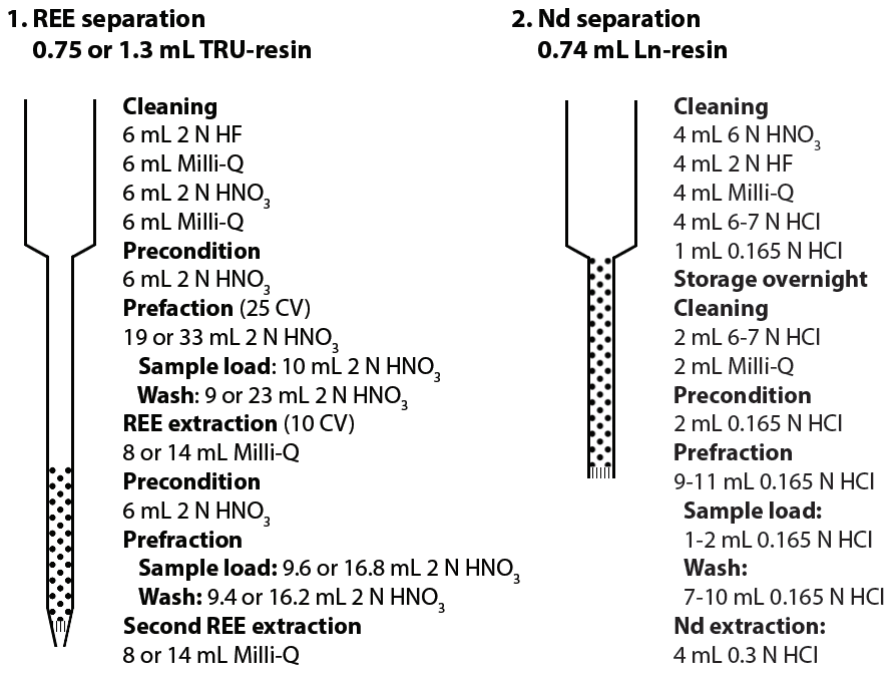

Figure 4.2 *Schematic overview of the chemical separation method for Nd separation for Ca-rich samples. REE from samples and standards were first extracted using TRU-resin employing Pasteur pipettes (35 µm polyethelene frit). Subsequently the Nd was extracted using Ln-resin. CV stands for column volume, which equals the volume of resin used.*

The efficiency of the new column extraction protocol was validated using both an internal synthetic tooth enamel Nd standard (see **Section 4.4.3**) and a standard Nd solution (Alfa Aesar, ICP standard code: 9301120). The Nd standard (3 ppb), to which 1000 mg of $Ca_3(PO_4)_2$ was added to mimic the enamel matrix, was analysed using a quadrapole Thermo X-Series II inductively coupled plasma mass spectrometer (ICP-MS) to determine the extraction efficiency. Yields approaching 90 % were achieved on samples (1 g) using 1.3 mL TRU-resin, similar to yields for standard TRU-resin procedure.

4.4.3 Tooth standard

A secondary standard was fabricated to validate the modified TRU-resin protocol and overall analytical procedures. Because the Nd concentration of teeth is low it was not viable to create a tooth standard from human teeth. The synthetic tooth standard (TSTD) consists of 400 g $CaHPO_4$ (Alfa Aesar) dissolved in 4 L 3 N HNO_3, doped with 100 ppm Sr (Alfa Duchefa, 1000 ppm Sr, ICP standard code: 970504), 1 ppm Pb (CPI International, 1000 ppm Pb, ICP standard code:

P/N 4400-1000281), and 4 ppb Nd (Alfa Aesar, ICP standard code: 9301120). Different sizes of TSTD aliquots were processed on both the standard 0.3 TRU-resin columns (1.25-3 mL TSTD, 0.5-1.2 ng Nd, 125-300 mg $CaHPO_4$) and on the new 0.75 and 1.3 mL TRU-resin columns (10 mL, 4 ng Nd, 1000 mg $CaHPO_4$).

4.4.4 TIMS

Neodymium analyses were performed on a Thermo Scientific Triton *Plus* TIMS. Standards and samples were loaded on out-gassed Re filaments in 1-2 µL 10 % HNO_3 with 1 µL H_3PO_4 (see *Koornneef et al.* (*2013*) for details). Analyses were performed using 10^{13} Ω resistors fitted to the amplifier system (see *Koornneef et al.* (*2014*) for analysis techniques) and 10^{11} Ω resistors if enough sample was available. Use of these 10^{13} Ω resistors results in a 100-fold higher output voltage compared to default 10^{11} Ω resistors, while the electronical noise level only increases by a factor of 10, improving the signal to noise ratio by a factor of 10. The 10^{13} Ω resistors therefore produce more precise data on small ion beams (*Koornneef et al. 2015*) and avoid the drawbacks of the NdO^+ technique (variation in oxygen isotope composition and multiple isobaric interferences (*Griselin et al. 2001; Koornneef et al. 2013*)).

For Nd^+ analyses four 10^{13} Ω amplifiers were connected to masses ^{143}Nd to ^{146}Nd, with ^{146}Nd in the centre cup. Masses ^{142}Nd, ^{147}Nd and ^{148}Nd were measured using 10^{11} Ω amplifiers. To optimise measurement time, amplifier baselines were measured during sample heating (11 minutes) and subtracted online from the raw intensity values. Instrumental mass fractionation was corrected using the exponential law and a $^{146}Nd/^{144}Nd$ value of 0.7219. A gain correction was performed by measuring the La Jolla reference standard (0.511841 ± 0.000002; *Koornneef et al. 2013*) overnight and using these values to calculate the gains for the 10^{13} Ω amplifiers. During the La Jolla measurement the four 10^{13} Ω resistors were connected to cups L3 (Nd^{143}), L1 (Nd^{145}), H2 (Nd^{148}) and H4 (Nd^{150}). The averaged results for $^{143}Nd/^{144}Nd$, $^{145}Nd/^{144}Nd$, $^{148}Nd/^{144}Nd$, $^{150}Nd/^{144}Nd$ from at least 7 separate La Jolla measurements were used to calculate the gain values for the 10^{13} Ω amplifiers using the following formula: gain value = 0.01*(true value La Jolla/measured value La Jolla). Beam intensities on 10^{13} Ω resistors were always kept below 0.03 V (30 mV if measured on a 10^{11} Ω amplifier) to avoid the effect of potential non-linearity of the amplifiers. A minimum of 70 scans was collected for each analysis on 10^{13} Ω amplifiers, and 60 scans for 10^{11} Ω amplifiers. Larger standards and samples were stopped after 300-400 cycles using 10^{13} Ω resistors and re-analysed using 10^{11} Ω to ensure optimal precision and accuracy. Standards (JNdi-1, CIGO (in-house standard, see *Koornneef et al.* (*2013*)) and TSTD)

were measured to check for accuracy and reproducibility and for normalisation purposes. Total procedural blanks yielded 1.1 ± 1.4 pg for Nd (n = 48) ($^{150}Nd/^{144}Nd$ = 142.93). Previous research in our lab demonstrated that samples as small as 30 pg Nd can be analysed without suffering from procedural blanks (*Koornneef et al. 2015*).

4.5 Results

4.5.1 Validation

Accuracy of analysis techniques using 10^{13} Ω resistors was assessed using large (~200 ng) and small (100 pg) aliquots of standards. For large aliquots the 10^{13} Ω CIGO ($^{143}Nd/^{144}Nd$ =0.511348 ± 0.000078, 2 SD, n = 61) and JNdi-1 results (0.512110 ± 0.000092, 2 SD, n = 21) are in excellent agreement with the long-term average of CIGO ($^{143}Nd/^{144}Nd$ = 0.511328 ± 0.000009, 2 SD, n = 39) and JNdi-1 ($^{143}Nd/^{144}Nd$ = 0.512096 ± 0.000009, 2 SD, n = 19) in this laboratory determined on default 10^{11} Ω amplifiers (**Table 4.3**).

The accuracy and reproducibility of small samples was assessed using 100 pg aliquots of the CIGO standard and analysis of the TSTD on both 10^{13} and 10^{11} Ω amplifiers. The 10^{13} Ω results for the 100 pg CIGO standards are in agreement with the 250 ng CIGO standards measured using 10^{13} Ω amplifiers (**Table 4.3**). The 100 pg CIGO standards did not contain enough Nd to be reanalysed using 10^{11} Ω resistors. To check for overall reproducibility of Ca-rich samples, TSTDs were analysed using the 10^{13} amplifiers and 10^{11} amplifiers if enough Nd (>1 ng Nd) was present. TSTDs (n = 43, >1 ng Nd) and larger samples (n = 5) were measured twice, using the same filament, first on 10^{13} Ω resisters and subsequently on 10^{11} Ω resistors. The results of the TSTD and samples on 10^{13} Ω and 10^{11} Ω are in agreement (**Tables 4.3** and **4.4**, **Figure 4.3**). The TSTD 10^{13} Ω analytical reproducibility (± 0.000071) in Nd isotope composition is an

Standard	Quantity	Amplifier	$^{143}Nd/^{144}Nd$	2 SE	n
CIGO	250 ng	10^{13}	0.511348	0.000078	61
		10^{11}	0.511328	0.000009	47
CIGO	100 pg	10^{13}	0.511346	0.000070	29
JNdi-1	200 ng	10^{13}	0.512107	0.000092	21
		10^{11}	0.512096	0.000009	19
TSTD	0.5-4.0 ng	10^{13}	0.512129	0.000030	74
	1-4 ng	10^{11}	0.512126	0.000061	43

Table 4.3 *Results of in-house standard (CIGO 250 ng, CIGO 0.1 ng), international standard (JNdi-1) and synthetic tooth standard (TSTD) for 10^{13} and 10^{11} Ω amplifiers when possible.*

Table 4.4 *Validation of measurement by repeat analyses (n = 5) on samples using both 10^{13} Ω and 10^{11} Ω resistors.*

Sample ID	10^{13}			10^{11}		
	$^{143}Nd/^{144}Nd$	2 SE	Scans	$^{143}Nd/^{144}Nd$	2 SE	Scans
4A-H	0.512229	0.000047	369	0.512238	0.000014	64
28R-14	0.512388	0.000032	332	0.512414	0.000018	263
29R-11	0.512080	0.000029	305	0.512183	0.000152	62
30R-13	0.511869	0.000028	281	0.511735	0.000123	63
31R-2	0.512048	0.000028	284	0.512106	0.000016	104

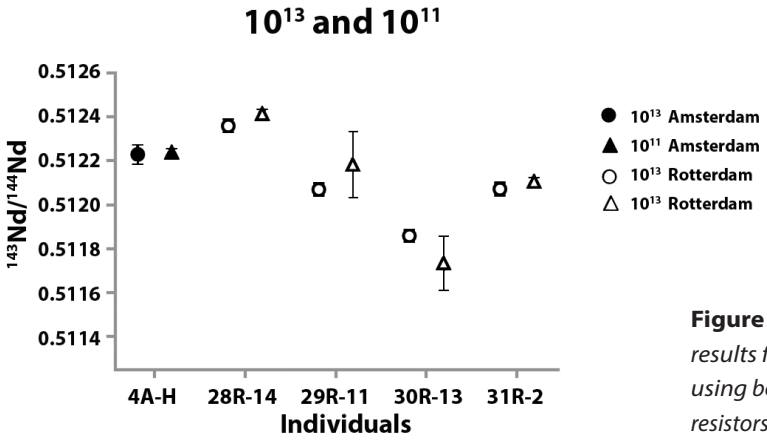

Figure 4.3 *$^{143}Nd/^{144}Nd$ results for enamel samples using both 10^{13} and 10^{11} Ω resistors (n = 4).*

indication of the reproducibility in Nd composition present in the samples undergoing the entire laboratory procedure, as the TSTD has a similar matrix and Nd concentration (4 ppb) as enamel (average 3.7 ppb).

4.5.2 Nd elemental concentration

The enamel of 23 Dutch individuals was analysed for Nd concentration. Concentrations ranged from 0.1 ppb to 21.0 ppb (**Figure 4.4**), with a median of 1.2 ppb. All but two values of 19.8 and 21.0 ppb fell in the range 0.1 to 7.0 ppb. Based on the concentration data, samples containing >100 pg were successfully measured for Nd isotope composition.

4.5.3 Nd isotope composition

Results for the enamel of the third molars are presented in **Table 4.5** and **Figure 4.5**. A total

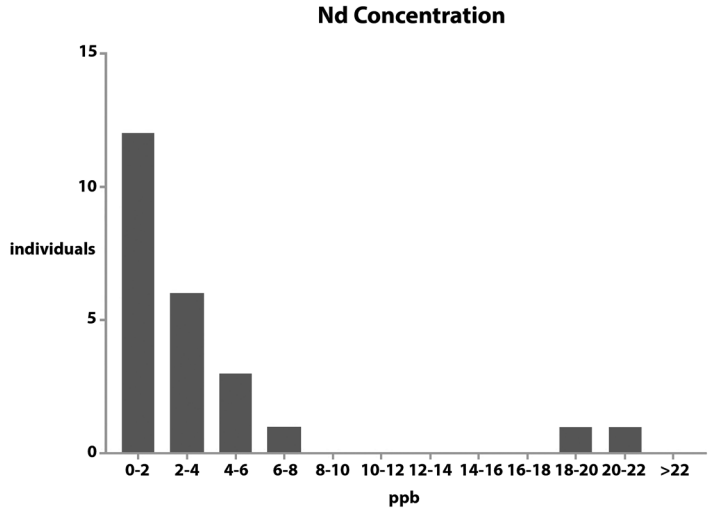

Figure 4.4 *Nd concentrations for enamel samples from 20 Dutch inhabitants (n = 23).*

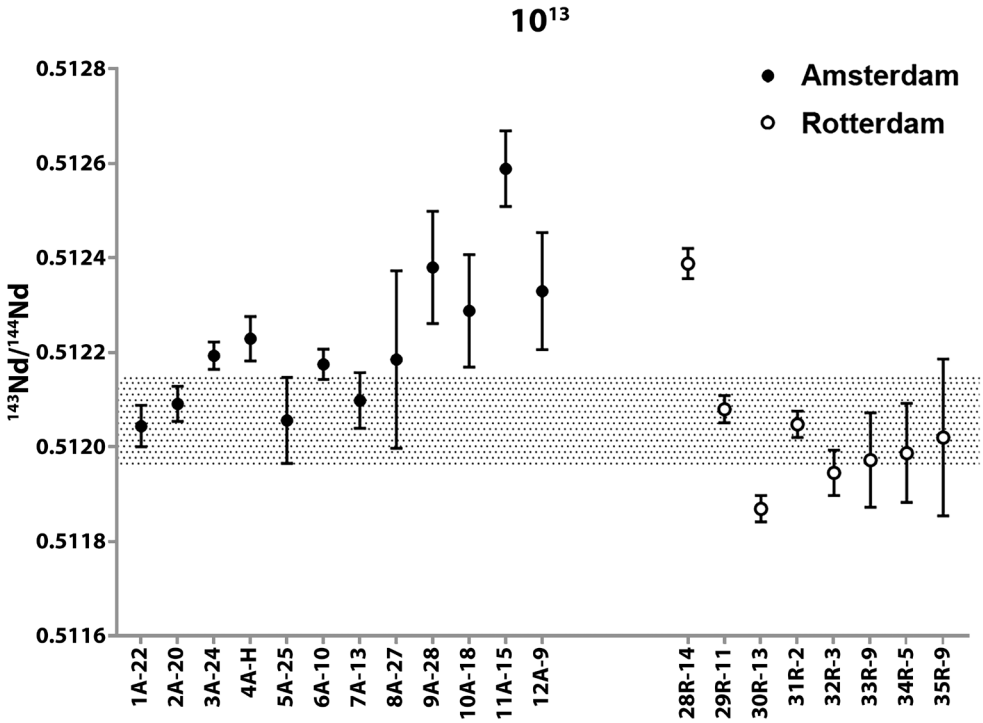

Figure 4.5 *Third molars analysed using 10^{13} Ω resistors from Dutch inhabitants of Amsterdam (n = 12) and Rotterdam (n = 8) and surrounding areas. The highlighted area ($^{143}Nd/^{144}Nd$ = 0.511983-0.512166) represents the Dutch range based on Rhine sediments analyses (see* **Section 4.3**).

Table 4.5 *Third molars (n = 35) analysed for Nd concentration and composition for 32 Dutch individuals. Third molars from Amsterdam (n = 12) and Rotterdam (n = 8) and surrounding areas were analysed for Nd composition using 10^{13} resistors. * = two third molars used.*

Sample	Location	Size (mg)	Nd (ppb)	$^{143}Nd/^{144}Nd$	2SE	Scans	εNd
1A-22	Amsterdam	530		0.512044	0.000044	377	-11.6
2A-20	Warmenhuizen	511	1.3	0.512091	0.000037	204	-10.7
3A-24	Amsterdam	529	2.3	0.512193	0.000029	373	-8.7
4A-H	Purmerend	320	19.8	0.512229	0.000047	369	-7.7
5A-25	Amsterdam	350	0.7	0.512056	0.000091	357	-11.4
6A-10	Amsterdam	276	3.1	0.512175	0.000032	80	-9.0
7A-13	Amsterdam	279	0.4	0.512098	0.000059	307	-10.5
8A-27	Alkmaar	273		0.512185	0.000188	141	-8.8
9A-28	Amsterdam	513		0.512380	0.000119	158	-5.0
10A-18	Amsterdam	418		0.512288	0.000119	161	-6.8
11A-15	Amsterdam	431		0.512589	0.000080	200	-1.0
12A-9	Amsterdam	299	1.1	0.512330	0.000124	150	-6.0
13A-6	Amsterdam	27	1.2				
14A-8	Amsterdam	16	0.9				
15A-12	Amsterdam	22	1.6				
16A-23	Amsterdam	24	0.2				
17A-32	Amsterdam	22	3.0				
18A-41	Amsterdam	23	3.4				
19A-42	Amsterdam	22	0.7				
20A-K	Purmerend	25	7.0				
21A-Sa	Zaandam	22	4.4				
22A-Sb	Zaandam	21	0.2				
23R-37	Rotterdam	27	1.1				
24R-1a	Dordrecht	69	5.7				
25R-1b	Dordrecht	29	3.0				
26R-4	Dordrecht	52	2.5				
27R-14b	Dordrecht	51	0.6				
28R-14a	Dordrecht	429	21.0	0.512388	0.000032	332	-4.9
29R-11	Rotterdam	1233*		0.512080	0.000029	305	-10.9
30R-13	Rotterdam	870*		0.511869	0.000028	281	-15.0
31R-2	Rotterdam	482		0.512048	0.000028	284	-11.5
32R-3	Rotterdam	746*		0.511945	0.000048	174	-13.5
33R-9	Rotterdam	589		0.511972	0.000100	172	-13.0
34R-5	Dordrecht	582		0.511987	0.000105	108	-12.7
35R-9	Rotterdam	636		0.512020	0.000166	72	-12.1

of 20 samples were analysed successfully (>70 scans) for their Nd isotope composition (out of a total of n = 32). On average samples ran for 223 scans using 10^{13} resistors. The $^{143}Nd/^{144}Nd$ isotope composition from individuals from Amsterdam ranged from 0.51204-0.51259 and values from Rotterdam ranged between 0.51187-0.51239. The $^{143}Nd/^{144}Nd$ isotope composition of enamel between Amsterdam and Rotterdam samples was significantly different (P value = 0.02, unpaired T-test).

4.6 Discussion

4.6.1 Analytical validation

Internal standard (CIGO and TSTD) results demonstrate that 100 pg (CIGO) and 500 pg (TSTD) Nd standards yield accurate and reproducible Nd isotope data (**Table 4.3**). The accuracy of measurements using 10^{13} Ω amplifiers is confirmed by successful repeat analysis of TSTDs (n = 43) and enamel samples (n = 5) using both the 10^{11} and 10^{13} Ω amplifiers (**Figure 4.3**, **Table 4.4**). Neodymium analysis using 10^{13} Ω resistors has been validated by previous research (*Klaver et al. 2015; Koornneef et al. 2015; Timmerman et al. 2017*). This study confirms the results of previous studies on melt inclusions (*Koornneef et al. 2015*) and diamonds (*Timmerman et al. 2017*), which show that the 10^{13} Ω resistors are beneficial to use for analyses of sub-nanogram sample sizes compared to 10^{11} Ω resistors, as the 10^{11} Ω amplifiers require ~10 ng Nd for successful analyses (*Tütken et al. 2011*). The successful analysis of small Nd samples (0.5–4.0 ng) in human enamel using 10^{13} Ω resistors demonstrates the potential for the study of Nd isotope composition in human tissues. Furthermore, TIMS analysis employing 10^{13} Ω resistors opens up new possibilities for studies with access to limited sample material (*Tütken et al. 2011*), and facilitates the analysis of Sr and Pb isotopes in human tissues previously considered too precious for destructive analysis (*Willmes et al. 2016*), as the sample size required for analysis is reduced.

4.6.2 Nd elemental concentration

Nd concentrations in human tooth enamel (1.2 ppb median with two outliers c. 20 ppb, **Figure 4.4**, **Table 4.5**) are consistent with the limited published data that concluded that Nd concentrations in human teeth are below 0.1 ppm (*Pye 2004*). The results of this study show that Nd concentration in enamel is generally lower than in other human tissues such as hair, nails, bone, blood, and soft tissues (see **Table 4.2**), although low values have also been reported for hair (*Tong et al. 2004*), urine and blood (*Pietra et al. 1985*). The mean Nd concentration in rib

bone (11 ppb; *Zaichick et al. 2011*) is more than three times higher than in enamel. Variation in Nd concentrations in human tissues may be the result of different formation times of the tissues. The rib bone analysed grew in adulthood, while third molar enamel is formed during childhood and early adolescence (8-16 years; *AlQahtani et al. 2010*). Little is known about the variation of Nd concentration in tissues between adults and children, as most studies focus on adult individuals. One study published Nd concentrations from children´s hair (*Tong et al. 2004*) that were almost 100 times lower than adult values (*Li et al. 2013; Ming & Bing 1998; Wei et al. 2013*), but these values may be affected by the use of EDTA in the cleaning procedure (*Tong et al. 2004*), possibly leaching Nd out of the children's hair. In the present study, the samples were only oxidised in 30 % H_20_2. The cleaning procedures used in the lab are therefore not the cause of the low Nd concentrations present in tooth enamel.

Low Nd concentrations in human tissues can partly be attributed to the generally low Nd concentrations in the food chain: plants and rivers have lower Nd concentrations (ppb range) than the underlying geology (*Goldstein & Jacobsen 1987; Kulaksiz & Bau 2013; Tyler 2004*). Although post-mortem absorption of Nd in fossil faunal remains has been investigated (*Kohn et al. 1999, 2013; Tütken et al. 2011*), little is known about the in vivo absorption of Nd as it is difficult to analyse in human biological systems. Low concentrations of Nd in human enamel may be caused by preferential exclusion of Nd, as the trivalent ion (Nd^{3+}) is less likely to substitute for Ca^{2+} in the hydroxyapatite crystal lattice, compared to for example Sr^{2+}. The moderately toxic nature of Nd may also explain its excretion by the liver, with poor intestinal absorption of REEs shown in animal experiments (*Bruce et al. 1963; Hayley 1965*). The combination of low bioavailable Nd to humans and its excretion by the liver is likely causing the generally low Nd concentrations in human tissues. Increased Nd concentrations in humans seem to be caused by absorption of Nd through the respiratory system (*Rim et al. 2013*).

The high Nd concentration analysed in the enamel of two individuals was atypical (19.8 and 21.0 ppb) and could not be explained based on their background information. The elevated Nd concentration in tissues from individuals that live in mining areas or have mining occupations (*Wei et al. 2013*) suggests that Nd uptake through air or dermal contact may overwrite the geological signal, similar to the Pb system (*Montgomery et al. 2010*). However, concentrations reported in this study do not reach the elevated values reported for mining areas (*Pietra et al. 1985; Wei et al. 2013*). Anthropogenic input from industrial products cannot be fully excluded however, as even small contributions would affect the low Nd concentrations in human enamel. Potential sources of Nd pollution include oil and petroleum refineries, fossil fuel

combustion, production of high performance magnets, waste incineration and metallurgic processes which can release REE emissions to air, soil and water (*Tyler 2004*). Industrial REE dust emission is usually low, however, and has decreased in the last decades in Europe due to improved emission control (*Tyler 2004*). The two individuals with increased Nd concentrations (4A-H and 28R-14) were furthermore not resident near industrial sites. Instead, individuals from Rotterdam that are situated near industrial sites do not show elevated Nd concentrations in their enamel. This makes industrial Nd emission an unlikely candidate for the increased Nd concentrations in the individuals from the Netherlands, although local exposure cannot be completely excluded. Based on current studies it thus remains difficult to explain why certain individuals have a marked increased Nd concentration present in their enamel. Large variation in Nd content with apparent outliers in the sample population is also present in the majority of previous studies on human tissues (**Table 4.1**). It is therefore highly likely that some variation in Nd concentration in enamel (0.1-21.0 ppb) is introduced by the human body.

4.6.3 Nd isotope composition

The $^{143}Nd/^{144}Nd$ ratios for 60 % of the individuals analysed in this study are compatible with expectations for local Dutch geology, as defined by analyses of Rhine sediments ($^{143}Nd/^{144}Nd$ = 0.511983-0.512166). The Rotterdam individuals are in closer agreement to the local range, which is consistent with Rotterdam's geographical position near the Rhine. It is possible that the expected local range was too narrowly defined, as 40 % of the samples in the study, particularly those from Amsterdam, had Nd isotope compositions outside the local range (7 are higher and 1 is lower, see **Figure 4.5**). In order to build solid interpretations of an individual's origin based on isotopes, appropriate background sampling is required. The current local range is based on a very limited background sediment dataset (n = 18), potentially explaining the large proportion (40 %) of individuals falling outside of these values. Nevertheless, the high Nd composition values ($^{143}Nd/^{144}Nd$ = >0.5122) seen here are incompatible with the geology of the Netherlands. Instead, elevated values are expected to be found in volcanic areas in Europe, such as Iceland and Italy (*Dickin 2005*). The variation and elevated Nd ratios found in this study suggests that either: (1) Nd in modern human diets in the Netherlands contains significant non-local contributions; (2) Nd is being fractionated significantly within the human body or in the food chain, for example with trophic level; or (3) there are local Nd sources other than geology (i.e. anthropogenic sources) contributing to human Nd composition in the Netherlands. It is unlikely that non-local food sources are completely overwriting the input of the local environment, as several studies have concluded that even with the globalisation

of the food market isotopes (H, O, C, N, S) can still be an indicator of geographical location of origin (*Chesson et al. 2012; Valenzuela et al. 2012*). Due to its relatively high mass, neodymium is not expected to be an indicator of trophic level by fractionation, as is recorded for $\delta^{15}N$, ^{2}H, $^{66}Zn/^{64}Zn$, and $\delta^{88}Sr$ (*Birchall et al. 2005; Jaouen et al. 2016; Lee-Thorp 2008; Lewis et al. 2017*). Interestingly, the highest Nd isotope composition measured in this study ($^{143}Nd/^{144}Nd$ = 0.512589 ± 0.0008) belongs to individual 10A-15, who was the only study participant with a vegetarian diet. It remains possible that anthropogenic contributions to Nd are important, especially given the weak negative correlation between Nd concentration and Nd isotope value in the data reported here (**Table 4.5**, $R^2 = 0.3$). However, *Tütken et al.* (*2011*) found similar elevated ratios for the enamel of two mammoth teeth from the region, one from the North Sea and one from the Rhine River in Germany ($^{143}Nd/^{144}Nd$ = 0.51261 and 0.51229 respectively, **Table 4.2**) which cannot be explained by anthropogenic contributions or diagenesis.

The statistical difference between Amsterdam and Rotterdam suggests that Nd analysis may provide information for provenance in the Netherlands that Sr analysis cannot (see discussion on Sr in *Kootker, van Lanen et al.* (*2016*)). This conclusion would, however, be more plausible if the source of variation in Nd isotope composition in enamel is identified. The limited data available on Nd in human tissue and in the local environment makes it difficult to assess the reported variation. This study establishes that Nd isotope analysis of human tooth enamel is viable but that the application of Nd analysis needs to be further validated by analysis of a larger sample set, including individuals from a variety of geological contexts, as well as more extensive background sampling, before it can be applied in archaeological and forensic contexts.

4.7 Conclusions

This study successfully establishes that Nd isotope composition can be measured in human tooth enamel. Low Nd concentrations in enamel with a Ca-rich sample matrix require an adapted Nd chemical separation procedure to process large samples while keeping the blank as low as possible, and TIMS measurements employing new 10^{13} Ω amplifiers to measure small ion beams at relatively high precision. The Nd concentration data confirms previous findings that the Nd concentration in human enamel is low (0.1 ppb to 21.0 ppb). High-precision Nd isotope analysis requires >100 pg of Nd, an amount which can only be obtained when an individual has a relatively high Nd concentration (>0.7 ppb) in the enamel, or if a larger sample size (>550 mg) can be achieved by analysing multiple teeth of one individual. The required

sample size for Nd analysis may limit the applicability of the technique. Neodymium isotope composition from Dutch inhabitants, though reliably measured, did not wholly correspond to expectations based on the limited available geological data. The lack of knowledge about Nd cycling in the environment and in human tissues meant that these discrepancies are difficult to interpret. In order to assess the potential of Nd isotopes for tracing the origins of human individuals, the variation in Nd composition in human tissue with residential geological context needs to be examined further.

Conflicts of interest

There are no conflicts to declare.

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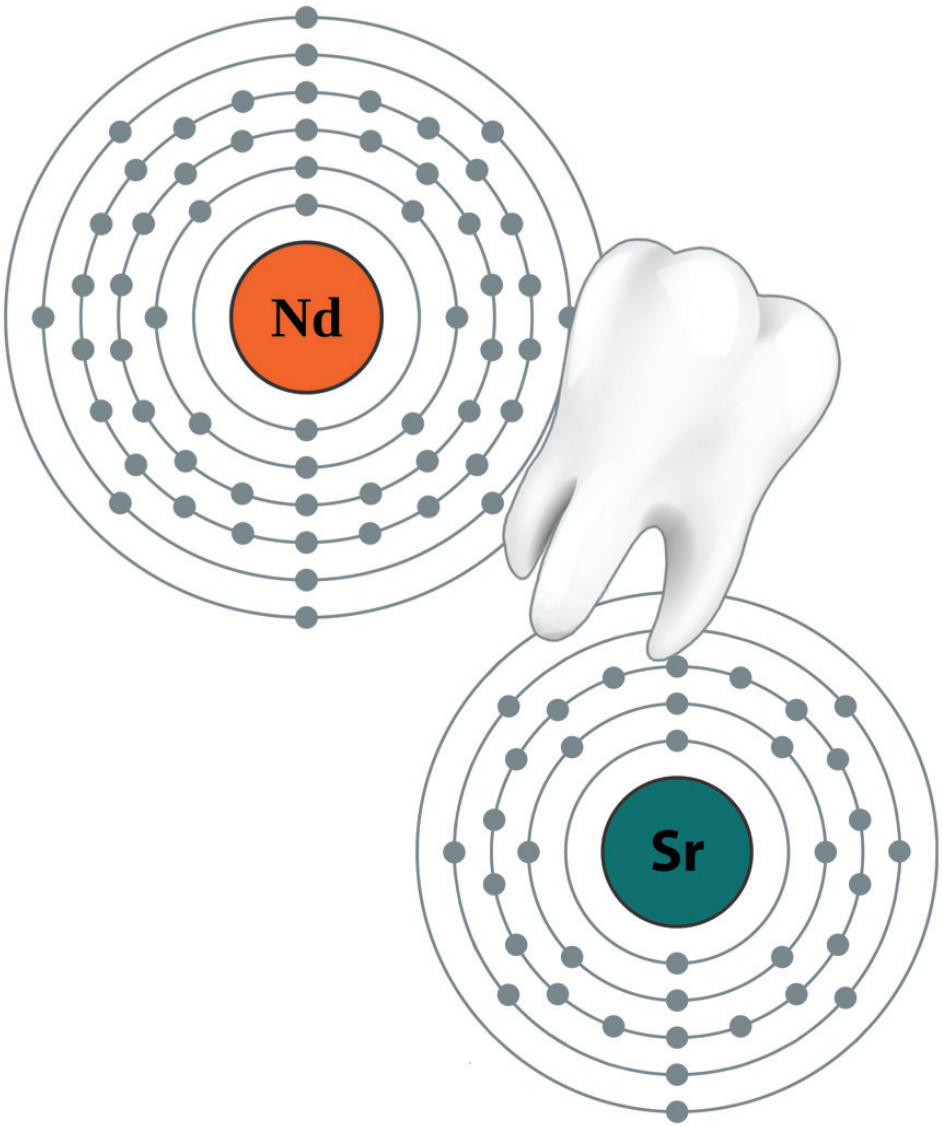
Nd
Sr

Chapter 5

Evaluation of neodymium isotope analysis of human dental enamel as a provenance indicator using 10^{13} Ω amplifiers (TIMS)

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Data: https://doi.org/10.4121/uuid:d541a402-2701-47b2-ac6a-eaaa14c8c111

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Abstract

Human provenance studies employing isotopic analysis have become an essential tool in forensic and archaeological sciences, with multi-isotope approaches providing more specific location estimates compared to single isotopic studies. This study reports on the human provenancing capability of neodymium isotopes ($^{143}Nd/^{144}Nd$), a relatively conservative tracer in the environment. Neodymium isotope ratios have only recently been determined on human remains due to low concentrations in human dental enamel (ppb range), requiring thermal ionisation mass spectrometry (TIMS) using 10^{13} Ω resistors. Dental elements (third molars) from 20 individuals born and raised in the Netherlands were analysed for Nd concentration (n = 12) and Nd isotope ratios (n = 15). The geological control on Nd isotope composition was examined using coupled Nd-Sr isotope analysis of the same third molar. Teeth from different geological environments were also analysed (Caribbean, Columbian, and Icelandic, n = 5). Neodymium elemental concentrations in dental elements ranged between 0.1 and 7.9 ppb (median 0.5 ppb). The Dutch $^{143}Nd/^{144}Nd$ ratios of the provinces of Limburg and Friesland were between 0.5118 and 0.5121, with Dutch $^{87}Sr/^{86}Sr$ ratios in agreement with the previously established local range (0.708-0.710). The current findings were compared to previously published results on Nd concentration and composition from Dutch individuals. The concentration of Nd and $^{143}Nd/^{144}Nd$ ratios were weakly correlated (R^2 = 0.47, n = 17) in Dutch human dental enamel. The majority (n = 25, 83.3 %) of individuals had Nd and Sr isotope values isotopically indistinguishable from the geological environment in which their third molars formed and mineralised. However, the Nd isotope ratios of the Icelandic individual and several Dutch individuals (n = 4) suggested that Nd in enamel is not solely influenced by geological environment. In order for neodymium isotopes to be quantitatively applied in forensic and archaeological settings further analyses of individuals from various geographical regions with well-defined dietary Nd isotope data are required.

5.1 Introduction

Isotope analysis of human tissues, such as hair, nails, skeletal and dental elements, can give insight into the mobility profile of an individual, as these tissues reflect the isotopic values of the environment in which the individual lived at the time of tissue formation. This mobility profile does not permit direct identification of unidentified victims, but provides forensic intelligence to construct a profile that may lead to identification of an individual when coupled with osteological and forensic information (*Meier-Augenstein 2017*). Isotopic systems which preserve environmental information in human tissue include strontium ($^{87}Sr/^{86}Sr$), oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$) and lead (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb). These isotopic systems have been applied to obtain information on the geographical region of origin and/or recent movements of individuals in forensic (*Chesson, Barnette et al. 2018; Ehleringer et al. 2010, 2015; Font et al. 2015; Kamenov & Curtis 2017; Kennedy et al. 2011; Lehn et al. 2015; Meier-Augenstein & Fraser 2008; Vautour et al. 2015*) and archaeological contexts (*Kamenov & Gulson 2014; Kootker, Mbeki et al. 2016; Kootker, van Lanen et al. 2016; Laffoon et al. 2017; Lamb et al. 2014; Mbeki et al. 2017; Sharpe et al. 2018*). The integration of multiple isotopic systems has been shown to be a powerful approach (*Font et al. 2015; Kootker, Mbeki et al. 2016; Laffoon et al. 2017; Lamb et al. 2014; Lehn et al. 2015; Vautour et al. 2015*).

This study examines the potential use of an additional isotope system for human provenancing: neodymium (Nd) isotope ratios. The addition of another isotopic system would allow for increased geographical discrimination as it provides complimentary information to the other isotopic systems. The potential for Nd analysis to be used for human provenancing is examined by evaluating the geological control on $^{143}Nd/^{144}Nd$ ratios in human enamel. Teeth (third molars) were sampled from individuals that resided in geological contexts with various isotopic compositions (the Netherlands, the Caribbean, Columbia and Iceland). Neodymium elemental concentrations as well as neodymium and strontium isotope ratios in modern human dental enamel were analysed using thermal ionisation mass spectrometry (TIMS) employing 10^{11} Ω and 10^{13} Ω amplifiers. The 10^{13} Ω amplifiers are essential for the measurement of small Nd samples, allowing reliable analysis of samples as small as 100 pg. These small Nd samples cannot be successfully analysed with the default 10^{11} Ω amplifiers that require > 1 ng Nd for analysis (*Koornneef et al. 2014; Plomp et al. 2017*). The findings of this study were examined and compared to previously published results on Nd and composition from Dutch individuals (*Plomp et al. 2017*) to evaluate the application of Nd isotopes for human provenancing.

5.2 Isotope method background

Despite widespread use, the application of isotopic analysis for human provenancing has several limitations:

(1) Sample selection may be biased by availability of human tissues recovered from forensic cases and archaeological sites. Moreover, tissues retrieved from these contexts can be affected by diagenesis, with the exception of dental enamel (*Trickett et al. 2003*).

(2) Accurate evaluation of isotopic data from human tissues requires bioavailable background data such as isoscapes: maps reporting bioavailable isotopic ratios in an environment. Unfortunately, detailed isoscapes are rarely available as they require extensive sampling and sophisticated modelling approaches (*Bataille et al. 2012, 2018; Bowen 2010a; Evans et al. 2010; Keller et al. 2016; Laffoon et al. 2017; Reimann et al. 2014*).

(3) The import of food grown in geological environments different to the residential area of an individual may influence the isotopic values of an individual, particularly in globalised modern societies (*Chesson et al. 2012; Valenzuela et al. 2012*).

(4) Anthropogenic Pb (*Gulson 2011*) or marine Sr (*Whipkey et al. 2000*) can overwrite the geological signature found in human remains.

(5) Identical isotopic signatures can be obtained from individuals originating from different geographic areas due to similar (geological) environments resulting in poor provenance discrimination.

These last three limitations could be partially addressed by applying a multi-isotope approach as the various isotopic systems reflect different parts of the environment: geology (Sr, Pb), drinking water (O, H) and pollution (Pb). Taken together, multiple isotope systems could provide greater spatial resolution by distinguishing between environments where a single isotopic system cannot (*Font et al. 2015; Kootker, Mbeki et al. 2016; Laffoon et al. 2017*). This study examines the potential of neodymium isotope ratios ($^{143}Nd/^{144}Nd$) for human provenancing. The variation of $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios in human enamel of the same dental element are determined to understand the geological control on the isotopic values.

Strontium isotope analysis ($^{87}Sr/^{86}Sr$) of human tissues is an established provenancing tool for modern and archaeological individuals (*Bentley 2006; Font et al. 2015; Kootker, Mbeki et al. 2016; Kootker, van Lanen et al. 2016; Mbeki et al. 2017; Snoeck et al. 2018; Vautour et al. 2015*). Strontium enters the human body through the diet, as vegetation and bodies of water take up strontium predominantly derived from the local geology (*Bentley 2006*). Strontium ratios vary spatially

dependent on rock type and age of formation. Low $^{87}Sr/^{86}Sr$ ratios (< 0.704) are generally found in geological young deposits (< 1-10 Mya) and high $^{87}Sr/^{86}Sr$ ratios (> 0.710) are found in older rocks (> 100 Mya) (*Bentley 2006*). Strontium ratios in human tissue can therefore be an indication of provenance when locally grown food dominates the diet.

Neodymium isotope ratios ($^{143}Nd/^{144}Nd$) have been successfully applied to provenance glass archaeological artefacts (*Boschetti et al. 2017; Brems et al. 2016; Gallo et al. 2015*) and modern animal bones (*Tütken et al. 2011*). Neodymium is a light rare earth element (LREE) which varies geologically in $^{143}Nd/^{144}Nd$ ratios as a result of the rock age, rock type/composition, and tectonic settings (*Banner 2004; Pye 2004*). Generally, older geological depositions have lower $^{143}Nd/^{144}Nd$ ratios compared to recently formed deposits, with $^{143}Nd/^{144}Nd$ ratios typically ranging between 0.510 and 0.514 (*Dickin 2005*). Neodymium isotope ratios are transferred from rocks to the vegetation and bodies of water, entering the human body through diet, inhalation and potentially dermal contact (*Pietra et al. 1985; Plomp et al. 2017; Wei et al. 2013*). It is expected that Nd isotopes are not isotopically fractionated during their uptake by the human body, thus reflecting the environmental ratios of the food, water and dust consumed (*Pye 2004; Tütken et al. 2011*). Due to the low concentrations of Nd present in human tissues (<0.7 ppm) there have been few studies addressing neodymium in biological systems (see *Plomp et al.* (*2017*) for a summary). Low Nd concentrations (0.1 to 58.0 ppb; *Kamenov et al. 2018; Plomp et al. 2017*) in dental enamel limit its analysis and application to human provenancing. The low Nd concentrations in human tissues can be explained by (1) the low levels of bioavailable Nd in the food chain (ppb range), as vegetation and bodies of water take up limited Nd from the underlying geology (*Goldstein & Jacobsen 1987; Kulaksiz & Bau 2013; Tyler 2004*), (2) the moderately toxic nature of Nd (*Evans 1990; Rim et al. 2013*) and lack of physiological or biological function of Nd in the human body (*Evans 1990*) and (3) the trivalent ion (Nd^{3+}), which is incompatible with calcium (Ca^{2+}) substitution in the hydroxyapatite crystal lattice of human bone and teeth (*Evans 1990; Plomp et al. 2017*).

Neodymium is a promising candidate for human provenancing due to its different geochemical characteristics in comparison to Sr (*Jung et al. 2004; Tütken et al. 2011*). Nd isotope ratios from coastal locations are less susceptible than Sr to sea spray effects (whereas geological Sr isotope ratios are dominated by seawater $^{87}Sr/^{86}Sr$ (*Bentley 2006*)). The Nd contents in water are low (typically 10-30 pmoL/L) and the residence time of Nd in the ocean is relatively short (in comparison to Sr) (*Tachikawa et al. 1999*). Hence, the $^{143}Nd/^{144}Nd$ ratios found in oceans reflect the surrounding geology (*Jeandel et al. 2007; Tachikawa et al. 2017*). The diminished influence

of sea spray makes Nd isotope analysis a promising candidate for human provenance analyses, particularly in coastal regions.

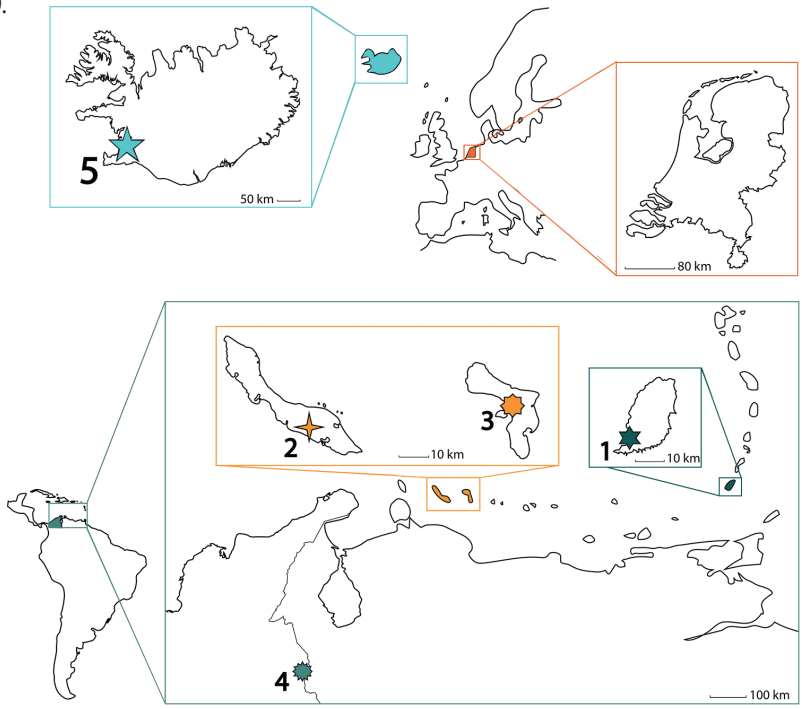
5.3 Material

Neodymium and strontium isotope analysis was performed on third molars (M3) from individuals who were known to have been residentially stable during the period of third molar formation and mineralisation. The enamel of third molars is formed between the age of 8-16 years (*AlQahtani et al. 2010*) and isotopic results are therefore representative of the environment in which the individual lived during that time period. Analysis was performed on the mineralised outer surface of the teeth, the enamel. Third molars were donated by inhabitants of the Netherlands (n = 56, including data from *Plomp et al.* (*2017*), **Figure 5.1**), the Caribbean (n = 3), Columbia (n = 1) and Iceland (n = 1) (**Figure 5.2**) of which the geological environments were expected to produce a sufficient range of Nd and Sr isotope compositions (see **Section 5.4**). The Dutch residents were grouped based on geographical residence and geological substrate at the age of 8-16 years. Dutch individuals lived in the provinces of North Holland (primarily Amsterdam, n = 22), South Holland (primarily Rotterdam, n = 13), Friesland (n = 7), Limburg (n = 9), and other regions in the Netherlands (n = 5) (**Figure 5.1**). The teeth from North Holland/Amsterdam were previously analysed for Sr, O, Pb (*Font et al. 2015*) and Nd isotopes (*Plomp et al. 2017*). The Nd results for the South Holland/Rotterdam individuals were previously published in *Plomp et al. (2017*). The current study reports the Sr and Nd results for the Friesland and Limburg provinces and the Nd results for other regions in the Netherlands (n = 20), as well as the Sr results for South Holland.

The analyses of the teeth were approved by the Medical Ethics Review Committee of the VU University Medical Center. Questionnaires provided anonymised background information on the donors and information on the geographic location of the individual at the time of tooth formation and mineralisation, as well as diet, health, smoking and exercise habits. Precise background information (other than geographic location during enamel mineralisation) was not available for the Icelandic and Grenadian individuals due to collection of these teeth outside the Netherlands (collection which was not covered by the Medical Ethics application).

Figure 5.1 *A topographic map of the Netherlands with localities where the individuals lived during formation and mineralisation of their third molars. 1 = Warmenhuizen, 2 = Alkmaar, 3 = Purmerend, 4 = Zaandam, 5 = Amsterdam, 6 = Maarsen, 7 = Utrecht, 8 = Rotterdam, 9 = Dordrecht, 10 = Kortgene, 11 = Holwerd, 12 = Leeuwarden, 13 = Oldeboorn, 14 = Lippenhuizen, 15 = Enschede, 16 = Den Bosch, 17 = Maastricht, 18 = Heerlen, 19 = Vaals.*

Figure 5.2. *A map of Europe and the Caribbean region indicating the location where the individuals lived during mineralisation of their third molars. 1 = St. George's (Grenada), 2 = Willemstad (Curaçao), 3 = Kralendijk (Bonaire), 4 = Cúcuta (Columbia), 5 = Reykjavik (Iceland).*



5.4 Background

The Netherlands is a European country (**Figures 5.1** and **5.2**) formed of geology consisting of Holocene deposits in the northwest, and Pleistocene areas in the south (*Vos 2015*). The surface deposits comprise marine, fluvial (Rhine, Meuse and Scheldt rivers) and glacial sediments of Quaternary age (2.6 Ma-present), with local loess and peat layers (*Mulder 2003; Van der Veer 2006*). Limited neodymium background sampling exists for the region. Rhine River sediment data range from $^{143}Nd/^{144}Nd$ = 0.51198 to 0.51217 (n = 18; *Bayon et al. 2015; Kuhlmann et al. 2004*) and is used here as a general indication for the local Dutch neodymium isotope variation. Neodymium isotope ratios in Dutch human enamel ranges from $^{143}Nd/^{144}Nd$ = 0.51187-0.51259 (n = 20; *Plomp et al. 2017*). The Sr local range ($^{87}Sr/^{86}Sr$ = 0.708-0.710; *Font et al. 2015*) is based on studies reporting human scalp hair and enamel data from modern Dutch individuals, tap water and soil/street dust. Dutch archaeological background samples exhibit higher variation with $^{87}Sr/^{86}Sr$ ratios up to 0.711 (*Kootker, van Lanen et al. 2016*).

The Caribbean samples originate from two distinct geological environments. Grenada is the southernmost island of the Lesser Antilles Island Arc (**Figure 5.2**) where the subduction induced mantle-derived magmas are contaminated with sediment at depth and in the crust (*Davidson 1987*). These sediments are derived from the Orinoco and Amazon deltaic systems (*Davidson 1987*). Volcanism on Grenada has $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios in the range 0.5123-0.5126 and 0.7038-0.7064 respectively (*White et al. 2017*). The island is subjected to sea spray influence ($^{87}Sr/^{86}Sr$ = 0.7092; *Bentley 2006*) and a significant dust flux from North Africa characterised by $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios between 0.5116-0.5126 and 0.715-0.718 respectively (*Aarons et al. 2013; Chapela et al. 2018; Pourmand et al. 2014; Zhao et al. 2018*). Bonaire and Curaçao are part of the Cretaceous Caribbean Flood basalt province, but both islands include more recent carbonate sediments. Estimated bioavailable Sr isotope ratios range from 0.703-0.709 (*Laffoon et al. 2017*) and estimated $^{143}Nd/^{144}Nd$ varies from 0.5120 in the limestone regions to values as high as 0.5130 in the volcanic regions (*Tachikawa et al. 2017; Thompson et al. 2004*). Like Grenada, the islands of Bonaire and Curaçao are influenced by sea spray and North African dust aerosol deposition (*Aarons et al. 2013; Chapela et al. 2018; Zhao et al. 2018*).

The individual from Colombia lived in Cúcuta, a city at the Venezuelan border in the Maraicaibo Basin lying outside the active volcanic zones of South America (**Figure 5.2**). The region is made up of Quaternary and Tertiary sediments derived from Cretaceous to Precambrian basement. Modelling estimates the local bioavailable Sr > 0.710 (*Bataille et al. 2012*). The basement in the

central and eastern Cordillera was metamorphosed at ~1.0 Ga and the limited data indicates this region has depleted mantle Nd model ages (T_{DM}) between 1.5 and 2.0 Ga and hence a $^{143}Nd/^{144}Nd$ ratio of ~0.5120 (*Restrepo-Pace et al. 1997*).

The individual from Iceland lived in the Reykjavik region (**Figure 5.2**) where the local basement lavas have $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios in the range 0.5130 to 0.5131 and 0.7031 to 0.7032 respectively (*Koornneef et al. 2012; Peate et al. 2009*). Iceland receives major sea spray influence (*Price & Gestsdóttir 2006; Voerkelius et al. 2010*) but dust flux is limited.

5.5 Methods

5.5.1 Sample preparation

The enamel was sampled, chemically processed and analysed at the Faculty of Science, Vrije Universiteit Amsterdam. Sample preparation and procedures are described in detail in *Plomp et al.* (*2017*). The enamel was sampled using a dental micro-drill fitted with a cleaned diamond-tipped rotary burr and blade (Minilor Perceuse). Sample weight for Nd composition in this study ranged from 222 to 1464 mg (average = 733 mg, n = 20) of which 1-2 % aliquots were taken for Sr analysis for the individuals from South Holland, Limburg, Friesland, the Caribbean, Columbia and Iceland (n = 25). If two third molars were available from a single donor, the enamel from both teeth was combined to increase available sample size.

5.5.2 Chemical separation

Sample dissolution and chromatographic separation was performed in a class 100 clean laboratory. All PFA laboratory equipment was cleaned according to standard procedure (*Plomp et al. 2017*). In order to assess the variability introduced by the laboratory procedures a synthetic tooth standard (TSTD) was used (*Plomp et al. 2017*). TSTD aliquots were processed on 0.75 and 1.3 mL TRU-resin columns (10 mL, 4 ng Nd, 1000 mg $CaHPO_4$) and Sr columns (0.05 mL, 500 ng Sr, 5 mg $CaHPO_4$).

In order to determine the range of Nd concentrations in human teeth, isotope dilution was performed on a subset of the samples before dissolution (*Koornneef et al. 2015, 2017; Timmerman et al. 2017*). This method allows for the simultaneous measurement of both Nd elemental concentration and Nd isotope composition of a single sample. The enamel was dissolved in two steps using 6.5 N HCl and a mixture of 6.5 N HCl and 14.0 N HNO_3 before

being taken up in 10 mL 2.0 N HNO_3 for column extraction (*Plomp et al. 2017*). Neodymium extraction followed the procedure described in *Plomp et al.* (*2017*) (available on *protocols.io: http://dx.doi.org/10.17504/protocols.io.xzmfp46*), using TRU-resin columns with resin volumes ranging from 0.75 mL (samples <550 mg) to 1.3 mL (samples >550 mg). After LREE extraction, Nd was separated from the other LREE using Ln-resin (Eichrom Technologies) following standard procedure (*Koornneef et al. 2015*).

An aliquot of 100-200 µL (depending on sample size) was taken from the samples for Sr analysis, which was separated using pipette tips (with 30µm pore size frit material (*Font et al. 2012*)) and 100 µL Sr-spec resin.

5.5.3 TIMS

Neodymium and Sr analyses were performed on a Thermo Scientific Triton *Plus* TIMS (*Koornneef et al. 2014*). Standards and samples were loaded on out-gassed Re filaments in 1-2 µL 10 % HNO_3 with 1 µL H_3PO_4 for Nd (see *Koornneef et al.* (*2013*) for details) and 50 % of the Sr fraction in 1 µL 10 % HNO_3, with 1.5 µL $TaCl_5$ for Sr.

Neodymium analyses were performed using 10^{13} Ω resistors fitted to the amplifier system (see *Koornneef et al.* (*2014*) for details) and 10^{11} Ω resistors if enough sample was available, following procedures described in detail in *Plomp et al.* (*2017*). $^{143}Nd/^{144}Nd$ ratios were corrected for mass-fractionation to $^{146}Nd/^{144}Nd = 0.7219$. A minimum of 70 scans were collected for each analysis on 10^{13} Ω amplifiers, and 60 scans for 10^{11} Ω amplifiers. Larger standards and samples (> 1 ng) were stopped after 300-400 cycles using 10^{13} Ω resistors and re-analysed using 10^{11} Ω amplifiers to check for precision and accuracy. Repeat sample analyses were within analytical error (*Plomp et al. 2017*).

Standards were measured to check for accuracy and reproducibility. Small aliquots, 100 pg, of an internal standard, CIGO (see *Koornneef et al.* (*2013*) for more details on CIGO), measured with 10^{13} Ω amplifiers ($^{143}Nd/^{144}Nd = 0.511344 \pm 70$, 2 SD, n = 40) were in agreement with 250 ng CIGO measurements determined using the 10^{11} Ω amplifiers ($^{143}Nd/^{144}Nd = 0.511328 \pm 9$, 2 SD, n = 50). JNdi-1 results using 10^{11} Ω amplifiers gave an average $^{143}Nd/^{144}Nd$ of 0.512096 (± 61, 2 SD, n = 22). Analysis of 0.5-4.0 ng Nd TSTD using 10^{13} Ω amplifiers ($^{143}Nd/^{144}Nd = 0.512134 \pm 72$, 2 SD, n = 81) are in agreement with measurements using 10^{11} Ω amplifiers ($^{143}Nd/^{144}Nd = 0.512125 \pm 61$, 2 SD, n = 49). Total procedural blanks yielded 1.1 ± 1.7 pg for Nd (n = 56).

Previous research in our lab demonstrates that blank contributions to samples as small as 30 pg Nd are negligible (*Koornneef et al. 2015, 2017*), hence blank corrections were not required.

Strontium analyses were performed using default 10^{11} Ω resistors. Isotope ratios were corrected for mass-fractionation to $^{86}Sr/^{88}Sr = 0.1194$. Standards measured for the period of a year resulted in $^{87}Sr/^{86}Sr = 0.710247 \pm 17$ (2 SD, n = 51, 100-200 ng) for NBS987 (accepted $^{87}Sr/^{86}Sr = 0.710248$) and $^{87}Sr/^{86}Sr = 0.707854 \pm 19$ (2 SD, n = 97) for the internal TSTD (first publication of $^{87}Sr/^{86}Sr$ ratios of the inhouse TSTD). The procedural blanks yielded an average of 24.7 pg strontium (± 38.9, n = 26), a negligible amount compared to the average amount of strontium present in enamel samples (100–800 ng; *Bentley 2006*).

5.6 Results

5.6.1 Neodymium elemental concentration

This paper reports new Nd concentration data from the enamel of a subset of the individuals (n = 15; 12 Dutch individuals and 3 individuals from Grenada, Bonaire and Colombia) (**Table 5.1**). Concentrations for these 15 individuals ranged from 0.1 ppb to 7.9 ppb, with a median of 0.5 ppb. These data are considered together with Nd concentration data from Dutch individuals previously published (total n = 39, *Plomp et al. 2017*, **Figure 5.3**). For the majority of the individuals tested, enamel contains < 1 ppb Nd (n = 20, 51.3 %, **Figure 5.3**). The total Dutch sample set records a weak correlation between Nd concentration and isotopic composition (R^2 = 0.47, n = 17, **Figure 5.4**).

5.6.2 Neodymium and strontium isotope composition

This study adds enamel Nd isotope ratios of 15 Dutch inhabitants and 5 inhabitants from Curaçao, Bonaire, Grenada, Colombia and Iceland to the existing dataset of 20 Dutch individuals (*Plomp et al. 2017*) (**Table 5.1**). Eight samples analysed for Nd isotope ratios did not contain enough Nd for reliable analysis (<70 scans). Paired Nd and Sr isotope ratios were determined for 33 out of 40 individuals (**Table 5.1**); 28 Dutch individuals (**Figure 5.5**) and 5 individuals from the Caribbean, Columbia and Iceland (**Figure 5.6**). This study reports Nd and Sr results on the same fraction for 25 individuals (South Holland, Limburg, Friesland, Caribbean, Columbia and Iceland). Neodymium and strontium isotope ratios for North Holland were performed on separate sample fractions (n = 8; *Font et al. 2015; Plomp et al. 2017*).

Table 5.1 *Nd concentration and isotope composition of third molars (n = 47). Nd was analysed using 10^{13} resistors and Sr isotope composition using 10^{11} resistors.*
εNd = [(^{143}Nd/^{144}Nd)sample/(^{143}Nd/^{144}Nd)CHUR) -1] x 10^4, with the accepted value of the Chondritic Uniform Reservoir (CHUR) = 0.512638 (Jacobsen & Wasserburg 1980).
Data available in .csv format at 4TU.ResearchData (http://doi.org/10.4121/uuid:d541a402-2701-47b2-ac6a-eaaa14c8c111).
**2 teeth combined*
[a] Results published in Font et al. (2015)
[b] Results published in Plomp et al. (2017)

Group	Sample	Location	Size (mg)	Nd (ppb)	^{143}Nd/^{144}Nd ± 2SD	εNd	^{87}Sr/^{86}Sr ± 2SD
North Holland	1A-22	Amsterdam	530		0.512044 ± 44[b]	-11.6[b]	
	2A-20	Warmenhuizen	511	1.3[b]	0.512091 ± 37[b]	-10.7[b]	0.709267 ± 7[a]
	3A-24	Amsterdam	529	2.3[b]	0.512193 ± 29[b]	-8.7[b]	0.709378 ± 7[a]
	4A-H	Purmerend	320	19.8[b]	0.512229 ± 47[b]	-8.0[b]	
	5A-25	Amsterdam	350	0.7[b]	0.512056 ± 91[b]	-11.4[b]	
	6A-10	Amsterdam	276	3.1[b]	0.512175 ± 32[b]	-9.0[b]	0.709315 ± 6[a]
	7A-13	Amsterdam	279	0.4[b]	0.512098 ± 59[b]	-10.5[b]	0.709409 ± 9[a]
	8A-27	Alkmaar	273		0.512185 ± 188[b]	-8.8[b]	0.709367 ± 7[a]
	9A-28	Amsterdam	513		0.512380 ± 119[b]	-5.0[b]	
	10A-18	Amsterdam	418	0.4[b]	0.512288 ± 119[b]	-6.8[b]	0.709584 ± 6[a]
	11A-15	Amsterdam	431		0.512589 ± 80[b]	-1.0[b]	0.709441 ± 4[a]
	12A-9	Amsterdam	299	1.1[b]	0.512330 ± 124[b]	-6.0[b]	0.709231 ± 4[a]
South Holland	28R-14a	Dordrecht	429	21.0[b]	0.512388 ± 32[b]	-4.9[b]	0.709153 ± 6
	29R-11	Rotterdam	1233*		0.512080 ± 29[b]	-10.9[b]	0.709375 ± 11
	30R-13	Rotterdam	870*		0.511869 ± 28[b]	-15.0[b]	0.709409 ± 9
	31R-2	Rotterdam	482		0.512048 ± 28[b]	-11.5[b]	
	32R-3	Rotterdam	746*		0.511945 ± 48[b]	-13.5[b]	
	33R-9	Rotterdam	589		0.511972 ± 100[b]	-13.0[b]	
	34R-5	Dordrecht	582		0.511987 ± 105[b]	-12.7[b]	0.709061 ± 8
	35R-9	Rotterdam	636		0.512020 ± 166[b]	-12.1[b]	0.709821 ± 9
Friesland	36-F1	Lippenhuizen	1310*		0.511959 ± 30	-13.2	0.709432 ± 9
	37-F3	Holwerd	652		0.511938 ± 130	-13.7	0.709619 ± 9
	38-F4	Leeuwarden	452		0.512011 ± 94	-12.2	0.708934 ± 10
	39-F8	Leeuwarden	510		0.511820 ± 107	-16.0	0.709469 ± 7
	40-F11	Leeuwarden	570		0.512046 ± 63	-11.5	0.709230 ± 9
	41-F12	Oldeboorn	361		0.512048 ± 35	-11.5	0.709122 ± 9
	42-F13	Leeuwarden	415		0.511928 ± 60	-13.8	0.709337 ± 9

Limburg	43-R6	Maastricht	1464*		0.511999 ± 29	-12.5	0.708942 ± 7
	44-M4	Maastricht	384		0.511820 ± 49	-16.0	0.709596 ± 7
	45-M5	Maastricht	712		0.511973 ± 56	-13.0	0.709644 ± 10
	46-M10	Maastricht	66	0.1			
	47-M14	Maastricht	1190*	0.1	0.511880 ± 117	-14.8	0.709546 ± 10
	48-ZH1	Heerlen	864*	0.1	0.511916 ± 112	-14.1	0.709424 ± 8
	49-ZH3	Heerlen	1226*	0.4	0.512061 ± 64	-11.3	0.709319 ± 9
	50-ZH4	Heerlen	969*	0.9	0.512075 ± 80	-11.0	0.709169 ± 9
	51-ZH9	Vaals	222	0.5	0.511924 ± 50	-13.9	0.709862 ± 8
Other Dutch	52-7	Utrecht	53	0.5			0.709382 ± 6[a]
	53-3	Maarssen	59	1.8			0.708951 ± 6[a]
	54-S3a	Kortgene	56	0.8			
	55-S2b	Kortgene	33	0.8			
	56-1e	Den Bosch	63	1.2			0.709611 ± 9[a]
	57-16e	Enschede	41	0.5			0.709674 ± 8[a]
World	W1-Gr	Grenada (St. George's)	421	7.9	0.512773 ± 30	2.6	0.707841 ± 9
	W2-R8	Curaçao (Willemstad)	489		0.512131 ± 43	-9.9	0.709375± 10
	W3-B4	Bonaire (Kralendijk)	873*	0.6	0.512127 ± 38	-10.0	0.709256 ± 9
	W4-B16	Columbia (Cúcuta)	1036*	0.2	0.512043 ± 142	-11.6	0.711749 ± 9
	W5-I	Iceland (Reykjavik)	548		0.511889 ± 29	-14.6	0.708740 ± 9

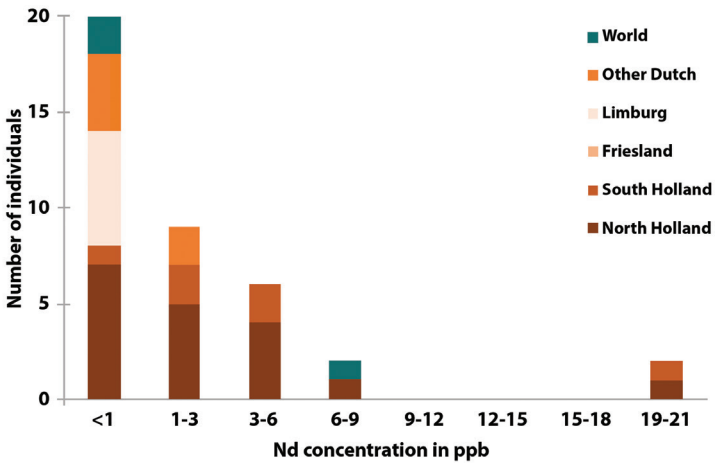


Figure 5.3 *Neodymium concentrations of individuals from North Holland (n = 18), South Holland (n = 6), Limburg (n = 6), other parts of the Netherlands (n = 6), and other parts of the world (n = 3) (total n = 39). Concentration results from the individuals from North and South Holland (n = 23) were previously published by Plomp et al. (2017).*

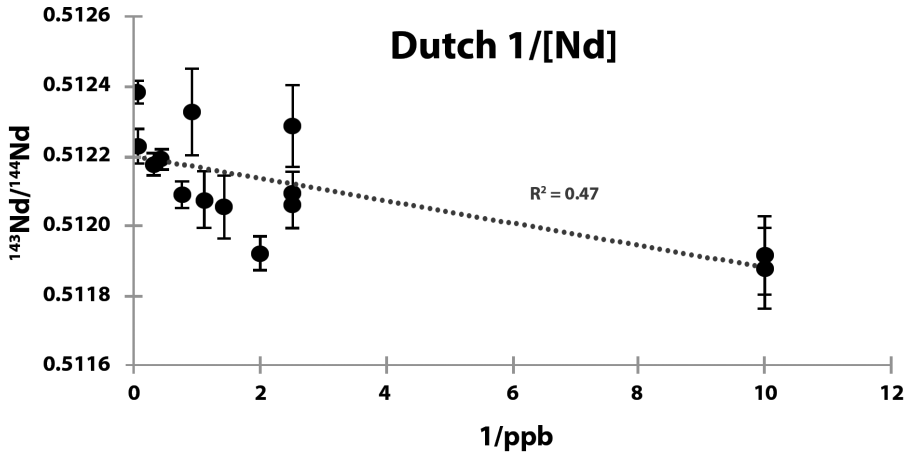


Figure 5.4 *$^{143}Nd/^{144}Nd$ vs the reciprocal of neodymium content (ppb) for Dutch samples (1/[Nd], n = 17). The two samples from Limburg containing 0.1 ppb Nd are at the right extreme of the graph.*

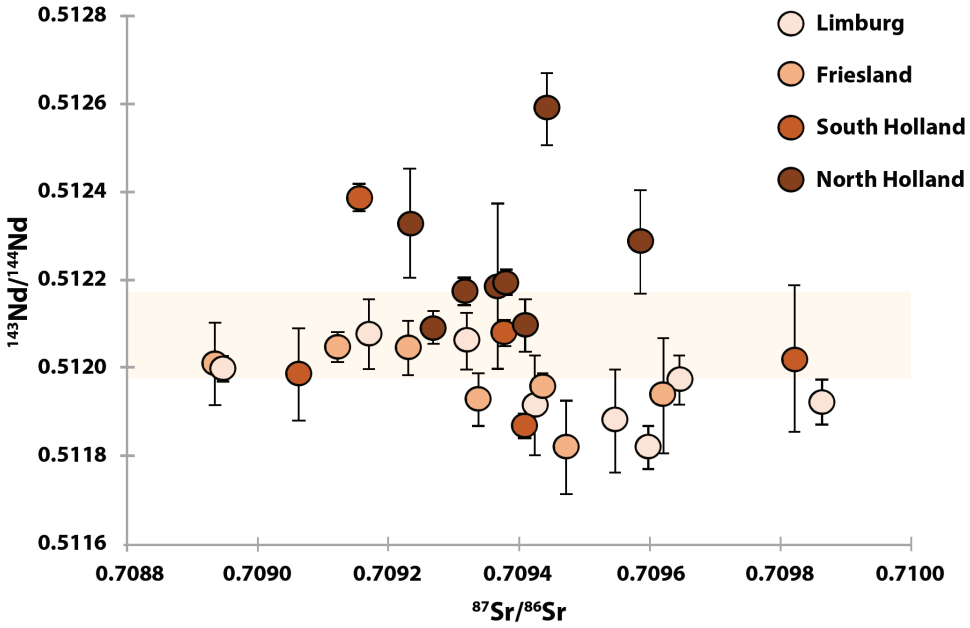


Figure 5.5 *Nd and Sr isotope compositions of third molars (n = 28) from Dutch individuals. The Dutch isotope range is represented by the orange box based on river sediment data (Nd, Bayon et al. 2015; Kuhlmann et al. 2004), human scalp hair and enamel data from modern Dutch individuals, tap water and soil/street dust (Sr, Font et al. 2015). Neodymium results for the individuals from North and South Holland were previously published by Plomp et al. (2017). Strontium results for the individuals from North Holland were previously published by Font et al. (2015).*

The $^{143}Nd/^{144}Nd$ isotope ratios from the Dutch individuals from Limburg (n = 8) ranged from 0.51182-0.51208 (median = 0.51195) and for Friesland (n = 7) between 0.51182-0.51205 (median = 0.51196). These results are compatible with or lower than the $^{143}Nd/^{144}Nd$ isotope range found in Dutch river sediments ($^{143}Nd/^{144}Nd$ = 0.51198-0.51217, n = 18, *Bayon et al. 2015; Kuhlmann et al. 2004*) and overlap with the results of the individuals from South Holland ($^{143}Nd/^{144}Nd$ = 0.51187–0.51239, n = 8) (**Figure 5.5**). The range in $^{87}Sr/^{86}Sr$ ratios in the Dutch inhabitants (0.70894-0.70982, **Figure 5.5**) is compatible with the defined modern Dutch range ($^{87}Sr/^{86}Sr$ = 0.708-0.710, *Font et al. 2015*).

The combined Sr-Nd isotope results from the individuals from Grenada, Curaçao, Bonaire, and Colombia are plotted in **Figure 5.6**. Both the Nd and Sr ratios are consistent with local geology for the individual from Colombia. The individual from Grenada exhibits Nd ratios compatible with local geology, but shows an elevated Sr ratio compared to the local volcanic geology. Elevated Sr isotope ratios are also seen in the Curaçao (0.7094) and Bonaire (0.7093) samples, with Nd ratios isotopically indistinguishable from the local geology. The Iceland sample has a

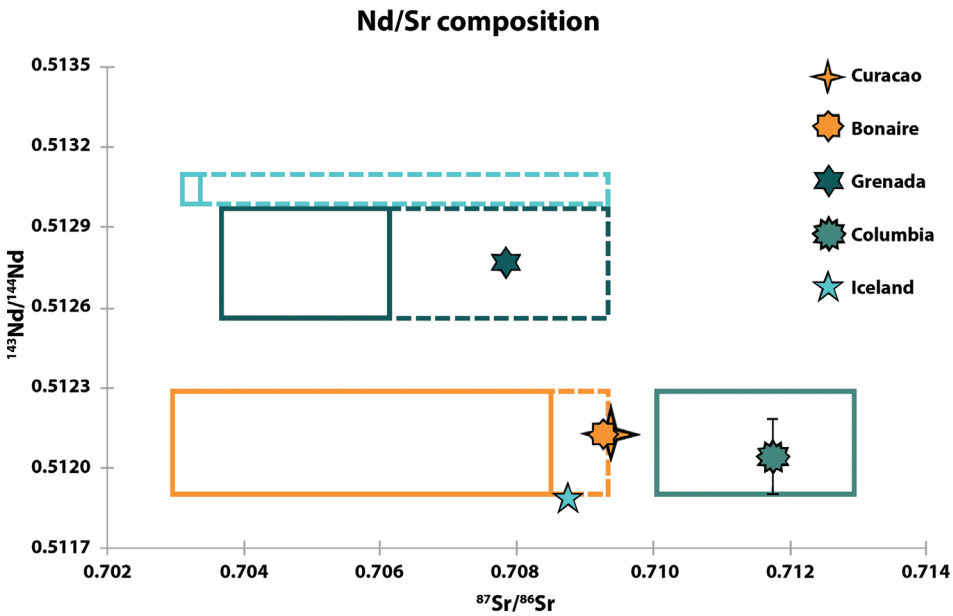


Figure 5.6 *Nd and Sr isotope compositions of third molars (n = 5) from Caribbean, Columbian and Icelandic individuals. The expected local isotope ranges, as described in* **Section 5.4**, *are represented by the solid line boxes, with stippled lines representing potential Sr sea spray influence. The standard deviations are smaller than the symbols (unless visible).*

Nd ratio ($^{143}Nd/^{144}Nd$ = 0.51189) significantly lower than the local volcanic rocks ($^{143}Nd/^{144}Nd$ = ~0.5130). The individual's Sr ratio ($^{87}Sr/^{86}Sr$ = 0.708740 ± 9) is also incompatible with the local volcanic geology.

5.7 Discussion

5.7.1 Nd elemental concentration variability

The low Nd concentration present in human tissue (<0.7 ppm) means that to date there are limited studies of Nd uptake into living tissue and bioavailable Nd, as well as the effect of anthropogenic contributions. Initial Nd concentration data reported low concentrations with significant variation in Dutch individuals (0.1 to 21.0 ppb, n = 23, *Plomp et al. 2017*), in which higher Nd concentrations (19.8 and 21.0 ppb) were explained by either (1) local exposure by industrial Nd products or (2) variation in the uptake of Nd in the human body due to individual differences in physiological factors such as sex, age, and activity patterns (or a combination of the two factors). The current study reports similar low concentrations ranging from 0.1 to 7.9 ppb (n = 16). The 0.9 ppb median (n = 39) is lower than previously reported for the individuals from North and South Holland (1.2 ppb median, <1 – 21 ppb), as individuals from Limburg show consistently lower Nd concentration in their enamel (<1 ppb). The weak correlation between Nd elemental concentration and isotope composition (R^2 = 0.47, **Figure 5.4**) suggests that local geology is not the only factor controlling neodymium in dental enamel. This correlation is still evident after removal of outliers with especially low Nd concentrations (0.1 ppb, n = 2, R^2 = 0.21) or elevated Nd isotope ratios ($^{143}Nd/^{144}Nd$ = > 0.5122, n = 4, R^2 = 0.64). The low Nd concentrations found in dental enamel (< 9 ppb) suggest that systemic pollution is unlikely to be a factor influencing the Dutch population, as Nd concentrations are much higher in lung (>50 ppb) and hair (>160 ppb) tissues reported for individuals affected by acute Nd pollution (*Pietra et al. 1985; Plomp et al. 2017; Wei et al. 2013*). Local Nd pollution caused by fossil fuel, fertilisers or waste combustion and metallurgic processes such as the production of magnets (*Tyler 2004*), or contact with these (electro)magnets in smart phones, computers and other electronic equipment could influence the Nd found in human tissues from individuals. Local anthropogenic Nd exposure cannot be excluded based on the available information of this dataset, as the originally low Nd concentrations in human enamel (< 1-9 ppb) would be easily affected by such influences. Smoking does not seem to increase Nd concentration in enamel, as two reported smokers during enamel mineralisation (7A-13 and 48-ZH1) had low Nd concentrations (0.1 and 0.4 ppb respectively).

5.7.2 Geological control of Nd-Sr isotopes

To determine whether Nd isotope ratios can be used as a provenance indicator, this study examined if the local geology controlled the Nd elemental concentration and isotope composition in modern human enamel. Both $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios of the same dental element were assessed to provide an additional geographical proxy next to information obtained from the questionnaires. The differences between an individual Nd or Sr isotope analysis and the maximum or minimum of the expected range is expressed as $\Delta^{143}Nd$ or $\Delta^{87}Sr$. The Sr range in the enamel of the Dutch inhabitants ($^{87}Sr/^{86}Sr$ = 0.70894-0.70982, **Figure 5.5**) is indistinguishable from the previously defined modern Dutch Sr range ($^{87}Sr/^{86}Sr$ = 0.708-0.710; *Font et al. 2015*). The $^{143}Nd/^{144}Nd$ ratios from the Dutch individuals from Limburg and Friesland were either compatible (n = 13) or lower than (n = 2) the currently defined Dutch geological range ($^{143}Nd/^{144}Nd$ = 0.51198-0.51217; *Bayon et al. 2015; Kuhlmann et al. 2004*) (**Table 5.1, Figure 5.5**). The difference of these two individuals compared to the minimum value of the Dutch geological range ($^{143}Nd/^{144}Nd$ = 0.51198) is $\Delta^{143}Nd$ = 0.0001-0.0002. The lower Nd isotope ratios recorded for three individuals from Limburg, Friesland and South Holland could potentially be consistent with regional geology, as results as low as $^{143}Nd/^{144}Nd$ = 0.5118 are found in the glacial sediment cover derived from geological old terrains in Scandinavia (*Mulder 2003; Vos 2015*). The $^{143}Nd/^{144}Nd$ ratios of the individuals from Friesland and Limburg were expected to differ based on the local geology (fluvial and glacial sediments in Friesland and fluvial and loess layers in Limburg), yet overlap in their $^{143}Nd/^{144}Nd$ ratio range and median results (Friesland = 0.51182-0.51205, median = 0.51196, and Limburg = 0.51182-0.51208, median = 0.51195). The $^{143}Nd/^{144}Nd$ ratios of Friesland and Limburg individuals are lower and less variable than $^{143}Nd/^{144}Nd$ ratios of the individuals from North Holland (0.51204-0.51259, median = 0.512189), where local geology consists of fluvial sediments.

Similarly, a local Nd-Sr isotope range was established for the enamel samples from the Caribbean, Columbia and Iceland, using previously published data (see **Section 5.4**). The isotope results from the individuals from Grenada, Curaçao, Bonaire, Colombia and Iceland are either (1) consistent with the local geology in both Sr and Nd isotopes (Colombia), (2) consistent with local geology in Nd isotopes but not Sr isotopes, where $^{87}Sr/^{86}Sr$ ratios are too high (Grenada, Curaçao and Bonaire) or are (3) incompatible with the local geology in both Sr and Nd isotope ratios (Iceland) (**Figure 5.6**). The elevated $^{87}Sr/^{86}Sr$ ratios seen in the individuals from Grenada (0.7078), Curaçao (0.7094) and Bonaire (0.7093) are consistent with the expected contribution from sea spray ($^{87}Sr/^{86}Sr$ = 0.709; *Bentley 2006*) and North African dust ($^{87}Sr/^{86}Sr$ = 0.715-0.718; *Aarons et al. 2013; Bataille et al. 2018*). The geologically compatible $^{143}Nd/^{144}Nd$

ratios of the Caribbean individuals suggest that Nd is less susceptible to sea spray and dust influences than Sr. Nevertheless, a dust input cannot be ruled out as the North African dust has $^{143}Nd/^{144}Nd$ ratios (0.5116-0.5126; *Aarons et al. 2013; Pourmand et al. 2014; Zhao et al. 2018*) compatible with the limestone regions of Curaçao and Bonaire (~0.5120; *Thompson et al. 2004*). While the $^{143}Nd/^{144}Nd$ ratios of the samples from Curacao, Bonaire and Colombia reflect the local geology they are indistinguishable from the Dutch population in their Nd isotope ratios as the predicted $^{143}Nd/^{144}Nd$ ratios of these countries are similar. The predominantly volcanic origin of Grenada, however, means that the island has a $^{143}Nd/^{144}Nd$ ratio distinct from the Dutch geology, and hence the Grenadian individual can be distinguished from the Dutch individuals based on Nd isotope composition. In summary, the $^{143}Nd/^{144}Nd$ ratios from the Dutch inhabitants from the provinces of Limburg, Friesland and South Holland as well as the individuals from the Caribbean and Columbia (n = 25 out of n = 30, 83.3 %) are consistent with the hypothesis that the Nd isotope composition of enamel primarily reflects local geology.

5

Incompatibilities between the Nd isotope ratios of local geology and enamel data were previously reported for 4 individuals from the Netherlands ($^{143}Nd/^{144}Nd = \geq 0.5122$, $\Delta^{143}Nd =$ 0.0002-0.0004; *Plomp et al. 2017*) and are seen in the current study for the Icelandic sample. The Icelandic individual has lower $^{143}Nd/^{144}Nd$ and higher $^{87}Sr/^{86}Sr$ ratios (0.51189 and 0.70874 respectively) than expected based on the recent volcanic origin of the island ($^{143}Nd/^{144}Nd =$ ~0.5130 and $^{87}Sr/^{86}Sr =$ ~0.70315; *Koornneef et al. 2012; Peate et al. 2009*; i.e., $\Delta^{143}Nd = -0.0011$ and $\Delta^{87}Sr = 0.0056$). The elevated Sr isotope ratio is consistent with sea spray contribution, as indicated by other biological datasets from Iceland (*Price & Gestsdóttir 2006; Voerkelius et al. 2010*). The Icelandic individual is distinguishable from the $^{87}Sr/^{86}Sr$ ratios seen in the enamel of the Dutch inhabitants in this study ($^{87}Sr/^{86}Sr = 0.70894$-$0.70982$). The relatively low Nd isotope ratio cannot be explained solely by local environment factors as Iceland does not receive a major dust input and marine influences should not predominate over the Nd derived from the local geology (*Jeandel et al. 2007; Tachikawa et al. 2017*). Incongruent release of Nd during weathering (*Hindshaw et al. 2018*) cannot explain the isotopic difference with the volcanic basement as the Icelandic basalt rocks are too young (< 5 Ma) to have developed minerals with significant isotopic differences. Although isotopic variations in geologically old terrains (such as Colombia) can be caused by weathering conditions (*Hindshaw et al. 2018; Tricca et al. 1999*) the $^{143}Nd/^{144}Nd$ ratio of the Colombian individual in this study is consistent with the expected geological isotopic range. The low $^{143}Nd/^{144}Nd$ value of the Icelandic individual is isotopically indistinguishable from the lowest $^{143}Nd/^{144}Nd$ ratios of modern Dutch enamel (~0.5118), despite major geological differences. Possible explanations for the unexpected Nd isotope

values include (1) contact with an anthropogenic Nd source (**Section 5.7.1**); or (2) individual dietary preferences for (non-local) food types with different Nd isotope ratios (**Section 5.7.3**).

5.7.3 The effect of dietary preferences on $^{143}Nd/^{144}Nd$

The highest $^{143}Nd/^{144}Nd$ ratio previously recorded (0.51259; *Plomp et al. 2017*) was a self-reported vegetarian individual from North Holland (11A-15). Two self-reported vegetarian individuals from Friesland, however, do not show elevated $^{143}Nd/^{144}Nd$ ratios (39-F8 = 0.51182, 40-F11 = 0.51205). Neodymium isotopes are not expected to be an indicator of trophic level, such as the isotope systems used for diet reconstruction ($\delta^{15}N$, ^{2}H and $^{66}Zn/^{64}Zn$; *Jaouen et al. 2016, 2018; Lee-Thorp 2008; Neuberger et al. 2013*), as the heavy mass of Nd inhibits biological fractionation during the uptake in the human body (*Evans 1990*). Based on the results of this study, it appears that vegetarianism does not result in a coherent isotopic fractionation.

The inconsistencies recorded in $^{143}Nd/^{144}Nd$ ratios between human enamel and local geology (n = 5 out of n = 30, 16.7 %), and unexpected similarities in $^{143}Nd/^{144}Nd$ ratios from individuals with variable Dutch geological backgrounds, may be explained by a significant input of non-local food. The globalisation of the food market is an important factor in the isotopic composition of modern human tissues (*Valenzuela et al. 2012*). Both Grenada and Iceland import a large proportion of their food (*The Observatory of Economic Complexity 2019; World Integrated Trade Solution 2019*), which may have lowered the Nd values of the Icelandic individual as primary import countries include the U.S.A., the United Kingdom, Germany, Scandinavian countries, and the Netherlands (*The Observatory of Economic Complexity 2019; World Integrated Trade Solution 2019*). An alternative explanation is that the low Nd isotope ratio of the Icelandic individual was influenced by the consumption of deep water fish, which are expected to have lower $^{143}Nd/^{144}Nd$ values as the Nd isotope composition of North Atlantic seawater ranges between 0.51187 and 0.51213 (*Lambelet et al. 2016; Tachikawa et al. 2017*). Unfortunately, the dietary background information of the Icelandic individual was unavailable, so this explanation remains speculative. The elevated $^{143}Nd/^{144}Nd$ ratios (≥ 0.5122) seen in four Dutch individuals may be explained by a reliance on food grown in geological areas with higher $^{143}Nd/^{144}Nd$ values (for example the volcanic areas such as East Africa, South America and the Caribbean (*Stern et al. 1990; Stern 2002; White et al. 2017*)). However, the four Dutch individuals with elevated $^{143}Nd/^{144}Nd$ ratios had $^{87}Sr/^{86}Sr$ ratios compatible with the Dutch Sr range, making a Nd provenance assignment improbable and suggesting that Sr and Nd in enamel may be affected by different environmental factors.

5.7.4 Suggestions for future research

The weak correlation between Nd concentration and Nd isotope composition in Dutch human enamel suggests that at least two Nd components are incorporated into the body, which may include the local geology, anthropogenic Nd, effects of dust and food import. Currently, however, a quantitative interpretation is hampered by the lack of studies on bioavailable neodymium and its uptake into the human body. Further research should include a more comprehensive study of the potential dietary control on Nd isotope ratios by, for example, coupled C and Zn isotope analyses on the enamel of the same dental element or C and N isotope analyses on the collagen of the dentine. This work should be linked to detailed questionnaires to address food consumption, including product origin. To establish a more robust local $^{143}Nd/^{144}Nd$ range, subsistence crops and potable water from multiple locations should be analysed for Nd isotope composition and mapped in sufficient numbers ($n = \geq 20$). Furthermore, local Nd pollution sources, such as rare earth element emission, the influence of phosphate-based fertilisers in food production, and the effect of exposure to electronic equipment should be examined. This approach should provide more information on if/how the globalisation of the food market and pollution affect the Nd isotope ratios in modern human enamel. The globalisation effect, or contamination by industrial Nd pollution and fertilisers, is expected to be less influential in archaeological populations that conducted limited long-distance trade and did not use rare earth elements such as Nd on an industrial scale. Archaeological samples, however, have the potential to be affected by diagenesis due to burial. This is particularly the case of buried bone, where the geological Nd signature will overwrite the individual's isotope signature (*Kohn et al. 2013; Tütken et al. 2011*). Currently, the contribution of diagenetic Nd and the rate of change is difficult to assess, hampering the isotopic analysis of bone tissue from cold cases in which remains have been buried for several years. Although enamel is a diagenetically resistant tissue, there are known instances where it has been affected by diagenesis (*Kamenov et al. 2018; Kohn et al. 1999; Schoeninger et al. 2003*). Work is therefore required to establish the effect of diagenesis on Nd in enamel, with the proviso that if removal of large amounts of the outer enamel layer is needed to avoid diagenetic contamination of archaeological samples (*Kootker, van Lanen et al. 2016; Laffoon et al. 2013*) there may be insufficient sample material available for neodymium analysis.

The analysis of Nd isotopes in human tissues is currently restricted by the large sample sizes required (~200-~1500 mg, > 90 % of the enamel of a molar) and the need for the latest analytical techniques for TIMS (10^{13} Ω resistors). Hence the use of Nd as part of a multi-isotope provenancing approach will probably be limited to exceptional research questions.

On-going developments in mass spectrometry may make it easier to explore the potential of neodymium as a routine tool in human provenance studies. Notably the latest generation multi-collector inducted coupled plasma mass spectrometers (MC-ICP-MS) are producing high quality Hf isotope data (± 1 εHf, 2SE) on ~0.3 ng of Hf (*Bauer & Horstwood 2018*). Addition of 10^{13} Ω resistors to such a system has the potential to increase sensitivity further and produce high quality Nd isotope data on <300 pg of Nd.

5.8 Conclusion

This study examined whether Nd isotope composition in human enamel reflects the geological area in which it was formed. For 83.3 % of the individuals the variation in Nd isotope composition of human enamel is indistinguishable from the geology of the location where the individual resided when the enamel was formed. This suggests that local geology is the major source of Nd in human dental enamel and in principle that Nd isotopes provide additional information on the mobility profile of an individual, potentially addressing some of the limitations associated with the current isotopic provenancing methods (Sr, Pb, O, H). There are, however, inconsistencies between enamel values and geological ranges in the current dataset. Therefore, further studies are required before Nd provenance studies can be applied to modern enamel samples. Influences on the Nd isotope ratio of human enamel other than local geology, such as dust or anthropogenic sources (electronics, use of fertilisers), and the effect of globalisation of the food market cannot be excluded based on the present dataset. The current uncertainty is due to the relatively limited number of individuals studied from various geological backgrounds and a lack of extensive background data on dietary resources which is required for thorough interpretation. On-going technical developments hold out the prospect that small sample sizes can be measured in the future making the technique more applicable for forensic and archaeological applications.

Conflicts of interest

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in Table 1 as well as openly available at the 4TU.ResearchData (http://doi.org/10.4121/uuid:d541a402-2701-47b2-ac6a-eaaa14c8c111) (Plomp, von Holstein, Koornneef & Davies 2019). The neodymium isotope protocol used in this study is available on protocols.io: dx.doi.org/10.17504/protocols.io.xzmfp46 (Plomp, Smeets et al. 2019).

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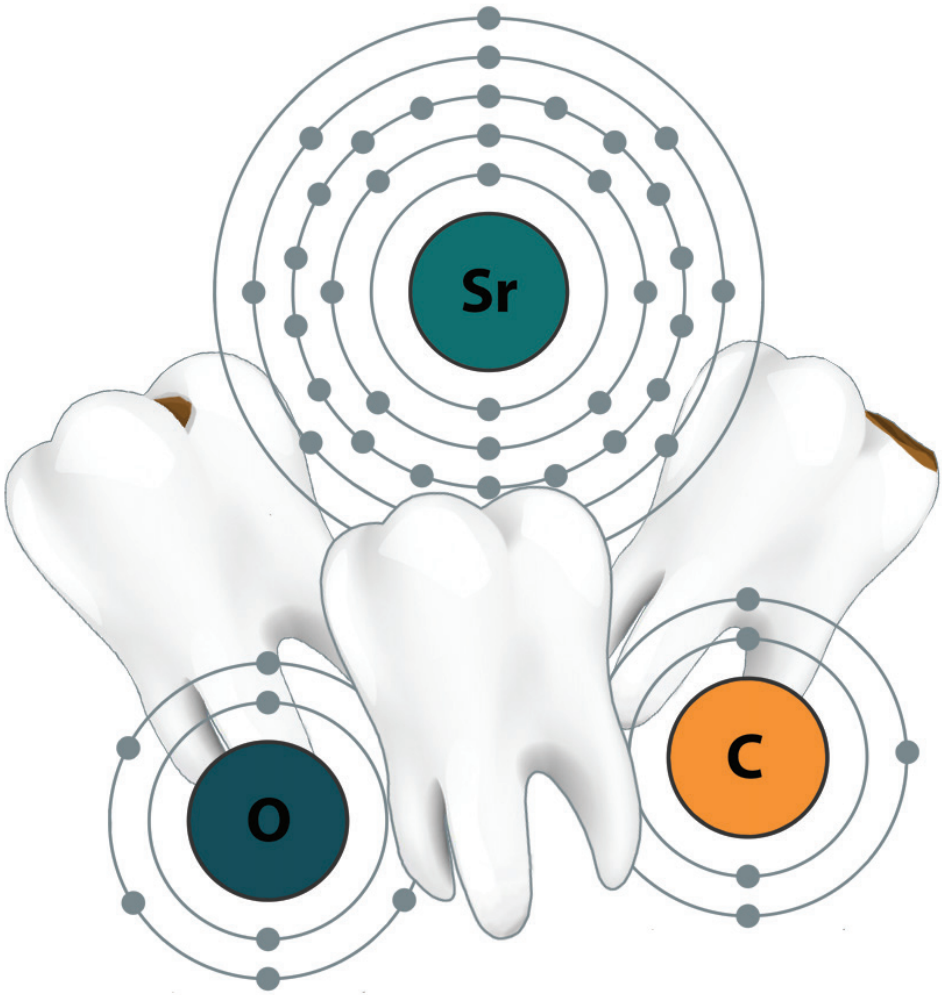
Sr
O
C

Chapter 6

Strontium, oxygen and carbon isotope variation in modern human dental enamel

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Abstract

Objectives: Isotopic analyses using human dental enamel provide information on the mobility and diet of individuals in forensic and archaeological studies. Thus far, no study has systematically examined intraindividual coupled strontium (Sr), oxygen (O) and carbon (C) isotope variation in human enamel, or the effect that caries have on the isotopic integrity of the enamel. The inadequate quantification of isotopic variation affects interpretations and may constrain sample selection of elements affected by caries. This study aims to quantify the intraindividual isotopic variation and provides recommendations for enamel sampling methods.

Material and Methods: This study presents the first systematic results on intraindividual variation in Sr-O-C isotope composition and Sr concentration in modern human dental enamel of third molars (affected and unaffected by caries). A multi-loci sampling approach (n = 6-20) was used to analyse surface and inner enamel, employing thermal ionisation mass spectrometry (TIMS) and isotope ratio mass spectrometry (IRMS). Third molars were analysed from 47 individuals from the Netherlands, Iceland, the United States, the Caribbean, Colombia, Somalia, and South Africa.

Results: Intradental isotopic variation in modern Dutch dental elements was recorded for Sr, O, and C and exceeded the variation introduced by the analytical error. Single loci and bulk sampling approaches of third molars established that a single analysis is only representative of the bulk Sr isotope composition in 60 % of the elements analysed. Dental elements affected by caries showed twice the variation seen in unaffected dental elements. Caries did not consistently incorporate the isotopic composition of the geographical environment in which they developed.

Discussion: The isotopic variability recorded in unaffected inner enamel indicates that variations greater than 0.000200 for $^{87}Sr/^{86}Sr$ and larger than 2 ‰ for $\delta^{18}O$ and $\delta^{13}C$ are required to demonstrate changes in modern Dutch human diet or geographic location.

6.1 Introduction

Human dental enamel contains information regarding the geographical origin and dietary patterns of an individual. Dental enamel records the isotopic signatures of the diet consumed during enamel mineralisation (*Bentley 2006; Lee-Thorp 2008; Montgomery 2002*), which for the permanent dentition takes place between birth and circa 16 years of age (*AlQahtani et al. 2010; Nanci 2012; Piesco & Avery 2002*). The isotopic signature of the enamel, representative of the diet and geographical location of the individual during childhood, is preserved because enamel does not remodel after mineralisation. Furthermore, enamel is markedly resistant to diagenetic alteration as it is a highly mineralised tissue, with low organic content and porosity (*Hoppe et al. 2003; Kohn et al. 1999; Lee-Thorp & Sponheimer 2003; Nanci 2012; Piesco & Simmelink 2002*). Strontium (Sr), oxygen (O) and carbon (C) isotope analyses are established techniques to infer information about human provenance ($^{87}Sr/^{86}Sr$ (e.g., *Bentley 2006*), $\delta^{18}O$ (e.g., *Blumenthal et al. 2014; Bowen 2010a; Lightfoot & O'Connell 2016; Pellegrini et al. 2016*)) and diet ($\delta^{13}C$, e.g., *Chesson, Barnette et al. 2018; France & Owsley 2015; Lee-Thorp 2008*). These isotopic analyses have been successfully applied to both modern (e.g., *Font et al. 2015; Vautour et al. 2015*) and archaeological individuals (e.g., *Bataille et al. 2018; Kootker, Mbeki et al. 2016; Laffoon et al. 2017; Panagiotopoulou et al. 2018; Snoeck et al. 2018*).

Despite the widespread use of human isotopic variation as an indicator for diet and migration, the relationship between intraindividual and intra-population variation has not been adequately quantified in humans, despite considerable geochemical variability in enamel demonstrated by previous studies (*Hare et al. 2011; Smith et al. 2018; Willmes et al. 2016; Wright 2013*). Both types of variation will be related to the variability of isotopic inputs over the time of enamel formation. Intraindividual variation may, however, also be related to (1) sampling location, (2) sampling method, and (3) enamel damage, specifically caries.

The analysis of strontium using thermal ionisation mass spectrometry (TIMS) and oxygen and carbon isotopes using isotope ratio mass spectrometry (IRMS) is now widespread in archaeological and forensic research due to the precision and accuracy that these analysis techniques provide (*Slovak & Paytan 2011*). Multiloci sampling methods (e.g., *Craig-Atkins et al. 2018*) are generally not applied on human enamel using TIMS and IRMS, however, because the final stage of enamel formation, mineralisation, has been suggested to overwrite any record of the isotopic composition of the initial incremental enamel deposition (*Fincham et al. 1999; Montgomery 2002; Montgomery et al. 2006, 2007; Müller et al. 2019; Trayler & Kohn 2017; Zazzo et al.*

2005). This re-equilibration of the isotopic composition during the mineralisation phase means that the isotopic composition of the sample taken along the incremental enamel layers would be representative of the isotopic composition during mineralisation rather than incremental enamel deposition (*Montgomery & Evans 2006; Trayler & Kohn 2017*). Moreover, sequential sampling is hampered by a poor understanding of enamel formation and mineralisation. The effects of spatial and temporal controls, as well as physiological factors (e.g., health, sex, diet, and physical activity) are unknown (*Balasse 2002, 2003; Blumenthal et al. 2014; Fincham et al. 1999; Reade et al. 2015; Simmer & Fincham 1995; Trayler & Kohn 2017*). In addition, the effect that these physiological factors have on enamel formation differs in various populations (*Tompkins 1996*). Isotopic values incorporated in the enamel are also influenced by geographical controls, especially O and Sr, which are controlled by the local precipitation (O, *Lightfoot and O'Connell 2016*) and geology (Sr, *Bentley 2006*). An example of temporal control is the introduction of the modern supermarket diet in the 1970s. The availability of a greater variety of products grown in different geological settings is expected to increase the isotopic variation seen in modern human dental enamel compared to archaeological dental enamel (C*hesson et al. 2012; Valenzuela et al. 2012; Vautour et al. 2015*).

Currently, no formal guidelines have been established for enamel sampling methods used in isotopic studies of human dental elements. The lack of a formal sampling approach may affect the intraindividual variation seen in individuals sampled as well as decrease the comparability between isotopic analyses of studies that use different sample loci. Presently, enamel sampling generally involves a single sample location of a dental element, collected across a tooth's inner enamel, indiscriminate of enamel growth phases (*Montgomery & Evans 2006; Slovak & Paytan 2011*). This sampling approach disregards the potential influence of intraindividual isotopic variation within a single dental element, that is, intradental variation. It is therefore unknown if a single sample location is representative of the total enamel Sr-O-C isotope composition of the dental element, referred to in this study as the bulk isotopic composition. Enamel is generally sampled using a handheld dental drill with tungsten or diamond burrs or saws (e.g., *Balasse 2003; Slovak and Paytan 2011; Trayler & Kohn 2017*). Some studies suggest that diagenetic Sr contaminates the surface enamel (~0.1 mm) after mineralisation due to diffusion of Sr in the saliva from the diet and water in the mouth (*Dufour et al. 2007; Horn & Müller-Sohnius 1999*), or because of interaction with the burial environment (*Kohn et al. 1999; Schoeninger et al. 2003*). As a result, tooth surfaces are usually mechanically cleaned by removing the outer surface layer prior to sampling (*Balasse 2002; Kootker, van Lanen et al. 2016; Reade et al. 2015; Slovak & Paytan 2011*). Although detailed sampling information is rarely provided in scientific

literature, researchers seem to prefer to avoid sampling surface enamel in contact with other dental elements or areas that are affected by caries or other defects (*Kootker, Mbeki et al. 2016; Montgomery 2002*). Therefore, the potential influence of carious processes, such as demineralisation and remineralisation (see references in *Li et al.* (*2014*) and *Cochrane et al.* (*2008*)) on Sr-O-C isotope ratios remains unknown.

A better understanding of the intradental isotopic variation of non-migratory individuals is therefore required to provide a baseline of intraindividual isotopic variation. This will improve the accuracy of the interpretation of mobility and dietary patterns in both archaeological and forensic contexts. Therefore, this study evaluated intraindividual isotope variation of Sr-O-C isotope composition, as well as Sr concentration, within modern human dental enamel of third molars (affected and unaffected by caries) from individuals known to have lived in one location during enamel formation and mineralisation.

This study aims to determine if:
(1) The variation of Sr-O-C isotope composition in modern human dental enamel is in the same order of magnitude between various sample locations within the same dental element (intradental), as well as within other dental elements (interdental) of the same individual. By quantifying the intradental variation it can be examined if there is any spatial control on the Sr-O-C isotope composition within a dental element.
(2) An individual's life history (year and region of birth) has an effect on the Sr-O-C isotope variation in modern human enamel.
(3) The Sr-O-C isotope values of single sample locations from the cusp match the average isotopic variation obtained from bulk sample analysis of the same dental element.
(4) The presence of caries affects the variation seen in Sr-O-C isotope composition of modern human dental elements.
Finally, these data are used to recommended a sampling protocol and to establish what Sr-O-C isotope variation is required to establish dietary change or mobility in modern Dutch humans.

6.2 Materials and Methods

6.2.1 Sample selection

Extracted third molars were donated to the Vrije Universiteit Amsterdam by patients of dental

clinics and medical centres in the Netherlands to be used for isotopic analyses. Background information was obtained through anonymous questionnaires, providing information on an individual's geographical location at the time of enamel formation (**Figure 6.1**), as well as diet, health, smoking and exercise habits. The isotopic analyses of the teeth were approved by the Medical Ethics Review Committee of the VU University Medical Center.

The enamel of third molars is formed between the age of 8-16 years (*AlQahtani et al. 2010*). Teeth were selected based on the mobility profiles of 38 Dutch individuals (residential stability during enamel formation and mineralisation) and presence of caries. In addition, third molars from 9 individuals from the Dutch Antilles (n = 3, Curaçao, Bonaire, Aruba), the Dominical Republic (n = 1), Colombia (n = 1), the U.S. (n = 1), Iceland (n = 1), Somalia (n = 1), and South Africa (n = 1), were sampled to compare their isotopic variation to the Dutch isotopic variation.

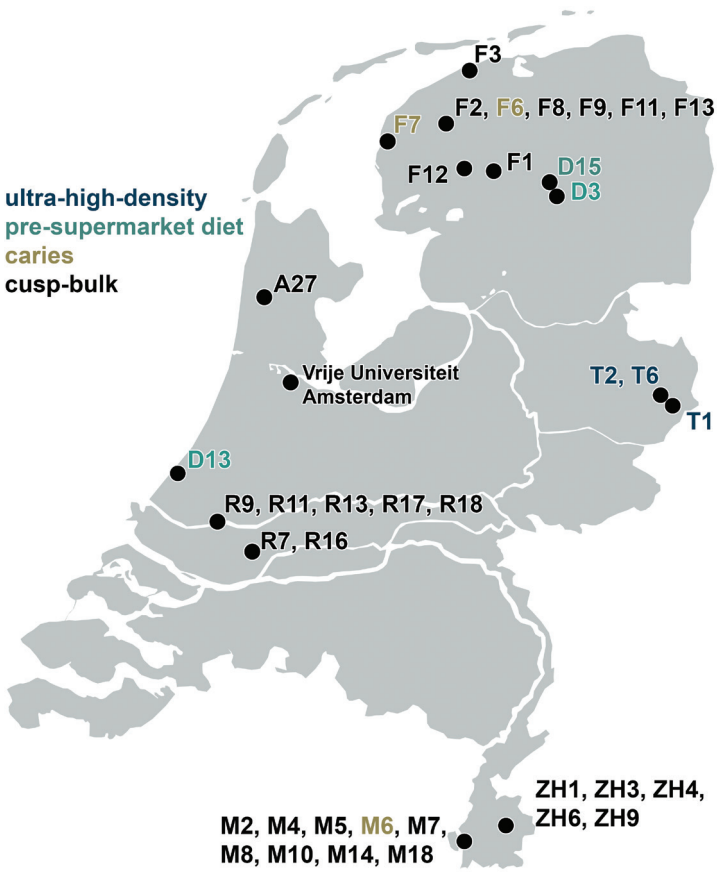


Figure 6.1 *A map of the Netherlands with localities where the individuals (n = 38) lived during formation of their third molars.*
F3 = Holwerd;
F2, F6, F8, F9, F11, F13 = Leeuwarden;
F7 = Wijnaldum;
F12 = Oldeboorn;
F1 = Lippenhuizen;
D15 = Veenhuizen;
D3 = Smilde;
A27 = Alkmaar;
T2, T6 = Hengelo;
T1 = Enschede;
D13 = Den Haag;
R9, R11, R13, R17, R18 = Rotterdam;
R7 = Dordrecht;
ZH1, ZH3, ZH4, ZH6, ZH9 = Heerlen;
M2, M4, M5, M6, M7, M8, M10, M14, M18 = Maastricht.

The following groups were examined:

(1) Three individuals born in the same decade in the late 20th century (years of birth 1989, 1995 and 1991 respectively) raised in cities in close proximity of each other in the Netherlands (T1, T2, T6), representative of inputs from a globalised supermarket diet that emerged in the 1970s. For each of these three individuals, one third molar was sampled using an ultrahigh-density approach (n = 20 samples per element), with other third molars sampled using a high-density approach (n = 6 samples per element).

(2) Three individuals born in the mid-20th century (years of birth 1949, 1964 and 1942) from the Netherlands (D3, D13, D15), representative of the pre-supermarket diet. These individuals were sampled using the high-density approach (n = 6).

(3) Single cusp location and bulk sampling approaches were compared for Sr isotope analysis of 35 individuals. The results from the bulk sampling approach were previously reported (Plomp, von Holstein et al. 2019). The results from the Dutch individuals (n = 29) were compared to non-Dutch individuals (n = 6). These individuals were born in the years 1972 – 1999 and are thus representative of increasing inputs from a globalised supermarket diet.

(4) Six individuals whose teeth developed caries. The unaffected enamel of these individuals was sampled using the high-density approach (n = 6), with caries being sampled from the surface towards the inner enamel (n = 3-4).

6.2.2 Sample preparation

The enamel was sampled, chemically processed and analysed at the Faculty of Science, Vrije Universiteit Amsterdam. Sample preparation and procedures are described in detail in *Plomp et al.* (*2017*) and *Plomp, Smeets et al.* (*2020*). The enamel was sampled perpendicular to the enamel dentine junction (EDJ) using a dental micro-drill fitted with an acid cleaned diamond-tipped rotary burr and blade (Minilor Perceuse). Enamel at the EDJ was not sampled as the thin enamel layer at the EDJ is difficult to isolate (*Reade et al. 2015*). Occlusal fissures were avoided as they (1) are difficult to mechanically clean and sample and (2) have been reported to be less mineralised (*He et al. 2010; Montgomery 2002*), making them potentially more prone to diagenesis.

To indicate the sample locations on each molar, a coding system was developed (**Table 6.1** and **Figure 6.2**). A distinction was made between the occlusal surface (cusp, or cuspal enamel; *Dean 2000*) and the sides of the dental element (wall, or lateral enamel; *Dean 2000*) (**Figure 6.2c**), where lateral enamel is secreted in a lateral direction and does not contribute to increase

Table 6.1 *Sample locations for the third molars used in this study.*

Location	Direction			
Wall	Lingual (L)	Buccal (B)	Mesial (M)	Distal (D)
Wall Surface (S)	SL	SB	SM	SD
Wall (W)	WL	WB	WM	WD
Cusp	Protocone/id (1)	Paracone/Metaconid (2)	Metacone/ entoconid (3)	Hypoconid (4)
	Mesio-lingual/buccal	Mesio-buccal/lingual	Disto-buccal/lingual	Disto-buccal
Cusp Surface (CS)	CS1	CS2	CS3	CS4
Cusp (C)	C1.1, C1.2, C1.3	C2.1, C2.2, C2.3	C3	C4

the tooth height (*Dean 2000*). The tooth wall was sampled on the wall surface (S) and the inner enamel wall (W). Similarly, the tooth cusp was sampled on the surface (CS) and from the inner enamel cusp (C). Sampling at increasing depth for the cusps is indicated by suffix .1 to .3 (in sample location numbers), representative of 0.2 to 0.5 mm. To indicate the difference between the four walls directional terms were used: Lingual, buccal, medial and distal (see **Table 6.1** and **Figure 6.2a**). The lingual tooth wall (WL) is next to the tongue, the buccal tooth wall (WB) is opposite the lingual tooth wall, towards the cheek. The mesial tooth wall (WM) is in contact with the second molar, towards the midpoint of the dental arch. The distal tooth wall (WD) is opposite the mesial tooth wall, towards the back of the dental arch. To indicate the difference between the three to four cusps on the third molar, cusps were classified based on the largest cusp (protocone/protoconid, with names ending in -cone indicative for the upper dentition and names ending with -id for the lower dentition, see **Table 6.1, Figure 6.2b**). As indicated by the incremental enamel layers in **Figure 6.2c**, the samples taken from the surface cusps (CS1, CS2, CS3, CS4) derive from the same incremental enamel layers. The (surface) wall samples (SL, SB, SM, SD and WL, WB, WM, WD) as well as the inner enamel cusps samples (C1.1, C2.1, C3, C4) cross multiple incremental enamel layers and do not necessarily represent the same or distinct time periods.

Molars with caries were described in a similar way, with carious enamel samples labelled with a G and followed by a number that indicates the increase in depth of sampling towards (and including) unaffected enamel. Some samples had multiple caries that were sampled (e.g., G1.1 – G1.3, G2.1 – G2.3). The locations of the caries sampled are indicated in **Table 6.2**.

Cusp samples (C1.1) and bulk samples were taken from the same third molar for Sr isotope analysis, as described above and in **Table 6.1**. The bulk enamel samples represent ~90 % of the enamel of a dental element (excluding the surface enamel and the enamel from C1.1). The bulk samples ranged from 273 to 1310 mg, of which 1-2 % aliquots were taken after sample dissolution (*Plomp, von Holstein et al. 2019*).

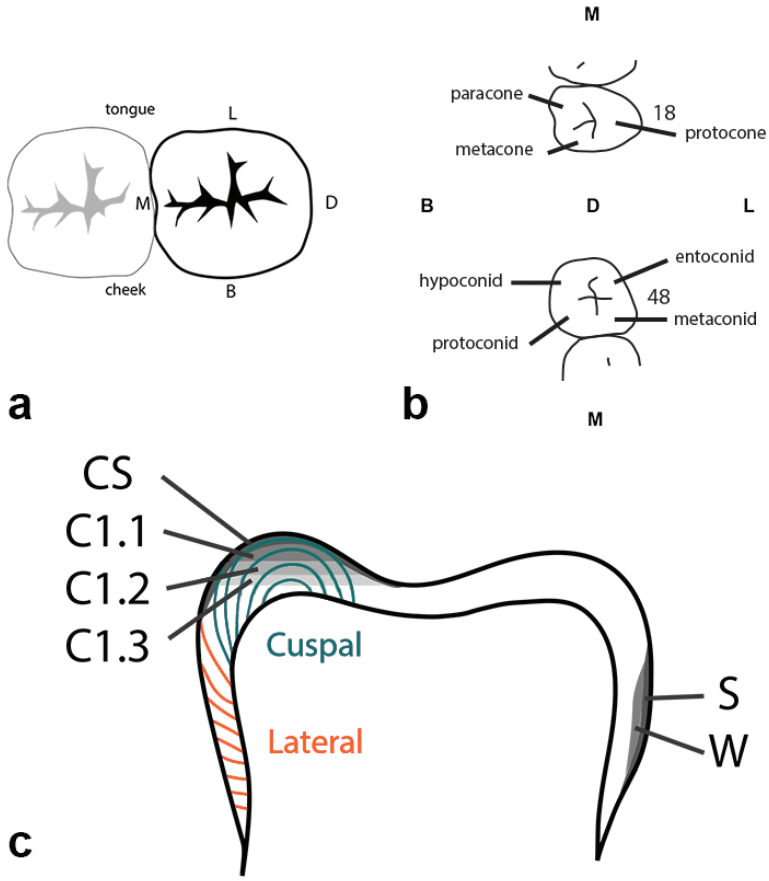


Figure 6.2a *Sample locations in third molars. Occlusal view (from above) indicating L = Lingual (towards the tongue), M = Mesial (toward the midline point/incisors of the dental arch), D = Distal (opposite of mesial, towards the back of the dental arch), B = Buccal (towards the cheek).* **Figure 6.2b** *Cusp names (see also* **Table 6.1***) for maxillary (above) and mandibular (below) third molars.* **Figure 6.2c** *Profile view indicating CS = Cusp Surface, C1.1 = Cusp layer 1, C1.2 = Cusp layer 2, C1.3 = Cusp layer 3, S = Wall Surface, W = Wall. Incremental enamel formation is indicated in purple (cuspal) and pink (lateral) lines (after Dean 2000).*

6.2.3 Strontium isotope analysis

Strontium isotope analysis (composition and concentration) was performed on powdered enamel samples (0.8-4.8 mg, median = 1.7 mg) and aliquots (1-2 %) of bulk enamel samples. To extract strontium from the enamel, samples were dissolved in 3N HNO_3 and chromatographic separation was performed in a class 100 clean laboratory. All PFA laboratory equipment was pre-cleaned (*Plomp, Smeets et al. 2020*). Aliquots of an in-house synthetic tooth standard (TSTD, 0.05 mL, 500 ng Sr, 5 mg $CaHPO_4$) were used as quality control (*Plomp et al. 2017*). The blanks and Sr concentrations were determined by isotope dilution using an ^{84}Sr spike (*Plomp, Smeets et al. 2020*). Strontium isotope analyses were performed on a Thermo Scientific Triton *Plus* thermal ionisation mass spectrometer (TIMS) using 10^{11} Ω resistors (*Koornneef et al. 2014*). Standards and 50 % of the samples were loaded on out-gassed annealed rhenium filaments in 1-2 µL 10 % HNO_3, with 1.5 µL $TaCl_5$. Strontium isotope ratios were corrected to $^{86}Sr/^{88}Sr$ = 0.1194 using the exponential mass-fractionation law. Standards measured during the study resulted in $^{87}Sr/^{86}Sr$ = 0.710247 ± 17 (n = 51) for NBS987 (100-200 ng) and 0.707854 ± 19 (n = 97) for the internal full procedure standard (TSTD). The error in the TSTD value is taken as the analytical error of the study. The procedural blanks ranged from 10.5-59.1 pg (n = 38, median = 18.4), negligible compared to typical presence of strontium in enamel (50-500 ppm; *Bentley 2006*).

6.2.4 Oxygen and carbon isotope analysis

Oxygen and carbon isotope analysis was performed on powdered enamel. The sample (0.3-0.8 mg) was weighed into an exetainer vial. The prepared vials were placed in a sample block interspaced with calibration and control standards VICS and IAEA-603. After flushing the vials with helium, samples and standards were acidified with water-free H_3PO_4 (100 %) at 45 °C and allowed to react for 24 hours. The gas mixture was analysed using a Thermo Finnigan Delta plus IRMS with a GasBench II. The isotopic values are reported as δ (delta) values in ‰ units. Values were normalised to international standard IAEA-603 ($\delta^{18}O$ = -2.6 ± 0.17 and $\delta^{13}C$ = 2.5 ± 0.04; 1 σ, n = 7) and are reported relative to the Vienna Peedee Belemnite (VPDB) standard.

6.2.5 Statistical analyses

Statistical assessments were performed using GraphPad Prism7. Data were examined for normality using D'Agostino & Pearson normality test (see *Plomp, Verdegaal-Warmerdam et al.* (*2020*) for details). Statistical significance used for the ultrahigh-density analyses (n = 20) of dental elements T1.1, T2.1 and T6.1 was determined using one-way ANOVA, followed by

Tukeys multiple comparisons post-hoc analysis. To facilitate comparisons between results, differences between the lowest and highest isotopic results are indicated ($\Delta_{max\text{-}min}$), as well as the average isotopic intraindividual variation, or avg_isovar (**Equation 6.1**, where n is the number of individuals analysed and where 2 σ is taken for strontium isotope and 1σ for oxygen and carbon isotope analyses).

$$\text{avg\_isovar} = \sqrt{\frac{1}{n} * \sum_{i=1}^{n} \sigma_i^2} \qquad \textbf{Equation 6.1}$$

6.3 Results

To evaluate the intraindividual variation in Sr-O-C isotopes in modern human enamel, the results of the multiloci sampling approach (**Table 6.2**) have been organised based on the density of the sampling approach. First the results of the ultrahigh-density samples are presented (**Section 6.3.1**), followed by the high-density samples (**Section 6.3.2**), and single cusp location versus bulk sampling approaches (**Section 6.3.3**). Lastly, the high-density sampling results from dental elements affected by caries are outlined (**Section 6.3.4**).

6.3.1 Intradental variation indicated by ultrahigh-density sampling

The Sr-O-C isotope results for the three individuals (T1, T2, T6) sampled using the ultrahigh-density approach are shown in **Figure 6.3**. Differences in strontium isotope ratios ($\Delta^{87}Sr/^{86}Sr_{max\text{-}min}$) ranged from 0.000091 to 0.000193 (up to 10 times larger than the analytical error) (**Table 6.3**). Sr concentrations appear randomly distributed, with the largest spread in Sr concentrations found in T1.1 (Δ Sr $ppm_{max\text{-}min}$ = 36.6 ppm, **Table 6.3**). Variation in $\delta^{18}O$ and $\delta^{13}C$ isotope values ranged between 1.3 ‰ and 2.0 ‰ (up to 12 times the analytical error for $\delta^{18}O$ and 50 times higher for $\delta^{13}C$) (**Table 6.3**).

There were no indications of linear correlation between enamel sample locations of T1.1, T2.1 and T6.1 and isotope system ($^{87}Sr/^{86}Sr$ R^2 <0.4, $\delta^{18}O$ R^2 <0.2, and $\delta^{13}C$ R^2 <0.4). Intradental variation between surface and inner enamel was recorded for $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$ in T1.1 ($P < 0.01$) and for both $^{87}Sr/^{86}Sr$ ($P < 0.04$) and $\delta^{13}C$ ($P < 0.01$) for T2.1 and T6.1. No consistent differences were found between the Cusp and Wall regions (with the exception of a significant difference for $^{87}Sr/^{86}Sr$ in T1.1 ($P = 0.01$; *Plomp, Verdegaal-Warmerdam et al. 2020*).

Table 6.2 *Isotopic results of individuals analysed in this study (n = 12). Information is provided on the geographical location (city), sample ID, dental element (using the FDI World Dental Federation notation - ISO 3950), sample location (described in* **Figure 6.2***), location of caries, strontium isotope ratio (n = 148) and concentration (n =146), and oxygen and carbon isotope values (n = 132).*

Sample						Strontium		Oxygen and Carbon	
Individual	City	Birth Year	ID	FDI	location	$^{87}Sr/^{86}Sr$	ppm	$\delta^{18}O$ (‰ VPDB)	$\delta^{13}C$ (‰ VPDB)
Twente 1	Enschede	1989	T1.1	38	SL	0.709785 ± 11	52.0	-6.4	-13.6
					SB	0.709785 ± 9	52.7	-6.5	-13.5
					SM	0.709732 ± 15	49.7	-6.6	-14.1
					SD	0.709785 ± 8	49.2	-6.3	-13.4
					WL	0.709776 ± 9	55.2	-6.5	-14.1
					WB	0.709787 ± 8	56.1	-6.8	-14.1
					WM	0.709871 ± 8	58.0	-6.9	-14.8
					WD	0.709762 ± 9	54.0	-6.1	-14.4
					CS1	0.709848 ± 9	46.6	-5.5	-13.7
					CS2	0.709826 ± 12	47.0	-5.9	-12.9
					CS3	0.709761 ± 11	48.9	-5.8	-12.9
					CS4	0.709772 ± 9	42.3	-6.3	-13.7
					C1.1	0.709884 ± 9	55.8	-6.3	-13.9
					C1.2	0.709877 ± 8	51.5		
					C1.3	0.709879 ± 9	53.6		
					C2.1	0.709890 ± 11	44.6	-6.3	-14.5
					C2.2	0.709890 ± 8	49.2		
					C2.3	0.709885 ± 7	53.7		
					C3	0.709822 ± 9	78.8	-6.2	-13.4
					C4	0.709851 ± 10	52.7	-6.1	-14.4
			T1.2	18	WL	0.709802 ± 9	55.9	-5.8	-13.9
					WB	0.709852 ± 9	50.1	-5.8	-14.0
					WM	0.709883 ± 10	48.5	-6.4	-14.4
					WD	0.709860 ± 9	53.3	-6.7	-14.3
					C1.1	0.709884 ± 8	49.3	-6.0	-14.5
					C3	0.709900 ± 9	52.5	-5.9	-14.6
			T1.3	28	SL			-5.0	-12.8
					SB			-5.7	-12.8
					SM			-5.6	-12.9
					SD			-5.6	-13.1

					WL	0.709891 ± 9	57.2	-6.2	-14.1
					WB	0.709897 ± 8	59.6	-6.2	-14.4
					WM	0.709908 ± 10	54.1	-6.0	-14.5
					WD	0.709864 ± 11	60.3	-5.9	-14.4
					CS1			-5.6	-13.8
					CS2			-5.5	-12.8
					CS3			-5.9	-13.7
					C1.1	0.709872 ± 9	48.3	-6.2	-14.6
					C2.1			-5.8	-14.8
					C3	0.709877 ± 9	33.9	-5.9	-14.9
Twente 2	Hengelo	1995	T2.1	48	SL	0.709294 ± 10	37.6	-7.1	-13.4
					SB	0.709304 ± 8	36.8	-7.2	-13.3
					SM	0.709313 ± 10	39.1	-6.4	-13.5
					SD	0.709303 ± 9	37.2	-6.4	-13.9
					WL	0.709266 ± 8	39.1	-7.2	-14.1
					WB	0.709279 ± 10	37.5	-7.2	-13.6
					WM	0.709295 ± 8	38.3	-6.6	-14.3
					WD	0.709312 ± 10	38.6	-6.5	-14.3
					CS1	0.709294 ± 9	31.1	-5.2	-12.8
					CS2	0.709329 ± 8	37.3	-6.0	-13.7
					CS3	0.709338 ± 10	37.9	-6.4	-13.9
					CS4	0.709357 ± 10	36.5	-6.2	-14.1
					C1.1	0.709311 ± 10	36.5	-6.2	-14.4
					C1.2	0.709276 ± 8	38.1		
					C1.3	0.709299 ± 10	37.5		
					C2.1	0.709302 ± 12	37.8	-6.3	-14.5
					C2.2	0.709293 ± 10	43.8		
					C2.3	0.709282 ± 11	40.1		
					C3	0.709321 ± 7	38.0	-6.4	-14.6
					C4	0.709322 ± 10	36.7	-6.6	-14.2
			T2.2	18	WL	0.709316 ± 10	39.3	-7.0	-14.2
					WB	0.709281 ± 10	42.7	-6.5	-14.3
					WM	0.709311 ± 9	42.1	-6.6	-14.4
					WD	0.709323 ± 7	39.8	-6.5	-14.4
					C1.1	0.709240 ± 9	38.7	-6.1	-14.7
					C2.1			-5.9	-14.2
					C3	0.709287 ± 10	39.2	-6.3	-14.5

Individual	City	Birth Year	ID	FDI	location	$^{87}Sr/^{86}Sr$	ppm	$\delta^{18}O$	$\delta^{13}C$
Twente 6	Hengelo	1991	T6.1	38	SL	0.709834 ± 9	59.3	-7.4	-14.0
					SB	0.709870 ± 10	69.4	-7.1	-14.2
					SM	0.709843 ± 9	60.8	-7.2	-13.3
					SD	0.709799 ± 9	55.8	-7.0	-14.0
					WL	0.709951 ± 8	74.8	-7.3	-14.5
					WB	0.709830 ± 8	62.6	-7.2	-14.2
					WM	0.709930 ± 9	74.5	-7.1	-14.1
					WD	0.709991 ± 9	61.4	-7.6	-14.7
					CS1	0.709960 ± 13	61.1	-5.7	-12.6
					CS2	0.709988 ± 10	68.9	-6.3	-13.0
					CS3	0.709857 ± 11	59.7	-6.5	-13.3
					CS4	0.709892 ± 10	65.3	-6.5	-13.0
					C1.1	0.709961 ± 10	64.6	-6.5	-14.4
					C1.2	0.709890 ± 10	76.0		
					C1.3	0.709940 ± 10	77.5		
					C2.1	0.709946 ± 9	66.6	-7.2	-14.4
					C2.2	0.709955 ± 9	66.1		
					C2.3	0.709957 ± 10	69.0		
					C3	0.709966 ± 8	68.5	-7.0	-14.3
					C4	0.709909 ± 9	56.5	-6.7	-14.3
			T6.2	28	WL	0.709835 ± 8	84.8	-6.8	-14.1
					WB	0.709817 ± 9	78.5	-6.3	-13.8
					WM	0.709823 ± 9	85.6	-6.5	-14.0
					WD	0.709808 ± 8	78.2	-6.9	-14.1
					C1.1	0.709799 ± 8	88.4	-6.6	-14.4
					C2.1			-6.0	-14.0
					C3	0.709830 ± 9	79.3	-6.0	-13.7
Drenthe 3	Smilde	1949	D3	48	WL	0.709575 ± 10	96.6	-6.1	-12.6
					WB	0.709558 ± 11	93.8	-6.1	-12.7
					WM	0.709552 ± 10	93.7	-6.2	-12.8
					WD	0.709600 ± 9	103.3	-6.9	-12.6
					C1.1	0.709584 ± 10	87.3	-6.2	-12.9
					C2.1	0.709539 ± 10	91.6	-5.5	-12.8

Individual	City	Birth Year	ID	FDI	location	$^{87}Sr/^{86}Sr$	ppm	$\delta^{18}O$	$\delta^{13}C$
South Holland 13	Den Haag	1942	D13	48	WL	0.709202 ± 9	96.2	-6.1	-13.5
					WB	0.709210 ± 7	95.9	-5.9	-14.0
					WM	0.709202 ± 9	100.6	-6.0	-13.8
					WD	0.709223 ± 7	97.9	-6.3	-13.9
					C1.1	0.709216 ± 9	94.6	-6.3	-13.9
					C2.1	0.709208 ± 8		-6.0	-14.0
Drenthe 15	Veenhuizen	1964	D15	38	WL	0.709412 ± 7	100.6	-6.4	-13.5
					WB	0.709392 ± 8	64.3	-6.1	-13.7
					WM	0.709383 ± 9	60.8	-6.0	-14.0
					WD	0.709392 ± 10	65.2	-6.6	-13.7
					C1.1	0.709395 ± 10	56.8	-5.9	-13.8
					C2.1	0.709405 ± 10	57.8	-6.0	-13.8
Friesland 6	Leeuw arden	1986	F6	28	WM	0.709583 ± 9	50.3	-6.2	-13.7
					C1.1	0.709535 ± 9	49.5	-5.8	-13.8
					G1.1 WL	0.709586 ± 10	54.3	-5.4	-13.8
					G1.2 WL	0.709605 ± 10	42.3		
					G1.3 WL	0.709587 ± 10	57.3		
					G1.4 WL	0.709571 ± 11	49.0	-4.9	-13.4
					G2.1 WB	0.709923 ± 18	115.2	-4.5	-13.5
					G2.2 WB	0.709935 ± 17	117.0		
					G2.3 WB	0.709984 ± 21	113.0	-6.0	-14.7
					G3.1 WD	0.709588 ± 12	49.6	-5.1	-13.9
					G3.2 WD	0.709607 ± 10	52.8		
					G3.3 WD	0.709651 ± 9	62.1		
					G3.4 WD	0.709587 ± 9	56.4	-5.5	-14.0
Friesland 7	Wijnaldum	1988	F7	28	WL	0.709199 ± 10	80.3	-6.4	-14.3
					WM	0.709206 ± 10	77.3	-6.8	-14.3
					C2.1	0.709178 ± 10	65.6	-6.6	-14.8
					G1.1 C1	0.709188 ± 10	61.1	-5.2	-14.8
					G1.2 C1	0.709181 ± 19	72.6		
					G1.4 C1	0.709185 ± 9	79.1	-5.6	-15.1
Limburg 6	Maastricht	1974	M6	48	WL	0.709351 ± 8	58.0	-6.2	-13.1
					C1.1	0.709206 ± 8	64.3	-6.0	-13.4
					G1.1 WM	0.709291 ± 10	62.5	-5.0	-13.1
					G1.2 WM	0.709296 ± 9	61.9		
					G1.3 WM	0.709285 ± 8	62.6		
					G1.4 WM	0.709268 ± 11	57.3	-5.1	-13.5

Individual	City	Birth Year	ID	FDI	location	$^{87}Sr/^{86}Sr$	ppm	$\delta^{18}O$	$\delta^{13}C$
South-Africa	Johannesburg		J	18	WL	0.713300 ± 7	67.6	-0.5	-9.1
					WM	0.713030 ± 10	58.5	-2.3	-9.2
					WD	0.713260 ± 10	52.9	-2.2	-9.3
					G1.1 WB	0.713280 ± 10	60.9	-0.8	-9.7
					G1.2 WB	0.713319 ± 9	58.2		
					G1.3 WB	0.713297 ± 10	56.4		
					G1.4 WB	0.713340 ± 10	61.8	-1.7	-10.0
Dominican Republic	Santo Domingo	1971	DR	18	WL	0.708310 ± 9	130.5	-4.3	-9.1
					WM	0.708301 ± 8		-4.2	-9.3
					C1.1	0.708299 ± 9	113.3	-4.5	-9.5
					C2.1	0.708309 ± 10	118.4	-4.5	-9.4
					G1.1 C3	0.708321 ± 9	107.0	-3.2	-9.3
					G1.2 C3	0.708299 ± 8	130.4		
					G1.3 C3	0.708307 ± 9	131.2		
					G1.4 C3	0.708309 ± 10	125.8	-3.8	-9.5
Somalia	unknown	1987	S	48	WB	0.707344 ± 11	301.3	-2.3	-12.3
					WD	0.707351 ± 7	315.0	-2.8	-12.1
					G1.1 WM	0.707397 ± 9	285.2	-1.8	-12.3
					G1.2 WM	0.707381 ± 9	323.6		
					G1.3 WM	0.707378 ± 9	304.8		
					G1.4 WM	0.707382 ± 10	301.1	-2.1	-12.0

Inter-dental variation: comparison of ultrahigh and high-density sampling methods

Additional third molars were sampled from the individuals sampled with the ultrahigh-density sampling approach (T1, T2, T6) using the high-density sampling approach, allowing the examination of intraindividual inter-dental Sr-O-C isotope variation (**Figure 6.4**). An increase in variation in $\Delta_{(max\text{-}min)}$ Sr isotope ratios (0.000117-0.000192) and Sr concentrations (13-45 ppm), and oxygen and carbon isotope values (1.8-2.1 ‰), is seen when multiple third molars from the same individual are combined (**Table 6.3**). Inter-dental variation was significant for strontium ($P < 0.02$) and oxygen ($P < 0.04$) isotopes in T1 and T6 (T1.1 and T1.3; T6.1 and T6.2 respectively), as well as carbon isotopes in T2 (T2.1 and T2.2, $P = 0.02$). No consistent differences were found with respect to isotopic system, location or dental element sampled (see *Plomp, Verdegaal-Warmerdam et al.* (*2020*) for more details).

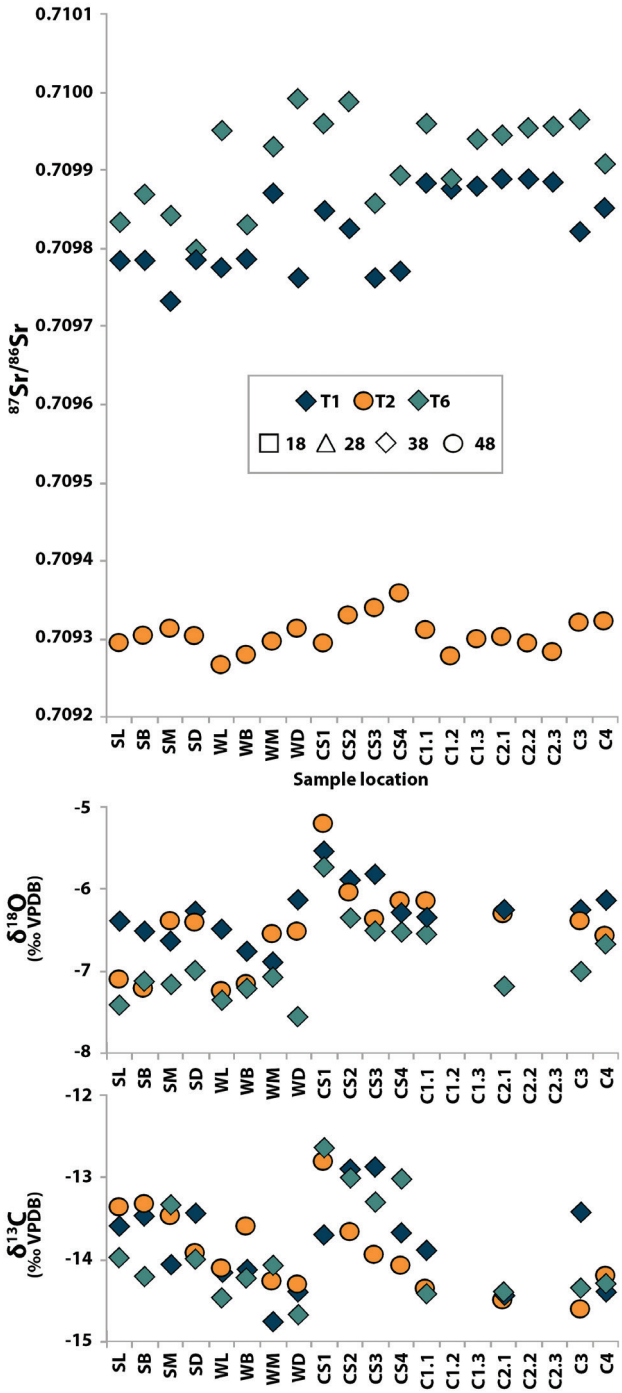
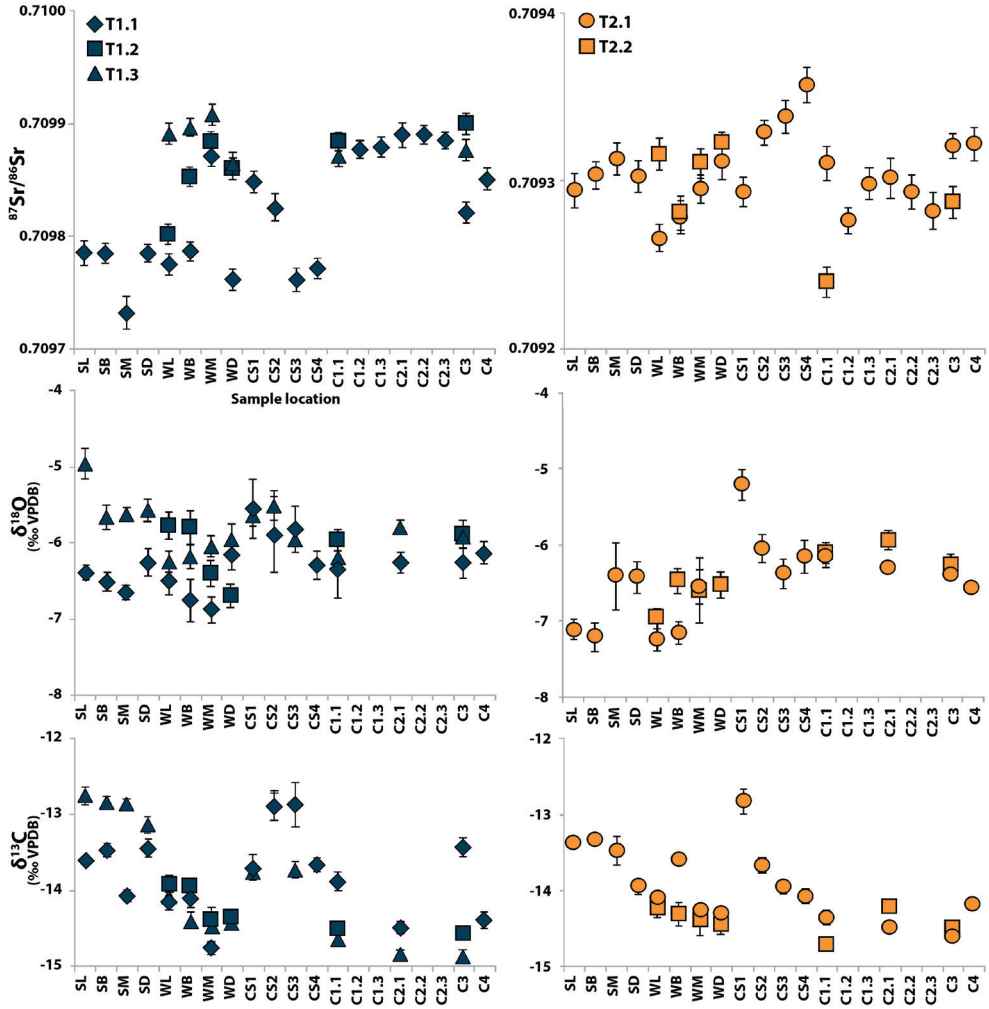


Figure 6.3 *Strontium, oxygen and carbon isotope data for individuals T1 (blue), T2 (orange) and T6 (teal). Dental element are indicated by markers using the FDI World Dental Federation notation (ISO 3950): Square = upper right M3 (18), Triangle = upper left M3 (28), Diamond = lower left M3 (38), Circle = lower right M3 (48). The x-axis indicates sampling location (see* **Figure 6.2** *and* **Table 6.1***).*

Table 6.3 *Strontium, oxygen and carbon isotope results for the individuals from the Netherlands, Johannesburg, Dominican Republic and Somalia (see* **Table 6.2** *for sample IDs). T1, T2 and T6 represent the combined results of all dental elements of these individuals analysed (e.g., T1 includes the combined results of T1.1, T1.2 and T1.3 etc.) The subset of 6 locations for T1.1, T2.1 and T6.1 are WL, WB, WM, WD, C1.1 and C3 (see* **Table 6.1** *for abbreviations), to match the locations with the other sampled teeth. Dental elements F6, F7, M6, J, DR, S, were affected by caries. Individuals J, DR, and S are non-Dutch.*

	$^{87}Sr/^{86}Sr$						Sr ppm			
	Min	Max	$\Delta_{(max-min)}$	Median	2 SD	n	Min	Max	$\Delta_{(max-min)}$	Median
T1 (T1.1, T1.2, T1.3)	0.709732	0.709908	0.000176	0.709862	± 102	32	33.9	78.8	44.9	52.6
T1.1	0.709732	0.709890	0.000157	0.709823	± 105	20	42.3	78.8	36.6	52.3
T1.1	0.709762	0.709884	0.000122	0.709804	± 102	6	54.0	78.8	24.8	56.0
T1.2	0.709802	0.709900	0.000098	0.709872	± 70	6	48.5	55.9	7.4	51.3
T1.3	0.709864	0.709908	0.000044	0.709884	± 33	6	33.9	60.3	26.3	55.7
T2 (T2.1, T2.2)	0.709240	0.709357	0.000117	0.709302	± 48	26	31.1	43.8	12.7	38.1
T2.1	0.709266	0.709357	0.000091	0.709302	± 44	20	31.1	43.8	12.7	37.7
T2.1	0.709266	0.709321	0.000055	0.709303	± 43	6	36.5	39.1	2.6	38.2
T2.2	0.709240	0.709323	0.000083	0.709299	± 61	6	38.7	42.7	4.0	39.6
T6 (T6.1, T6.2)	0.709799	0.709991	0.000192	0.709891	± 130	26	55.8	88.4	32.6	68.7
T6.1	0.709799	0.709991	0.000192	0.709935	± 115	20	55.8	77.5	21.7	65.7
T6.1	0.709830	0.709991	0.000161	0.709956	± 113	6	61.4	74.8	13.4	66.5
T6.2	0.709799	0.709835	0.000036	0.709820	± 27	6	78.2	88.4	10.2	82.1
D3	0.709539	0.709600	0.000061	0.709567	± 45	6	87.3	103.3	16.0	93.7
D13	0.709202	0.709223	0.000021	0.709209	± 16	6	94.6	100.6	6.0	96.2
D15	0.709383	0.709412	0.000029	0.709394	± 21	6	56.8	100.6	43.8	62.5
Dutch Caries										
F6	0.709535	0.709984	0.000449	0.709588	± 319	13	42.3	117.0	74.7	54.3
F7	0.709178	0.709206	0.000029	0.709187	± 22	6	61.1	80.3	19.2	74.9
M6	0.709206	0.709351	0.000145	0.709288	± 94	6	57.3	64.3	7.0	62.2
Non-Dutch Caries										
J	0.713030	0.713340	0.000309	0.713297	± 210	7	52.9	67.6	14.8	58.5
DR	0.708299	0.708321	0.000022	0.708308	± 15	8	107.0	131.2	24.3	125.8
S	0.707344	0.707397	0.000053	0.707380	± 41	6	285.2	323.6	38.4	303.1

Sr ppm		$\delta^{18}O$ (‰ VPDB)				$\delta^{13}C$ (‰ VPDB)						
2 SD	n	Min	Max	$\Delta_{(max-min)}$	Median	2 SD	Min	Max	$\Delta_{(max-min)}$	Median	2 SD	n
14.3	32	-6.9	-5.0	1.9	-6.1	0.8	-14.9	-12.8	2.1	-14.0	1.3	36
14.8	20	-6.9	-5.5	1.3	-6.3	0.7	-14.8	-12.9	1.9	-13.8	1.1	16
18.9	6	-6.9	-6.1	0.7	-6.4	0.6	-14.8	-13.4	1.3	-14.1	0.9	6
5.6	6	-6.7	-5.8	0.9	-5.9	0.8	-14.6	-13.9	0.6	-14.4	0.6	6
20.0	6	-6.2	-5.8	0.4	-6.0	0.3	-14.9	-14.1	0.8	-14.5	0.5	7
4.7	26	-7.2	-5.2	2.0	-6.4	0.9	-14.7	-12.8	1.9	-14.2	1.0	23
4.5	6	-7.2	-5.2	2.0	-6.4	1.0	-14.6	-12.8	1.8	-14.0	1.0	16
1.8	6	-7.2	-6.2	1.1	-6.5	0.9	-14.6	-13.6	1.0	-14.3	0.7	6
3.3	6	-7.0	-5.9	1.0	-6.5	0.7	-14.7	-14.2	0.5	-14.4	0.3	7
18.5	26	-7.6	-5.7	1.8	-6.8	1.0	-14.7	-12.7	2.0	-14.1	1.1	23
12.8	20	-7.6	-5.7	1.8	-7.0	1.2	-14.7	-12.6	2.0	-14.1	1.2	16
11.8	6	-7.6	-6.5	1.0	-7.1	0.7	-14.7	-14.1	0.6	-14.4	0.4	6
8.7	6	-6.9	-6.0	0.9	-6.5	0.7	-14.4	-13.7	0.6	-14.0	0.4	7
10.7	6	-6.9	-5.5	1.4	-6.2	0.9	-12.9	-12.6	0.3	-12.8	0.3	6
4.6	5	-6.3	-5.9	0.4	-6.1	0.3	-14.0	-13.6	0.4	-13.9	0.3	6
33.1	6	-6.6	-5.9	0.7	-6.1	0.6	-14.0	-13.5	0.5	-13.7	0.3	6
55.8	13	-6.2	-4.5	1.7	-5.5	1.1	-14.7	-13.4	1.3	-13.8	0.8	8
15.6	6	-6.8	-5.2	1.6	-6.4	1.3	-15.1	-14.3	0.8	-14.8	0.7	5
5.6	6	-6.2	-5.0	1.2	-5.6	1.3	-13.5	-13.1	0.4	-13.2	0.4	4
9.3	7	-2.3	-0.5	1.8	-1.7	1.6	-10.0	-9.1	0.9	-9.3	0.8	5
19.3	7	-4.5	-3.2	1.3	-4.2	1.0	-9.5	-9.1	0.5	-9.3	0.3	6
26.3	6	-2.8	-1.8	1.0	-2.2	0.8	-12.3	-12.0	0.3	-12.2	0.3	4



6.3.2 Population variation indicated by high-density sampling

To compare the variation seen in Sr-O-C isotopes between individuals (inter-individual variation) the high-density sampling approach was applied to six individuals from the Netherlands (T1, T2, T6, D3, D13, D15; 10 teeth in total) (**Figure 6.5**, **Table 6.3**).

6.3.2.1 High-density sampling across the Netherlands

The difference in $^{87}Sr/^{86}Sr$ ($\Delta_{max\text{-}min}$) within the six Dutch individuals using the high-density-sampling approach on inner enamel ranged from 0.000021 to 0.000161 (2 SD ± 16-115, avg_

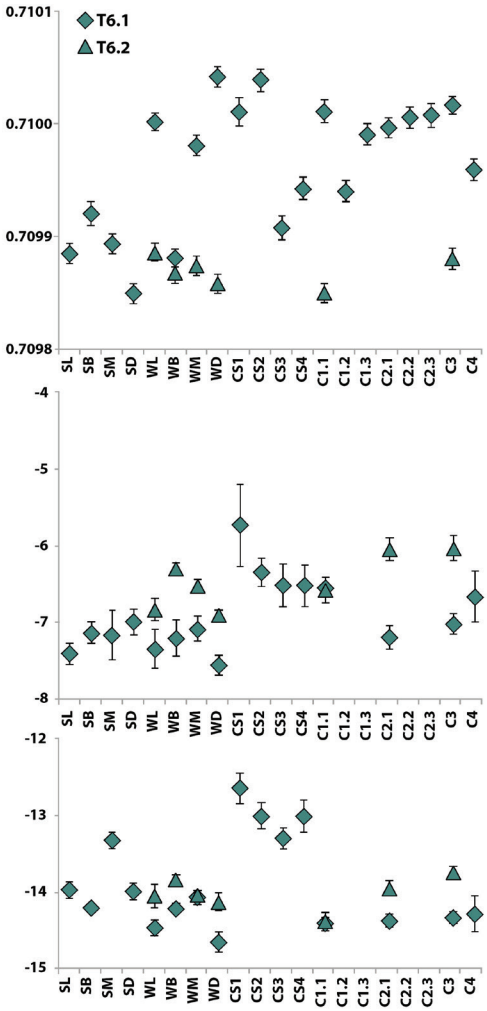


Figure 6.4 *Inter-dental Sr-O-C isotope variation of T1, T2 and T6. The x-axis represents the sample locations as described in* **Figure 6.2.**

isovar ± 62, **Table 6.3**). Differences in Sr concentrations (ΔSr ppm$_{max\text{-}min}$) ranged between 3 and 44 ppm (avg_isovar ± 15 ppm, **Table 6.3**). Variation seen in $\Delta\delta^{18}O_{max\text{-}min}$ ranged from 0.3 ‰ to 1.4 ‰, and $\Delta\delta^{13}C_{max\text{-}min}$ from 0.3 ‰ to 1.3 ‰ (avg_isovar for $\delta^{18}O$ and $\delta^{13}C$ ± 0.7 ‰, **Tables 6.2** and **6.3**). The average Dutch isotopic variation (avg_isovar) is three times larger than the analytical error for $^{87}Sr/^{86}Sr$, four times for $\delta^{18}O$ and eighteen times for $\delta^{13}C$. The maximal differences in the inner enamel of a single dental element found in this study are $^{87}Sr/^{86}Sr$ = 0.000161, 44 ppm Sr, $\delta^{18}O$ and $\delta^{13}C$ ~1.4 ‰, with eight times larger values seen compared to the analytical error for $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ and thirty-three times larger for $\delta^{13}C$.

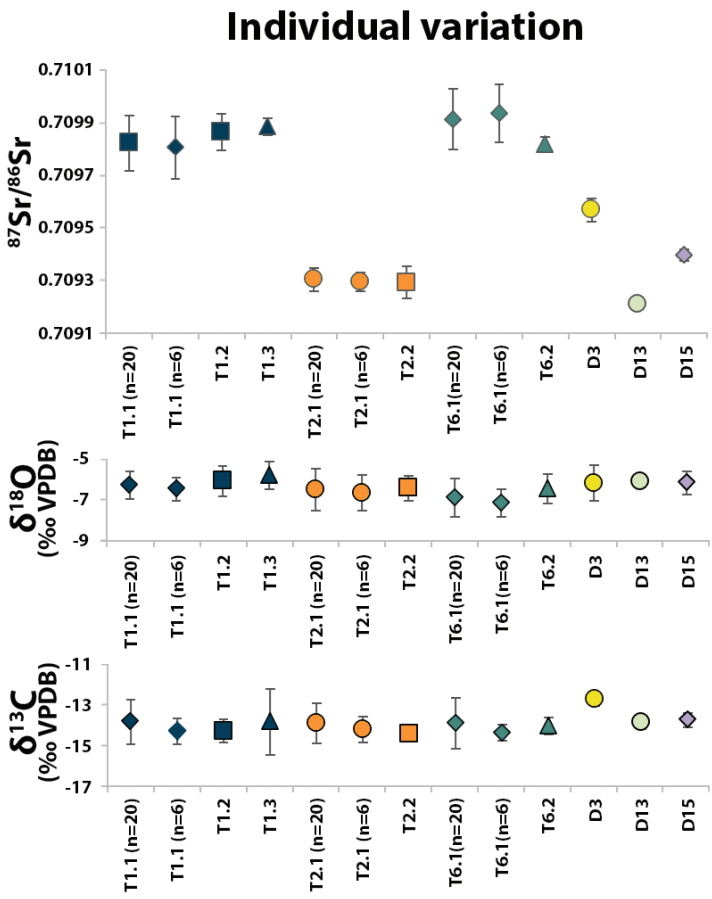


Figure 6.5 *Isotopic variation plotted for each dental element per Dutch individual sampled using the (ultra)high-density approach. The high-density subset (n = 6) of T1.1, T2.1 and T6.1 consists of the same sampling locations as the other individuals sampled using the high-density sampling approach (WL, WB, WM, WD and C1.1, C2.1).*

6

6.3.2.2 Effect of the globalised supermarket diet

The $^{87}Sr/^{86}Sr$ variation seen in inner enamel from the late 20th century Dutch individuals ranged from 0.709240-0.709991 (Δ = 0.000751, with $\Delta^{87}Sr/^{86}Sr_{max\text{-}min}$ = 0.000036-0.000122, 2 SD ± 43-113), with Sr concentrations ranging between 37-88 ppm. Variation is also seen in the Sr isotope data from the mid-20th century individuals (Δ = 0.000398, with $\Delta^{87}Sr/^{86}Sr_{max\text{-}min}$ = 0.000021-0.000061, 2 SD ± 21-45 - Sr concentrations ranging between 57-103 ppm). In late 20th century enamel $\delta^{18}O$ ranged from -7.6 to -5.8 (Δ = 1.8 ‰, 2 SD ± 0.6-0.9) and $\delta^{13}C$ ranged between -14.8 to -13.4 (Δ = 1.4 ‰, 2 SD ± 0.4-0.9) (**Tables 6.2** and **6.3**). In earlier material, $\delta^{18}O$ ranged from -6.9 to -5.5 (Δ = 1.4 ‰, 2 SD ± 0.3-0.9) and $\delta^{13}C$ ranged between -14.0 to -12.6 (Δ = 1.4 ‰, 2 SD ± 0.3-0.5) (**Table 6.3**).

6.3.3 Single locus Cusp versus Bulk sampling

The $^{87}Sr/^{86}Sr$ ratios of the cusp and bulk samples of the same individual were within analytical error ($\Delta^{87}Sr/^{86}Sr_{Bulk\text{-}Cusp}$ 2 SD ± 19) in only 60 % of the cases (18 out of 30 individuals; **Table 6.4**, **Figure 6.6**). When the average Dutch intraindividual variation is taken (avg_isovar ± 62), C1.1 is representative for the Bulk isotopic results in 93.3 % of the individuals (n = 28) (**Figure 6.6**). The variation in $^{87}Sr/^{86}Sr$ seen in non-Dutch dental elements (n = 6) was similar, ranging from $\Delta_{Cusp\text{-}Bulk}$ = 0.000020–0.000080.

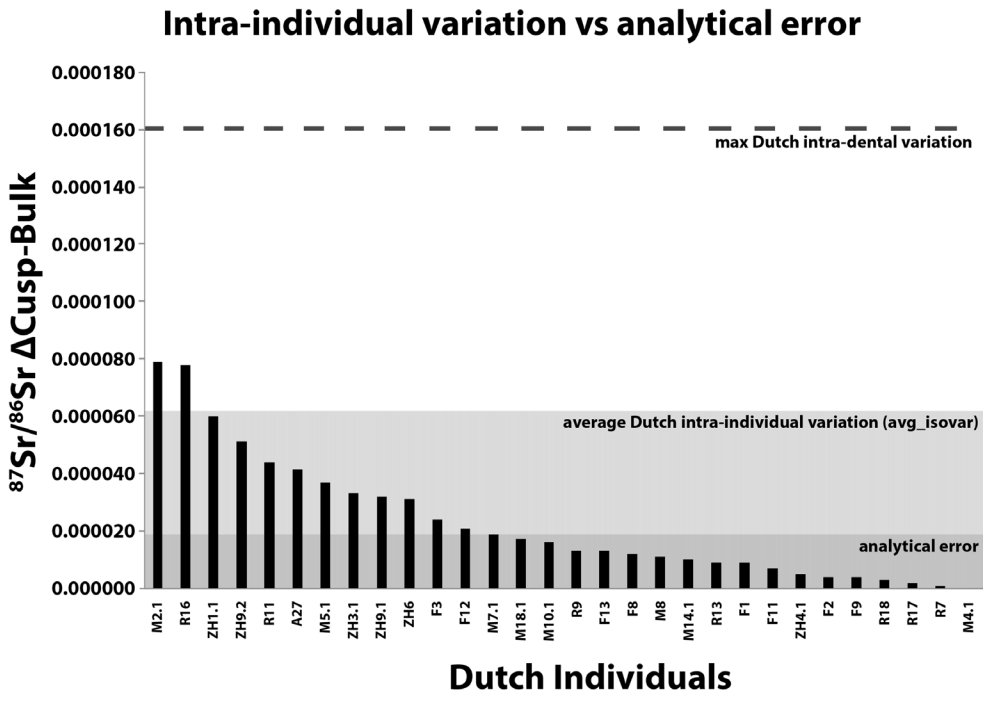


Figure 6.6 *The difference in Sr isotope ratio recorded between bulk and cusp samples from an individual. Note that the analytical error does not accurately capture the intraindividual variation seen in Sr isotope composition of Dutch individuals. See* **Table 6.4** *for all Δ Cusp-Bulk values.*

6.3.4 The effect of caries on isotopic composition

To evaluate the effect of caries on the isotopic composition of dental enamel, both unaffected and affected locations were sampled from the same dental element (**Table 6.3**, individuals F6, F7, M6, J, DR and S; **Figure 6.7**). The Sr isotope ratios of carious enamel is generally within error of unaffected enamel (**Figure 6.7**), with $\Delta^{87}Sr/^{86}Sr_{max\text{-}min}$ ranging from 0.000022-0.000449 (avg_

isovar ± 162) and ΔSr ppm $_{max\text{-}min}$ ranging from 7.0 to 74.7 ppm (avg_isovar ± 28). Variation seen in $\delta^{18}O$ $\Delta_{max\text{-}min}$ ranged from 1.0 ‰ to 1.8 ‰, and $\Delta\delta^{13}C_{max\text{-}min}$ from 0.3 ‰ to 1.3 ‰ (avg_isovar for $\delta^{18}O$ = 1.2 ‰ and $\delta^{13}C$ ± 0.6 ‰, **Table 6.3**). Elevated $\delta^{18}O$ values were found in caries for all 6 individuals, with significant differences (p = 0.01) in F7, M6 and DR. Unaffected and carious enamel showed similar $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ values (**Table 6.3**, **Figure 6.7**), with the exception (n = 1 out of 8) of the buccal caries in F6 (G2) which showed elevated Sr values ($\Delta^{87}Sr/^{86}Sr$ = 0.0004) as well as higher Sr concentrations (ΔSr ppm = 64). Despite these isotopic variations in Sr and O, all the data from the Dutch individuals was compatible with the Dutch Sr-O isotope range (**Figure 6.7**).

6.4 Discussion

The maximum intraindividual variation in inner dental enamel seen in this study ($^{87}Sr/^{86}Sr$ = 0.000161, 44 ppm Sr, $\delta^{18}O$ and $\delta^{13}C$ ~1.4 ‰) highlights the importance of quantifying intraindividual isotopic variation before interpretations on mobility and diet are made.

6.4.1 Intra- and inter-individual variation

Previous studies proposed possible diagenetic Sr contributions to surface enamel (*Dufour et al. 2007; Horn & Müller-Sohnius 1999*). Differences in Sr ratios in surface and inner enamel were present in all three individuals (T1, T2, T6) examined using the ultrahigh-density sampling approach (**Section 6.3.1**). Nevertheless, inner enamel of both wall and cusp regions in the high-density samples (excluding surface enamel) were representative of the results of the ultrahigh-density (including surface samples) Sr-O-C isotope results of the same third molar (**Table 6.3**). Omitting the surface measurements decreased the total Sr isotope variation by 20 % ($^{87}Sr/^{86}Sr_{all}$ 2 SD ± 40-120 to $^{87}Sr/^{86}Sr_{inner}$ 2 SD ± 40-100). The median $^{87}Sr/^{86}Sr$ results for individuals are, however, essentially unchanged when surface measurements are excluded (with the exception of T1.1 where $\Delta^{87}Sr/^{86}Sr_{median(all\text{-}inner)}$ = 0.000050, three times the analytical error). Future research involving more individuals sampled (n > 20) with a similar number of sample loci (n > 6) is required to provide conclusive evidence of Sr contamination of enamel surface. Such results would be particularly relevant for unburied dental elements in forensic cases.

Differences between surface and inner enamel were also present in $\delta^{13}C$ for all three individuals (T1, T2, T6) analysed using the ultrahigh sampling approach, and for one individual (T1) in

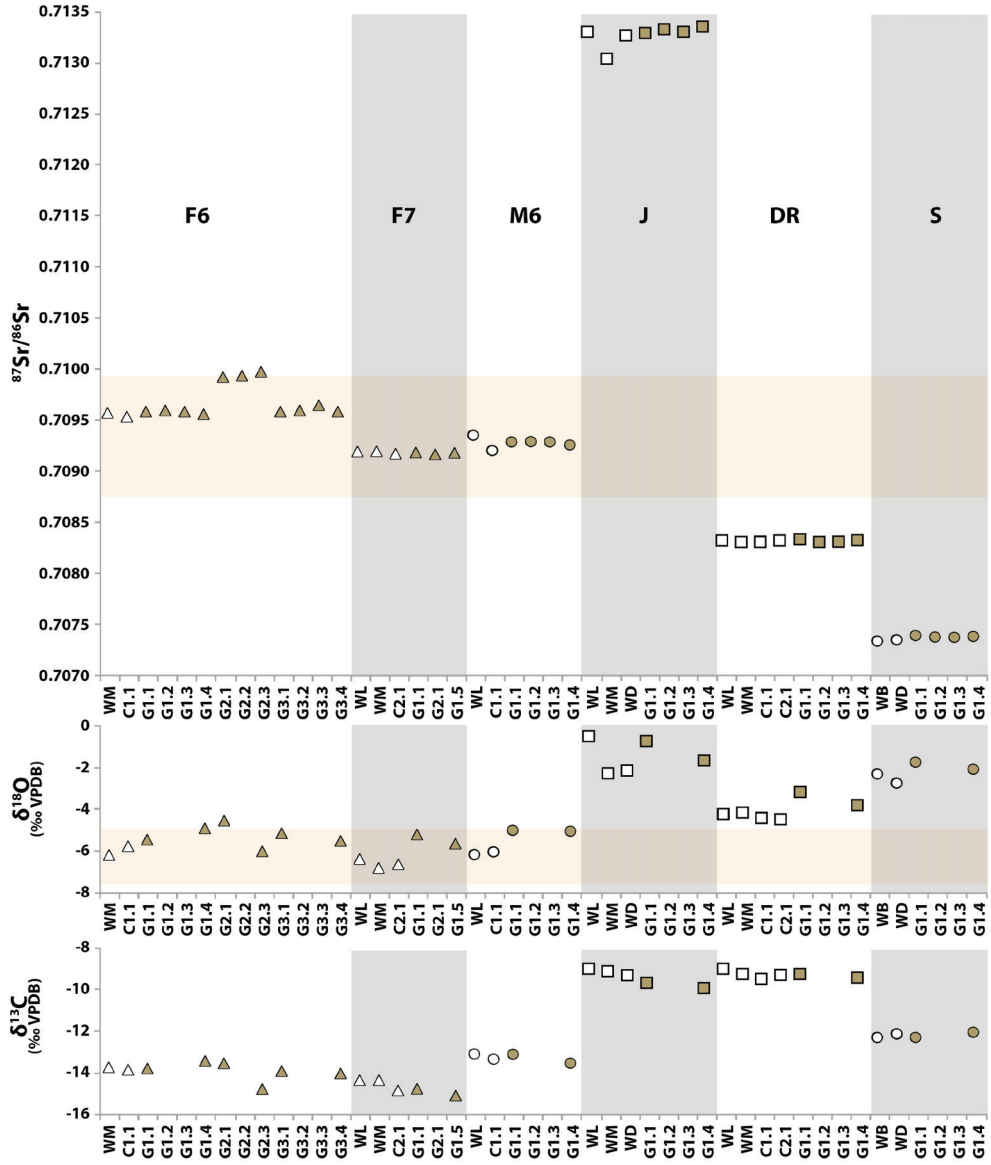


Figure 6.7 *Sr-O-C isotope variation seen in dental elements affected by caries. Unaffected enamel in white, carious enamel in brown. The light orange area represents the Dutch range based on human enamel from Dutch residents reported in this study ($^{87}Sr/^{86}Sr$ = 0.7088–0.7099, $\delta^{18}O$ = -7.6 ‰ to -5.0 ‰).*

$\delta^{18}O$. When omitting the surface measurements, the oxygen and carbon variation decreased by 15-25 % for $\delta^{18}O$ and 25-60 % for $\delta^{13}C$ ($\delta^{18}O$ 2 SD_{total} = 0.7-1.2 compared to $\delta^{18}O$ 2 SD_{inner}

= 0.6-0.9 and $\delta^{13}C$ 2 SD_{total} = 1.0-1.2 compared to $\delta^{13}C$ 2 SD_{inner} = 0.4-0.9), with lower median differences (0.6-1.0 ‰ for $\delta^{18}O$ and 0.3 ‰ for $\delta^{13}C$) in the inner enamel. Omitting the surface measurements has a greater effect on the median O and C isotope results in comparison to Sr (up to six times the analytical error for oxygen and eight times for carbon). Significantly elevated $\delta^{13}C$ values are found in surface enamel ($P < 0.02$) (**Figure 6.3**). Greater variability in C isotope values might be explained by differential isotopic incorporation in surface enamel or possible surface exchange. A change in diet at the time of the formation of the surface enamel, which is secreted later than the inner enamel (*Piesco & Avery 2002*), may also explain the difference seen in surface and inner enamel seen in carbon isotopes. As the surface cusp samples (CS1, CS2, CS3, CS4) are taken from the same incremental enamel layer, this could indicate that incremental isotopic signatures are retained instead of being averaged during the mineralisation phase. Nevertheless, there is large variation seen in the cusp surface samples (**Figure 6.2**). Furthermore, a potential temporal influence is difficult to assess for the current study as the formation of the dental elements were not recorded in such detail, most of the samples do not represent restricted time periods in enamel formation, and specific dietary information during the enamel formation is unavailable. These data do, however, suggest that surface enamel sampling should be avoided for carbon isotope analysis until incorporation of $\delta^{13}C$ values in surface enamel is better understood.

The ultrahigh-density sampling approach showed limited intradental variation within inner enamel, with no differences recorded between the inner Cusp and Wall regions (with the exception of elevated $^{87}Sr/^{86}Sr$ in the cusp samples of T1.1). This indicates that the currently preferred sampling regions (buccal/lingual tooth wall) can be extended to include cusp regions (where attrition allows occlusal sampling), as these regions of inner enamel are expected to give comparable results.

Comparison of Cusp and Bulk Sr isotope analyses indicate that a single inner enamel cusp measurement (C1.1) of Dutch third molars is representative of the bulk enamel value in only 60 % of the dental elements analysed (**Figure 6.6**). The two samples with the largest differences in $^{87}Sr/^{86}Sr$ in Cusp and Bulk samples (0.000078/9) belong to individuals M2.1 and R16, raised in a single location (Maastricht and Dordrecht, respectively), with individual R16 indicating that they did not consume fish. These data demonstrate that even where individuals are sedentary, the dental Sr isotope ratios are heterogeneous. Although the current study did not contrast single versus bulk samples for oxygen and carbon isotopes, results for oxygen and carbon isotopes in caprid (*Ammotragus Lervia*, *Reade et al.* (*2015*) similarly suggest that single location

samples may not represent the average isotopic value of the dental element, and that bulk sampling condenses the full isotopic variation within a dental element.

Future studies are encouraged select their sampling strategies based on the type of isotopic variation they would like to evaluate. In cases where intraindividual variation should be assessed, or when the life history of an individual is examined, the multiloci or high-density approach is more effective than single loci sampling. If inter-individual variation is determined and only an estimation of the isotopic signature is required, single loci sampling may be sufficient. As bulk sampling averages the total isotopic variation and requires large sample sizes, this method may not be applicable. Compared to bulk analyses, single-loci sampling approaches provide similar information, are more efficient and less destructive. In situ sampling analysis using laser ablation inductively coupled mass spectrometry (LA-ICP-MS) analysis may be better suited to assess the intraindividual variation in Sr concentration and composition in a dental element (*Smith et al. 2018; Willmes et al. 2016*).

The Sr-O-C isotope results from Dutch individuals in this study contribute to the already established Dutch isotopic ranges based on modern enamel for strontium and oxygen, and provide an indication of the Dutch carbon isotope range. The $^{87}Sr/^{86}Sr$ results of this study (0.708838 to 0.709991) confirm ranges reported in previous studies (0.7078 –0.7099; *Font et al. 2015; Plomp et al. 2019*). The $\delta^{18}O$ values in the current study range from -7.6 ‰ to -5.0 ‰ (Δ = 2.6 ‰), confirm results of a previous study reporting a wider range (-7.6 ‰ to -4.5 ‰, Δ = 3.1 ‰; *Font et al. 2015*), as well as previous estimations for archaeological populations of 2-3 ‰ (*Lightfoot & O'Connell 2016; Wright 2013*). Modern Dutch enamel $\delta^{13}C$ values in the current study range from -14.9 ‰ to -12.6 ‰ (Δ = 2.3 ‰).

The (ultra)high-density sampling approach showed considerable intraindividual isotopic variation within modern Dutch individuals. Significant inter-dental variation was seen in strontium and oxygen isotopes in two out of three individuals (T1 and T6), indicating that a single third molar is not always representative of the isotopic results of other third molars, and possibly other dental elements. Using the high-density sampling approach, the maximum differences in isotopic results from inner enamel of a single dental element reached 0.000161 for strontium, 1.4 ‰ for oxygen, and up to 1.3 ‰ for carbon. Increased variation is seen using the ultrahigh-density sampling approach (including results from additional molars from the same individual), with maximum intraindividual variation ($^{87}Sr/^{86}Sr$ = 0.000192, ~2 ‰ for oxygen and carbon, **Table 6.3**) approaching levels of variability in the Dutch population for

oxygen ($\delta^{18}O$ = 3.1 ‰; *Font et al. 2015*) and carbon ($\delta^{13}C$ = 2.3 ‰). Intraindividual Sr variation did not reach inter-individual/population variation, which was ten times higher (Δ = ~0.002). The analytical precision ($^{87}Sr/^{86}Sr$ ± 0.000019, $\delta^{18}O$ ± 0.17 ‰ and $\delta^{13}C$ ± 0.04 ‰) is therefore significantly less than the intraindividual and population variability recorded here. The estimated variation based on the average Dutch isotopic intraindividual variation (avg_isovar) of the inner enamel of single dental elements in this study ($^{87}Sr/^{86}Sr$ ± 0.000062, Sr ppm ± 15, $\delta^{18}O$ and $\delta^{13}C$ ± 0.7 ‰) provide estimations for the expected variation in modern Dutch third molars. The maximum intraindividual differences seen in this study for inner enamel ($^{87}Sr/^{86}Sr$ = 0.000161, Sr ppm = 44, $\delta^{18}O$ = 1.4 ‰ $\delta^{13}C$ = 1.3 ‰) can be used as an indication for the maximal expected variation within inner enamel of a dental element, and may increase in future studies when more individuals are analysed using a high-density sampling approach. Third molars are the most variable dental element in the human dentition in terms of enamel formation and eruption (*AlQahtani et al. 2010; Reid & Dean 2006*), and can therefore be expected to record the largest isotopic variation in the dentition of habitual diet and residence. Consequently, studies using other dental elements may be expected to exhibit less isotopic variation as time frames of dental development are shorter and more constrained. In order to establish how representative this study is of the isotopic variability recorded in human dentition, it would be of particular interest to study first/second molars and pre-molars, as these are most often sampled in archaeological/forensic provenance studies. A comparative study of archaeological inner enamel of dental elements would also be of interest, keeping in mind the effects that diagenesis may have on the isotopic composition of archaeological dental elements.

6.4.2 Temporal and spatial effects on Sr-O-C isotope variation

Previous studies (*Chesson et al. 2012; Valenzuela et al. 2012; Vatour et al. 2015*) have highlighted the potential influence of the modern global supermarket diet on the isotopic results of modern human tissues. Assessing the impact of globalisation on the individuals in this study is complicated as the individuals originate from various areas in the Netherlands, which will likely result in some degree of isotopic variation due to different sources of potable water and variation in local food availability. In addition, variation is expected due to different ages of the individuals. Most importantly, only three individuals representative of the pre-supermarket era were sampled. More samples from individuals born before the 1970s are therefore required to allow for a comprehensive comparison for pre- and post-globalisation intraindividual variation. In this study, the individuals born in the 1980s and 1990s (T1, T2, T6) recorded more variation in their Sr-O-C isotope ratios and lower Sr concentrations (37-88 ppm) than the individuals born

in the 1940s and 1960s (D3, D13, D15; 57-103 ppm). Interestingly, one of the individuals in the younger group (T2) was a self-reported vegetarian from the age of 10 onwards and had lower Sr concentrations than the other individuals in the same age group (T2, T6) while Sr content are reported to be higher in plants (*Pate 1994*). It should be noted that not all individuals raised on supermarket diets show increased variation in $^{87}Sr/^{86}Sr$: a total of 26 individuals born after 1972 showed little variation between $^{87}Sr/^{86}Sr$ ratios of their Cusp and Bulk enamel ($^{87}Sr/^{86}Sr\Delta_{Cusp\text{-}Bulk}$ 0.000000 – 0.000045, **Table 6.4**, **Figure 6.6**).

6.4.3 Increased Sr-O-C isotope variation and elevated oxygen values in carious enamel

This study indicates that caries do not seem to have a major isotopic effect on the macroscopically unaffected enamel of the same dental element, indicating that if a dental element is affected by caries it is still possible to sample the unaffected areas. Future studies should compare the results of carious dental elements to the isotopic values of an unaffected dental element from the same individual to provide more conclusive evidence, while taking into account the intraindividual variation described here.

Dental elements with caries showed twice the variation in their $^{87}Sr/^{86}Sr$ ratios ($\Delta_{max\text{-}min}$ = 0.000022-0.000449, Δ = 0.000427; avg_isovar ± 0.000162) and Sr concentrations 7 to 75 ppm (Δ = 68, avg_isovar ± 28 ppm) compared to healthy dental elements ($\Delta^{87}Sr/^{86}Sr_{max\text{-}min}$ = 0.000021 to 0.000193, Δ = 0.000172; avg_isovar ± 0.000062; $\Delta Sr\ ppm_{max\text{-}min}$ = 3-44 ppm, Δ = 41, avg_isovar ± 15 ppm). This increased variation is caused by elevated $^{87}Sr/^{86}Sr$ values in caries (n = 2 of 6) and increased variation in Sr concentrations and Sr isotope composition in caries (n = 4 out of 6). Variation seen in $\Delta\delta^{18}O_{max\text{-}min}$ was higher on average in dental elements affected by caries than enamel from healthy individuals (1.0-1.8 ‰ compared to 0.4-2.0 ‰). The variation in carbon isotopes in dental elements affected by caries was less than in healthy individuals ($\Delta\delta^{13}C_{max\text{-}min}$ = 0.3 ‰ to 1.3 ‰ compared to 2.1 ‰). The avg_isovar is similar for carbon in carious and healthy enamel, but almost twice as high in oxygen (1.2 ‰), due to significant elevated $\delta^{18}O$ values in caries (n = 3 out of 6, see *Plomp, Verdegaal-Warmerdam et al.* (*2020*) for details). While the increased variation in Sr isotopes and the decreased variation in C isotopes could also be explained by the small sample size, the significant differences between carious and healthy enamel in oxygen isotopes indicate that caries should not be sampled for oxygen isotopes.

Strontium concentration in caries is indistinguishable from unaffected enamel in the same dental element (see also *Little & Steadman* (*1966*)), with the exception of one caries (F6-G2, **Figure 6.7**). The increased Sr concentrations (+ 64 ppm) and elevated $^{87}Sr/^{86}Sr$ values ($\Delta^{87}Sr/^{86}Sr$ = ~0.0004) in the buccal caries of F6 remain unexplained, as the other F6 caries sampled are within error of the Sr isotope compositions and concentrations of the unaffected sample locations. The results of the buccal caries of F6 cannot be explained by background information provided by the questionnaire as the individual did not report moving and it appears likely that the three caries were active at the same time.

The non-Dutch data strongly suggest that the de- and re-mineralisation processes involved in the development of caries (*Piesco & Simmelink 2002; Wazen & Nanci 2012*) are not likely to incorporate Sr from the diet consumed when the caries were active. The individuals that grew up in the Dominican Republic and Somalia developed their caries in the Netherlands, yet the isotopic results (Sr, O) of both unaffected and carious enamel are representative of the Dominican Republic and Somalia, and thus distinct from the Dutch isotopic signal.

While in most cases caries do not significantly affect the Sr-C isotope composition, the data presented here indicates that sampling caries is not recommended for modern dental elements. Oxygen isotopes values are altered and the elemental incorporation process in caries remains poorly understood, as well as the time frame involved in the development of the caries.

6.5 Conclusion

Assessing the intradental, interdental and population isotopic variability is a vital step in providing a framework for provenance and dietary interpretations. This work establishes that a single sample location is not representative for the total intradental enamel isotopic variation and that bulk analyses average the total variation present in the modern third molars.

This study indicates that drilled samples should be taken from the inner enamel, with no preference for a particular cusp/wall region as these locations offer comparable isotopic results. Sampling approaches should avoid carious enamel as this study indicated that caries produce inconsistent results. The unaffected enamel of carious dental elements seems to be isotopically unaltered and can be used for isotopic analyses.

Further studies are required to quantitatively evaluate the intraindividual variability in modern and archaeological enamel in dental elements other than third molars, as well as the effect of caries on the isotopic composition of enamel. The intraindividual isotopic variation is expected to be controlled by a combination of the geological area in which food is grown and personal diet preferences of individuals. The resulting isotopic variation needs to be quantified for other modern or archaeological populations living in regions with larger topographical and geological variation by analysing the enamel of multiple individuals (>20) to provide a baseline to which intraindividual isotopic variation can be compared.

For Dutch modern enamel the average isotopic variation (avg_isovar: $^{87}Sr/^{86}Sr \pm 0.000062$, Sr ppm ± 15 ppm, $\delta^{18}O$ and $\delta^{13}C \pm 0.7$ ‰) provides a more accurate estimation of the intraindividual variation than reporting the results and analytical error of a single-locus sample. The maximal differences seen in this study should also be taken into account ($^{87}Sr/^{86}Sr$ ~0.000200, 44 Sr ppm, $\delta^{18}O$ and $\delta^{13}C$ ~1.4 ‰). Therefore, interpretations of diet and mobility should be made cautiously until isotopic variation is adequately quantified in the relevant region. For modern Dutch individuals Sr isotope variation > 0.0002 is required to argue for mobility and differences under 2 ‰ are negligible for $\delta^{18}O$ and $\delta^{13}C$.

Data Availability Statement

The data that support the findings of this study are available in **Tables 6.2-6.4** *as well as openly available at the 4TU.Centre for Research Data (Plomp, Verdegaal-Warmerdam et al. 2020): http://doi.org/10.4121/uuid:f6dc4f20-a6e0-4b2f-b2f8-b79a4f9061c3).*

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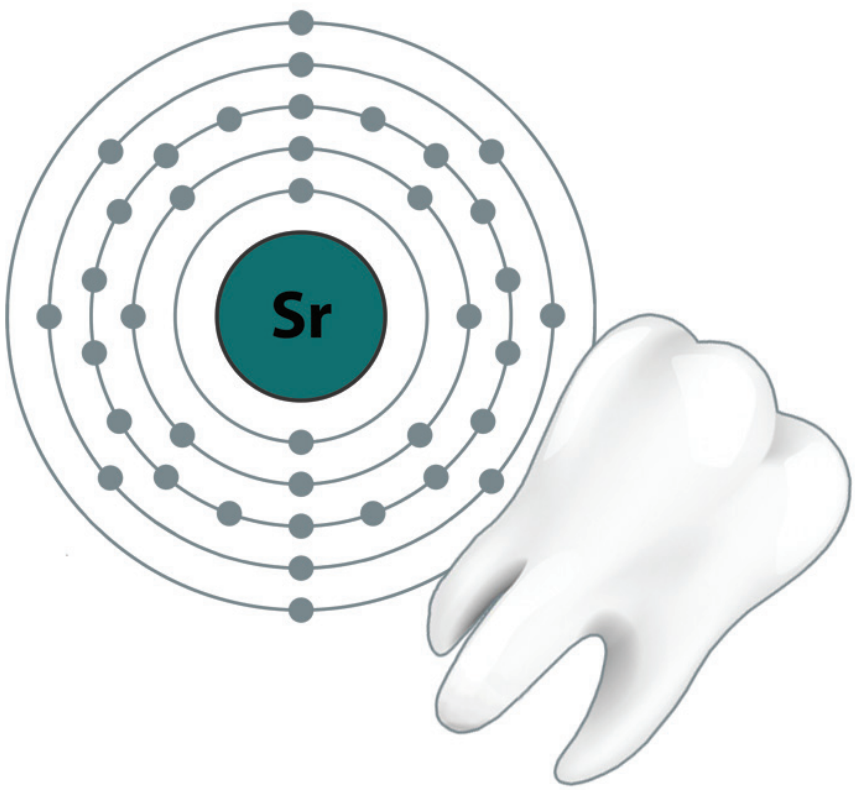
Sr

Chapter 7

Strontium isotopes in modern human dental enamel and tap water from the Netherlands: implications for forensic provenancing

This is a pre-submission draft of the paper 'Spatial patterns in $^{87}Sr/^{86}Sr$ ratios in modern human dental enamel and tap water from the Netherlands: implications for forensic provenancing' by Lisette M. Kootker, Esther Plomp, Saskia T.M. Ammer, Vera Hoogland and Gareth R. Davies

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Abstract

The analysis of strontium (Sr) isotope ratios in human dental enamel has become increasingly important in the fields of archaeological and forensic science for determining provenance. The prerequisite for the success of this approach relies on a correlation between dietary Sr intake and the underlying local geology. Due to the increasing globalisation of food supply, the establishment of nation-wide or international supermarket chains, and increasing urbanisation, Sr isotope signatures are expected to reflect, at least partially, the more uniform supermarket-diet. These globalised Sr isotope signatures could potentially compromise anthropological forensic investigations. This requires greater insights into the processes that cause spatial variation of Sr isotope ratios in modern environments. This study presents an extensive overview of the range of $^{87}Sr/^{86}Sr$ ratios in the modern Dutch environment based on 296 modern human dental enamel and tap water samples. Tap water $^{87}Sr/^{86}Sr$ ratios from the Netherlands range between 0.70837 to 0.71278 (ΔSr 0.0044, n = 143) and are predominantly determined by the underlying bedrock geology at the sampling point. In contrast, the human enamel data record no correlation with water supply or local geology. Hence, the main principle behind the application of $^{87}Sr/^{86}Sr$ as a proxy for mobility appears invalid in the modern globalised Dutch context. Based on the data presented here, a Dutch $^{87}Sr/^{86}Sr$ range is established for modern humans, ranging between 0.7085 and 0.7100 (ΔSr 0.0015, n = 153), with 98.0% of individuals between 0.7088 and 0.7099.

7.1 Introduction

Dental enamel has become increasingly important in the fields of archaeological and forensic science for determining the dietary intake and geological provenance of humans (*Bartelink et al. 2016; Bentley 2006; Meier-Augenstein & Fraser 2008*). The most common isotopic systems applied to dental enamel in both archaeological and modern contexts are strontium ($^{87}Sr/^{86}Sr$), oxygen ($\delta^{18}O$), and carbon ($\delta^{13}C$). Recent research, however, shows promising potential for the application of various other isotope systems, such as neodymium ($^{143}Nd/^{144}Nd$; P*lomp et al. 2017; Plomp, von Holstein, et al. 2019*), calcium ($\delta^{44}/^{42}Ca$; *Tacail et al. 2017, 2019*) and zinc ($\delta^{66}Zn$; *Jaouen et al. 2016, 2018*).

Chemical elements enter the human body through the ingestion of food and water and become incorporated into the crystal lattice of bioapatite, the principle component of dental enamel, dentine, and bone (*Zapanta LeGeros 1981*). In the case of strontium, Sr^{2+} replaces Ca^{2+} due to comparable ionic radius and identical ionic charge^{+} (*Bentley 2006; Eanes 1979; Pate 1994; Schroeder et al. 1972; Zapanta LeGeros 1981*). As ameloblasts, enamel forming cells, disappear post-tooth formation, enamel cannot be repaired or remodelled. Consequently, the isotopic signatures of dental enamel are indicative of the environment of the diet consumed during enamel formation (*Montgomery 2002; Ubelaker et al. 2006; Weatherell 1975; Zazzo et al. 2010*). In human individuals, mineralisation of the permanent molars occurs between birth and circa 16 years of age, with slight variations observed between European, Asian and African populations (e.g., *Reid and Dean 2006*) (see **Chapter 3** for more details).

Strontium isotope analyses may provide forensic intelligence by providing information about the geographical origin of individuals, as the isotopic values of human hair, nail, bone and teeth provide a reflection of the isotopic values of the environment in which an individual lived when these tissues formed (*Aggarwal et al. 2008; Bentley 2006; Degryse et al. 2012; Font et al. 2012, 2015; Juarez 2008; Meier-Augenstein 2017*). In the Netherlands, for example, strontium isotope analysis of dental enamel has been used to solve cold cases (*Font et al. 2015*). The interpretation of isotopic data to provide provenance information requires sufficient background information, or a bioavailable baseline, of the individual or population under study. This bioavailable baseline represents the isotopic composition that is incorporated into human tissues through consumption of plants, animals, potable water and respiration. This baseline can be used to compare the isotopic values and establish whether an individual derived from the local environment. The bioavailable baseline can be established by using

a reference dataset or, increasingly more popular, by establishing an isoscape. An isoscape is a graphical display of spatial variations in isotope landscapes (*West et al. 2006*). Extensive reference datasets or isoscapes are essential to allow for accurate data interpretation in respect of potential provenance (*Bataille et al. 2018; Bowen 2010a; Ehleringer et al. 2010*). There are currently, however, only a limited number of reference datasets or isoscapes that have been based on primarily human isotopic values (*Keller et al. 2016; Laffoon et al. 2017*).

Oxygen isoscapes in particular are usually generated based on isotope values of local waters: seawater, river water, surface water, lake water, or inferred precipitation (*Bowen 2010a, 2010b; Bowen & Revenaugh 2003; Evans et al. 2012; Giustini et al. 2016; Ryan et al. 2018; Terzer et al. 2013; Wassenaar et al. 2009; West et al. 2006*). While these isoscapes may give an indication of the oxygen isotope values expected in the local region, they do not directly represent the isotopic values of water that is consumed by most humans. Hence, several oxygen isoscapes have also been established using potable water (*Bowen et al. 2007; Ehleringer et al. 2008, 2010; Warner et al. 2018; West et al. 2014; Zhao et al. 2017*). Results from these studies indicated that bottled water samples (generally produced from local tap water) have similar oxygen isotopic compositions as local meteoric water at the location of purchase (*Bowen et al. 2005, 2007; Ehleringer et al. 2010*). Water sources can therefore be used as reference data or isoscapes for comparison with human oxygen isotope values (*Ehleringer et al. 2010; Warner et al. 2018; West et al. 2014*).

For strontium isotope ratios, isoscapes based on potable water remain more limited (*Montgomery et al. 2006; Voerkelius et al. 2010*) and there is a heavy reliance on geological based isoscapes (*Adams et al. 2019; Bataille et al. 2012, 2018; Bataille & Bowen 2012; Beard & Johnson 2000; Bentley & Knipper 2005; Evans et al. 2009, 2010; Hoogewerff et al. 2019*). Strontium isoscapes based on plants (*Ryan et al. 2018; Snoeck et al. 2020; Willmes, Bataille et al. 2018*) and archaeological animal remains (*Kootker, van Lanen et al. 2016*) have also been published, indicating that these sources may be more representative of the bioavailable isotope ratios than geological sources as the geological isotopic composition is not directly incorporated into human tissues (*Maurer et al. 2012; Montgomery & Jay 2013; Ryan et al. 2018; Snoeck et al. 2020*). This is especially the case for modern societies, where agricultural practices can influence the Sr isotope composition of a region (*Maurer et al. 2012; Thomsen & Andreasen 2019*).

More importantly, due to the current global 'supermarket diet', the range of background isotopic values reported by isoscapes based on archaeological remains or plants may not be correlated to the isotopic values seen in modern humans. The use of environmental reference

databases and isoscapes for provenance determinations is based upon the assumption that the vast majority of the consumed foods, or Sr intake, is from local origin. For the Netherlands, a densely populated and prosperous country that has the world's fourth largest economy supported by foreign trade, this may not be the case (*Kootker et al. 2020*). Here, due to the increasing globalisation of food supply, the establishment of nation-wide or international supermarket chains, and increasing urbanisation, an isotopic signature that reflects the more uniform supermarket-diet can be expected in anthropological forensic investigations (*Kootker et al 2020*). The imported food will influence the isotopic composition of human tissues, and could overwrite the isotopic values of the local geology. This could hamper the application of strontium isotope analysis in forensic studies in the Netherlands. Nonetheless, this overwriting of isotopic signatures may not be applicable to other parts of Europe or the rest of the world. This is evidenced by $^{87}Sr/^{86}Sr$ ratios of modern keratin samples correlating with geography in other regions of the world, although this may in part be a consequence of the tendency of hair keratin to incorporate exogeneous Sr through interactions with local tap water (e.g., during showering and bathing (*Ehleringer et al. 2008; Nardoto et al. 2006; Tipple et al. 2018*)).

A promising potential reference material for human isotopic values is tap water, which even in a globalising world is generally extracted locally, as indicated by the oxygen isoscapes and previous strontium isotope studies (*Kootker et al. 2020; Montgomery et al. 2006; Voerkelius et al. 2010; West et al. 2014*). Previous studies have indicated that strontium in water is absorbed by vegetables from cooking water (*Losee & Adkins 1969*), and studies of mineral water indicated a local Sr origin (*Montgomery et al. 2006; Voerkelius et al. 2010*). Despite these promising results the contribution of local water sources to the $^{87}Sr/^{86}Sr$ in dental enamel of modern humans has not been quantified. To evaluate if $^{87}Sr/^{86}Sr$ ratios in tap water are representative of Sr in dental enamel of modern humans, and can therefore be used as a proxy to human values in forensic case studies, the current study reports an extensive isotope study of modern human dental enamel (n = 153) and tap water (n = 143) samples from the Netherlands (*Kootker et al. 2020; Font et al. 2015; Plomp, von Holstein et al. 2019; 2020*). These results will establish if (1) Dutch tap water is correlated to the water source and/or geological substrate, and whether (2) Sr isotopic ratios in turn correspond to the modern dental enamel of the Dutch individuals living in that location. Then the question can be addressed (3) whether either of these sample types can be used as reference materials to geolocate unidentified human remains in forensic investigations.

7.2 Strontium isotope system

The principle behind strontium isotope analyses of human remains is based on the premise that 'you are (isotopically) what you eat". Strontium enters our system though ingestion of food and drinking water (*Bentley 2006*). Mass-dependent fractionation of $^{87}Sr/^{86}Sr$ is negligible because of the large atomic mass of strontium, and the fact that ^{87}Sr is only 1.16 % heavier than ^{86}Sr (*Bentley 2006*). Moreover, any possible mass-dependent fractionation in $^{87}Sr/^{86}Sr$ is corrected during mass spectrometric measurement by the routine normalisation to a constant $^{88}Sr/^{86}Sr$ ratio (*Beard & Johnson 2000; Faure & Mensing 2005*). During weathering processes and soil formation, mineral breakdown is associated with some incongruent reactions such that bioavailable Sr isotope ratios will be similar but not identical to the underlying rocks. This means that Sr passes from bedrock to soil into biologically-available solutions with a predictable $^{87}Sr/^{86}Sr$ ratio (see discussion in *Bataille et al.* (*2018*)). Although international trade and the import of food is not restricted to the modern period (*Wright 2005*), the assumption is made that the vast majority of the food available for ancient populations were of local decent, allowing a direct comparison to be made between the human enamel $^{87}Sr/^{86}Sr$ ratios and biologically available $^{87}Sr/^{86}Srr$ ratios of the surrounding region that are linked to the underlying geology. For modern populations, however, the import and national distribution of foods potentially has a major impact on human $^{87}Sr/^{86}Sr$ ratios.

7

7.3 The Netherlands

7.3.1 Previous Sr isotope research

For the Netherlands, an archaeological Sr isoscape based on animal remains has been published with $^{87}Sr/^{86}Sr$ ratios ranging between 0.708-0.711 (*Kootker, van Lanen et al. 2016*). The first established modern Sr Dutch range ($^{87}Sr/^{86}Sr$ = 0.708-0.710; *Font et al. 2015*) was based on human scalp hair and enamel data from modern Dutch individuals, tap water and soil/street dust. This range was confirmed by the analyses on dental enamel from Dutch inhabitants presented in **Chapter 5** ($^{87}Sr/^{86}Sr$ = 0.709-0.710; *Plomp, von Holstein et al. 2019*). The results from tap water and human enamel from these previous studies (*Font et al. 2015; Plomp, von Holstein et al. 2019; 2020*) are combined with a new dataset (*Kootker et al. 2020*) to explore the correlation between $^{87}Sr/^{86}Sr$ ratios in tap water and dental enamel.

7.3.2 Geology

The Netherlands consists of a mixed geology, with Holocene sediments in the north and western part of the country and Pleistocene sediments in the south and eastern part of the country (*Vos 2015*). These different deposits are expected to influence the isotopic values of particularly the groundwater resources (*Zhou et al. 2018*). Holocene age sediments are expected to exhibit $^{87}Sr/^{86}Sr$ ratios approximating precipitation/seawater (0.7092; *Veizer 1989*). Pleistocene sediments are likely to exhibit more radiogenic signatures due to their age and provenance (>0.7095) (*Kootker et al. 2020*).

7.3.3 Tap water resources

Water supply in the Netherlands is divided into ten different areas managed by different drinking water companies (**Figure 7.1**). Four types of raw water sources are used: groundwater (58 %), natural dune water (1 %), riverbank filtration water (6 %) and surface water (35 %) (*Kootker et al. in 2020; Vewin 2017*). Tap water in the coastal provinces of Noord-Holland, Zuid-Holland, and Zeeland is dominated by water abstracted from infiltration, surface, dunes and riverbank water sites. All other provinces receive tap water from groundwater sources, with a few exceptions in Overijssel (riverbank infiltration), Gelderland (push moraine - infiltration), and Limburg (combination of all) (*Kootker et al. 2020*).

The $^{87}Sr/^{86}Sr$ ratios of tap water are expected to be at least partially related to the type of abstraction site, raw water source, and water quality (*Kootker et al. 2020*). Strontium concentration and hardness of water are for instance directly related (*Schroeder et al. 1972*). The raw water sources may also have an impact on the strontium isotope composition of the water: **(1)** Ground water sources potentially exhibit a wide range of $^{87}Sr/^{86}Sr$ ratios. Groundwater from shallow aquifers is likely to reflect a mixed isotopic composition of recent rainwater and the infiltrated soil (*Kootker et al. 2020*). In the Netherlands, ground water used for tap water production is generally abstracted at depths between 15 and 200+ meter below surface (*Kootker et al. 2020*). Groundwater, as well as riverbank infiltration water, remains in the soil for years (e.g., at Oasen's abstraction sites: 2-50 years) before abstraction (*Kootker et al. 2020*). Water-rock interaction during this period results in groundwater with a Sr isotope ratio that reflects the soil composition (*Johnson & DePaolo 1997; Zou et al. 2018*).
(2) Subsurface water is influenced by infiltration processes, that may take several months, to improve the water quality. The tap water $^{87}Sr/^{86}Sr$ ratios are expected to represent a mix of the infiltrated river water and that of the filtering sediments (Holocene sands), and thus to be close

Figure 7.1 *Overview of the drinking water companies in the Netherlands (after https://www.vewin.nl/sector-in-beeld)*

to 0.7091 (*Kootker, van Lanen, et al. 2016*).

(3) Surface water is influenced by multiple factors such as groundwater discharge and surface runoff (*Ehleringer et al. 2010; West et al. 2014*). Surface water extraction sites can be influenced by human activities such as agriculture, industry, and filtration systems (*Kootker et al. 2020; Thomsen & Andreasen 2019; Zou et al. 2018*). Moreover, surface water may have been transported across great distance within the Greater Rhine river system. The effect of this transport, as well

as human activities, on the Sr isotope composition of the purified Dutch tap water is unclear.

The Sr intake of humans can be expected to include a mixture of sources, such as public tap water, commercial natural mineral water, and water based beverages (*Ehleringer et al. 2010; Montgomery et al. 2006*).

7.4 Material and Methods

7.4.1 Sampling strategy

Dental enamel

Extracted mandibular and maxillary third molars were donated to the Vrije Universiteit Amsterdam by 153 individuals that were born and raised in the Netherlands. The use of the human dental elements for scientific research was approved by the Medical Ethics Review Committee of the Amsterdam UMC, location VUmc. Background information on the donors was obtained by anonymous questionnaires, providing information on the donor's geographical location at the time of tooth formation, dietary preferences and health. None of the individuals relocated during the formation and mineralisation period of the dental enamel.

After removing the outermost surface of the enamel, circa 1-3 mg of dental enamel powder was collected using a diamond-tipped burr pre-cleaned in 10 % HCl. The samples were taken from the mesial or distal side of either the buccal or lingual surface, depending on the physical quality of the molar and the presence of carious lesions (*Kootker et al. 2020; Font et al. 2015*). The samples were collected in acid-cleaned polyethylene Eppendorf centrifuge tubes and transferred to a class 100 clean laboratory at the Vrije Universiteit Amsterdam (*Kootker et al. 2020*). For the 20 samples from **Chapter 5** (*Plomp, von Holstein et al. 2019*), the cuspal enamel was sampled. For the 9 samples from **Chapter 6** (*Plomp, von Holstein et al. 2020*) the Sr isotope results from the lateral lingual enamel were chosen where possible (WM or WB where selected if WL was unavailable due to presence of caries, see **Chapter 6**). Samples processed by *Plomp, von Holstein et al.* (*2019, 2020*) were collected into clean glass vials before processing them in the clean laboratory (see *Plomp, Smeets et al. 2020*).

Tap water

A total of 124 tap water samples from all twelve provinces were collected between May and November 2018. Together with the 19 tap water samples previously published by *Font et al.* (*2015*) the 143 samples represent 120 locations from all ten Dutch regional water companies as well as all twelve provinces (**Figure 7.1**). The 50 mL polyethylene centrifuge tubes were rinsed three times with tap water before circa 45 mL of tap water was collected (*Kootker et al. 2020*). The samples were then transferred to the Vrije Universiteit Amsterdam and stored in a fridge at 4 °C to avoid evaporation. Circa 10 mL of these vials were subsampled into 30 mL acid-cleaned Savillex PFA beakers in a class 100 clean laboratory at the Vrije Universiteit Amsterdam. These 10 mL subsamples were dried down over night, capped and stored (see *Kootker et al. 2020*).

In addition, 60 tap water samples were selected for concentration measurements. These 60 samples represent 60 locations divided over the twelve provinces and ten Dutch regional water companies (**Figure 7.1**). For concentration measurements, a 2 mL aliquot of tap water was pipetted into a 10 mL acid-cleaned ICP Exetainer® vial and acidified with 118 µL 14M HNO_3 (see *Kootker et al. 2020*).

7.4.2 Strontium isotope analysis

The dental enamel samples and tap water residues were dissolved in 500 µl 3M HNO_3 for ion exchange chromatography. Detailed descriptions of the Sr chromatography protocols and sample loading procedures are provided in *Font et al.* (*2012*), *Kootker, Mbeki et al.* (*2016*), and *Plomp, Smeets et al.* (*2020*). The strontium isotope compositions were measured on a Thermo Finnigan Triton *Plus* thermal ionisation mass spectrometer (TIMS) at the Vrije Universiteit Amsterdam. The ratios were determined using a static routine and were corrected for mass-fractionation to $^{86}Sr/^{88}Sr$ of 0.1194. The NBS987 standard gave mean $^{87}Sr/^{86}Sr$ values of 0.710258 ± 0.000009 (2 SD, n = 15; *Kootker et al. 2020*), 0.710247 ± 17 (2 SD, n = 51; *Plomp, von Holstein 2019*) and 0.710242 ± 0.000009 (2 SD, n = 36; *Font et al. 2015*). The measurements from *Kootker et al.* (*2020*) were normalised to 0.710240 for NBS987: for every turret the correction factor was calculated ($0.710240/^{87}Sr/^{86}Sr_{measured\ NBS}$) and applied to all samples within that turret. Procedural blanks contained <75 pg strontium (n = 9; *Kootker et al. 2020*). The in-house tooth standard (TSTD) gave mean values of $^{87}Sr/^{86}Sr$ = 0.707854 ± 19 (n = 97) over the period of a year, with procedural blanks containing <60 pg (n = 38, median = 18.4 pg) in the *Plomp, von Holstein et al.* (*2019*) study. *Font et al.* (*2012*) reported blanks below <50 pg. As these are minor contributions blank corrections have not been applied.

Concentration measurements

The acidified 60 tap water samples were analysed using a Thermo X-Series II Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The aliquot solutions were introduced via a quartz dual cyclonic spray chamber equipped with a PFA-ST MicroFlow nebulizer (Elemental Scientific) with a sample uptake rate of about 100 µL min-1. Changes in sensitivity over time were monitored and corrected for using the geological reference material BHVO-2, which was analysed after every second sample (modified after *Eggins et al.* (*1997*)). After interference correction, elemental concentrations were calculated using a two-point calibration of blank and BHVO-2. Long-term precision determined with multiple geological reference materials is about 10% (RSD) (see *Kootker et al. 2020*).

7.5 Results & Discussion

7.5.1 Sr isotope variation

A total of 143 tap water samples were analysed (n = 19, *Font et al. 2015*; n = 124, *Kootker et al. 2020*) and 153 human enamel samples (n = 30, *Font et al. 2015*; n = 94, *Kootker et al. 2020*; n = 20, *Plomp, von Holstein et al. 2019*; n = 9, *Plomp, von Holstein et al. 2020*). The observed range of $^{87}Sr/^{86}Sr$ ratios was larger for tap water (0.7084 – 0.7128, $\Delta Sr_{max\text{-}min}$ = 0.0044) than for enamel samples in the Netherlands (0.7085 to 0.7100, $\Delta Sr_{max\text{-}min}$ = 0.0015) (**Table 7.1**).

7.5.2 Tap water

The distribution of the tap water $^{87}Sr/^{86}Sr$ ratios is displayed in **Figure 7.2**. Little variation is seen in tap water from Waternet (n = 3, 0.7089), PWN (n = 7, 0.7088-0.7089, $\Delta Sr_{max\text{-}min}$ = 0.0001), Dunea (n = 9, 0.7089-0.7094, $\Delta Sr_{max\text{-}min}$ = 0.0005), Oasen (n = 9, 0.7088-0.7093, $\Delta Sr_{max\text{-}min}$ = 0.0005), Waterbedrijf Groningen (n = 8, 0.7086-0.7092, $\Delta Sr_{max\text{-}min}$ = 0.0006), and Evides Waterbedrijf (n =

Table 7.1 *Descriptive statistics for the Dutch tap water (Font et al. 2015; Kootker et al. 2020) and human enamel samples (Font et al. 2015; Kootker et al. 2020; Plomp, von Holsten et al. 2019; 2020)*

	Tap water	Enamel
n	143	153
Mean	0.709268	0.709350
Median	0.709085	0.709351
Minimum	0.708369	0.708469
Maximum	0.712783	0.709951
Range	0.004414	0.001482
$\sigma 2$	0.001344	0.000515

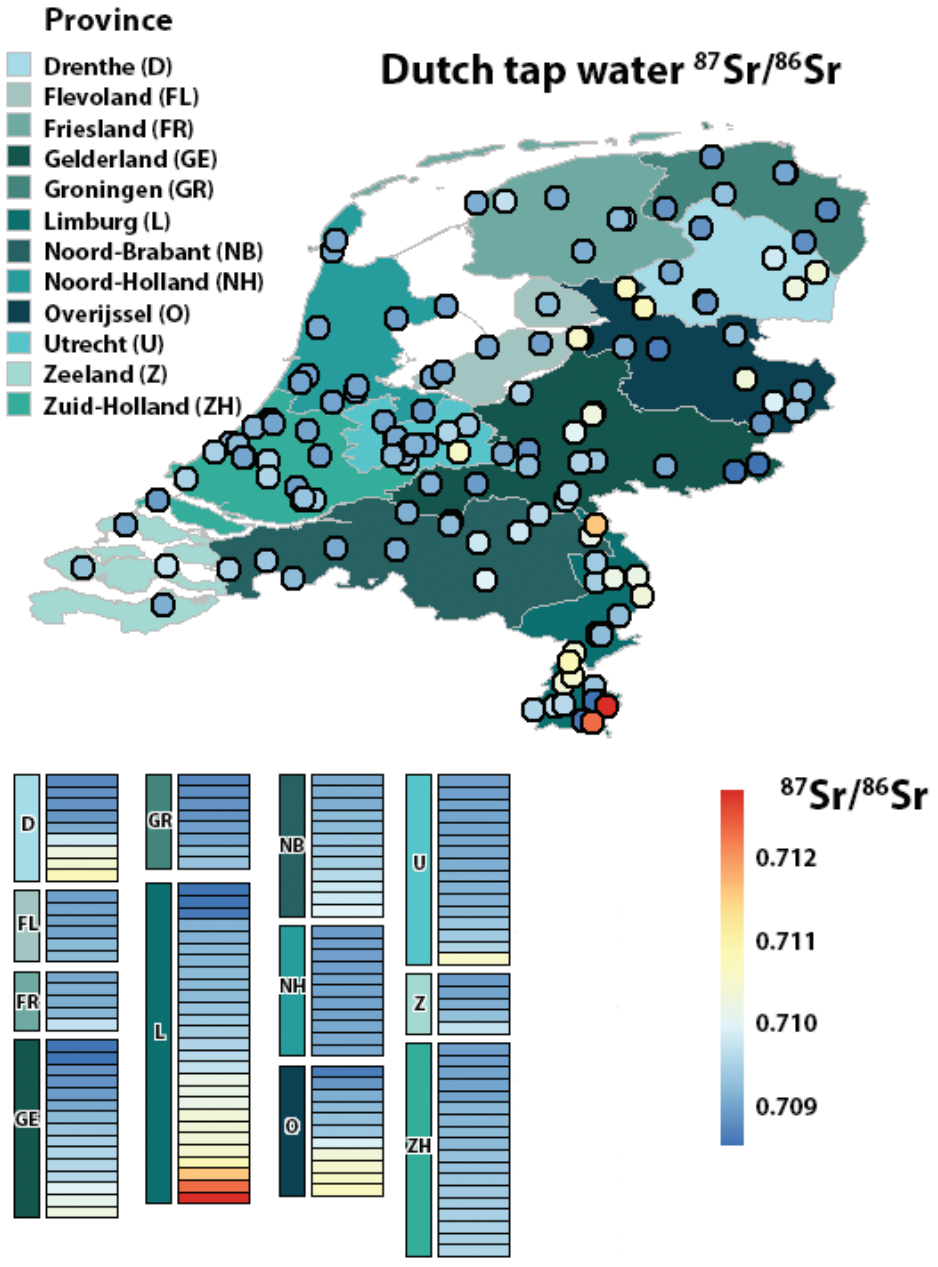

Figure 7.2 *Locations and heat map of the tap water values separated by province (Plomp & Peterson 2020). The most variable Sr isotope composition was found in tap water from Limburg, Drenthe and Overijssel. Note the outlier from Kerkrade in Limburg in red.*

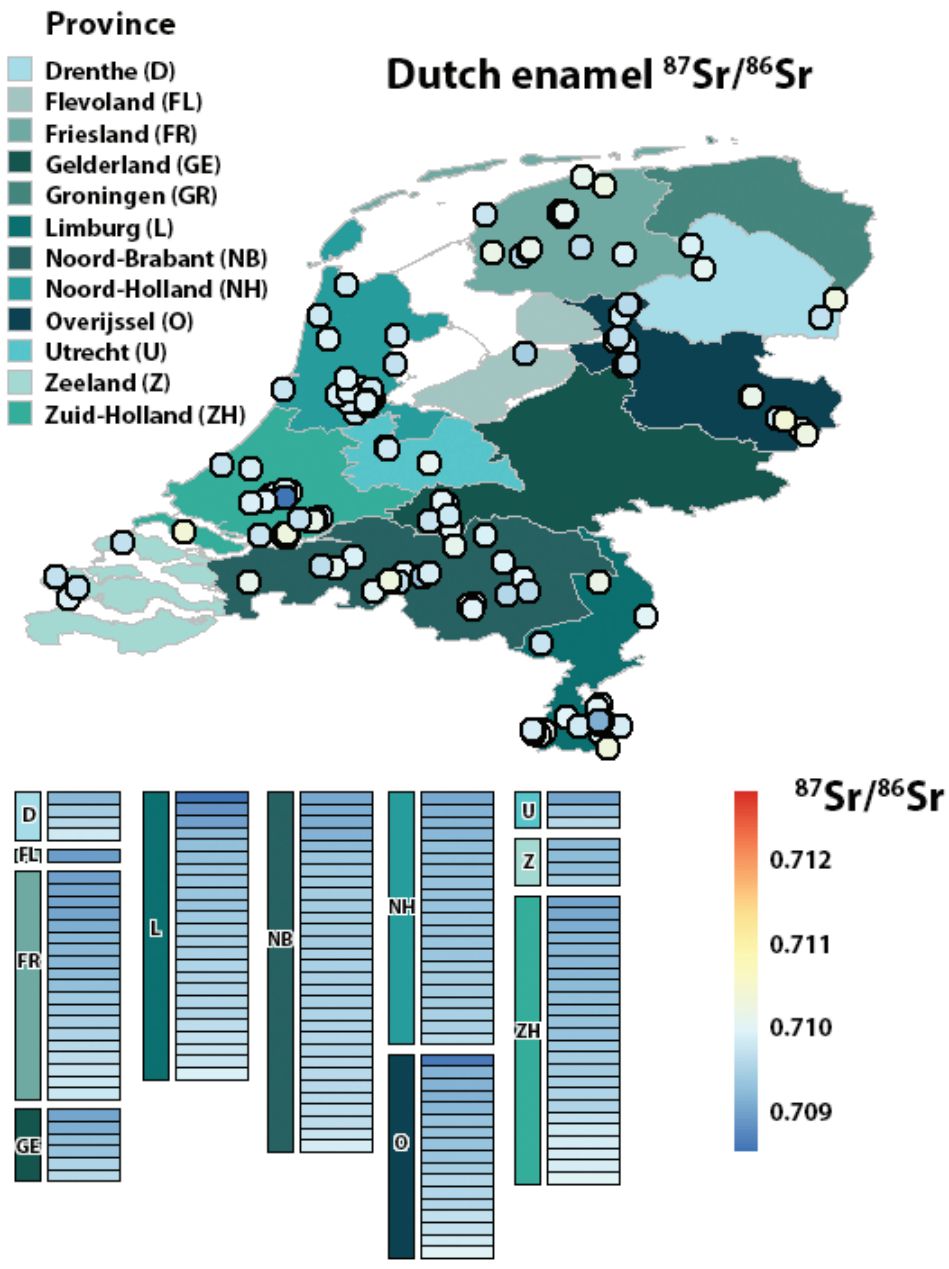

Figure 7.3 *Locations and heat map of the enamel values separated by province (Plomp & Peterson 2020). The most variable Sr isotope composition was found in individuals from Limburg, Overijssel and Zuid-Holland.*

7, 0.7088-0.7096, $\Delta Sr_{max\text{-}min}$ = 0.0008). Except for Waterbedrijf Groningen, these water companies almost exclusively rely on surface water, riverbank filtration and infiltration abstraction sites that are situated in an underlying geology dominated by Holocene sediments, explaining the limited variation in observed $^{87}Sr/^{86}Sr$ ratios (*Kootker et al. 2020*). The groundwater abstraction sites in Noord-Brabant extract water from the thick layers of clay, sand, and loam that exhibit a wide range of $^{87}Sr/^{86}Sr$ ratios (*Kootker et al. 2020*), as seen in the tap water isotope compositions, ranging from 0.7089-0.7098 (n = 12, $\Delta Sr_{max\text{-}min}$ = 0.0009).

The largest variations in tap water $^{87}Sr/^{86}Sr$ ratios are seen in water managed by WMD Drinkwater (n = 8, 0.7086-0.7103, $\Delta Sr_{max\text{-}min}$ = 0.0017), Vitens (n = 53, 0.7084-0.7106, $\Delta Sr_{max\text{-}min}$ = 0.0022), and WML (n = 27, 0.7084-0.7128, $\Delta Sr_{max\text{-}min}$ = 0.0044).

(1) All WMD Drinkwater groundwater stations abstract water from coarse sand and boulder clay layers, which are expected to exhibit more radiogenic Sr isotope ratios (*Kootker et al. 2020*). This is reflected in some of the observed tap water $^{87}Sr/^{86}Sr$ ratios. However, some WMD Drinkwater samples exhibit low Sr isotope ratios ($^{87}Sr/^{86}Sr$ = 0.7086).

(2) Vitens covers almost 50 % of the Netherlands, and therefore abstracts groundwater from all types of sediments (Holocene clays – Pleistocene loam) and consequently distribute tap water with varying Sr isotope ratios. For example, tap water from Zwolle (Overijssel) is abstracted at a depth of circa 120-160 meters from a local groundwater source (*Vitens 2020*). These sediments belong to the Upper North Sea Group that are expected to exhibit Sr isotope ratios comparable to seawater (0.7092; *Kootker et al. 2020; Veizer 1989*). Kampen is located 15 km west of Zwolle. Here, tap water is extracted about 15 km south of Zwolle from a push moraine (Veluwe). This ice push ridge consists of radiogenic Pleistocene sediments, which is reflected in the high $^{87}Sr/^{86}Sr$ ratios of the Kampen tap water samples (n = 2, 0.7104; *Kootker et al. 2020*).

(3) The most complex tap water abstraction and distribution system, WML, is found in the province of Limburg (**Figure 7.2**). The tap water from Limburg represents a mix of groundwater, riverbank filtration, infiltration and surface water. This diversity, in combination with the various types of sediments present (e.g., Holocene fluviatile sediments and Pleistocene loess) results in a wide range of observed tap water $^{87}Sr/^{86}Sr$ ratios (*Kootker et al. 2020*).

The $^{87}Sr/^{86}Sr$ ratios of tap water therefore seem to be correlated with the local geology (*Kootker et al. 2020*). These results are consistent with previous research, where $^{87}Sr/^{86}Sr$ ratios of mineral water were correlated to the surface geology (*Kamenov & Curtis 2017; Montgomery et al. 2006; Voerkelius et al. 2010*).

Similar as previously demonstrated for oxygen isotopes (*Bowen et al. 2007*), the annual variation in Sr ratios seems to be limited as indicated by duplicate tap water samples. Duplicate tap water samples had maximum differences ranging between $\Delta^{87}Sr/^{86}Sr_{max\text{-}min}$ = 0.000003-0.000445 (**Table 7.2**), with Utrecht, Vianen, and Delft showing the most variation ($\Delta Sr_{max\text{-}min}$ = 0.000208, 0.000324 and 0.000445 respectively). The limited variation seen in the majority of the locations (n = 15, $\Delta Sr_{max\text{-}min}$ < 0.0002*)* is not surprising as Sr isotope values are not influenced by seasonal effects as seen for the oxygen isotope system (see **Section 2.3**).

7.5.3 Human dental enamel

The distribution of the modern human dental enamel $^{87}Sr/^{86}Sr$ ratios is displayed in **Figure 7.3**. The $^{87}Sr/^{86}Sr$ atios range between 0.7085 and 0.7100 (n = 153). The greatest variance in human dental enamel $^{87}Sr/^{86}Sr$ ratios ($\Delta Sr_{max\text{-}min}$ >0.0008) is seen in the samples from the provinces of Friesland, Noord-Brabant, Overijssel, and Zuid-Holland (**Figure 7.3**, **Table 7.3**). The observed variation seems to be independent of the degree of urbanisation, of which the highest degrees are found in Noord-Holland, Zuid-Holland and Noord-Brabant (*Vanham et al. 2016*).

Table 7.2 *Maximum $^{87}Sr/^{86}Sr\Delta$ differences (0.000003-0.000445) between duplicate Dutch tap water samples from 17 locations. Two tap water samples were taken for each of these locations, with the exception of Roermond and Utrecht for which five samples were analysed.*

Tap water location	maximum difference
Apeldoorn	0.000186
Appingedam	0.000029
Delft	0.000445
Drachten	0.000007
Groningen	0.000038
Heerlen	0.000023
Hoogeveen	0.000106
Kampen	0.000063
Leiden	0.000117
Nijmegen	0.000025
Norg	0.000011
Roermond	0.000089
's-Gravenhage	0.000038
's-Hertogenbosch	0.000180
Utrecht	0.000208
Vianen	0.000324
Zwijndrecht	0.000003

Province	n	minimum	maximum	Δmax-min
Drenthe	4	0.709142	0.709800	0.000658
Friesland	19	0.708934	0.709754	0.000820
Gelderland	6	0.708964	0.709562	0.000598
Limburg	23	0.708469	0.709862	0.001393
Noord-Brabant	31	0.708774	0.709822	0.001048
Noord-Holland	21	0.708991	0.709584	0.000593
Overijssel	17	0.708532	0.709951	0.001419
Utrecht	3	0.708951	0.709570	0.000619
Zeeland	4	0.709162	0.709384	0.000222
Zuid-Holland	24	0.708974	0.709944	0.000970

Table 7.3 *Minimum and maximum $^{87}Sr/^{86}Sr$ ratios of modern enamel from provinces with more than one sample, ranging between Δ = 0.000222-0.001419.*

Two individuals from Almelo (Overijssel) and Heerlen (Limburg) exhibit low $^{87}Sr/^{86}Sr$ ratios (0.7085). In one molar (Almelo 1) an amalgam filling was present. To date, no research has been executed to investigate the effect filling materials on the isotopic integrity of dental enamel. The effect of the carious lesion itself is considered of limited importance, as the biogenic $^{87}Sr/^{86}Sr$ ratio in unaffected enamel is not overwritten during the carious processes (*Plomp, von Holstein et al. 2020*). The absence of dental fillings in the other individual (IDIS 5, Heerlen) suggests that the isotopic composition reflects the dietary Sr intake. Nevertheless, the reasons behind these low $^{87}Sr/^{86}Sr$ ratios remain unclear.

7.5.4 Tap water contribution to dietary Sr

The Sr concentrations in 60 tap water samples range from 0.035 to 0.357 ppm (µg/g), (mean = 0.174 ppm, median = 0.157 ppm). Based on an intake of 2L drinking water per day, tap water is expected to contribute between circa 70 to 720 µg (average 340 µg) strontium to the human dietary intake (*Kootker et al. 2020*). The contribution of tap water to the isotope composition of human dental enamel is therefore considered to be limited. This is further supported by the data in **Table 7.4** and **Figure 7.4.** Human dental enamel and tap water samples were available for 24 locations. There is a poor correlation between the two sample sources ($R^2 = 0.006$; **Figure 7.4**). There is no evidence of major systematic changes in the water distribution network in the past four decades, hence, based on this dataset the conclusion can be drawn that the Sr isotope signature of the human dental enamel samples in the Netherlands are independent of the consumed tap water $^{87}Sr/^{86}Sr$ ratios. The lack of correlation between water and human enamel suggests that even if the water or human enamel database were expanded significantly (> x 5) an accurate predictive isoscape cannot be established for the Netherlands (*Kootker et al. 2020*).

Table 7.4 *Human dental enamel and tap water $^{87}Sr/^{86}Sr$ ratios from the same sample location (n = 24). For several sample locations multiple enamel samples were available and an average of was taken to compare these to the tap water values.*

Location	$^{87}Sr/^{86}Sr$ enamel	$^{87}Sr/^{86}Sr$ tap water
Almelo	0.709103	0.710229
Amsterdam	0.709299	0.708877
Amstelveen	0.709231	0.708883
Breda	0.709466	0.708932
Brunssum	0.709490	0.709207
Bunnik	0.709570	0.708896
Den Bosch	0.709611	0.709288
Den Haag	0.709202	0.709066
Dordrecht	0.709242	0.709279
Enschede	0.709662	0.709219
Heerlen	0.709095	0.708406
Hengelo	0.709598	0.709785
Hoorn	0.709229	0.708838
Leeuwarden	0.709255	0.708936
Maastricht	0.709437	0.709408
Middelburg	0.709187	0.709125
Rotterdam	0.709502	0.709386
Serooskerke Schouwen	0.709176	0.708871
Steenwijk	0.709152	0.710540
Tilburg	0.709455	0.708976
Venlo	0.709493	0.710226
Venray	0.709711	0.709264
Zwijndrecht	0.709153	0.709204
Zwolle	0.709259	0.708966

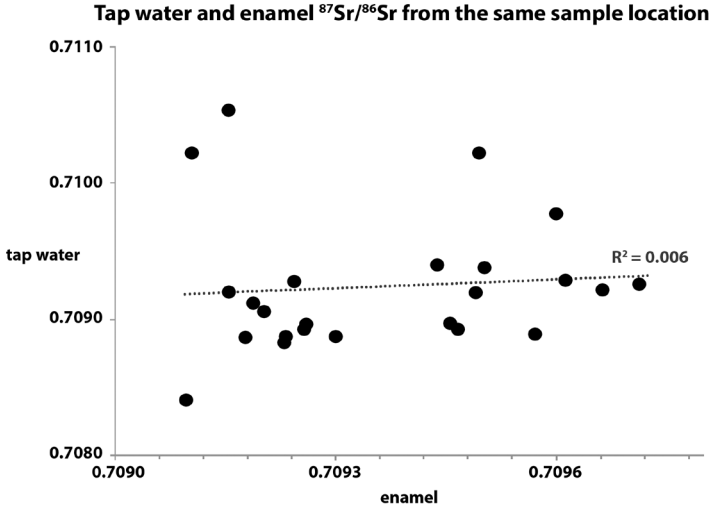

Figure 7.4 *Human dental enamel and tap water $^{87}Sr/^{86}Sr$ ratios from the same sample location (n = 24). For several sample locations multiple enamel samples were available and an average was taken to compare to the tap water values (see* **Table 7.4** *for the data).*

7.5.5 Implications for forensic provenancing

Although the consumed tap water in the Netherlands is related to the local geology, the modern human Sr intake appears to have become detached from the local geological strontium isotope composition. This is likely caused by the import of food from which the majority of the Sr isotope intake derives (*Kootker et al. 2020*). Hence, local reference materials, such as soil and tap water samples, may not be applicable as a proxy for human strontium values in modern globalised population societies. This may also be the case for other densely populated and wealthy cities and countries worldwide. Larger and less densely populated countries, especially with a more complex geologies, need to be examined to establish if the variation in human Sr isotope ratios are dampened by globalisation of the food supply in other regions of the world.

The effective application of Sr isotopes in modern populations strongly depends on the existence of a reference database containing a vast number of modern human enamel data from individuals with known provenance history. Based on the data collected in this study (*Kootker et al. 2020*), *Font et al.* (*2015*), and *Plomp, von Holstein et al.* (*2019; 2020*), a Dutch $^{87}Sr/^{86}Sr$ range for the Netherlands can be defined, varying between 0.7085 to 0.7010 (n = 153), with 98.0 % of the individuals (n = 150) ranging between 0.7088-0.7099. Future research is required to assess whether local dietary plant samples provide a better proxy for human enamel values than tap water. Additional isotopic data on local and imported food resources, as well as information from other isotopic systems, may help to gain more insight into the spatial variation of human dental enamel in the Netherlands, allowing for a more accurate interpretation of forensic Sr isotope data.

7.6 Conclusion

The accurate interpretation of $^{87}Sr/^{86}Sr$ ratios in archaeological and forensic case studies requires sufficient background information, or a bioavailable baseline. For the successful application of strontium isotope analysis of human tissues, the dietary intake and the underlying local geology should be correlated. While this may be valid for archaeological studies, forensic provenancing studies have to address the challenge of a globalising supermarket-diet and its homogenising effect on human $^{87}Sr/^{86}Sr$ ratios. The current Sr isoscapes and baseline datasets are based on modern vegetation samples and/or archaeological faunal samples that reflect the strontium isotope composition of the geological subsurface. Forensic isotope investigations, however,

require tailored baseline $^{87}Sr/^{86}Sr$ datasets and isoscapes as human isotopic signatures do not necessarily reflect the local geological values.

This study examined tap water and modern dental enamel with the aim to examine spatial constrains on the expected local strontium isotopic signature in the Netherlands. Tap water values (0.7084 – 0.7128, n = 143) were found to reflect the local geology, as they exhibited expected Sr isotope values and outliers could be explained by divergent extraction processes that were influenced by the local geology. Tap water $^{87}Sr/^{86}Sr$ ratios do not correlate, however, with the modern human dental enamel $^{87}Sr/^{86}Sr$ ratios (i.e., tap water is not dominating the dietary Sr intake). This is likely the result of the low Sr concentrations in Dutch tap water and the increasing globalisation of the food distribution. The latter is especially important for the Netherlands, a country which depends heavily on the import of food. Hence, for forensic provenance investigations in the Netherlands, tap water should not be used as comparative reference material for modern dental enamel for Sr isotopes. Where possible, future studies should use human tissues to establish a baseline or isoscape to determine the range of expected isotopic ratios. Based on the available data (*Font et al. 2015, Plomp, von Holstein et al. 2019, 2020; Kootker et al. 2020*), the Dutch $^{87}Sr/^{86}Sr$ range in human enamel is between 0.7085 and 0.7100 (n = 153), with 98.0 % of the individuals ranging between 0.7088 and 0.7099 (n = 151). Although clear spatial variations in $^{87}Sr/^{86}Sr$ within the Netherlands are absent, the obtained baseline data for the Netherlands are of great importance for forensic human identification cases using strontium isotopes as an investigative tool. Additional isotopic data on the bioavailable Sr from imported and local foods will allow for better insights into the isotopic variation of modern human dental enamel. In combination with the application of a multi-isotope approach (Sr-Pb-C-H-O), such information is needed for more accurate isotopic baselines that are representatives of human isotopic variation. This will improve interpretations of modern isotopic data and the application of isotopic techniques to forensic case studies.

Data Availability Statement

The data and code that support the findings of this study are available in **Tables 7.1-7-4,** *as well as openly available at GitHub and Zenodo (Plomp & Peterson 2020, https://github.com/EstherPlomp/IsoMapNL, https://doi.org/10.5281/zenodo.3941066).*

Acknowledgements

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Chapter 8

Discussion and Conclusion

This thesis had two main aims: First, to assess the applicability of neodymium isotopes as a new isotopic technique to determine human provenance. Second, to evaluate the application of more traditional techniques (strontium, oxygen and carbon) by quantifying the isotopic variation seen in modern dental enamel. Both the application of new techniques and the refinement of traditional techniques is expected to influence interpretations of human diet and mobility patterns. This chapter discusses the implications of the research presented in the previous chapters and suggests potential future directions of isotopic research in forensic and archaeological studies.

8.1 Technological advances

Developments in mass spectrometry have improved the precision, accuracy and sensitivity of isotopic measurements, decreased sample size requirements, and analyses have increasingly become more automated (*Bartelink et al. 2016; Coelho et al. 2017; Hoefs 2015; Katzenberg 2008; Klaver et al. 2015; Koornneef et al. 2015; Lee-Thorp 2008; Oulhote et al. 2011; Willmes et al. 2016*). These developments will likely continue in the upcoming years, enabling the application of new isotopic systems (such as neodymium isotopes), to assess the isotopic composition of human tissues.

Neodymium isotopes

This thesis presents the first results of neodymium (Nd) isotope ratios in modern human dental enamel. The total number of individuals analysed (n = 40), provides a base for an initial evaluation of the technique. Nevertheless, this sample size is limited and requires future expansion to evaluate the neodymium isotope variation in human populations. The dental enamel of the majority of the individuals (83.3 %) was compatible with the local geology where the individual resided at the time of enamel formation. This geological compatibility indicates that Nd composition of dental enamel is likely mainly controlled by geological factors. As a result, Nd could provide additional information on the mobility of individuals, complementary to the current isotopes used for provenancing (Sr, Pb, O, H). Nevertheless, there are several discrepancies in the dataset that do not reflect the neodymium isotope composition of the local geology and remain difficult to interpret given the limited data available. Routine analyses of Nd isotope analyses are, however, limited by the sample size required, the time and cost investments in the analyses, as well as the required measurement equipment (10^{13} Ω amplifiers). As these costs decrease and the equipment becomes more standardised (with increasingly

improved sensitivity), the analyses may become more straightforward and applicable outside specialised research questions. Additional samples from other countries/geological areas will complement the results from the six geographical areas explored in this dissertation. An expanded database of human and background data will improve the understanding of spatial variation in Nd. Results of bioavailable samples such as plants and food items may shed more light on the uptake of Nd in the human body, and improve the understanding of Nd isotope composition within human tissues, as well as provide a background signal to compare to human neodymium isotope ratios. Additional influences on the Nd isotope ratio of human enamel, such as dust or anthropogenic sources (e.g., electronics, fertilisers), as well as the effect of the globalisation of the food market, will require further investigation.

Synchrotron imaging

Synchrotron imaging (third/fourth generation X-rays) provides high resolution, three dimensional, spatial information of dental elements (*Gherase & Fleming 2019; Smith & Tafforeau 2008; Tafforeau et al. 2006*). This method is non-destructive and overcomes the limitations of tradition light electron microscopy (*Gherase & Fleming 2019*). Synchrotron imaging can provide more information on microstructure of enamel. This information is needed to improve current understandings of the formation and (de)mineralisation processes of dental elements (*Green et al. 2017; Sui et al. 2018*). Moreover, synchrotron imaging provides information on trace and major element concentration without preparation of samples (*Dean et al. 2019; Gherase & Fleming 2019*). This type of imaging can therefore provide new insights in the life history, growth, diet of an individual, particularly in cases where preservation of samples is essential due to their limited availability. Integrating imaging and isotopic variation studies (intra- and interdental element), will improve our understanding of how the enamel mineralisation process controls the isotopic variation in dental elements.

8.2 Isotopic variation and background data

Isotopic variation within individuals and populations remain an important parameter within the field of isotope biochemistry. It remains important to quantify the degree of isotopic variability resulting from human variation versus the degree of variation resulting from different environmental and geographical settings.

In archaeological studies the degree of typical isotopic variation within the enamel of a single individual (between different dental elements or interdental variation) and dental isotopic variation within populations has been better characterised than in modern populations (*Alt et al. 2013; Brandt et al. 2014; Chenery et al. 2011; Cook & Price 2015; Eerkens et al. 2014; Eerkens, Carlson et al. 2016; Eerkens, Sullivan et al. 2016; Evans et al. 2012; Gregoricka 2014; Hakenbeck et al. 2017; Haverkort et al. 2010; Knipper et al. 2012, 2014, 2016, 2017, 2018; Kootker, Mbeki et al. 2016; Kutterer & Uerpmann 2017; Marsteller et al. 2017; Mbeki et al. 2017; Montgomery et al. 2000; Neil et al. 2016, 2017; Price et al. 2010, 2012; Schroeder et al. 2009; Sorrentino et al. 2018; Stojanowski & Knudson 2011, 2014; Thompson et al. 2015; Turner et al. 2012; Valentine et al. 2015; Weber & Goriunova 2013; Wright et al. 2010*), particularly for carbon and nitrogen isotope results obtained from incremental dentine samples (*Beaumont et al. 2013, 2015; Beaumont & Montgomery 2016; Burt 2015; Eerkens et al. 2011; Eerkens, Sullivan et al. 2016; Fuller et al. 2003*). Nevertheless, previous studies have not explored multiloci analysis on the enamel from a single dental element as the isotopic signal of enamel is assumed to represent an average isotopic signature (see **Section 3.2.7**). For strontium, a minimum offset of ~0.00100 between different teeth is generally assumed to be indicative of migration (*Hrnčíř & Laffoon 2019; Knipper et al. 2014, 2018; Kootker, Mbeki et al. 2016; Price et al. 1998; Scheeres et al. 2013, 2014; Slater et al. 2014*). The estimations of the typical isotopic variation in oxygen in archaeological population ranges between 2-3 ‰ (*Lightfoot & O'Connell 2016; Wright 2013*). These estimations confirm the findings of **Chapter 6**, where the maximal differences in modern individuals from the Netherlands with sedentary residential histories range up to $^{87}Sr/^{86}Sr$ ~0.000200 and ~1.4 ‰ for $\delta^{18}O$ and $\delta^{13}C$. These large intraindividual and interindividual variations indicate that we need to be more conservative with interpretations of changes in location and diet. The use of conservative margins and larger local variation estimates is required, especially in cases where no bioavailable background values are available and where limited individuals are analysed for their dental isotopic composition. Multiloci analyses can help establish the isotopic variation within populations, which is likely to be context specific.

Our understanding of the causes of intraindividual and interindividual carbon and nitrogen isotope variation can potentially be improved through the application of compound specific analyses (*Bowes & Thorp 2015; Corr et al. 2005; Honch et al. 2012; Reitsema 2013*). Currently collagen is analysed in bulk, while it is made up out of a group of 20 amino acids that can be individually analysed for their isotopic composition. The traditional bulk analyses thus present an averaged signal of these amino acids (*Bowes & Thorp 2015; Corr et al. 2005; Montgomery & Jay 2013*). Compound specific carbon and nitrogen isotope analyses can provide more nuanced

information about the diet. The analysis of essential amino acids can provide more accurate information about the protein ingestion of an individual and may serve as a marine dietary indicator. This approach would be particularly applicable in arid and marine regions where $\delta^{15}N$ is influenced by factors other than just the trophic levels of the diet (*Bartelink et al. 2016; Bowes & Thorp 2015; Choy et al. 2010; Corr et al. 2005; Honch et al. 2012; Lee-Thorp 2008; Petzke et al. 2005, 2006; Reitsema 2013; Styring et al. 2010*). The analysis of nonessential amino acids may shed light on the effect of diseases or nutritional stress on the isotopic composition of human tissues (*Bartelink et al. 2016; Petzke et al. 2005, 2006; Reitsema 2013; Webb et al. 2015*).

The application of multi-isotopic approaches, additional isotopic systems (such as Nd, **Chapters 4** and **5**), compound-specific analyses, and intra/multi-tissue comparisons (such as **Chapter 6**), and the establishment of isotopic background data (**Chapter 7**), must be applied to a broad range of environments and populations in order to distinguish more quantitatively between dietary, physiological, environmental or other influences on the isotopic variation.

8.3 Findable, Accessible, Interoperable and Reusable (FAIR)

To improve the applicability of new isotopic research and conduct original research using previously published studies, all research outputs should be made more accessible and openly available. This should be done in accordance with the FAIR principles (Findable, Accessible, Interoperable and Reusable), which strive to stimulate reuse of existing research outputs. Most of the current literature is still published behind paywalls (where literature cannot be accessed unless a purchase is made or a subscription fee is paid) and research outputs are not always assigned a DOI (Digital Object Identifier, required to be Findable). This can make it difficult to find research outputs and paywalls restrict access to anyone that is not affiliated to an institution that has a deal or subscription with the journal (**Figure 8.1**).

Furthermore, these openly available publications should be accompanied with the full datasets upon which the conclusions are based upon. These datasets should be shared in a format that will make data understandable and easy to reuse (.xls and .csv instead of .pdf format). Making such datasets available will enable the creation and analysis of large datasets, which can be explored using meta-analysis, Bayesian models (such as FRUITS), GIS (*Britton 2017; Fernandes et al. 2014; Marroquin et al. 2017; Willmes et al. 2014*) and analyses using R and Python (*Willmes, Ransom et al. 2018*). The publication of such datasets is becoming increasingly more common

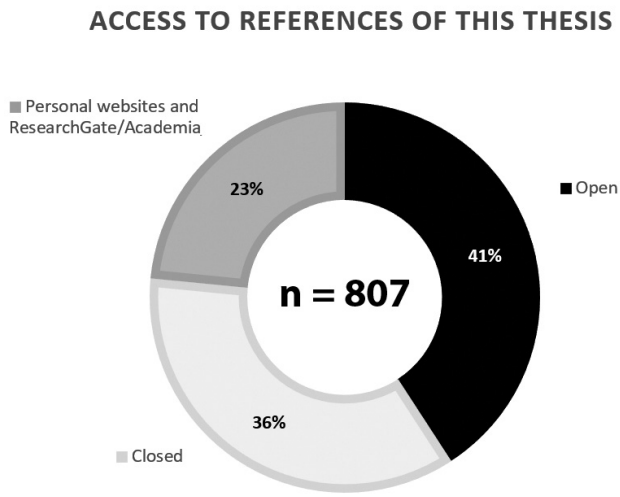

Figure 8.1 *Overview of the references used in this work (n = 807) and their availability. The majority of the literature used was either published open access or archived in an institutional or discipline specific repository (n = 332). Some of the literature is openly available using personal websites or commercial providers such as ResearchGate and Academia, which are not sustainable ways of providing access to these publications (n = 188). A limited amount of the works used here is restricted to anyone without institutional access (n = 287). The reference list in this work does not include any output to which there was no access, even with institutional privileges. (See https://doi.org/10.5281/zenodo.3929551 for the data.)*

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(*Britton 2017; Pauli et al. 2017*), but the practices in data reporting and documentation require improvement before composite datasets are created and direct sample comparisons are possible (*Ambrose 1990; Bartelink & Chesson 2019; Carter & Barwick 2011; Carter & Fry 2013; Chesson et al. 2019; Demény et al. 2019; Gentile et al. 2011; Hakenbeck 2013; Marroquin et al. 2017; Roberts et al. 2018; Stansbie & Mallet 2015; Szpak et al. 2017; van Klinken 1999*). To enable data compatibility between studies undertaken in different parts of the world and in different time periods, it is essential that analytical procedures become more transparent. Detailed information should be made available about the rationale behind sample selection, pre-treatment and sampling protocols, measurement procedures, standards and calibrations/calculation used, blank and interference corrections, and quantification of measurement accuracy and precision (*Bartelink & Chesson 2019; Bond & Hobson 2012; Carter & Fry 2013; Coelho et al. 2017; Coleman & Meier-Augenstein 2014; Coplen 2011; Demény et al. 2019; Dunn et al. 2015, 2017, 2018; Etu-Sihvola et al. 2019; Horsky et al. 2016; Irrgeher & Prohaska 2016; Killick 2015; Meier-Augenstein & Schimmelmann*

2019; Pestle et al. 2014; Pilaar Birch & Graham 2015; Roberts et al. 2018; Szpak et al. 2017; Willmes, Ransom et al. 2018). To evaluate the interoperability of results between different labs, repeated extraction and analysis of comparable human tissue samples with different sample matrixes (hair, bone, dentine and enamel) is required (*Chavagnac et al. 2007; Chesson et al. 2019; Demény et al. 2019; Dunn et al. 2017, 2018; Orlowski et al. 2018; Pestle et al. 2014; Roberts et al. 2018; Sealy et al. 2014; Wassenaar et al. 2018*). This will lead to standardisation of analysis protocols (*Demény et al. 2019; Dunn et al. 2015; Jørkov et al. 2007; Roberts et al. 2018; Szpak et al. 2017*) and requires the exchange of analytical protocols (for which online repository platforms such as Protocols.io can be used, e.g., *Plomp, Smeets et al.* (*2019, 2020*)). Transparent laboratory and measurement procedures, inter-lab interoperability and standardisation of practices will improve the reproducibility of isotopic research. Only after these practices have been improved can we adopt new approaches based on machine learning and create uniform isoscapes or reference data based on multiple different datasets (while still keeping in mind the limitations of each isotopic analysis, outlined in **Chapter 2**). An example of the combination of multiple datasets can be found in **Chapter 7**, which presents the results of four comparable datasets (equivalent time period and geographical context) that were all generated in the same lab over a short time period of ~five years (F*ont et al. 2015; Plomp, von Holstein et al. 2019, 2020; and Kootker et al. 2020*). The combination of multiple datasets will allow the exploration of different types of research questions, identify gaps in current knowledge (*Salesse et al. 2017*), and improve the robustness of interpretations of diet and mobility in human populations. This improved reproducibility and robustness of interpretations will also potentially increase the impact and importance of isotopic interpretations in forensic cases (*Chesson et al. 2019; Dunn et al. 2017; Ehleringer & Matheson 2010*).

Developments of online platforms that curate isotopic results are crucial to enable the creation and use of larger datasets. This is currently being led by IsoArch (www.isoarch.eu; *Salesse et al. 2017*), IsoMem (www.isomemo.com), Biosphere Isotope Domains (http://mapapps.bgs.ac.uk/biosphereisotopedomains; *Evans et al. 2010*), and IsoMAP (https://isomap.rcac.purdue.edu/isomap/). Other initiatives are a future IsoBank (*Pauli et al. 2017; Pilaar Birch & Graham 2015*), Isotopic Reconstruction of Human Migration (IRHUM; *Willmes et al. 2014*), dIANA (https://www.oasisnorth.org/diana.html; *Etu-Sihvola et al. 2019*), and ISO-FOOD (http://isofood.eu/). Radiocarbon databases are more common: 14SEA – (www.14sea.org/), Radiocarbon Palaeolithic Europe Database – (https://ees.kuleuven.be/geography/projects/14c-palaeolithic/), KIK-IRPA (*Van Strydonck & De Roock 2011*), RADON (http://radon-b.ufg.uni-kiel.de/), and CARD (https://www.canadianarchaeology.ca/).

Data repositories for archaeological data include NARCIS (https://www.narcis.nl/), DANS-EASY (https://easy.dans.knaw.nl/), Open Context (https://opencontext.org/), and Archaeological Data Services (https://archaeologydataservice.ac.uk/), as well as the Qualitative Data Repository (QDR - https://qdr.syr.edu/). There is an established repository for ancient mitochondrial sequences (Ancient mtDNA - https://amtdb.org/). More general purpose repositories where data could be shared include Zenodo (https://zenodo.org/), Figshare (https://figshare.com/), Dataverse (https://dataverse.org) and the Open Science Framework (https://osf.io/).

Most of the isotopic datasets are currently published in peer reviewed journals or in the grey/unpublished literature, and are thus not very well known as there are no communication strategies in place to reach the broader isotopic community. In addition to limited awareness about these datasets, maintaining databases is time consuming and costly. For these platforms and repositories to be sustainable, the management and costs will have to be addressed in a transparent way by the research community (*Britton 2017; Pauli et al. 2017*). Furthermore, the data must be FAIR (*Eftimov et al. 2019; Pauli et al. 2017; Roberts et al. 2018*), which is currently not always the case. Most of the datasets and databases use their own documentation systems, complicating comparison between datasets and reducing their interoperability and routine use (*Eftimov et al. 2019*). In order for datasets to become more FAIR, they must be accompanied with a persistent identifier (DOI), sufficient metadata (creator, date, methods, standards, accuracy and precision), and metadata standards (such as the FDI World Dental Federation notation, or ISO3950). The assignment of persistent identifiers to isotope labs (Research Organization Registry (ROR) - https://ror.org/) and measurement equipment (see ongoing developments by the Research Data Alliance; https://www.rd-alliance.org/groups/persistent-identification-instruments-wg), would further improve the reusability of isotopic data.

The adoption of common terminology and ontologies (*Eftimov et al. 2019; Roberts et al. 2018*), **Figure 8.2**), will further increase the interoperability and reusability of the data. As common terminology and ontology will need to be established and employed by the community, efforts will need to be undertaken to organise the different sub-groups within diverse field of isotope geochemistry.

To ensure that data are reusable, our data collection, analyses and reporting will have to become increasingly standardised. Using software to process data will speed up the process compared to manual analysis (*Mânica et al. 2018; Marroquin et al. 2017; Marwick et al. 2020*) and improve reproducibility of analyses as it minimises error associated with the observer or

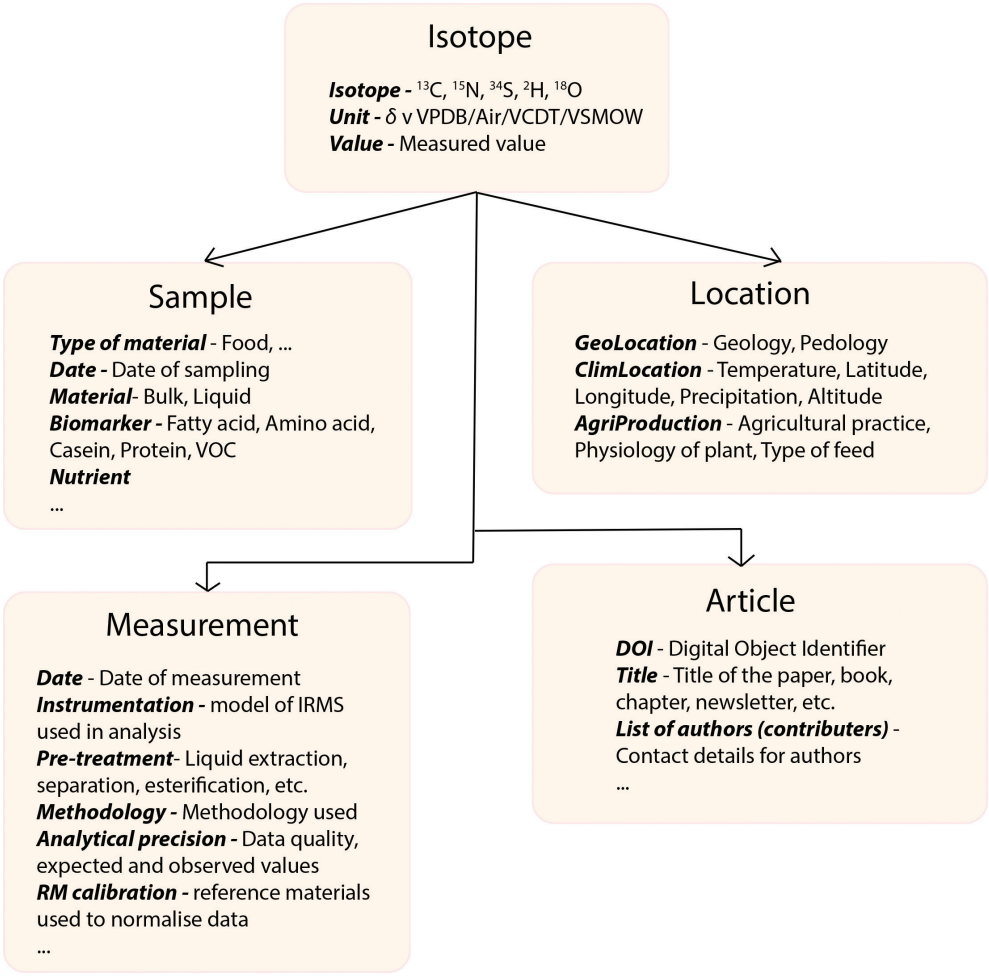

Figure 8.2 *Outline of the ISO-FOOD ontology by Eftimov et al. (2019). An ontology is a formal specification to organise knowledge (in a machine-readable manner). It contains a set of concepts and relationships between that connect them.*

analyst (*Beck & Smith 2019; Ma & Bowen 2019; Mânica et al. 2018; Marroquin et al. 2017; Willmes, Ransom et al. 2018; Wilson et al. 2017*). Software can also be used to make publications more reproducible: by defining the parameters of our hypotheses clearly, in a machine readable way (*Lakens & DeBruine 2020*), it becomes easier to interpret the results of the publication and build upon previous research.

8.4 Future Research Directions

New developments in the field of bioengineering may have an impact on the application of forensic isotopic analysis. By inducing artificial enamel mineralisation using modified calcium phosphate ion clusters, teeth affected by caries or wear are able to repair themselves in a way where the morphological structure is indistinguishable from the original enamel (*Shao et al. 2019*). While these artificial remineralisation techniques are beneficial for the dental health of individuals (*Moradian-Oldak 2012*), they have the potential to overwrite original isotopic signatures in the enamel. Another modern influence on the isotopic composition are fillings or restorative elements (*Curzon & Cutress 1983; Jaouen et al. 2017*). This is currently preventing the sampling of restored dental elements, which can complicate the sample selection for isotopic analyses in forensic cases. The effect that these restorations have on the isotopic variation of the dental element need to be properly addressed in order to potentially enable isotopic analysis of unaffected areas of restored dental elements.

The potential information recorded by additional isotopes remains to be explored in detail. Calcium, lithium, hydrogen, copper and zinc show potential for dietary applications and the study of weaning (*Balter & Vigier 2014; Britton 2017; Jaouen et al. 2016, 2017; Jaouen & Pons 2017; Lee-Thorp 2008; Tacail et al. 2017; 2019; van der Sluis et al. 2015*). Cadmium may shed light on dietary patterns or smoking behaviour of individuals (*Irrgeher & Prohaska 2016; Scott et al. 2019*). Vanadium has recently been shown to vary in river waters (*Schuth et al. 2019*), which could hold potential for its use as a human provenance indicator similar to oxygen and hydrogen (*Warner et al. 2018*). It should be noted that vanadium isotopes are, like neodymium isotopes, only present in low concentrations in the food chain as well as in human teeth (<1 ppm) (*Curzon 1983; Golden & Golden 1981*). The increasing adoption of Pb isotope analysis can also continue to provide information on the life history and mobility patterns of human individuals (*Evans et al. 2018; Kamenov et al. 2018; Kamenov & Curtis 2017; Laffoon et al. 2020; Sharpe et al. 2018*).

While osteocalcin is unsuitable for isotopic analysis due to diagenesis, the search for additional human tissues that can be reliably analysed for their isotopic composition continues. The potential of petrous bone to preserve biogenetic isotopic signals (*Harvig et al. 2014; Kontopoulos et al. 2019*) should be established, and the Sr isotope analysis of cremated remains opens up new research where the availability of dental material is limited (*Snoeck et al. 2016, 2018*).

8.5 Conclusion / Summary

This research was conducted as part of the international research project NEXUS1492 which studied the impacts of the colonial encounters in the Caribbean. As part of the second project that focused on the development and application of biogeochemical methods to address human mobility, this work combined the exploration of a new isotopic technique (Nd isotope analysis) and evaluated already established methods (Sr, O, C isotope analysis).

This work successfully applied Nd isotope analysis to human dental enamel. This required a modified chemical chromatographic separation procedure that allowed the processing of large samples while keeping the blank as low as possible due to small Nd concentrations in dental enamel (0.1 – 21.0 ppb). This work indicated that Nd isotope can provide additional information on mobility, potentially addressing the limitations associated with other isotopic provenancing techniques (Sr, Pb, O, H). Successful analyses required >100 pg of Nd which limits the applicability of the technique as this amount of Nd is not always present in dental elements. Furthermore, while the majority of human enamel is indistinguishable from the geological location in which the enamel was formed, Nd isotope composition in dental enamel did not always correspond to expectations based on the geological locations. Further research is needed to understand Nd cycling in the environment and human tissues, and the variation of Nd in dental tissues needs to be evaluated by analysing dental elements from various geological contexts. Technical developments resulting in improved sensitive of measurements may make this technique more applicable to forensic and archaeological studies and open up new opportunities to study the past. The addition of Nd to the human provenancing repertoire would be of particular use in the Caribbean, where mobility patterns in individuals from coastal areas could be more reliably assessed. This is due to the differential characteristics of the Nd isotope system compared to other isotope systems as strontium and oxygen. Compared to strontium, the Nd isotope composition in coastal environments is not affected by sea spray and thus reflecting the isotopic variation of the local geology rather than the sea. Unlike oxygen isotopes, which have similar values in coastal regions, Nd isotopes are more likely to discern differences between various coastal environments. This improved spatial resolution could thus contribute to better understanding of past human mobility patterns in the Caribbean.

To increase the robustness of archaeological and forensic interpretations based on isotopic analyses, it is crucial that isotopic variability within a single dental element (intradental), between multiple dental elements of the same individual (interdental) and populational

isotopic variability is quantified. This work established that a single sample location is not representative for the total dental enamel Sr, O and C isotope variation. Enamel samples should be taken from the inner enamel, with no preference for a particular region as lateral and cuspal enamel are expected to provide comparable results. This research indicated that carious enamel should be avoided for sampling as this produced inconsistent isotopic data. This work highlighted that for modern Dutch individuals Sr isotope variation > 0.0002 is required to argue for mobility and differences under 2 ‰ are negligible for $\delta^{18}O$ and $\delta^{13}C$. To quantify the isotopic (intraindividual) variability in other modern and archaeological populations from geologically more complex regions than the Netherlands, studies will need to analyse multiple samples of the same dental element. More work is needed on dental elements other than third molars, and on the isotopic composition of enamel affected by caries. This will result in more robust interpretations of diet and mobility in archaeological and forensic studies. For the Caribbean, improving the robustness of isotopic techniques provides a more detailed characterisation of mobility and dietary patterns in Amerindian populations allowing for enhanced reconstructions of the impact of the interactions with European and African populations after 1492.

Reference materials, also known as isotopic baselines or isoscapes, are needed to interpret the results from isotopic analyses of human tissues. It is essential that these reference materials, such as the local geology, tap water, and dietary resources, are correlated to human tissue values. For modern globalised societies the preferred reference materials are human tissues, as the isotopic values of modern human tissues may become incompatible with from those of the local environment and geology due to increasing globalisation. In the Caribbean the archaeological isotopic variation across the islands has been well established. To be able to apply isotopic techniques in forensic cases in the Caribbean area, however, modern baselines or isoscapes should first be established.

Isotope research should always be performed complementary to other analyses and not be taken lightly as the destruction of the tooth enamel can impair other analyses (wear, aging, DNA, metrics, etc.) or future techniques that are still being developed. Furthermore, the teeth derived from an individual come from a specific archaeological or forensic context, and isotopic results should be interpreted within that local framework. This becomes particularly important in the data driven age, where multiple datasets are combined in order to address new research questions. Improving the standardisation and transparency of analytical procedures in isotopic research will result in more interoperability and optimisation of techniques between labs. Combining isotopic data from different labs and complementing this with the information

from other techniques and analyses will allow the field to address research questions on a new scale, further unlocking the potential information that human teeth contain.

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Nederlandse samenvatting

Tanden ontsloten

Ontwikkeling en toepassing van isotopenanalyses voor onderzoek naar de herkomst van mensen

Hoofdstuk 1: Introductie

Dit onderzoek maakt onderdeel uit van een groot internationaal onderzoeksproject: NEXUS1492. Het NEXUS1492 project onderzocht de impact van de interacties tussen Amerindianen, Europeanen en Afrikanen in de tijd van Columbus. Lang werd gedacht dat de inheemse samenlevingen vrij snel verdwenen nadat Columbus in 1492 de Caraïben 'ontdekte'. Met het NEXUS1492 project is de kant van het verhaal van de inheemse samenlevingen beter belicht door technieken van verschillende onderzoeksdisciplines te combineren om zo tot een betere reconstructie van het verleden te komen. Onderzoekers van drie universiteiten (Universiteit Leiden, Vrije Universiteit Amsterdam en Universiteit Konstanz) en verschillende onderzoeksvelden (archeologie, antropologie, bioarcheologie, genetica, fysische geografie, computerwetenschappen, bio- en geochemie en erfgoedstudies) kwamen bij elkaar en hebben het bedreigde erfgoed van de Caraïben beter in kaart gebracht. De Caraïbische archeologie wordt bedreigd door natuurrampen (klimaatverandering, stijgende zeespiegel, aardbevingen, vulkanen en orkanen), plunderaars die erfgoed illegaal verhandelen en bouwprojecten. Om verdere vernietiging van het archeologisch bodemarchief te voorkomen moet het verleden van het Caraïbisch gebied op de erfgoedagenda worden geplaatst om zo het bewustzijn voor dit erfgoed te vergroten. NEXUS1492 heeft hieraan bijgedragen door de lokale Caraïbische experts en bevolking van de eilanden te betrekken bij het onderzoek en bij het opzetten van duurzaam erfgoedbeheer.

Isotopenanalyses van menselijke tanden

Dit onderzoek richt zich specifiek op de ontwikkeling en toepassing van biogeochemische methoden, ook wel isotopenanalyses genoemd. Isotopenanalyses van menselijke weefsels kunnen inzicht geven over drie aspecten van menselijk gedrag: (1) wat de persoon consumeerde; (2) mobiliteitspatronen; en (3) hoe oud de menselijke resten zijn. Isotopenanalyses zijn een uniek hulpmiddel voor het bestuderen van individueel menselijk gedrag. Archeologische interpretaties zijn vaak gebaseerd op analyses van de groep in plaats van het individu, omdat het archeologisch bodemarchief gefragmenteerd is. In forensische zaken kunnen isotopenanalyses bijdragen aan de identificatie van een lijk. De toepassing van forensische isotopenanalyses geeft bijvoorbeeld informatie over potentiële herkomstregio's, dieet, geboortejaar en tijdstip van overlijden, of diagnoses van overlijden door verdrinking.
Ondanks het toenemende gebruik van isotopenanalyses in archeologisch en forensisch onderzoek zijn er nog wel onzekerheden en grenzen in de toepasbaarheid van deze technieken.

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(1) Er is niet altijd (voldoende) materiaal beschikbaar voor isotopenonderzoek. Als materiaal niet bemonsterd kan worden, omdat het niet aanwezig is of beïnvloed is door diagenese (veranderingen in de fysische en/of chemische samenstelling van het materiaal), kunnen isotopenanalyses niet worden toegepast. Dit is met name een probleem in archeologisch onderzoek.

(2) De resolutie van isotopendata is vaak niet gedetailleerd genoeg. Er kan geen onderscheid gemaakt worden in diëten die op elkaar lijken, of geografische omgevingen die vergelijkbaar zijn. Wat betreft dieet kan er vaak alleen een schatting gemaakt worden van het soort voedsel wat geconsumeerd is, zoals maritiem of verbouwd voedsel, plantaardig of dierlijke eiwitten. Tevens kan er onderscheid gemaakt worden tussen bepaalde planten. Zo heeft mais bijvoorbeeld een ander isotoopsignaal dan tarwe.

(3) Import van voedsel uit andere omgevingen kan een effect hebben op de isotopenwaarden van de mens: als dit voedsel uit een omgeving komt met een ander isotopensignaal kan het erop lijken dat de mens is verplaatst.

(4) Alhoewel isotopenanalyses een generiek beeld kunnen geven over wat mensen eten en waar zij vandaan komen, geven de analyses zelf geen informatie over welke sociaal-politieke factoren een rol spelen in toegang tot eten, of de redenen voor migratie.

(5) Om te bepalen of er een verandering in het dieet of in de locatie van mensen heeft plaatsgevonden is er data nodig over de isotopenwaarden van dit dieet en de omgeving. Zo zal er eerst een 'lokaal' signaal vastgesteld moeten worden. Daarna kan het isotoopsignaal van het menselijk weefsel hiermee worden vergeleken en dan kan er worden vastgesteld of iemand lokaal is of niet. Deze achtergronddata zijn niet altijd beschikbaar vanwege gebrekkige preservatie van archeologisch materiaal of beperkte (financiële) middelen. Daarnaast wordt niet altijd het meest geschikte materiaal gebruikt om dit lokale signaal te construeren. Zo heeft eerder onderzoek vaak de isotopenresultaten van de lokale geologie of planten gebruikt voor de reconstructie van het lokale signaal. Maar de isotopenwaarden van de lokale geologie en planten hoeven niet altijd direct gerelateerd te zijn aan die van mensen. Isotopen in menselijk weefsel worden namelijk niet direct opgenomen uit de grond. Ook is het de vraag hoe vergelijkbaar data van planten en mensen zijn als de geanalyseerde planten niet geconsumeerd werden door de mens.

(6) Op dit moment is de verwachtte isotopenvariatie in menselijk weefsel nog niet goed in kaart gebracht. Zo is het onduidelijk of een verschil in isotopenwaarden het resultaat is van een verandering in dieet of locatie, of het wordt bepaald door een verschil in menselijk weefsel (als bot vergeleken wordt met een tand) of door biologische variatie (als er verschillende waarden aangetroffen worden in hetzelfde bot of tand). Het is daarom vaak onduidelijk hoeveel variatie

in de isotopenwaarden genoeg zou zijn om een verandering in dieet of locatie aan te kunnen tonen.
(7) De isotopendata die gegenereerd worden door verschillende laboratoria zijn niet altijd direct vergelijkbaar. Dit komt omdat er verschillen zijn in de uitvoering en toepassing van isotopen technieken binnen deze laboratoria.

Om een aantal van deze genoemde beperkingen te adresseren is er in dit proefschrift gekeken naar de ontwikkeling van een nieuwe isotopentechniek (neodymium) om aanvullende informatie te verkrijgen over de geografische oorsprong van individuen. De toepassing van meerdere isotopentechnieken geeft meer informatie over het dieet of de locatie van een individu, omdat de informatie per isotoopsysteem verschilt. Zuurstofisotopen geven bijvoorbeeld een indicatie waar het water vandaan komt wat een individu drinkt. Strontiumisotopen zijn afhankelijk van de geologie in plaats van het drinkwater en geven daardoor een ander beeld, namelijk over waar het eten wat een individu consumeert vandaan komt. Een combinatie van de technieken geeft daarom een gedetailleerder beeld over de isotopen in menselijk weefsel en over de leefomgeving van een individu. In dit proefschrift werd gekeken of neodymiumisotopen in tanden informatie toe kunnen voegen over de geografische locatie van mensen (zie **Hoofdstukken 4** en **5**).

Ook zijn bestaande isotopentechnieken (strontium, zuurstof, koolstof) nader onderzocht om de toepassingen hiervan te verbeteren. Zo is er bijvoorbeeld gekeken naar de variatie in de isotopenwaarden van mensen die niet van dieet of locatie zijn veranderd. Dit is gedaan door verschillende stukken tand te bemonsteren en zo te kijken of er een verschil zichtbaar is tussen de isotopenwaarden van deze monsters (zie **Hoofdstuk 6**). Ook is er gekeken naar het verband tussen de isotopenwaarden van kraanwater en van menselijke tanden (zie **Hoofdstuk 7**). Voor dit onderzoek werden de verstandskiezen van mensen die geboren en getogen waren in Nederland onderzocht.

Hoofdstuk 2: Isotopenanalyses

Isotopenanalyses worden sinds de jaren zeventig gebruikt om menselijke mobiliteit en dieet in archeologische samenlevingen te bestuderen. De toepassing van isotopenanalyses in forensische zaken begon later, namelijk rond 2000.

Isotoop, afgeleid van de Griekse woorden *isos* (zelfde) en *topos* (plaats), is een woord dat bedacht werd door Margaret Todd in 1912. Isotopen bestaan uit neutronen en protonen, de bouwstenen van atomen (de kleinste eenheden van een chemisch element). Isotopen hebben hetzelfde aantal protonen en behoren derhalve tot hetzelfde chemische element, maar kunnen een verschillend aantal neutronen in hun kern hebben. Strontium (Sr) isotopen ^{87}Sr en ^{86}Sr hebben bijvoorbeeld beide 38 protonen (en alle atomen met 38 protonen zijn altijd Sr-atomen), maar ^{87}Sr heeft 49 neutronen en ^{86}Sr heeft 48 neutronen. De atoommassa (de optelling van het totaal aantal protonen en neutronen) varieert dus aan de hand van het aantal neutronen.

Dit massaverschil resulteert in kleine variaties die leiden tot verschillende reactiesnelheden in chemische en biologische processen. Zwaardere isotopen reageren langzamer dan lichtere isotopen. Als de verhouding in isotopen verandert tijdens processen, wordt dit fractionering genoemd. Doordat lichtere isotopen, zoals zuurstof ($^{16,18}O$) en koolstof ($^{12,13}C$), sneller opgenomen kunnen worden tijdens biologische processen, zijn deze lichtere isotoopsystemen eerder onderhevig aan fractionering dan zwaardere isotopen. Zwaardere isotoopsystemen, zoals strontium ($^{86,87}Sr$) en neodymium ($^{143,144}Nd$), worden niet zo gemakkelijk gefractioneerd tijdens biologische processen. Zo is ^{13}C is bijvoorbeeld 7,7% zwaarder dan ^{12}C, terwijl ^{87}Sr slechts 1,2% zwaarder is dan ^{86}Sr en ^{144}Nd is slechts 0,7% zwaarder dan ^{143}Nd. Hoe groter het verschil in gewicht, hoe groter het effect van fractionering.

Isotopen kunnen stabiel zijn ($^{16,18}O$, $^{12,13}C$, ^{86}Sr, ^{144}Nd), radiogeen (^{87}Sr, ^{143}Nd) of radioactief (^{14}C, ^{90}Sr). De verhoudingen van stabiele isotopen veranderen niet in de loop van de tijd, terwijl radiogeen en radioactieve isotopen afnemen of vervallen gedurende voorspelbare perioden omdat de halveringstijd van de radioactieve isotopen bekend is.

Planten nemen de isotopensamenstelling op van de grond en het water van de omgeving waarin zij groeien en de koolstofdioxide (CO_2) uit de atmosfeer. De isotopenwaarden van planten wordt doorgegeven aan dieren via het dieet, drinkwater en de lucht die het dier inademt. De isotopen in het menselijk lichaam zijn afkomstig van het eten van deze planten

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en dieren, drinkwater en de lucht die wordt ingeademd. Hierdoor worden de isotopen in de tanden van een persoon bepaald door de chemische samenstelling van de geografische en klimatologische omgeving waarin een persoon leeft. Hierdoor zeggen de isotopen in menselijk weefsel, zoals haar, bot, nagels en tanden (zie **Hoofstuk 3**) wat over de woonplaats, migratie- en voedingspatronen van mensen.

De verschillende isotoopsystemen vertegenwoordigen verschillende aspecten van de omgeving waarin individuen leefden. De samenstelling van de zuurstofisotoop is voornamelijk afhankelijk van drinkwater. Hierdoor kunnen zuurstofisotopen gebruikt worden als herkomstindicator, omdat de zuurstofisotoopsamenstelling van drinkwater verandert naarmate een omgeving verder is verwijderd van de evenaar en/of zee en daarnaast afhankelijk is van de hoogteligging van een gebied. Strontiumisotopen geven ook informatie over de locatie van een individu, omdat de samenstelling van strontiumisotopen voornamelijk wordt bepaald door de geologie waarin het geconsumeerde voedsel werd verbouwd. Strontiumisotopenwaarden in kustgebieden worden echter beïnvloed door de isotopenwaarden van zeewater in plaats van de lokale geologie. Koolstofisotopen geven informatie over het type planten en dieren dat door een individu werd geconsumeerd en worden daarom hoofdzakelijk als dieetindicator gebruikt. De gecombineerde analyse van meerdere isotopensystemen levert daarom betrouwbaardere gegevens op, omdat elk isotoopsysteem verschillende aspecten van menselijk gedrag belicht. In dit proefschrift wordt daarom gekeken of een nieuw isotoopsysteem, neodymium, gebruikt zou kunnen worden als herkomstindicator om zo nieuwe informatie toe te voegen aan al bestaande isotooptechnieken (zie **Hoofdstukken 4** en **5**). Ook worden bestaande isotooptechnieken kritisch geëvalueerd, door te kijken naar de isotopenvariatie van strontium, zuurstof en koolstof in tandglazuur. Dit werd gedaan door meerdere monsters te nemen van het glazuur van dezelfde kies (zie **Hoofdstuk 6**). Zowel de toevoeging van informatie van nieuwe isotoopsystemen als de verbetering van de toepassing van bestaande isotopentechnieken zorgt ervoor dat de interpretaties die gebaseerd zijn op deze technieken verfijnd kunnen worden.

Hoofdstuk 3: Menselijke weefsels voor isotopenanalyses

Isotopenanalyses kunnen worden toegepast op menselijke weefsels om informatie te verkrijgen over de mobiliteit en het dieet van een persoon tijdens verschillende periodes in het leven van een individu. De analyse van tandglazuur geeft inzicht in de kindertijd, omdat de tanden groeien tijdens deze periode en vervolgens niet meer veranderen. Omdat bot zich constant vernieuwt, geven isotopenanalyses van bot informatie over een langere periode. De duur van deze periode verschilt per botelement: zo worden de ribben over een kortere periode vernieuwd dan de schedel of beenderen. Als de ribben geanalyseerd worden, geeft dit informatie over ongeveer de laatste 10 jaar van het leven van een individu, terwijl dit voor de schedel ongeveer 50 jaar is. Een isotopenanalyse van het haar geeft informatie over de laatste maanden of jaren van een individu afhankelijk van de lengte van het haar. Hoewel haar een belangrijk weefsel is in forensische zaken, blijft het helaas minder goed bewaard in het archeologische bodemarchief, omdat haar een zacht en poreus weefsel is. Daarom ligt de nadruk van dit proefschrift op het tandglazuur, de "diamant" van het menselijk lichaam. Tandglazuur is een menselijk weefsel wat goed bestand is tegen diagenese (fysieke of chemische aantasting), omdat glazuur het hardste menselijke weefsel is. Tandglazuur wordt daarom met name in de archeologie veel gebruikt voor isotopenanalyses.

Tanden kunnen geanalyseerd worden voor de isotopensamenstelling, maar worden ook voor andere doeleinden gebruikt binnen de biologische antropologie en forensische geneeskunde. Zo kunnen de vorm, volgorde en snelheid van de ontwikkeling van tanden inzicht geven over het geslacht van een individu, de leeftijd, gezondheid, dieet en afkomst.

Mensen hebben twee gebitten (ook wel diphyodont genoemd). Het melkgebit wordt gevormd in de baarmoeder (vanaf ongeveer 14 weken) tot ongeveer een jaar na de geboorte. Dit melkgebit wordt tijdens de eerste levensjaren vervangen door het permanente gebit. Elke tand (voortanden en hoektanden) of kies (achterste tanden) bestaat uit een kroon en een wortel (zie **Figuur 3.2**). De buitenste laag van de kroon heet het tandglazuur, wat een zachtere binnenlaag bedekt dat dentine wordt genoemd. Omdat deze laag glazuur niet verandert nadat het gevormd is, blijft de isotopensamenstelling van de kinderjaren bewaard. Gezien verschillende tanden over andere jaren ontwikkelen (zie **Tabel 3.2**, en **Figuren 3.3** en **3.4**, pagina's 46-47) is het mogelijk om meerdere tanden te analyseren van één individu om zo een beeld te krijgen over bepaalde periodes in de kindertijd.

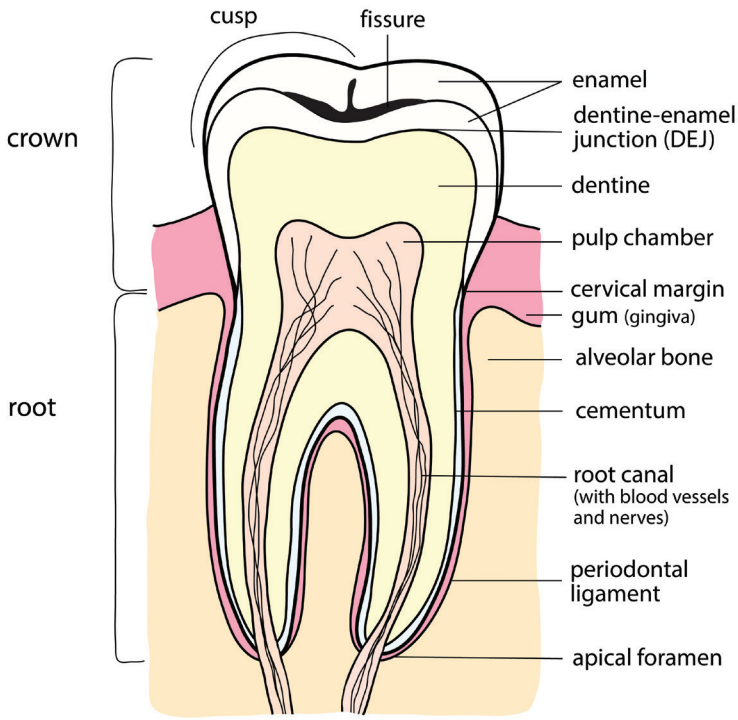
De analyses van dit proefschrift zijn gedaan op verstandskiezen, gedoneerd door mensen na extractie tussen de jaren 2011-2016. Deze verstandskiezen zijn geschikt voor isotopenanalyses omdat zij preventief getrokken kunnen worden, waardoor de kies vaak nog gezond is (in tegen stelling tot andere getrokken tanden). Verstandskiezen zijn anders dan andere tanden en kiezen van het gebit, omdat er veel variatie zit in de grootte, ontwikkeling en het doorkomen van de tanden. Zo ontwikkelen verstandskiezen zich niet altijd of zijn ze misvormd. De verstandskiezen in de bovenkaak worden meestal eerder gevormd dan de verstandskiezen in de onderkaak. Er lijkt geen verschil te zijn tussen de linker- en rechterkant van het gebit in de ontwikkeling van verstandskiezen. Wel vindt de ontwikkeling van verstandskiezen eerder plaats bij jongens dan bij meisjes (in tegenstelling tot de ontwikkeling van de rest van het gebit).

De vorming van tandglazuur is een complex proces wat bestaat uit verschillende fases. In de eerste fase vindt de eerste vorming van het glazuur plaats binnen in de tand, bovenop de laag dentine. Vervolgens breidt het glazuur zich uit in lagen die zich langzaam opstapelen in een patroon. Dit patroon zorgt ervoor dat het glazuur later resistent is voor de druk die het ondergaat tijdens het kauwen. De aanleg van de lagen glazuur vindt plaats in een regelmatige tijdsperiode, waardoor deze lagen gebruikt kunnen worden om naar de tijdsduur van glazuurvorming te kijken en naar de leeftijd van de eigenaar van de tand. Het glazuur verhardt zich pas tijdens de laatste fase van het vormingsproces. Aan het einde van dit verhardingsproces, ook wel mineralisering genoemd, wordt er geen nieuw glazuur meer aangemaakt.

Tijdens de vorming van glazuur kunnen er defecten ontstaan door verstoring in de groei of door tekorten in het dieet. Ook kan na de vorming het glazuur aangetast worden door de vorming van gaatjes of cariës. Cariës zorgen voor de geleidelijke demineralisatie van het glazuur. Dit proces wordt vooral veroorzaakt door de zuren die worden gevormd tijdens de fermentatie van koolhydraten, voornamelijk suikers, door de bacteriën in de mond. Het proces van demineralisatie kan gestopt worden en soms treedt er ook re-mineralisatie op. Of cariës verder ontwikkelen hangt af van vele factoren en het effect wat cariës hebben op de isotoopsamenstelling van glazuur is momenteel nog niet goed onderzocht (zie **Hoofstuk 6**).

Omdat de vorming van tandglazuur een ingewikkeld proces is, is het momenteel niet duidelijk hoe isotopen in glazuur worden geïncorporeerd. Worden de isotopen op dezelfde manier opgenomen als de opbouw van het glazuur zelf, waarbij er onderscheid gemaakt kan

worden tussen verschillende lagen? Is er een discrepantie in de opbouw van het glazuur en de incorporatie van de isotopen, waardoor de glazuurlagen en de isotopenwaarden verschillende tijdsperiodes representeren? Of worden de isotopen pas helemaal aan het einde, tijdens het mineralisatieproces, vastgelegd in het glazuur? Omdat dit momenteel nog niet goed wetenschappelijk onderzocht is, weten we niet exact welke tijdsperiode de monsters voor isotopenanalyses representeren en of het mogelijk is om informatie over meerdere tijdsperiodes te verkrijgen vanuit één tand. Als de isotopen voornamelijk tijdens het mineralisatieproces vastgelegd worden in het glazuur - iets waar de meeste onderzoekers momenteel vanuit gaan - zou de gehele glazuurlaag ongeveer dezelfde isotopenwaarden moeten hebben. Daarom richten de meeste isotopenstudies zich op het bemonsteren van één locatie van de tand. De resultaten van deze bemonsteringslocaties worden gezien als representatief voor de gehele tijdsperiode waarin de tand zich heeft gevormd. **Hoofdstuk 6** onderzoekt of dit daadwerkelijk het geval is, maar eerst wordt de gehele glazuurlaag geanalyseerd voor neodymiumisotopen in **Hoofdstukken 4** en **5**.



Figuur 3.2 *Schematische tekening van een kies.*

NL

Hoofdstuk 4: Neodymiumisotopen in menselijke tanden

De analyse van een nieuw isotoopsysteem, neodymiumisotopen ($^{143}Nd/^{144}Nd$), zou nieuwe informatie kunnen geven over de mobiliteit van mensen in archeologische en forensische studies. Neodymium zou hiervoor een geschikt isotoopsysteem kunnen zijn, omdat neodymiumisotopen zich conservatief gedragen of onveranderd blijven in chemische en biologische processen dankzij de zware massa. Hierdoor geven neodymiumisotopen een betere weerspiegeling van de geologische ondergrond dan strontiumisotopen. Dit is met name een voordeel in kustgebieden - zoals grote delen van het Caraïbisch gebied - waar strontiumisotopen beïnvloed worden door de strontiumwaarden van de oceaan.

De analyse van neodymiumisotopen werd nog niet toegepast op menselijke weefsels, omdat de concentratie van neodymiumisotopen in het menselijk lichaam heel laag is. Dit is vanwege de lage neodymiumisotopenconcentratie in het dieet van de mens. Planten nemen neodymiumisotopen uit de grond slecht op, waardoor de hoeveelheid neodymiumisotopen in de voedselketen laag blijft. Naast opname via het dieet kunnen neodymiumisotopen ook ingeademd worden of via de huid het lichaam binnentreden. Zo werden verhoogde concentraties aangetroffen in menselijk weefsel van mensen die in contact waren geweest met neodymium zoals mijnwerkers. Neodymium vervult geen functie in het menselijk lichaam en kan in grote hoeveelheden zelfs giftig zijn, waardoor het slecht wordt opgenomen. De kleine hoeveelheden neodymiumisotopen in menselijke weefsels bemoeilijkt de analyse, waardoor er nog weinig bekend is over hoe neodymiumisotopen zich gedragen in het biologische systeem van de mens. Dit proefschrift is het eerste werk wat naar de neodymiumisotopenratio's ($^{143}Nd/^{144}Nd$) van meerdere individuen heeft gekeken.

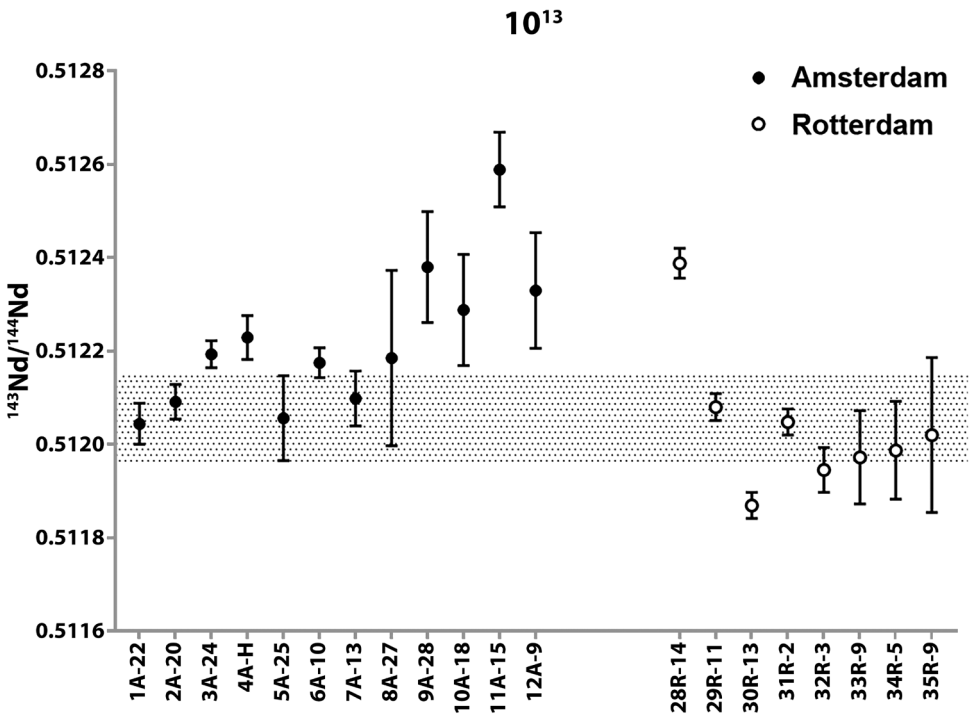
Voor de isotopenanalyse van strontium, zuurstof en koolstof is het gebruikelijk om een klein beetje glazuur van de tand te bemonsteren met behulp van een micro Dremel boor. Voor de analyse van neodymiumisotopen is echter de gehele laag glazuur van de tand nodig, omdat er anders niet genoeg neodymium beschikbaar is voor de meting. Om deze grote hoeveelheid glazuur te verwerken (voordat het klaar is voor de analyse) moesten bestaande labprocedures voor neodymiumisotopenextractie worden aangepast.

Voor zowel strontium- als neodymiumisotopenanalyse moeten de isotopen uit het bemonsterde glazuur geïsoleerd worden. Dit gebeurt door een kolomprocedure in het lab. Daarvoor moet het bemonsterde glazuur opgelost worden in zuur, waarna het vloeibare

monster op een kolom wordt overgebracht. Met behulp van deze kolomprocedure worden de chemische elementen van elkaar gescheiden. Alleen het neodymium (of strontium) wordt opgevangen aan het einde van de kolomprocedure. Door het scheiden van de elementen kan de geselecteerde isotoop geanalyseerd worden zonder interferenties van andere elementen die zich in het glazuur bevinden. Vervolgens kunnen strontium- en neodymiumisotopen gemeten worden met behulp van een massaspectrometer. Voor de monsters in dit proefschrift is een 'thermal ionisation mass spectrometer' (TIMS) gebruikt, een Thermo Scientific Triton *Plus* TIMS. Met behulp van dit instrument wordt het monster opgewarmd, waardoor de neodymium- of strontiumisotopen in het instrument terecht komen en met behulp van magneten door het apparaat worden getrokken. Aan het einde van het apparaat bevinden zich bekers die de isotopen opvangen en bijhouden hoeveel isotopen zij opvangen. Deze aantallen worden vervolgens gecommuniceerd naar de computer waarmee het instrument bediend wordt, waardoor de hoeveelheid en de verhouding van de strontium- of neodymiumisotopen berekend kan worden. Deze verhouding, of de ratio, is de isotopenwaarde van het geanalyseerde monster. Omdat er zulke lage concentraties neodymiumisotopen in de tandmonsters zat, moest er gebruik worden gemaakt van speciale versterkers (10^{13} Ω) voor de TIMS.

Uit de resultaten bleek dat de hoeveelheid neodymiumisotopen in de verstandskiezen erg verschillend was. Hierdoor kon een gedeelte van de monsters niet geanalyseerd worden, omdat er zich onvoldoende neodymiumisotopen in de tand bevonden voor de meting. Hoeveel neodymiumisotopen er aanwezig zijn in de verstandskiezen wordt mogelijk veroorzaakt door biologische processen in het lichaam van de mens, wat voor variabele neodymiumisotopenconcentraties zorgt. Uit de gemeten monsters bleek dat ongeveer 60% van de neodymiumwaarden van verstandskiezen overeenkwamen met de geologie waar de donoren waren opgegroeid (gebaseerd op data van vorig onderzoek). De verstandskiezen van inwoners uit Rotterdam en Amsterdam werden geanalyseerd en bleken onderling verschillend in hun neodymiumwaarden. Over het algemeen kwamen de waarden van individuen van Rotterdam beter overeen met de verwachte neodymiumwaarden van de omgeving (**Figuur 4.5**). Dit werd mogelijk veroorzaakt omdat het geologische achtergrondsignaal gebaseerd was op een klein aantal monsters (18 in totaal) afkomstig uit de buurt van Rotterdam. De reden voor het verschil tussen de inwoners van Rotterdam en Amsterdam is lastig te bepalen met de beperkt beschikbare data. Daarnaast hadden een paar individuen afwijkende neodymiumwaarden die niet overeenkwamen met de geologie van Nederland, maar eerder met de geologie van vulkanische gebieden zoals IJsland en Italië. Deze afwijkende waarden kunnen veroorzaakt worden door meerdere factoren. Zo is het mogelijk dat neodymiumisotopen gefractioneerd

worden tijdens de opname in het menselijk lichaam, alhoewel dit onwaarschijnlijk is vanwege de zware massa van neodymiumisotopen. Daarnaast kan het neodymiumisotopensignaal beïnvloed worden als het dieet een niet-Nederlandse isotoopsamenstelling heeft door bijvoorbeeld geïmporteerd eten. Het is lastig vast te stellen hoeveel invloed dit heeft op neodymiumisotopen in tanden vanwege de gelimiteerde hoeveelheid data, maar voor andere isotoopsystemen als zuurstof, koolstof en strontium bleek dat de waarden nog steeds gebonden waren aan de lokale omgeving ondanks de globalisering van de Nederlandse voedselmarkt. Neodymiumisotopen in verstandskiezen kunnen ook nog beïnvloed worden door niet-geologische bronnen, zoals bijvoorbeeld industriële emissie die wordt ingeademd. Dit laatste leek onwaarschijnlijk, alhoewel lokale blootstelling niet kon worden uitgesloten. Het blijft mogelijk dat andere bronnen van neodymium een grote invloed hebben op de neodymiumwaarden in verstandskiezen, maar om hier een beter beeld van te vormen is verder onderzoek nodig (zie **Hoofdstuk 5**).



Figuur 4.5 *Verstandskiezen geanalyseerd met speciale versterkers (10^{13} Ω) van inwoners uit Amsterdam (n = 12) en Rotterdam (n=8). Het grijsgekleurde vlak ($^{143}Nd/^{144}Nd$ = 0.511983-0.512166) zijn de verwachtte neodymiumisotopenwaarden, gebaseerd op waarden van Rijn sedimenten.*

NL

Hoofdstuk 5: Evaluatie van de analyse van neodymiumisotopen in menselijke tanden

Om te kijken of de analyse van neodymiumisotopen ($^{143}Nd/^{144}Nd$) in menselijke tanden kan worden toegepast om mobiliteit van mensen te bepalen zijn voor dit hoofdstuk meer tanden geanalyseerd met behulp van de methoden en technieken die beschreven zijn in **Hoofdstuk 4**. Aan de bestaande data zijn nieuwe Nederlandse resultaten toevoegt van individuen die geboren en getogen zijn in Limburg en Friesland (**Figuur 5.1,** pagina 91). De bestaande dataset is hiermee verdubbeld. Het is belangrijk om te bepalen of de neodymiumisotopenwaarden ook overeenkomen met een geologische achtergrond buiten Nederland. Hiervoor zijn de verstandskiezen van vijf individuen uit IJsland, Colombia en het Caraïbisch gebied (Bonaire, Curaçao) geanalyseerd (**Figuur 5.2**, pagina 91). In totaal zijn de neodymiumisotopenwaarden van 40 individuen geanalyseerd.

De neodymiumisotopendata uit dit hoofdstuk komen overeen met eerder gegenereerde data: de concentratie neodymiumisotopen in de tanden was laag en het is onwaarschijnlijk dat deze lage concentraties beïnvloed waren door bijvoorbeeld luchtvervuiling. Neodymiumisotopen in stof in de lucht zorgen namelijk voor veel hogere concentraties van neodymiumisotopen in menselijk weefsel dan aangetoond in dit onderzoek. Het lijkt echter onwaarschijnlijk dat neodymium volledig door de geologie wordt bepaald, wat bijvoorbeeld wel het geval is voor strontiumisotopen. De neodymiumisotopenwaarden van menselijke tanden kunnen onder andere worden beïnvloed door fossiele brandstof, mest, verbranding van afval, metallurgische verwerkingsprocessen (zoals de productie van magneten) of contact met magneten in smartphones, computers en andere elektrische apparatuur. De invloed van roken op de $^{143}Nd/^{144}Nd$ ratio's kon wel worden uitgesloten, omdat twee individuen rookten tijdens de vorming van hun verstandskiezen. Ondanks het roken hadden zij nog steeds een lage neodymiumisotopenconcentratie in hun tanden. De $^{143}Nd/^{144}Nd$ ratio's worden waarschijnlijk ook niet beïnvloed door het dieet: In **Hoofdstuk 4** was de eigenaar van de hoogste waarde een vegetariër, maar nu hadden twee andere vegetariërs gemiddelde waarden.

De meerderheid van de individuen (83%) heeft neodymium- en strontiumisotopenwaarden die overeenkomen met de geologische omgeving waar hun verstandskiezen in vormden. Dit is een indicatie dat de analyse van neodymiumisotopen gebruikt zou kunnen worden als herkomstindicator. In vijf individuen (vier Nederlanders en één IJslander) weken deze waarden af van die van de geologie. Deze afwijkende $^{143}Nd/^{144}Nd$ ratio's zouden veroorzaakt kunnen

worden door invloed van de mens op neodymiumisotopen (zoals mest, fijnstof of elektronica) en import van voedsel. Zowel in Nederland als in IJsland wordt veel eten geïmporteerd uit gebieden met $^{143}Nd/^{144}Nd$ ratio's die overeenkomen met de waarden van de geanalyseerde individuen. Dit verklaart echter niet waarom de strontiumisotopendata van alle Nederlandse individuen wel overeenkomen met de verwachte strontiumisotopenwaarden voor Nederland. Mogelijk worden strontium- en neodymiumisotopenwaarden in menselijke tanden beïnvloed door verschillende factoren. De strontiumwaarden van het IJslandse individu weken ook af van de verwachte waarden van de IJslandse geologie. Deze afwijking is waarschijnlijk het gevolg van de invloed van de strontiumisotopenwaarden van de zee. Een andere oorzaak voor de afwijkende isotopenwaarden van dit individu kan het dieet zijn. Zo is het mogelijk dat het individu uit IJsland veel vis uit de diepzee heeft gegeten, waar de $^{143}Nd/^{144}Nd$ ratio's lager zijn die van de IJslandse geologie. Helaas is er geen gedetailleerde informatie beschikbaar over het dieet van dit individu en blijft dit slechts een interpretatie.

Industriële vervuiling en het gebruik van kunstmest kan invloed kan hebben op de neodymiumisotopen in menselijk weefsel. Deze invloed is waarschijnlijk beperkt in archeologische populaties, omdat er toen weinig tot geen sprake was van lange-afstandshandel, grootschalige industrialisering of het gebruik van magneten en elektronica. Voordat neodymiumisotopenanalyses toegepast kunnen worden op archeologisch materiaal moet er eerst worden vastgesteld of neodymiumisotopen in het glazuur niet worden beïnvloed door diagenese (fysieke of chemische veranderingen). Als de buitenste laag van het glazuur verwijderd moet worden om er zeker van te zijn dat de resterende laag glazuur onaangetast is gebleven, kan het namelijk zijn dat er te weinig glazuur overblijft voor de analyse van neodymiumisotopen.

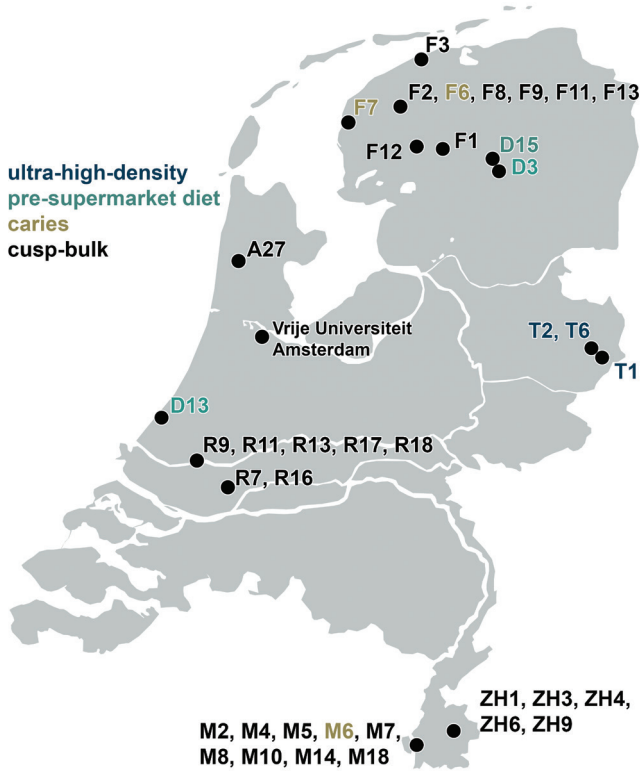
De analyse van neodymiumisotopen in menselijke weefsels wordt momenteel beperkt doordat de gehele laag glazuur nodig is en daarnaast meetapparatuur nodig is die gebruikt maakt van de nieuwste technieken (10^{13} Ω versterkers). Omdat het op dit moment nog niet zeker is of de neodymiumisotopenwaarden volledig door de geologie worden bepaald, is het nu nog niet mogelijk om neodymiumisotopen routinematig toe te passen voor de analyse van het glazuur van menselijke tanden. Hiervoor is verder onderzoek nodig naar de $^{143}Nd/^{144}Nd$ ratio's van andere geografische regio's. Ook is er meer achtergronddata nodig over de herkomst van het dieet en eventuele andere neodymiumisotopenbronnen zoals elektronische apparatuur, magneten, meststoffen en luchtvervuiling. In de toekomst zal de analyse van neodymiumisotopen waarschijnlijk makkelijker worden door technische verbeteringen.

Hoofdstuk 6: Variatie in isotoopsystemen (strontium, zuurstof en koolstof) in modern menselijk tandglazuur

De vorming van tandglazuur is een ingewikkeld proces (zie **Hoofdstuk 3**) waardoor niet zeker is wanneer isotoopsystemen worden opgenomen in het glazuur. De meeste onderzoekers gaan er nu vanuit dat de gehele glazuurlaag ongeveer dezelfde isotopenwaarden heeft. Om deze hypothese te testen, beschrijft dit hoofdstuk de resultaten van meerdere bemonsteringslocaties van het glazuur van dezelfde verstandskies (6 tot 20 monsters) en werden deze resultaten vergeleken met de resultaten van zes bemonsteringslocaties van een andere verstandskies van hetzelfde individu. Hiervoor werden verstandskiezen geanalyseerd van 47 personen uit Nederland (zie **Figuur 6.1**), het Caraïbisch gebied, Colombia, Amerika, Somalië en Zuid-Afrika. Er werden drie isotoopsystemen geanalyseerd: strontium, zuurstof en koolstof. Daarbij is alleen voor strontiumisotopen ook de aanwezige concentratie gemeten.

Voor isotopenanalyses wordt het glazuur bemonsterd met behulp van een handboor (micro Dremel). Eerst wordt de buitenste oppervlaktelaag vóór bemonstering verwijderd om contaminatie van het monster te voorkomen. Vaak wordt er in isotopenstudies niet duidelijk beschreven waar het monster exact genomen is en momenteel bestaan hier geen formele richtlijnen voor. Doorgaans worden de tandoppervlaktes in contact met andere tanden of gebieden aangetast door gaatjes of defecten (zie **Hoofdstuk 3**) vermeden. Hierdoor is er momenteel geen data beschikbaar over het effect van gaatjes of defecten op de isotopenwaarden in het glazuur. Om dit effect te onderzoeken zijn er in dit hoofdstuk ook verstandskiezen met gaatjes geanalyseerd, waarbij zowel de gaatjes als het gezonde glazuur is bemonsterd.

Omdat er geen formele bemonsteringsrichtlijnen bestaan, is het onduidelijk in hoeverre de isotopenresultaten van verschillende bemonsteringstechnieken vergelijkbaar zijn. Omdat er nu vaak maar één locatie wordt bemonsterd, is het ook niet duidelijk hoeveel onderlinge variatie er tussen de isotopenanalyses van verschillende bemonsteringslocaties van één tand zou zijn. Kortom, de verwachtte spreiding in isotopenwaarden (of de isotopenvariatie) in tanden is momenteel onbekend en wordt voor moderne Nederlanders in dit hoofdstuk beschreven.



Figuur 6.1 *Een kaart van Nederland met de plaatsen waarin de geanalyseerde individuen (n = 38) woonden tijdens de vorming van hun verstandskiezen.*
F3 = Holwerd
F2, F6, F8, F9, F11, F13 = Leeuwarden
7 = Wijnaldum
F12 = Oldeboorn
F1 = Lippenhuizen
D15 = Veenhuizen
D3 = Smilde
A27 = Alkmaar
T2, T6 = Hengelo
T1 = Enschede
D13 = Den Haag
R9, R11, R13, R17, R18 = Rotterdam
R7 = Dordrecht
ZH1, ZH3, ZH4, ZH6, ZH9 = Heerlen
M2, M4, M5, M6, M7, M8, M10, M14, M18 = Maastricht.

Isotopenvariatie

De 6 tot 20 bemonsteringslocaties van de moderne Nederlandse verstandskiezen lieten een aanzienlijke spreiding in de isotopenwaarden zien (**Figuur 6.3**, pagina 125). Vooral de waarden van strontium- en zuurstofisotopen van verschillende verstandskiezen van hetzelfde individu kwamen niet volledig overeen. Dit demonstreert dat een bemonsteringslocatie van één verstandskies niet altijd representatief is voor de andere verstandskiezen (of andere tanden en kiezen) in het gebit. Naarmate het aantal bemonsteringslocaties toeneemt, is er meer variatie in de isotopenwaarden zichtbaar. De isotopenvariatie binnen de verstandskiezen van één individu lijkt zelfs op de variatie die normaal zichtbaar is tussen verschillende individuen (variatie in een populatie). Met name de variatie in zuurstof- en koolstofisotopen was groot. Verstandskiezen vertonen de meeste variatie in de ontwikkeling van alle tanden in het gebit (zie **Hoofdstuk 3**), waardoor de spreiding van isotopenwaarden waarschijnlijk groter is dan in

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andere tanden en kiezen. Uit nieuw onderzoek moet blijken of de isotopenvariatie in andere tanden en kiezen te vergelijken is met de verstandskiesdata.
Er was geen duidelijk verschil tussen het oppervlakte-glazuur en het binnenste-glazuur voor strontiumisotopen. Wel was er variatie in koolstof- en zuurstofisotopen tussen deze bemonsteringslocaties. Met name in het oppervlakte-glazuur werden verhoogde waarden van koolstofisotopen gevonden. Deze verhoogde waarden in het oppervlakte-glazuur kunnen drie verklaringen hebben:
(1) Het glazuur wisselt koolstofisotopen uit binnen de mond, bijvoorbeeld als het individu eten consumeert met andere isotopenwaarden dan het binnenste-glazuur.
(2) Het is mogelijk dat koolstofisotopen in het glazuur op een andere manier worden opgenomen dan de andere isotopen, waarbij de opname van koolstof de vorming van de lagen tijdens glazuurvorming volgt (in plaats van aan het einde van het vormingsproces een gemiddelde waarde vormt zoals nu wordt gedacht).
(3) Strontium- en zuurstofisotopen worden ook in lagen opgenomen in het glazuur, maar dit is nu onzichtbaar omdat alleen het dieet van de geanalyseerde individuen veranderde (en niet de locatie), waardoor er alleen een verschil in waarden zichtbaar is in de koolstofisotopen van het oppervlakte- en binnenste-glazuur.

Omdat we geen exacte informatie hebben over het dieet tijdens de vorming van de verstandskiezen is het lastig te bepalen waarom de koolstofisotopen verhoogd zijn in het oppervlakte-glazuur. Dit suggereert dat bemonstering van het oppervlakte-glazuur moet worden vermeden, voordat met name de opname van koolstofisotopen in glazuur beter is onderzocht.

Uit vergelijking van strontiumisotopenanalyses van de gehele laag glazuur en één bemonsteringslocatie van het binnenste-glazuur bleek dat de waarden van deze twee analyses in 40% van de gevallen niet overeenkomen. De twee individuen die hierbij de grootste verschillen vertoonden, waren opgegroeid in één locatie. Hieruit blijkt dat zelfs als individuen sedentair zijn, de isotopenwaarden van hun tanden een grote spreiding kunnen hebben. Hierdoor is één bemonsteringslocatie niet altijd representatief voor de gemiddelde isotopenwaarde van het glazuur. Het bemonsteren van de gehele glazuurlaag is echter ook geen ideale optie omdat dit een gemiddelde waarde is. De waarneembare variatie in kleine bemonsteringslocaties zou daarmee onzichtbaar zjn, omdat alles wordt samengevoegd in één isotopenwaarde.

Globalisatie

Om te kijken of de globalisering van supermarktproducten een effect heeft op de isotopenwaarden in verstandskiezen werden de resultaten van individuen die geboren in de jaren '40-60 vergeleken met individuen geboren in de jaren '80 en '90. Van elke verstandskies werden zes monsters genomen. Een directe vergelijking blijft lastig omdat deze individuen niet allemaal op exact dezelfde locatie zijn opgegroeid (zie **Figuur 6.1**). Dit leidt waarschijnlijk al tot verschillen in de isotopenwaarden tussen de individuen. De individuen geboren in de jaren '80 en '90 hadden een bredere spreiding in hun isotopenwaarden (en dus een grotere isotopenvariatie) en lagere strontiumisotopenconcentraties in hun verstandskiezen dan de eerder geboren individuen. Deze vergelijking is echter gebaseerd op een kleine steekproef van zes individuen; er is vooral meer informatie nodig van individuen die geboren zijn voor de jaren '70 om iets te kunnen zeggen over het effect van de globalisering van het aanbod van supermarkten. Zo was er niet altijd een grote isotopenvariatie zichtbaar in de resultaten van individuen die geboren zijn na de jaren '70. Een groot aantal individuen in dit onderzoek (26 in totaal) geboren na 1972 vertoonden net als de individuen geboren in de jaren '40-60 weinig variatie in hun strontiumisotopenwaarden van de gehele glazuurlaag en de enkele bemonsteringlocatie.

Cariës

Deze studie geeft aan dat cariës geen noemenswaardig effect hebben op de isotopenwaarden van het onaangetaste glazuur van de verstandkies, waardoor het mogelijk is om een verstandskies met cariës te bemonsteren (zolang de cariës zelf niet bemonsterd worden). Om het effect van cariës nog beter in kaart te brengen, zouden toekomstige studies kunnen kijken naar de isotopenwaarden in hetzelfde type tanden (ontwikkeld tijdens dezelfde tijdsperiode) van hetzelfde individu waarvan in ieder geval één tand cariës heeft ontwikkeld en één tand gezond is. De resultaten van dit soort onderzoek zouden verder uitsluitsel kunnen geven of cariës ook een effect hebben op de isotopenwaarden van het gezonde tandglazuur.

Wel is duidelijk dat de gaatjes zelf niet bemonsterd moeten worden: met name de zuurstofisotopen zijn hoger in de gaatjes dan in het gezonde glazuur. Ondanks dat cariës in de meeste gevallen geen effect lijken te hebben op de strontium- en koolstofisotopen is de bemonstering van cariës niet aan te raden omdat het effect van cariës nog niet voldoende in kaart is gebracht en het onzeker is welke tijdsperiode geanalyseerd wordt. (Wanneer worden de cariës gevormd? Wanneer tasten de cariës de originele isotopenwaarde aan?)

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Ook is er gekeken of cariës de isotopenwaarden opnemen van de omgeving waarin zij werden gevormd. Hiervoor zijn verstandskiezen met gaatjes geanalyseerd van individuen die opgegroeid zijn in de Dominicaanse Republiek en Somalië en waarvan cariës ontwikkeld zijn in Nederland. De isotopenwaarden van de gaatjes kwamen nog steeds overeen met de verwachte isotopenwaarden van de geologie in de Dominicaanse Republiek en Somalië. Het lijkt er dus op dat cariës niet altijd de lokale isotopenwaarden overnemen. Als dit wel het geval zou zijn, zouden de gaatjes van deze individuen Nederlandse isotopenwaarden moeten vertonen.

Toekomstige studies

Uit deze studie blijkt dat bemonstering van het binnenste glazuur de voorkeur heeft. Daarbij maakt het niet uit welke locatie in het binnenste glazuur wordt bemonsterd, omdat deze verschillende locaties (aan de bovenkant en zijkant van de kies) doorgaans vergelijkbare isotopenwaarden hebben. Hoeveel monsters genomen moeten worden van één tand of kies hangt af van de onderzoeksvraag. Zo kan het zijn dat de isotopenvariatie van een individu nog vastgesteld moet worden of dat er wordt gekeken naar de levensgeschiedenis. Hiervoor is het handig om meerdere glazuurmonsters te nemen. Als er alleen een schatting nodig is van de isotopenwaarden is één bemonsteringslocatie echter vaak voldoende, omdat de isotopenvariatie niet groter zal zijn dan die binnen een populatie.

De huidige resultaten zijn voornamelijk gebaseerd op verstandskiezen van Nederlanders. Of dezelfde resultaten gevonden zouden worden in verstandskiezen van individuen afkomstig uit andere landen is momenteel nog onduidelijk. Hiervoor zouden moderne (of archeologische) samenlevingen onderzocht moeten worden uit andere omgevingen dan Nederland. Bij voorkeur zouden meer dan 20 individuen moeten worden geanalyseerd om een betrouwbare schatting te maken over de isotopenwaarden die kunnen voorkomen in één individu. Met name voor zuurstof- en koolstofisotopen zijn er grote veranderingen in de isotopenwaarden nodig om een verandering in dieet of locatie aan te kunnen tonen, omdat kleine afwijkingen veroorzaakt kunnen worden door biologische processen in het menselijk lichaam.

Hoofdstuk 7: Strontiumisotopen in modern menselijk tandglazuur en drinkwater in Nederland

Strontiumisotopenanalyse kan in forensische zaken gebruikt worden om informatie te geven over de geografische herkomst van een individu. In Nederland wordt dit soort onderzoek sinds 2015 gebruikt in onopgeloste zaken. Om betrouwbare informatie te verkrijgen is het belangrijk om genoeg referentiemateriaal (strontiumisotopenwaarden van de omgeving, zoals de lokale geologie, planten of dieren) te hebben om de isotopenwaarden van een individu of populatie te kunnen vergelijken. Dankzij referentiemateriaal kunnen de verwachte isotopenwaarden voor een omgeving worden bepaald. Tegenwoordig worden deze verwachte waarden ook wel grafisch weergegeven op kaarten, een zogenaamde isoscape (isotopenlandschap). Op het moment zijn er nog maar weinig isoscapes gebaseerd op voornamelijk menselijke isotopenwaarden.

Om de strontiumisotopenvariatie in de Nederlandse populatie beter in kaart te brengen, zodat er in de toekomst een isoscape geconstrueerd kan worden, zijn verstandskiezen van 153 Nederlanders geanalyseerd. **Figuur 7.3** illustreert de strontiumisotopenvariatie tussen verschillende individuen die geboren en getogen zijn in Nederland. De data gebruikt voor dit figuur zijn afkomstig van vier verschillende datasets, waaronder de data van **Hoofdstuk 5** en **6**.

Om te bepalen of kraanwater representatief is voor de strontiumisotopenwaarden van het tandglazuur van mensen, zijn er naast de verstandskiezen ook nog 143 kraanwatermonsters geanalyseerd. De isotopenwaarden van het kraanwater kwamen overeen met de verwachte isotopenwaarden van de Nederlandse geologie (**Figuur 7.2**, pagina 152).

De isotopenwaarden van kraanwater en van mensen van dezelfde locatie zijn echter niet aan elkaar gerelateerd. Dit betekent dat de strontiumisotopenwaarden van kraanwater niet representatief zijn voor de isotopenwaarden van mensen en dat isoscapes gebaseerd op water waarschijnlijk onbruikbaar zijn om menselijke data direct mee te vergelijken. Het verschil tussen de data van kraanwater en verstandskiezen wordt waarschijnlijk veroorzaakt door de lage concentratie strontium in het kraanwater. Hierdoor draagt het kraanwater weinig bij aan het uiteindelijke isotopensignaal van menselijke weefsels. Omdat de menselijke strontiumisotopenwaarden afwijken van die van kraanwater, en daarmee dus ook van de lokale geologie, worden de strontiumisotopenwaarden van mensen waarschijnlijk voornamelijk bepaald door de strontiumisotopen in het eten. Dit eten is echter niet altijd geproduceerd

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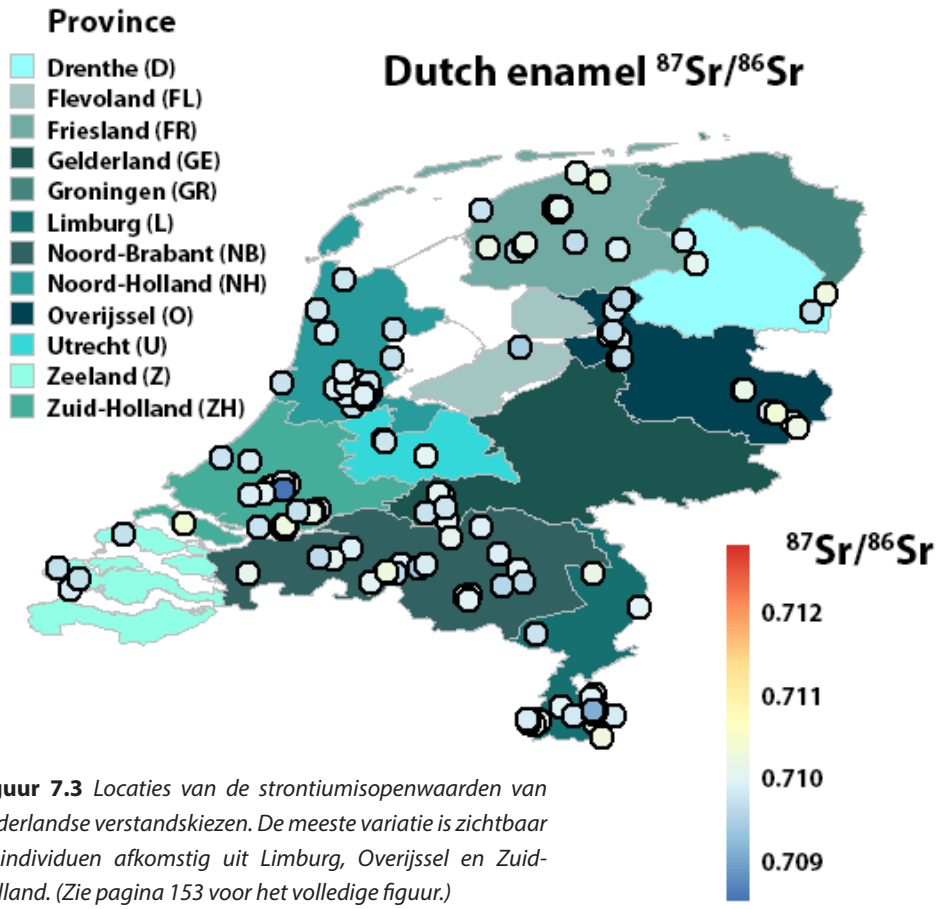
in de lokale omgeving en reflecteert daardoor niet altijd de isotopenwaarden van de lokale geologie. Vooral in een land als Nederland, wat sterk afhankelijk is van de import en export van voedsel, worden isotopenwaarden van eten afkomstig uit landen met andere geologische isotopenwaarden in menselijke weefsels opgenomen.

Het is daarom aan te raden om referentiewaarden voor isotopenanalyses niet te baseren op de isotopenwaarden van de lokale geologie of kraanwater, maar indien mogelijk menselijke weefsels te analyseren. Extra informatie, zoals data over de herkomst van geïmporteerd voedsel en isotopenanalyses van andere isotopensystemen zoals zuurstof, lood, koolstof en eventueel neodymium, kunnen aanvullende informatie geven. Hierdoor kunnen interpretaties gebaseerd op strontiumisotopenwaarden beter worden toegepast in forensische zaken.



Figuur 7.3 *Locaties van de strontiumisopenwaarden van Nederlandse verstandskiezen. De meeste variatie is zichtbaar in individuen afkomstig uit Limburg, Overijssel en Zuid-Holland. (Zie pagina 153 voor het volledige figuur.)*

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Hoofdstuk 8: Discussie & Conclusie

Dit proefschrift heeft twee hoofddoelen. Allereerst de ontwikkeling van de neodymiumisotopentechniek voor de analyse van menselijk tandglazuur om zo informatie te verkrijgen over de geografische herkomst van een individu. Ten tweede om de toepassing van bestaande isotopentechnieken (strontium, zuurstof en koolstof) kritisch te evalueren door de variatie in isotopenwaarden te kwantificeren. Zowel de ontwikkeling van nieuwe technieken als de verfijning van bestaande technieken zullen het mogelijk maken om de interpretaties van het dieet en de mobiliteit van mensen te verbeteren.

Discussie

Door technologische ontwikkelingen kunnen nieuwe isotopensystemen, zoals neodymium, worden gebruikt om menselijke weefsels te analyseren. Dit proefschrift beschrijft de eerste resultaten van analyse van neodymiumisotopen in menselijk tandglazuur (zie **Hoofdstuk 4** en **5**). De resultaten van deze veertig individuen vormen de basis voor de eerste evaluatie van de techniek. De neodymiumisotopenwaarden van de meerderheid van deze individuen komen overeen met de lokale geologie waar de individu verbleef op het moment dat de verstandskies werd gevormd. Hierdoor lijkt het erop dat de geologie de bepalende factor is in de samenstelling van de neodymiumisotopenwaarden in het tandglazuur. Dit betekent dat neodymiumisotopenanalyses kunnen worden toegepast om aanvullende informatie over mobiliteit van individuen te geven. Deze informatie kan worden gebruikt in combinatie met informatie die bestaande isotopenanalyses zoals strontium en zuurstof geven. Desondanks komen de neodymiumisotopenwaarden van vijf van de 30 individuen niet overeen met die van de lokale geologie. Deze afwijkingen zijn lastig te interpreteren met de beperkte data.

De analyse van neodymiumisotopen wordt vooralsnog beperkt door de grootte hoeveelheid monster die nodig is en de benodigde meetapparatuur (met de laatste versterkers, 10^{13} Ω). Naarmate de technologie zich verder ontwikkeld zal de analyse toegankelijker worden en breder kunnen worden toegepast. Voor deze toepassing is de analyse van monsters uit andere landen en geologische gebieden nodig. Ook is er meer onderzoek nodig naar neodymiumisotopen in de voedselketen. Resultaten van planten en voedselproducten kunnen meer licht werpen op het opnameproces van neodymiumisotopen in het menselijk lichaam en gebruikt worden als achtergrondsignaal waarmee menselijke neodymiumisotopenwaarden kunnen worden vergeleken. Om de invloed van andere bronnen van neodymiumisotopen te bepalen, is ook verder onderzoek nodig. Hierdoor krijgen wij een beter beeld van de rol van fijnstof,

antropogene bronnen als elektronica en kunstmest en de globalisering van de voedselmarkt.

Voor een beter inzicht over de vorming van tandglazuur zijn de laatste technologische ontwikkelingen ook belangrijk. Zo kan synchrotron imaging, de laatste generatie aan röntgenstraling techniek, 3D informatie geven over de structuur en samenstelling van tanden. Deze afbeeldingen worden gegenereerd zonder de tand te beschadigen en geven een hogere resolutie dan traditionele microscopie. Dit bied mogelijkheden om de kennis over de vorming van glazuur te verbeteren (zie **Hoofdstuk 3**).

De variatie in isotopenwaarden binnen één individu en binnen één populatie blijft een belangrijke factor binnen het veld van isotopenbiochemie (zie **Hoofdstuk 6**). Archeologische studies hebben de variatie binnen populaties en tussen verschillende populaties al in kaart gebracht, maar de isotopenvariatie in de menselijke weefsels van één individu zijn minder goed onderzocht. Er bestaan nog altijd geen studies waar meerdere bemonsteringslocaties van archeologisch tandglazuur van dezelfde tand worden geanalyseerd op dezelfde wijze als in **Hoofdstuk 6.** Dit komt omdat onderzoekers aannemen dat de isotopenvariatie in het glazuur een gemiddelde waarde representeert wat de analyse van meerdere monsters van dezelfde tand overbodig zou maken. De grote variatie in de isotoopsystemen beschreven in **Hoofdstuk 6** toont echter aan dat we voorzichtig moeten zijn met interpretaties over veranderingen in locatie en dieet van individuen op basis van één monster. Als de isotopenvariatie binnen een individu of een populatie nog niet vastgesteld is (of als er geen achtergrondinformatie over het dieet en de omgeving beschikbaar is), is het lastig om veranderingen in dieet en locatie vast te stellen, omdat afwijkende waarden ook veroorzaakt kunnen worden door biologische processen in het menselijk lichaam. Meer analyses van verschillende weefsels van hetzelfde individu zijn nodig om deze processen beter te begrijpen. Nieuwe technieken, zoals de isotopenanalyse van specifieke aminozuren in bot kunnen een beter beeld geven over het dieet van een individu en de verwachte variatie in de isotopenwaarden van koolstof. Ook de toepassing van meerdere isotopentechnieken, ook wel multi-isotopenanalyses genoemd, geven aanvullende informatie. Het toepassen van meerdere technieken voorkomt dat we te veel waarde hechten aan afwijkende resultaten van één isotoopsysteem die niet altijd representatief zijn voor een daadwerkelijke verandering in het dieet of locatie.

Om de kwaliteit en toepasbaarheid van isotopenonderzoek te verbeteren, moeten de resultaten van het onderzoek toegankelijk worden gemaakt voor andere onderzoekers en het bredere publiek. Op dit moment vindt de communicatie van onderzoeksresultaten voornamelijk

plaats via artikelen in wetenschappelijke tijdschriften. Deze tijdschriften zijn echter niet voor iedereen toegankelijk (zie **Figuur 8.1**, pagina 168). Bovendien is er in deze tijdschriften meestal geen plaats voor de gebruikte data. Het is noodzakelijk dat niet alleen de artikelen, maar ook de data openlijk worden gedeeld zonder dat men hiervoor moet betalen. Het delen van deze resultaten kan daarbij het beste de FAIR-principes volgen: Findable, Accessible, Interoperable en Reusable (vindbaar, toegankelijk, uitwisselbaar en herbruikbaar). Volgens de FAIR-principes zou elke onderzoekoutput online vindbaar en toegankelijk moeten zijn via een vaste link.

De publicatie van datasets wordt steeds gebruikelijker. De documentatie van de data moet echter verbeterd worden voordat deze datasets hergebruikt of gecombineerd kunnen worden met andere datasets voor nieuw onderzoek. Zo is het essentieel dat de gebruikte onderzoeksprocedures transparanter en inzichtelijker worden, zoals bijvoorbeeld de gebruikte bemonsteringsprotocollen, meetprocedures, berekeningen en instellingen van de meetapparatuur. Door de standaardisatie van de onderzoeksprocedures (door bijvoorbeeld uitwisseling van monsters en labprotocollen tussen verschillende isotopenlaboratoria) verbetert de compatibiliteit van de verschillende datasets. Als datasets beter vergelijkbaar zijn, kunnen er bijvoorbeeld isoscapes (kaarten met daarop de verwachte spreiding van de isotopenwaarden) gemaakt worden voor grotere gebieden. Hiermee is het mogelijk om nieuwe onderzoeksvragen te beantwoorden en de huidige interpretaties verder te verbeteren. Om data gemakkelijk te kunnen delen met anderen en om de data te bewaren voor de toekomst is de ontwikkeling van online data-archieven essentieel. Een voorbeeld hiervan is IsoArch (www.isoarch.eu).

Om ervoor te zorgen dat data herbruikbaar is, zullen de gegevensverzameling, analyses en rapportages steeds meer gestandaardiseerd moeten worden. Het gebruik van software om gegevens te analyseren zal het proces standaardiseren en versnellen in vergelijking met handmatige analyse. Daarnaast bevatten geautomatiseerde analyses minder fouten dan handmatige analyses. Zo wordt het gemakkelijker om resultaten te interpreteren en om voort te bouwen op eerder onderzoek.

In forensische zaken hebben de laatste ontwikkelingen in het biotechnologische veld een effect op de interpretatie van isotopenanalyses. Zo is het nu mogelijk om kunstmatig het glazuurvormingsproces opnieuw op te starten. Hoewel dit een gunstige ontwikkeling is voor de tandheelkundige gezondheid van de moderne mens, kan de nieuwe vorming van glazuur het oorspronkelijke isotopensignaal overschrijven waardoor het isotopensignaal van de

kindertijd verloren gaat. Ook restoratie-elementen (zoals vullingen) kunnen een effect hebben op de isotopenwaarden in de tand. Op dit moment worden deze gerestaureerde tanden niet geanalyseerd, waardoor de selectie voor monsters in met name forensische zaken wordt beperkt.

Naast neodymium zijn er ook nog andere isotopensystemen die toegepast zouden kunnen worden op menselijk weefsel. Potentiële kandidaten voor dieetanalyses zijn calcium, lithium, waterstof, koper en zink. Cadmiumisotopen zouden bijvoorbeeld informatie kunnen verschaffen over voedingspatronen of rookgedrag. De toenemende toepassing van loodisotopenanalyse kan ook meer licht werpen op de levensgeschiedenis en mobiliteitspatronen van mensen.

Hoewel bot vaak ongeschikt is voor isotopenanalyses, gaat de zoektocht naar nieuwe toepassingen op menselijk weefsel verder. Momenteel wordt onderzocht of er in het harde stuk bot van de schedel bij het oor isotopenwaarden bewaard blijven. Het lijkt erop dat dit het geval is, mits het bot gecremeerd is. Dankzij de verbranding van het bot kan het net zo hard worden als tandglazuur, waardoor de isotopenwaarden bewaard blijven.

Conclusie

In het kader van het NEXUS1492 project is er succesvol een nieuwe isotopentechniek voor de analyse van menselijk tandglazuur opgezet (neodymiumisotopen) en is er kritisch gekeken naar al bestaande isotopenmethodes (strontium, zuurstof en koolstof).

Neodymiumisotopenanalyse kan aanvullende informatie geven over mobiliteitspatronen, wat momenteel niet mogelijk is met enkel het gebruik van de bestaande technieken. De toepassing van neodymiumisotopenanalyse zou vooral uitkomst kunnen bieden in het Caraïbisch gebied. Omdat neodymiumisotopen minder beïnvloed worden dan andere isotoopsystemen als strontium en zuurstof in kustregio's, zoals de Caraïben, geven zij betrouwbaardere informatie over de geografische omgeving. Vergeleken met strontiumisotopen worden neodymiumisotopen in kustmilieus niet beïnvloed door de isotopenwaarden van zeewater. In tegenstelling tot zuurstofisotopen, die vergelijkbare waarden hebben in kustgebieden, zullen neodymiumisotopen makkelijker onderscheid kunnen maken in verschillende kustregio's. Deze informatie kan daarmee bijdragen aan een gedetailleerder beeld van vroegere menselijke mobiliteitspatronen in het Caraïbisch gebied.

Het is van belang dat de variatie in isotopenwaarden van tanden beter wordt gekwantificeerd om de archeologische en forensische interpretaties op basis van deze resultaten te verbeteren. In dit proefschrift is aangetoond dat een enkele bemonsteringslocatie niet representatief is voor de totale isotopenvariatie van strontium, zuurstof en koolstof in het tandglazuur. Wel is aangetoond dat het niet uitmaakt waar de bemonstering plaats vindt (aan de zijkant of bovenkant van de tand) zolang het binnenste glazuur wordt bemonsterd. Als cariës ontwikkelen in een tand kan dit gedeelte van de tand niet gebruikt worden voor isotopenanalyses, omdat het niet duidelijk is wat het effect van cariës is op de isotopenwaarden.

Dit onderzoek kwantificeert de isotopenvariatie voor de moderne mens in Nederland. Verder onderzoek is nodig voor andere populaties in andere geologische en klimatologische omgevingen om de variatie in isotoopsystemen beter vast te stellen. De kwantificatie van de isotopenvariatie in tanden zal leiden tot robuustere interpretaties van dieet en mobiliteit in archeologisch en forensisch onderzoek. Voor het Caraïbisch gebied betekent dit dat de reconstructie van de impact van de interacties van de Amerindiaanse bevolking met de Europese en Afrikaanse populaties na 1492 kan worden verbeterd.

Isotopenanalyses moeten altijd toegepast worden in combinatie met andere technieken. Isotopenanalyses zijn destructief, waardoor andere analyses (zoals slijtage, leeftijd schattingen, DNA, of metrische analyses) eerst moeten worden uitgevoerd. De isotopenanalyses van een individu moeten altijd worden geïnterpreteerd binnen de specifieke archeologische of forensische context van het individu. Dit is belangrijk, omdat we steeds beter in staat zijn om verschillende datasets samen te voegen. De verbetering in de standaardisatie en transparantie van de analytische procedures in isotopenanalyses maakt het makkelijker om resultaten van verschillende laboratoria te interpreteren en te vergelijken. Door isotopenanalyses van verschillende laboratoria te combineren en deze aan te vullen met de informatie van andere technieken en analyses kunnen nieuwe onderzoeksvragen beantwoord worden, waardoor de informatie die menselijke tanden bevatten steeds verder wordt ontsloten.