The Concept of Isotopic Landscapes: Modern Ecogeochemistry versus Bioarchaeology

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Abstract

The term "isotopic landscape" or "isoscape" is used to indicate a map depicting isotopic variation in the environment. The spatial distribution of isotopic ratios in environmental samples is an indispensable prerequisite for generating an isotopic landscape yet represents more than simply an assessment of this distribution. An isotopic landscape also includes the fundamental parameters of prediction and modelling, thus providing estimated isotopic signatures at sites for which no values are known. When calibrated, such models are very helpful in assessing the origin of geological and biological materials. Reconstructing the place of origin of primarily non-local archaeological finds is a major topic in bioarchaeology because it gives clues to major driving forces for population development through time such as mobility, migration, and trade. These are fundamental aspects of the past human behaviour. For decades, stable isotope analysis has been the method of choice, but still has its limitations. Bioarchaeological sciences have adopted "isoscapes" mainly as a term, but not as a contextual concept.

This chapter briefly introduces the research substrate of bioarchaeology, which mainly consists of human and animal skeletal finds, provides a concise

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overview of selected stable isotopic ratios in these remains, and explains their research potential for migration research. State of the art in bioarchaeology, including efforts towards the generation of predictive models, is discussed within the framework of existing isotopic maps and landscapes relevant to bioarchaeology. The persisting challenges in this field of research, which gave rise to research efforts summarized in this book, are also addressed.

Introduction

Stable isotopes are very useful and indispensable markers for the monitoring of the flow of matter through biogeochemical cycles. Isotopes of an element differ in the number of neutrons and are generated, e.g. by the decay of parent isotopes or by reactions with subatomic particles in the environment. Differences in the atomic mass of isotopes of the same element lead to differences in molecular bond strength and vibration energies, whereby the vibrational frequency of a molecule is inversely related to the atomic masses of its compounds. This, and the different thermodynamic reactivity of light and heavy isotopes or molecules consisting of light or heavy isotopes, leads to isotopic fractionation, i.e. uneven partitioning of isotopes between source and product. Isotopic fractionation is mostly considered for non-radiogenic isotopes of light elements because these effects are often difficult to distinguish from decay effects in radiogenic isotopes (Porcelli and Baskaran 2012) and decrease with increasing atomic mass. In general, three fractionation processes are possible and do occur in nature: In the course of equilibrium fractionation, isotopes are separated between the source and reaction products in the form of a chemical or physical equilibrium such as the reversible exchange of molecules between two phases (e.g. water vapour and liquid water). Kinetic fractionation describes mass-dependent isotopic splitting in the course of a unidirectional process such as an enzymatic reaction (e.g. photosynthesis), and diffusion fractionation occurs in the gas phase only, which is due to the slower diffusion velocity of molecules containing or consisting of heavy isotopes.

Isotopic fractionation and mixing in an ecosystem, thus, can generate compartments with characteristic isotopic signatures (see, e.g. Fry 2006). For instance, evaporation and condensation in the course of hydrological processes lead to predictable distributions of hydrogen and oxygen isotopes in the atmosphere and in precipitation, while photosynthesis is the crucial process of carbon isotope fractionation on the level of the primary producers. Isotopic labels shared by certain ecological components such as soil, water, plants, microbia and animals are successfully used for the generation of isotopic maps for the investigation of landscape ecology. Source inputs such as wastewater discharge into rivers or changing floral communities in time and space are tracked this way (Fry 2006). Such isotopic maps are empirically generated by sampling the relevant environmental components and by subsequent analyses of their isotopic signatures. However, isotopic maps differ substantially from an “isotopic landscape”.

The term "isotopic landscape" or "isoscape" emerged around the turn of the millennium and describes "maps of isotopic variation produced by iteratively applying (predictive) models across regions of space using gridded environmental data sets", whereby one "common use of isoscapes is as a source of estimated isotopic values at unmonitored sites, which can be an important implementation for both local- and global-scale studies if the isoscape is based on a robust and well-studied model" (Bowen 2010). In April 2008, a conference on isoscapes was held in Santa Barbara, California, where research interests in the fields of ecology, climate change, biogeochemistry, hydrology, forensic sciences, anthropology, atmospheric chemistry and trade regulation were addressed in an attempt to better understand and quantify the distributions of stable isotopic ratios in time and space. The conference proceedings were published by West et al. (2010a) as a monograph and received high international attention.

Bioarchaeological sciences adopted the measurement and interpretation of stable isotopes in preserved archaeological finds rapidly after their potential as ecological markers became evident and long before the concept of "isotopic landscapes" was developed. Early studies concerned the reconstruction of palaeodiet and ancient food webs by stable carbon and nitrogen isotopes in bone collagen (e.g. Vogel and van der Merwe 1977; Bumsted 1981; Schoeninger et al. 1983; Norr 1984; Schwarcz et al. 1985; DeNiro 1985) and provenance analysis by stable strontium and lead isotopic ratios in bone minerals (Ericson 1985; Molleson et al. 1986). Decades later, "isoscapes" have been adopted by bioarchaeologists, but mainly just as a term and not as a contextual concept (Grupe and McGlynn 2016). The vast majority of stable isotope studies in this field lack the fundamental parameters of prediction and modelling and are still restricted to the evaluation of the spatial variability of isotopic data. To quote Bowen et al. (2009), "the underlying premise behind isoscapes is that isotopic composition can be predicted as a function of time, location, and spatially explicit variables describing isotope-discriminating processes" and that "well calibrated models also help predict patterns of environmental isotope variation that can be used to 'fingerprint' the origin of geological and biological materials". Bioarchaeology cannot claim to use this concept before these prerequisites are fulfilled. To identify the origin of humans, animals or goods in prehistory, existing gaps in empirical data sets have to be filled, and continuous predictions of isotope distributions in time and space are needed (Bowen 2010).

In the beginning, stable isotopes in bioarchaeological finds were measured and simply compared to the known spatial distribution of the isotopic system under study such as $^{87}Sr/^{86}Sr$ in geological maps or the climate and habitat-dependent distribution of C_3 and C_4 plants which is reflected in the $\delta^{13}C$ values of the consumers' tissues. Outliers, detectable by univariate statistics (e.g. Grupe et al. 1997), were readily interpreted as immigrant individuals. Soon it became obvious, however, that the use of stable isotopes for the reconstruction of migration and trade in bioarchaeology is not an end in itself but frequently necessitates accompanying data (e.g. analysis of not only human but also animal bones or soil sampled from the same site) for the assessment of ecogeographical baseline values to account for the

small-scale variability in time and space. The deliberate a priori establishment of maps of bioavailable stable isotopes in modern environments or archaeological strata was a first approximation to "archaeological isotopic landscapes" and was developed only slowly in the course of the last decade (see below). The accumulating knowledge on the distribution of stable isotopes in the environment in time and space was followed by a refinement of the simplified notion that outliers necessarily represent primarily non-local individuals. Growing insights into the small-scale variability in isotopically characterized ecogeographical compartments gave rise to more fruitful discussions on mobility versus migration/trade in the past. In the case of individual or collective residence change, as depicted by "non-local" stable isotope signatures in the skeletal remains, distance travelled is a crucial aspect. A single micro-region might be patchy in terms of stable isotopic signatures, and simple mobility within such a region can be easily mistaken as migration and trade.

Brief Introduction into the Research Substrate: Archaeological Skeletal Remains

Bioarchaeological finds are preserved organic remains, either the remnants of former beings or preserved artefacts manufactured from organic material. Soft tissue preservation requires special burial conditions (e.g. bog bodies, fossils) or post-mortem treatments such as intended mummification. While stable isotope analysis is also applied to such remains, this will not be considered in this book because the vast majority of bioarchaeological research substrates are made up of mineralized tissues such as bones, teeth and shells. Biominerals are formed by living organisms and are under genetic control, permitting for sizes and shapes that do not occur in the course of inorganic mineralization (e.g. dissymmetry). Also, biominerals are primarily composite materials consisting of minerogenic nanocrystals that are surrounded and penetrated by organic material. In the living being, the structured composition of organic and inorganic components guarantees for material properties such as pressure and tension resistance. Since the research efforts that led to this book concentrate on how to evaluate migration and culture transfer in a defined reference area, focus is on vertebrate skeletal remains because both humans and many non-human vertebrates are mobile by nature. Recovered shells are not considered because they are either the remnants of the local fauna or were transported to the site of their recovery by their owners or as trade goods.

With the exception of cell-free tissue, such as mature dental enamel, the major constituents of the vertebrate skeleton are the elastic structural protein collagen (type I) and the pressure-resistant calcium phosphate mineral. Mature human bone consists of about 70 % mineral and 21 % collagen, mature enamel of >96 % mineral and a few weight percentages of non-collagenous proteins, while tooth dentine largely resembles bone in its gross composition (Grupe et al. 2015). The minerogenic fraction corresponds to hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), but is both calcium deficient and carbonated and is therefore named "bioapatite". Calcium

lattice positions may be substituted by trace elements such as the non-essential elements strontium and lead that are sequestered into the skeleton after assimilation. As a result, the calcium/phosphate ratio in bioapatite is somewhat lower than the respective ratio in the ideal hydroxyapatite (1.4–1.6 opposed to 1.67, Pate 1994). Both the phosphate and the hydroxyl group are substituted by carbonate anions in vivo (Peroos et al. 2006) but do not amount to more than 2–4 % in the living being. Bone mineral crystals are extremely small and thin platelets in vivo with an average size of only 50 × 25 nm and a thickness of 1.5–4.0 nm (Berna et al. 2004; Schmahl et al. 2017). This size and shape guarantees for a high reactive surface that is a necessity for an active metabolic organ, but requires a constant energy supply for its maintenance. After death, energy supply ceases and the crystals readily start growing in size. At the same rate as the surrounding organic material is degraded in the course of dead bone decomposition, this growth will continue until all intracrystalline porosities are filled and the bone turns into a closed system (Trueman et al. 2008). Mineral crystals of dental enamel are much larger and of µm size and are combined into bundles with a diameter of about 4 µm (Hillson 1996).

Collagen type I is responsible for the elasticity of bone and makes up about 90 % of all organic molecules in the living skeleton. It is a highly conservative structural protein that occurs in all connective tissues that have to stand tension forces. Mature collagen type I is a triple helix consisting of two α1(I) and one α2(I) chain, each made up of 338 tripeptides corresponding to 1014 amino acids of the glycine-X–Y type. Being the smallest of all physiological amino acids, the presence of glycine at every third position of the helix permits for a particularly tightly twisted chain. The triple helix is stabilized by a high abundance of the amino acid hydroxyproline by forming hydrogen bonds and pyridinoline cross-links which are specific for bone collagen (Grupe et al. 2015). While the single collagen molecule has an average length of about 300 nm and a thickness of about 1.5 nm, its combination into fibrils leads to bundles that can reach a length of several millimetres and a thickness of several hundred nanometres (Weiner and Wagner 1998; Persikov et al. 2000). Bone collagen is therefore a highly stable and hardly soluble molecule. These properties and its embedding into the bioapatite are the reasons why this organic molecule is at all capable of surviving hundreds and thousands of years after death in the soil and may serve as a substrate for several archaeometric methods such as radiocarbon dating, among others. This does not imply that bone collagen is infinitely stable and not subject to dead bone decomposition, but its state of integrity after purification from a bioarchaeological find is securely and easily assessable by its amino acid profile. This availability of a routine molecular biological method for the assessment of the molecule's state of integrity contrasts with the definition of the state of preservation of archaeological bone and tooth mineral (see Schmahl et al. 2017).

Stable Isotopes in Archaeological Skeletons and Their Research Potential for Migration Research

Stable isotopes in vertebrate skeletal remains which are suitable for an ecogeographical isotope mapping concern on the one hand the light elements hydrogen (H), carbon (C), nitrogen (N) and sulfur (S) in bone collagen, whereby carbon, hydrogen and in addition oxygen isotopic ratios are also measurable in the bone mineral (phosphate and structural carbonate groups), and on the other hand the heavy elements strontium (Sr) and lead (Pb) that substitute for calcium lattice positions in the bioapatite (Fig. 1). Since the mass differences of isotopes of light elements are relatively large with regard to the element's atomic weight, stable isotope abundances are expressed by the δ-notation as $\delta = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}]*1000$ in ‰ with R being the molar ratio of the heavy to the light isotope. A quasi-linear relationship exists between the δ-value and the abundance of the heavy isotope in a natural sample. For heavy elements with an atomic mass exceeding about 50 mass units, absolute abundance ratios are used (e.g. $^{87}Sr/^{86}Sr$) because fractionation is negligible. While this has long been assumed for logical reasons, it has been verified experimentally only very recently (Flockhart et al. 2015). *Per definition*, the fractionation factor α between source x and product y is expressed as $\alpha_{x-y} = R_x/R_y$. In most bioarchaeological publications, this fractionation factor is expressed in a simplified way as the mere difference of the δ-values between source and product $\Delta_{x-y} = \delta_x - \delta_y$ although this is not mathematically correct. However, Δ is suitable for an empirical assessment of the amount of isotopic partitioning during element

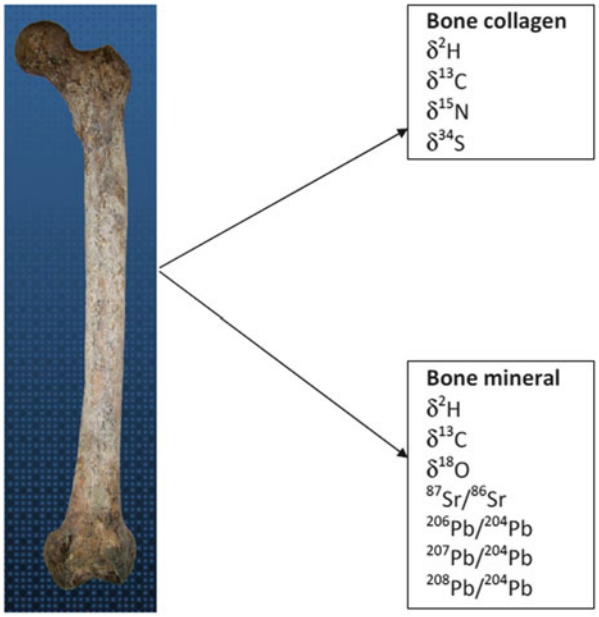

Fig. 1 Isotopic ratios routinely measured in archaeological skeletal remains

Table 1 Average atomic fraction (abundance %) of selected isotopes, and standard reference material for analysis. Abundance data from Hobson (1999), Ben-David and Flaherty (2012), and West et al. (2010b)

Element	Isotope	Abundance (%)	Standard
Hydrogen	^{1}H	99.985	V-SMOW
	^{2}H (=D)	0.015	
Carbon	^{12}C	98.90	V-PDB
	^{13}C	1.10	
Nitrogen	^{14}N	99.63	AIR
	^{15}N	0.37	
Oxygen	^{16}O	99.76	V-SMOW
	^{18}O	0.20	
Sulfur	^{32}S	95.02	CDT
	^{34}S	4.21	
Strontium	^{86}Sr	9.86	SRM 987
	^{87}Sr	7.0	
Lead	^{204}Pb	1.4	SRM 981
	^{206}Pb	24.1	
	^{207}Pb	22.1	
	^{208}Pb	52.4	

transport, e.g. through the food chain. As long as Δ does not exceed about 10 ‰, it constitutes a reasonable approximation for α because $\Delta_{x-y} \approx 10^3 \ln \alpha_{x-y}$ (West et al. 2010b). An overview of the average abundance of stable isotopes in elements which are suitable for bioarchaeological purposes is given in Table 1.

Stable isotope ratios in archaeological skeletal finds that are frequently used for the reconstruction of migration and trade in prehistory concern the radiogenic strontium and lead isotopes and $\delta^{18}O_{phosphate}$ in bioapatite. The radiogenic isotopes are related to the overall geochemistry at a site, while $\delta^{18}O$ is dependent on hydrological cycles and therefore on ecogeographical parameters. $\delta^{13}C$ and $\delta^{15}N$ in bone collagen are strongly related to diet and may serve as additional markers for provenance analysis in cases where the presumed place of origin of the finds and the site of their recovery are likely to differ in terms of the spectrum of edible plants and animals (see Fry 2006; Ben-David and Flaherty 2012). $\delta^{34}S$ in bone collagen mainly differentiates between marine/coastal and inland environments (Richards et al. 2001; Fry 2006) and is also related to diet. $\delta^{2}H$ can be measured both in bone collagen and the bioapatite. It is again governed by hydrological cycles and therefore strongly coupled with $\delta^{18}O$. Normally, a deuterium excess d is observed in stable isotopes in precipitation ($d = \delta^{2}H - \delta^{18}O \times 8$, Dansgaard 1964). However, $\delta^{2}H$ is still rather infrequently used for bioarchaeological purposes. First, a strong interference of ecogeography and diet is evident (Reynard and Hedges 2008; Petzke et al. 2010), and, second, hydrogen in both bone collagen and apatite is subject to exchange processes in the course of decomposition rendering the authentication of $\delta^{2}H$ in bone very difficult.

Isotope Maps and Isotopic Landscapes of Relevance for Bioarchaeology

The most advanced isotopic landscapes that are augmented on a regular basis concern the global hydrological cycles. The "Global Network of Isotopes in Precipitation" (GNIP) arose from a joint cooperation of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) that started a worldwide survey of the oxygen and hydrogen isotopic composition in precipitation (Dansgaard 1964; Aggarwal et al. 2010). Since the year 2007, the "Global Network of Isotopes in Rivers" (GNIR) is operated by the IAEA Water Resources Programme and monitors the isotopic composition of large river run-offs (Vitvar et al. 2007). Other projects initiated and supported by the IAEA are the "Moisture Isotopes in the Biosphere and Atmosphere" (MIBA, launched in 2004) and "Isotope Composition of Surface Waters and Groundwaters" (IAEA-TWIN, launched in 2003) networks (Aggarwal et al. 2010). For a prediction of stable isotope ratios in water, soils and plants, the IsoMAP modelling tool was first released in 2011 (Bowen et al. 2014). With regard to the global climate change, these networks are of outstanding importance for a deep understanding of the water flux in the course of environmental processes.

Empirical local maps of $\delta^{18}O$ in precipitation exist worldwide, of relevance for the transalpine passage investigated in this book are, e.g. the publications by Humer et al. (1995), Longinelli and Selmo (2003) and Kern et al. (2014). Bioarchaeology tries to make use of these existing isotopic landscapes and isotope maps by transforming stable oxygen (and to a far lesser extent also hydrogen) isotopes in the bioapatite of human and animal skeletal remains to $\delta^{18}O$ in precipitation in an attempt to gain insights into palaeoclimates and individual place of origin. Longinelli and Nuti (1973) were the first to relate $\delta^{18}O_{phosphate}$ to water and temperature and gave way to numerous studies using archaeological bones and teeth as substrate for the reconstruction of palaeoclimate proxies (e.g. Fricke et al. 1998; Luz and Kolodny 1985, 1989; Shemesh et al. 1983, 1988). Technical and methodological progress, as well as corrections with regard to the standard reference material NBS 120c, led Pucéat et al. (2010) to publish a revised regression between $\delta^{18}O_{phosphate}$, $\delta^{18}O_{water}$ and temperature (T):

$$T(^{\circ}C) = 118.7 - 4.22\left[\left(\delta^{18}O_{phosphate} + \left(22.6 - \delta^{18}O_{NBS120c}\right)\right) - \delta^{18}O_{water}\right],$$

with the result that previously published applications of $\delta^{18}O_{phosphate}$ for the reconstruction of past climates underestimated the palaeotemperature of water by 4–8 °C. But still, stable oxygen isotopic ratios prove to be accepted climate proxies.

Closely linked with climatic conditions are stable carbon isotope ratios in vegetation. Terrestrial plants preferentially assimilate the $^{12}CO_2$ over the $^{13}CO_2$ molecule in the course of photosynthesis, whereby plants using the photosynthetic C_3 and C_4 pathways differ in their isotopic fractionation leading to significantly different plant $\delta^{13}C$ values (Farquhar et al. 1989). The majority of terrestrial vegetation in the temperate climates follows the C_3 photosynthesis, while the C_4

pathway is largely restricted to herbaceous plants that prefer open, warmer and more arid environments. The overall higher flexibility towards different growth conditions in addition leads to a smaller variability of C_4 plant $\delta^{13}C$ values (about −15 ‰ to −11 ‰) compared to those of C_3 plants (on average −27 ‰ to −22 ‰, but with much lower values under closed canopies; Still and Powell 2010; Ben-David and Flaherty 2012). These isotopic differences in the primary producers are transferred into the consumer's tissues and are therefore frequently used by bioarchaeologists for the reconstruction of palaeodiets from the skeleton (with consideration of some *caveats*; see Grupe et al. 2015). $\delta^{13}C$ values of aquatic primary producers can differ from terrestrial ones, but are highly variable and related to the assimilation of different inorganic carbon species (bicarbonate versus dissolved CO_2, Mook et al. 1974; Keeley and Sandquist 1992), water temperature, salinity, amount of solubilized CO_2, water depth, etc. (Fry 2006). Differences in $\delta^{13}C$ of human bone collagen from the same archaeological site are basically indicators of different dietary preferences of the consumers and can give clues to the general past subsistence economy such as fishing versus farming (e.g. Grupe et al. 2013) and can assist in identifying immigrated human or animal individuals which originated from regions with a different vegetation cover. Because of a fairly constant offset between $\delta^{13}C_{collagen}$ and $\delta^{13}C_{carbonate}$ in the skeleton (Passey et al. 2005), also $\delta^{13}C$ in the bone structural carbonate can be successfully measured for the scope of palaeodiet reconstruction and migration research. The creation of vegetation $\delta^{13}C$ isotopic landscapes that will be of great benefit for bioarchaeological research is straightforward (Still and Powell 2010).

Stable isotope ratios in bone collagen are related to the growth metabolism of a vertebrate and mirror the respective isotopic composition of the protein part of the diet. While $\delta^{34}S_{collagen}$ reliably differentiates between terrestrial and marine environments and is therefore also a useful isotopic system for palaeodietary and potentially related migration research in bioarchaeology (Privat et al. 2007), the relationship of $\delta^{15}N$ and diet can be rather variable and less useful for migration research despite an overall enrichment of proteins with ^{15}N in marine environments. Since heavy isotopes prefer the stronger molecular bonds, ^{14}N is enriched in excreta in the course of protein metabolism, leaving the consumer's tissues enriched with ^{15}N. This leads to a significant trophic level effect in the course of the food chain (Caut et al. 2008), but the nitrogen cycle as such is complex. As a result, nitrogen uptake by the primary producers and the soil properties in terrestrial environments can be highly variable and dependent on former land use, among other factors (Pardo and Nadelhoffer 2010). $\delta^{15}N_{collagen}$ therefore does not contribute much to bioarchaeological migration research, with the exception of special scenarios related to mobility and residence change between coastal and inland sites.

Stable strontium isotope ratios ($^{87}Sr/^{86}Sr$) have long been used in ecological and bioarchaeological studies for the reconstruction of place of origin and migration of modern and past humans and animals (e.g. Bentley 2006; Crowley et al. 2015). ^{87}Sr is a radiogenic isotope and the decay product of ^{87}Rb, which has a half-life of 48.8×10^9 years which by far exceeds the age of our planet. In the course of our

earth's history, stable strontium isotopes with the masses 84, 86 and 88 gained constant ratios, while the abundance of ^{87}Sr in rocks is a function of the initial ^{87}Rb concentration in rock and its age. Therefore, geochemistry has greatly benefited from the $^{87}Sr/^{86}Sr$ ratio for dating rocks (Faure 1986). Since soil is largely generated from weathering rock, $^{87}Sr/^{86}Sr$ in terrestrial ecosystems is related to parent rocks, whereby oceanic basalts and young volcanic rocks typically exhibit $^{87}Sr/^{86}Sr$ isotopic ratios around 0.7036, while Rb-rich continental rocks have much higher ratios such as around 0.737 (Faure 1986). Due to global mixing, modern ocean water has a relative constant $^{87}Sr/^{86}Sr$ isotopic ratio of 0.7092, however, with some variability dependent on the salinity (e.g. Andersson et al. 1992). Today, a geological map exists for nearly every place on the planet that gives clues to the smaller and larger scale variability of stable strontium isotope ratios in bedrock. While such empirically generated maps may be helpful in defining expected $^{87}Sr/^{86}Sr$ values in bioarchaeological finds, they can at the same time be very misleading because the bioavailable strontium which enters the biosphere can significantly differ in its isotopic composition from the respective bedrock (Sillen et al. 1998). Let alone that some soils are not at all related to local parent rock such as glacial till introduced into carbonate-dominated regions in the North German Plain in the course of the last glaciation, most rocks do not have a uniform mineral composition. First, some constituents of parent rock weather faster than others. Beard and Johnson (2000) have already pinpointed that carbonates are both rich in strontium and weather fast, and therefore, bioavailable strontium from a region characterized by, e.g. both carbonates and siliciclastics, is heavily biased towards the carbonate portion in terms of its isotopic signature. Second, in contrast to Rb, which is an alkali metal, Sr is an alkaline earth element and behaves differently in geological reactions. Resulting differences in the Rb/Sr ratio of rocks are accordingly reflected in variations of $^{87}Sr/^{86}Sr$ isotopic ratios in ecosystems (Capo et al. 1998; Porcelli and Baskaran 2012) what basically permits the routing of $^{87}Sr/^{86}Sr$ to its geological source.

However, discerning local from non-local $^{87}Sr/^{86}Sr$ isotopic ratios in bioarchaeological finds necessitates both some geological variability between place of origin and place of recovery and at the same time a relative geological homogeneity at the latter (Slovak and Paytan 2012). This prerequisite is rarely met: The worldwide variability of archaeological human dental enamel is significantly compressed compared to the geological variability at any site (Burton and Hahn 2016) because consumer $^{87}Sr/^{86}Sr$ ratios are dependent from a finite number of calcium-rich food items (Meiggs 2007; Fenner and Wright 2014). 95 % of $^{87}Sr/^{86}Sr$ isotopic ratios of 4885 human dental enamel samples originating from six continents fall within the narrow range between 0.7047 and 0.7190 (Burton and Price 2013). Definition of the typical "local" bioavailable $^{87}Sr/^{86}Sr$ isotopic ratio is therefore far from easy. Several methods for the assessment of local strontium isotope ratios in archaeological strata have been suggested, such as the accompanying analysis of archaeological remains of the residential fauna (Price et al. 2002), sampling of modern reference material such as soil, water, snails and flora (Frei and Frei 2011; Maurer et al. 2012) or simply by referring to the majority

of measured $^{87}Sr/^{86}Sr$ isotopic ratios in an archaeological human population under the assumption that the majority of individuals should have been local to the site (Wright 2005). While the latter is a plausible assumption for any settlement chamber, it may however lead to circular conclusions and will be misleading in case of pioneering populations (Grupe and McGlynn 2010). Also, imported food such as salt (Fenner and Wright 2014) or the reliance on marine resources may obscure the data.

As a result, isotopic mapping for a detection of immigrant people or imported animals is still mainly performed by gathering as many data as possible from the finds themselves and from accompanying archaeological or modern ecological samples to get an overview of the isotopic variability in the region of interest. Without doubt, such empirical data are the indispensable prerequisite for model predictions. Geological maps can be used for a gross estimation of expected isotopic ratios to assess possible places of origin of finds which do not fit into the "regional" isotopic range. A list of major such radiogenic strontium isotope studies in bioarchaeology with regard to Europe, the Mediterranean and the Americas is provided by Slovak and Paytan (2012, pp 756–757). Such isotopic maps however do not fulfil the requirements for a definition of an "isotopic landscape". Primarily non-local individuals are readily identified by the exclusion principle, but their possible place of origin remains ambiguous because of the spatial redundancy of isotopic ratios. Slovak and Paytan (2012) are therefore right in claiming that "scientists should formulate hypotheses and devise their sampling strategy", because "the interpretation of $^{87}Sr/^{86}Sr$ data is hardly straight forward". Bioarchaeological strontium isotope maps are thus useful for supporting or rejecting any archaeological hypothesis about possible place of origin of immigrants to a site, but still cannot predict it with a certain probability.

Meanwhile, the simple amount of accumulated data resulted in regional archaeological isotopic maps covering several regions worldwide (e.g. Sillen et al. 1998; Porder et al. 2003; Hodell et al. 2004; Hedman et al. 2009; Maurer et al. 2012; Evans et al. 2010). Alternatively, an a priori isotopic mapping of suitable material can be performed for a defined region of interest for a subsequent application to bioarchaeological finds to come to answer precise questions related to migration and trade. Several such studies already exist, but are still the exception to the rule (e.g. Price and Gestsdóttir 2006; Gillmaier et al. 2009; Nafplioti 2011; Voerkelius et al. 2010; Frei and Frei 2011; Brems et al. 2013; Willmes et al. 2014). This latter procedure was chosen for the study of transalpine mobility in our project (see Toncala et al. 2017). A few years ago, a major step towards strontium isotopic landscapes was made by Bataille and Bowen (2012) by the development of a "local water model" capable of predicting $^{87}Sr/^{86}Sr$ in surface waters. Essentially this prediction relies on the relationship of bedrock with a weathering model and the resulting contributions of dissolved strontium in water. Shortly thereafter, Bataille et al. (2014) issued an independent sub-model for siliciclastic sediments. Crowley et al. (2015) undertook large efforts in compiling hundreds of published $^{87}Sr/^{86}Sr$ ratios of surface water, soil, vegetation, fish and mammalian bone across the USA and compared the accuracy of predictability by the use of the aforementioned local

water model. Besides the expected outcome that the predictability is higher in geologically homogenous regions compared to more complex ones, one result is of particular interest for bioarchaeology, namely, the fact that mammalian skeletons were most accurately predicted. This led the authors to conclude that at least in their study, mammal bone and the local water model "integrated Sr in similar ways"…"making mammal tissues particularly well suited for the model" (Crowley et al. 2015). Larger mammals (>100 kg) exhibited lower offsets between modelled and empirically measured isotopic ratios than smaller mammals, possibly because they integrate Sr "across broader spatial scales" (Crowley et al. 2015). In a small pilot study performed in the frame of the transalpine project, Söllner et al. (2016) had modelled and predicted local $^{87}Sr/^{86}Sr$ isotopic ratios in archaeological skeletons of cattle, pig and red deer from modern ecological reference samples. While at some sites, soil $^{87}Sr/^{86}Sr$ in the archaeological horizons had greatly influenced the respective isotopic ratio in mammalian bones, skeletal $^{87}Sr/^{86}Sr$ was almost exclusively related to the isotopic ratio of available Sr in water at a single site. It is apparent that soil/water/atmosphere/vegetation interdependencies resulting in bioavailable strontium for the vertebrate consumer are more complex than expected and that the spatial distribution of $^{87}Sr/^{86}Sr$ in bioarchaeological samples has been too focussed on the underlying bedrock and overlying soil properties. These interdependencies need much more research efforts in the future, but the development of "strontium isotopic landscapes" for bioarchaeological purposes is straightforward.

Like strontium, lead becomes fixed into the skeletal hydroxyapatite at calcium lattice positions. Therefore, lead and strontium are not independent in terms of mineral metabolism. More than 90 % of lead that is not excreted is stored in the skeleton where it has a particular long biological half-life of up to 10 years in compact bone (Smith et al. 1996). Basically, lead isotopes in the mammalian skeleton can therefore be used as a georeferencing tool (Kamenov and Gulson 2014). Compared to $^{87}Sr/^{86}Sr$, however, lead isotopic ratios have less frequently been used for provenance studies in bioarchaeology (e.g. Carlson 1996; Yoshinga et al. 1998; Åberg et al. 1998; Chiaradia et al. 2003; Bower et al. 2005; Montgomery et al. 2005; Turner et al. 2009; Fitch et al. 2012). The often very low lead content in archaeological finds and in particular the technical difficulties in accurately measuring the least abundant isotope ^{204}Pb constituted only one limiting factor (Albarède et al. 2012; see below). It has been strongly advised that all four stable lead isotopes need to be taken into account for any georeferencing purpose (Kamenov and Gulson 2014; Villa 2016).

In general, lead isotopes should be very promising for provenance studies because radiogenic lead is the product of three different decay series: $^{238}U \rightarrow {}^{206}Pb$, $^{235}U \rightarrow {}^{207}Pb$ and $^{232}Th \rightarrow {}^{208}Pb$. Only ^{204}Pb is not a radiogenic isotope. Therefore, the variability of lead isotopic ratios in rocks is far higher than for $^{87}Sr/^{86}Sr$ (Bullen and Kendall 1998). Just as in the case of $^{87}Sr/^{86}Sr$, stationary and bioavailable lead and its respective isotopic ratios need to be distinguished from each other. While lead is absorbed tighter to mineral surfaces than strontium and therefore only

soluble at low pH values, it can also be transported in the form of organic lead complexes and is highly mobile in nature. Consequently, the assessment of a typical "local" stable lead isotopic ratio is much more difficult. In addition to the lithological sources, the atmospheric introduction of lead into a certain catchment area is also of crucial importance (Bullen and Kendall 1998). While such airborne lead is concentrated in the topsoil layers, lead and its respective isotopic ratios in groundwater are largely a function of rock weathering. Both lead sources will mix in stream water accordingly. Ombrotrophic bogs are to a large extent fed with water and nutrients from the atmosphere and are considered "long-term traps of airborne particles" (Dunlap et al. 1999). Early metal working by humans already had a measurable impact on atmospheric lead, and bog analyses indicate that since at least 2.300 years, atmospheric lead over Europe "has not had a natural background lead isotope signature" (Shotyk et al. 1996; Dunlap et al. 1999). According to several relevant studies, preindustrial lead isotopic ratios should fall into the following ranges: $^{206}Pb/^{207}Pb$, 1.21 ± 0.05; $^{206}Pb/^{204}Pb$, 18.90 ± 0.86; $^{207}Pb/^{204}Pb$, 15.66 ± 0.10; and $^{208}Pb/^{204}Pb$, 38.74 ± 0.57 (Shotyk et al. 1996; Kylander et al. 2010; Breitenlechner et al. 2010; Kamenov and Gulson 2014). With regard to the topic of this book, typical ratios for ore deposits in the Alps are $^{206}Pb/^{204}Pb$, 18.3–18.5; $^{207}Pb/^{204}Pb$, 15.6–15.7; and $^{208}Pb/^{204}Pb$, 38.3–38.7 (Villa 2016). Due to the impact of industrial lead sources such as leaded gasoline and their worldwide distribution, modern lead isotopic signatures are significantly different (Bollhöfer and Rosman 2001).

With regard to bioarchaeological applications of lead isotopes for the assessment of mobility and migration, it is logical to expect that residential vertebrates will also best reflect the local lead isotopic ratios at a site. But in contrast to Sr, lead sources and lead uptake may significantly differ in humans and animals. In general, lead enters the organism through the ingestion of food and drinking water, but also through the skin and lungs. While soil ingestion is a major source of lead in herbivores (the bones of which should therefore reflect local isotopic signatures), leachable Pb released from soil and dust dominates over dietary intake in modern humans (Kamenov and Gulson 2014; Keller et al. 2016). Since vertebrates also discriminate against ingested lead in favour of calcium, the lead content of mineralized tissues is by far lower than environmental lead contents. Only in recent times, the global heavy metal contamination led to more similar lead contents in tissues and the surrounding habitat (Elias et al. 1982). Neolithic human skeletons exhibit typical lead concentrations between <1 and 3 ppm only (Grupe 1991), a level that was named "physiological zero level" by Drasch (1982). Modern human skeletons in contrast may exhibit lead concentrations up to 70 ppm without any accompanying symptoms of lead intoxication (Fergusson 1990). But lead exposure can have been particularly high also during several epochs in human history which is of relevance for bioarchaeological studies. Ore smelting for the purification of, e.g. silver by the process known as *cupellation* leads to the formation of lead oxide that is highly toxic because of its solubility in body fluids (Waldron 1988). Extensive metal working in antiquity has resulted in the generation of regional anthropogenic "hot spots" which are contaminated to an extent that they were no

longer suitable for agriculture until modern times (Thornton and Abrahams 1984). Since it takes a particularly long time until soils are generated by weathering of rocks and sediments, soils belong to the non-renewable resources and are an important topic in the frame of modern efforts for environment protection (Reimann et al. 2012). But also daily life in history offered many opportunities for lead exposure, such as the lead contamination of acidic food that was cooked or otherwise prepared in lead vessels by formation of lead acetate. Because of its sweet taste (synonymous "lead sugar"), preparation of *sapa*, a concentrated fruit juice widely used both as sweetener and as preservative in Roman antiquity, was preferably performed in leaden cooking ware. *Sapa* should have been a major lead source for the population at that time (Alföldi-Rosenbaum 1984). With regard to stable isotope mapping, lead isotopes from such utensils of daily life are likely to overprint the isotopic ratios of locally occurring lead. Lead ores are characterized by fairly typical isotopic fingerprints which are reflected in manufactured artefacts and are helpful in provenancing items belonging to the material culture, whereby the isotopic ratios are often augmented by trace element analysis (Frotzscher et al. 2007; Fabian and Fortunato 2010; Ling et al. 2014; Villa 2016). The custom of reusing metals by smelting broken or otherwise useless artefacts introduces an additional problem because this will lead to mixed isotopic fingerprints that are not easy to resolve. With regard to the reconstruction of human mobility and migration, primarily local individuals may therefore exhibit stable lead isotopic signatures that are no longer compatible with the respective local ratios in their native environment simply because of daily contact with traded and therefore non-local lead artefacts.

Provenancing metal objects by lead isotopic ratios has a long history in archaeometry, and extensive isotopic data bases do exist (for Europe, e.g. Durali-Mueller et al. 2007; Stos-Gale 1993; Stos-Gale and Gale 2009). Reimann et al. (2012) published a lead isotopic map of European agricultural soils a few years ago. Recently, Albarède et al. (2012) suggested to additionally focus on the geological age of the tectonic provinces where the ores have been generated and presented a model to evaluate a "geological model age" and the necessary U/Pb (μ) and Th/U (κ) ratios from lead isotopic ratios, thereby reorganizing existing Pb isotopic databases to better decipher these measurements for provenance studies of metals. But still, most provenance studies relying on lead isotopes make use of the normal "isotopic fingerprint" provided by the raw measurement data (Klein 2007). In this field, archaeometry is probably much further away from the generation of an isotopic landscape compared with stable strontium and oxygen isotope analyses. While prehistoric, historic and modern lead isotopic signatures are significantly different from each other, telling the place of origin is still not easily achieved because of the geological redundancy and the quite large catchment area of airborne lead. Villa (2016) is therefore right in claiming that archaeometry should rely on "Occam's razor: the nearest ore source, as small as it may be is the most likely choice of origin".

Persistent Challenges

In contrast to archaeological finds of artefacts manufactured from inorganic materials, stable isotope ratios in bioarchaeological finds were generated in the course of individual metabolism and have been under physiological control. When it comes to provenance analyses, these physiological parameters need to be taken into account, but still, they are largely unknown or at least known in insufficient detail. This is probably the largest obstacle for the generation of bioarchaeological isotopic landscapes.

Considering the most frequently used isotopic systems for provenance analysis, namely, oxygen, strontium and lead isotopes in the skeleton, $\delta^{18}O$ is independent from lead and strontium isotope ratios, but the latter two are not independent in terms of mineral metabolism because strontium and lead compete over calcium lattice positions in the bone/tooth mineral (see above). Reconstructing human mobility is more complex than residence change of herbivorous mammals, since omnivores assimilate a variety of different food items and the measured isotopic ratio in any tissue is made up of the weighted average of the respective dietary isotopic signatures. The first challenge therefore lies in the definition of the most important element sources which automatically implies that although stable isotope ratios are important data with a high explanatory value, they will always remain approximations. The question is how closely a past reality can be approximated at all.

Accompanying analyses of animal bone finds still are the main clue for defining the most probable local isotopic signatures for humans. Since humans and animals have different water and food sources, the human isotopic fingerprints should be similar to those of the animals (provided that all animals were in fact local to a site and not imported), but not identical. With regard to $\delta^{18}O$, average ambient humidity may have a considerable impact on animal bone $\delta^{18}O$ depending on the species (Kohn 1996). Humans are known to seldom drink surface water but rather prefer water from springs, wells or cisterns. Standing water is in constant exchange with the atmosphere, and $H_2{}^{16}O$ molecules will preferably evaporate, opening up the possibility of generating a $\delta^{18}O$ value of drinking water that significantly differs from $\delta^{18}O$ in precipitation. Another issue that has been raised early by Luz and Kolodny (1989) but has not received much attention afterwards is the fact that the residence time of phosphate in a skeleton varies between different types of bone. In the event that people migrate across climatic boundaries and ingest water of a different stable oxygen isotopic composition, the bones of the skeleton will respond to this at different rates. The resulting heterogeneous isotopic composition of a single skeleton can be very useful for the reconstruction of past migration, but necessitates a standardized sampling procedure. This holds also for the analysis of stable strontium and lead isotopes because of a strong reservoir effect in the mammalian body (Montgomery et al. 2010) and the faster turnover rate of trabecular opposed to compact bone.

It took many years until the significant impact of dietary preferences on consumer $^{87}Sr/^{86}Sr$ isotopic ratio was accepted (Burton and Hahn 2016), and still, this

important topic is often neglected in relevant publications. With regard to the variety of lead sources in the environment, sourcing the accumulated lead isotopic signatures in a skeleton is still in its infancy. In other words, while it is at present technically possible to measure original stable lead isotopic ratios in bioarchaeological finds after application of appropriate laboratory protocols, the information hidden in the measurement data is far from being deciphered. This constitutes a big obstacle especially in any attempt to generate lead isotopic landscapes.

The spatial variability of oxygen, strontium and lead isotopes in a given region of interest is mostly at hand or can be generated for archaeological strata. It has also been accepted that the spatial redundancy of all three isotopic systems necessitates the establishment of a "multi-isotope fingerprint" for each individual. Such multi-isotope studies are gaining importance, but frequently, the measured stable isotopic ratios are still compared and related to each other one by one (e.g. Müller et al. 2003). Modern mathematical tools are seldom applied, such as the hierarchical clustering of Pb, Sr and O isotopic parameters by Turner et al. (2009) or clustering of lead and oxygen isotopic ratios by Keller et al. (2016). Since the isotopic ratios $\delta^{18}O$, $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ may be taken as seven different, partly dependent and partly independent features capable of characterizing an individual bone find, data mining methods such as Gaussian mixture model clustering and application of an expectation-maximization algorithm have been tested in our transalpine project with a promising outcome (Mauder et al. 2016, 2017).

Resolving isotopic mixtures in geological systems is not trivial, but mixing in the biosphere and the evaluation of the involved metabolic processes is even more difficult. Many efforts have been and still are undertaken to generate bioarchaeological isotopic landscapes, and there is a strong reason to believe that the information hidden in multi-isotopic fingerprints of biominerals is far from being fully exploited. The isotopic mapping of one of the most frequently used Alpine passages, which demonstrates that a geographical obstacle does not prevent culture transfer and population admixture, is just one of the ongoing research efforts in the field.

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