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Modelling strontium isotopes in past biospheres – Assessment of bioavailable $^{87}Sr/^{86}Sr$ ratios in local archaeological vertebrates based on environmental signatures

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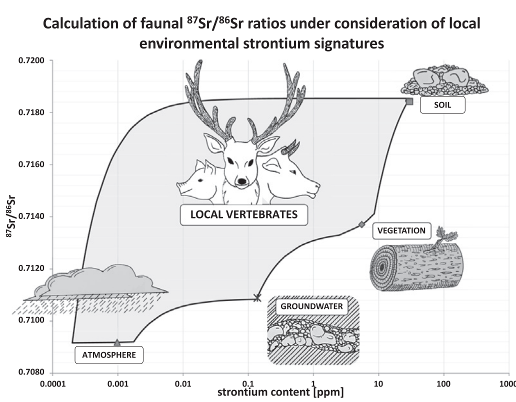
HIGHLIGHTS

- A mixing model for the prediction of local archaeofaunal $^{87}Sr/^{86}Sr$ was established.
- $^{87}Sr/^{86}Sr$ and Sr content of environmental samples were measured: soil, groundwater and wood.
- Local $^{87}Sr/^{86}Sr$ spans were calculated for 24 sites and compared with archaeozoological material.
- Results suggest the model to be a valuable tool for the determination of local $^{87}Sr/^{86}Sr$ spans.

GRAPHICAL ABSTRACT



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ABSTRACT

$^{87}Sr/^{86}Sr$ isotopic ratios in skeletal remains of archaeological vertebrates are used for provenance analysis since long. However, the definition of the past bioavailable isotopic ratio at the site of recovery is not known beforehand and geological maps can provide no more than gross expectations. Therefore, the assessment of the "local Sr isotopic signature" is still of crucial importance. In this study, we present a tool for the prediction of such local isotopic signatures by creating a concentration weighted mixing model that links lithospheric, biospheric, and atmospheric strontium per site. The major strontium sources and their input into an animal's body were assessed by choosing elemental strontium and its isotopic signature in groundwater, soil, vegetation, and precipitation as components for the mixing model, augmented by literature values. The model was applied to 24 sites located in the alpine transect of the Inn-Eisack-Adige-Brenner passage across the European Alps, a passage used since the Mesolithic. Predicted local bioavailable $^{87}Sr/^{86}Sr$ ratios were compared with measured values from locally excavated archaeozoological bone samples from three taxa of large and mainly residential vertebrates (cattle, pig, red deer) to verify the models' accuracy. With regard to the fact that the environmental samples predict the past local bioavailable $^{87}Sr/^{86}Sr$ at a specific site while the vertebrates had different and species-specific home ranges, thereby integrating strontium from a region of primarily unknown size, the model is capable of assigning reasonable expectation values. For 11 sites, up to 100% of the vertebrate isotopic signatures were

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correctly predicted. Mismatches at the remaining sites are explainable by special environmental factors, and also the fact that some import of animals can never be excluded beforehand. Suggestions for site-specific adjustments of the model are made.

1. Introduction

Strontium isotope studies are performed by several sciences such as physical anthropology, archaeology, zoology, forensics, geology, pedology, ecology and hydrology (see e.g. reviews by Bataille and Bowen, 2012; Hajj et al., 2017). Since strontium is a heavy element with a standard atomic mass of 87.62 u (Meija et al., 2016), mass differences between its isotopes, in particular between ^{86}Sr and ^{87}Sr, are very small in relation to the atomic mass and isotopic fractionations in biochemical reactions are undetected so far (Flockhart et al., 2015; Pouilly et al., 2014; Song et al., 2014). Therefore, ^{87}Sr/^{86}Sr as such is not altered in the course of its flux through the biosphere due to higher reactivity or preferential reactant of one isotope over another, but rather due to concentration weighted mixing of strontium sources with differing ^{87}Sr/^{86}Sr ratios.

Strontium in terrestrial ecosystems is mainly derived from the geosphere, where soils formed by erosion of the underlying bedrock have similar strontium isotopic compositions (Beard and Johnson, 2000; Capo et al., 1998). By weathering of the bio-available mineral components of soil, geology derived strontium is released into the biosphere (Bataille and Bowen, 2012). Residential vertebrates integrate different strontium sources of their home range. Different local bio-available ^{87}Sr/^{86}Sr signatures of distinct home ranges are accordingly reflected in the tissue of animals and humans which can thus be distinguished by their strontium isotopic signatures. Using strontium isotopes for the reconstruction of the place of origin as well as trade and migration patterns of both living and dead organic specimens, be they animal or human, however requires both the definition of local strontium isotopic signatures and an appropriate cut-off value between place of origin and place of recovery. In most bioarchaeological provenance studies, immigrants/imports to a site are thus identified by the exclusion principle only.

In general, two possible approaches for the determination of local bio-available strontium isotopic signatures exist. The first one is the measurement of ^{87}Sr/^{86}Sr ratios in presumably local animals and humans at a site because these are assumed to have mainly incorporated the locally bio-available strontium. The local strontium isotopic signature is conservatively defined as the observed mean ^{87}Sr/^{86}Sr ratio $\pm$ the double standard deviation, or a fixed cut-off value of 0.001 (e.g. Ezzo et al., 1997; Grupe et al., 1997; Knipper et al., 2012; Price et al., 1994, 2004, 2015; Schweissing and Grupe, 2003). While this procedure assumes that the majority of the sampled individuals were residential, parameters like animal husbandry, species-specific home ranges, import of food and drinking water, as well as migration and trade might obscure the result. The second approach is the measurement of the strontium isotopic composition of local environmental reference material, such as plants, water, soil, and bedrock (Frei and Frei, 2011; Maurer et al., 2012; Price et al., 2002; Ryan et al., 2018). Unfortunately local isotopic signatures of bedrock, soil, water, flora and fauna do not always match with ^{87}Sr/^{86}Sr ratios in vertebrate body tissues since their strontium originates from various sources in different amounts and animal strontium uptake is heavily diet dependent (Burton and Price, 2013; Grupe et al., 2011). In addition, mixing strontium sources will result in mixed ^{87}Sr/^{86}Sr ratios and non-local sources such as river- or rainwater are of further influence.

The current state of research has advanced to a level where strontium isotopic ratios are available for several archaeological sites world-wide, and where attempts of creating “isotopic landscapes” for bioarchaeology by mapping strontium isotopic compositions of a variety of materials over small and large scaled areas are made (Brems et al., 2013; Gillmaier et al., 2009; Nafplioti, 2011; Price and Gestsdóttir, 2006; Toncala et al., 2017; Voerkelius et al., 2010; Willmes et al., 2014). While more or less detailed geological maps exist for almost every place on earth (Grupe et al., 2017), mixing models were generated to quantify the strontium flux from bedrock formation to bedrock and soil weathering into the bio- and hydrosphere, with the aim of assessing local bio-available ^{87}Sr/^{86}Sr ratios (Bataille and Bowen, 2012; Beard and Johnson, 2000; Brennan et al., 2016; Stewart et al., 1998). While isotopic maps and mixing model improvements constitute innovations for every newly exploited region and material type, prediction of strontium isotopic signatures of residential archaeological animals and humans have only recently been attempted (Söllner et al., 2016).

In the frame of the multidisciplinary research unit “Transalpine Mobility and Cultural Transfer” (www.for1670-transalpine.uni-muenchen.de), a concentration weighted mixing model for the calculation of local bio-available ^{87}Sr/^{86}Sr ratios in several archaeological strata was developed with the aim of providing reference data for provenance analysis in bioarchaeology, especially for cases of material scarcity. In doing this, the primary strontium sources of a vertebrate were reduced to the origins of elemental strontium, namely groundwater, soil, vegetation, and precipitation. Strontium isotopic signatures and concentrations of locally gathered groundwater, soil and vegetation samples were therefore measured for 24 archaeological sites in a reference area along an alpine transect, the Inn-Eisack-Adige passage through the European Alps. This reference area was chosen because of its particular archaeological importance in Central Europe (Grupe et al., 2017). Calculated local isotopic ratios were compared with those measured in the skeletons of three taxa of assumed residential vertebrates recovered at the same sites (cattle, pigs, red deer). The measurements of the environmental samples were augmented with published ^{87}Sr/^{86}Sr ratios in global precipitation. In this paper, we describe the establishment of the mixing model as well as its strengths and weaknesses in the prediction of ^{87}Sr/^{86}Sr values in archaeological vertebrate skeletons. This is done in the attempt to proceed a step forward with regard to the establishment of isotopic landscapes (“isoscapes”) for bioarchaeological purposes, since “isoscapes” include the fundamental parameters of prediction and modelling (Bowen, 2010).

2. Material and methods

2.1. Material

Environmental samples were collected at the archaeological sites or – if no longer accessible – at closest distance. Animal bones had been recovered, analysed and discussed previously (with geological site descriptions: Toncala et al., 2017, pp. 131–132). Sites with different archaeological dates were deliberately chosen to test whether the isotopic mapping would be applicable to different archaeological strata. Dating was performed according to the archaeological context. All 24 sites where environmental samples were gathered are located within the range of the European Alps, and therefore represent a high variability in geological strontium signatures and environmental conditions. Names and GPS-coordinates of the investigated sites as well as the linked site codes for each location are listed in Table 1, the geographical locations are visualized in Fig. 1. The sites are located in three countries,