DFG Research - Group FOR 1670

TRANSALPINE MOBILITY AND CULTURAL TRANSFER

Intraindividual variability of Pb and Sr in human skeletons from the Roman site of Stettfeld

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1 Introduction

Contrary to the determination of $^{87}Sr/^{86}Sr$ ratios in archaeological human bones and teeth for provenance analysis, investigations using stable Pb isotopes in bioarchaeology are relatively rare. Especially systematic investigations of lead isotopes and the related concentrations in skeletal tissue of different ontogenetic age (such as enamel versus bone) are mostly lacking. For this purpose 12 human bone and corresponding enamel samples from the Roman site in Stettfeld, near Stuttgart, were analyzed. The Stettfeld settlement is situated on a small jurassic islet (mudstone and limestone) bordering the Upper Triassic sand and mudstones (Keuper) and the loess to the east and the Pleistocene alluvial deposits of the Rhine to the west.

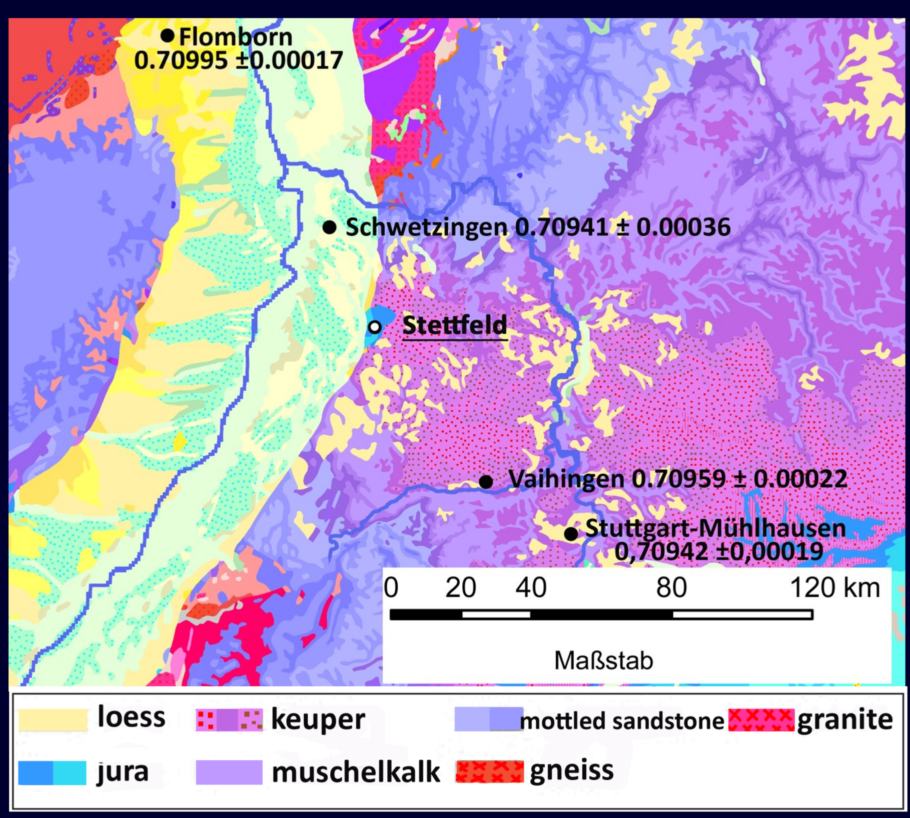

Fig. 1: Geological map of the area of Stettfeld. Figure modified after GBR GK1000 with human bone data taken from Price et al. (2003).

2 Material and Methods

In this pilot study, 20 enamel and 22 bone samples from 12 individuals from the Roman Stettfeld site in Baden-Württemberg (110 – 260 AD) have been taken and – if available – recently remodeled bone such as periostitis or callus. Per individual, different ontogenetic stages from early childhood until a few years prior to death are thus represented. Choice of the skeletons was due to the availability of an in-depth anthropological investigation (Wahl & Kokabi 1988), and the fact that the individuals most probably belonged to a sedentary population.

For Sr and Pb concentration analysis 10 mg of sample were microwave digested in 1 ml conc. HNO3 (suprapure) and finaly diluted to 10 ml. The concentrations were determined using an AAS with graphite furnace at the university Weihenstephan-Triesdorf. For quality control of the measurements NIST 1400 ware used (Tab. 1).

Sr and Pb isotope ratios were measured by TIMS Finnigan MAT 261.5 at the RiesKraterMuseum Nördlingen. The cleaning steps and column separation are reported elsewhere (Toncala et al. 2017). The isotope ratios of the SRM 987 and SRM 982 standard were stable during analysis and are in compliance with the appropriate certificate (Tab. 2). The blanks of the analytical procedure were below 1 ng Pb.

Tab. 1: Concentrations of the standard NIST 1400 and its associated certificate values

	Standard (N=6)	measured value ± σ	Certificate value ± σ
Sr µg/g	NIST 1400 (bone ash)	259 ± 22.7	249 ± 7
Pb µg/g	NIST 1400 (bone ash)	9.87 ± 1.42	9.07 ± 0.12

Tab. 2: Isotope ratios of the standards SRM 987 and SRM 982 and their associated certificate values

	Ratio	measured value ± σ	Certificate value ± σ
SRM 987 (N=4)	$^{87}Sr/^{86}Sr$	0.710206 ± 0.000029	0.71034 ± 0.00026
SRM 982 (N=5)	$^{206}Pb/^{204}Pb$	36.7294 ± 0.0129	36.7390 ± 0.0364
SRM 982 (N=5)	$^{206}Pb/^{207}Pb$	2.14118 ± 0.00045	2.14101 ± 0.00092

3 Results: Sr & Pb concentrations

In comparison to the literature (Schuh et al. 2016, Bentley et al. 2012, Oelze et al 2012), our samples show elevated Sr concentrations (Tab. 3). Additionally the Sr concentration correlates with the isotopy (Tab. 4) thus contamination by diagenesis can not be fully excluded.

The concentration of Sr and Pb in bone is significantly higher than in the enamel samples (Mann-Whitney-U-Test: twosided, α=0.05; Sr (U = 200; p>0.000); Pb (U = 188; p>0.001), Fig. 2). This is due to the accumulation of Sr and Pb in the body during life and/or diagenetic processes (Fig. 2).

The Pb concentrations on the other hand show no correlations with the Pb isotope ratios (Tab. 4). The data correspond to the expected values for a Roman settlement (median enamel Pb burden 3.6 ppm after Montgomery et

Tab. 3: Sr and Pb concentrations of the different sample types analyzed

		N	Mean	σ	Median	Min	Max	Range
Sr µg/g	enamel	20	224.57	151.86	189.50	94.40	674.00	579.60
	long bone	11	459.55	116.61	408.00	343.00	699.00	356.00
	rib	6	438.67	111.41	407.50	304.00	593.00	289.00
	new bone	4	317.75	79.16	327.50	221.00	395.00	174.00
Pb µg/g	enamel	20	2.22	2.88	1.01	0.30	10.90	10.60
	long bone	11	6.79	5.76	4.11	2.00	18.20	16.20
	rib	6	5.33	3.14	3.90	2.78	10.70	7.92
	new bone	4	9.76	7.22	6.83	4.90	20.50	15.60

al. 2010), indicate purity of the samples and contamination seems improbable. Furthermore the average Pb content for jurassic mudstones in Baden-Württemberg is 46,9 mg/kg (26-81 mg/kg) and for jurassic limestone 66,0 mg/kg (2,1-184 mg/kg) (LfU 1994), clearly above the Pb content of the samples.

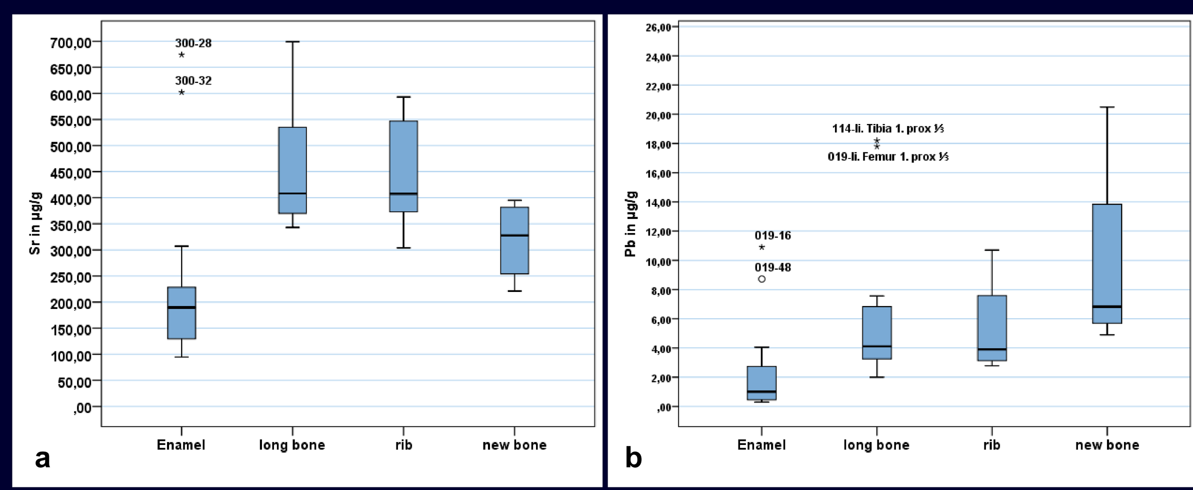

Fig. 2: a) Comparison of Sr concentrations in different sample types. b) Comparison of Pb concentrations in different sample types

4 Results: Sr & Pb isotope ratios

The results of all human samples are shown in figure 3 and table 5. To define a more specific local isotopic range, calculations with Isoplot were carried out and the kernel density evaluation was included as well (Tab. 6). A local range for example for $^{87}Sr/^{86}Sr$ via Isoplot (σ=1.82) from 0.70901 to 0.70975 (0.70938±0.0002) was the result.

Based on different chemical properties and their behaviour in the environment, the radiogenic Sr and Pb stable isotopes provide independent potential information about the place of origin of primarily non-local individuals. No correlation between Sr and Pb isotopic ratios was evidenced accordingly (Tab. 4).

In figure 3 all human samples from this study and geological samples from Ströbele et al. (2012) are depicted in a $^{207}Pb/^{204}Pb$ to $^{206}Pb/^{204}Pb$ plot. Additionally values of gasoline and soot (triangle) as source of contamination are plotted. The nearest available aerosole data (circles) stemming from Constance, Kehl und Strasbourg illustrate a mixed isotopy between natural geogene and anthropogene sources.

A clear differentiation between the human samples and anthropogene sources can be seen.

Human samples mostly plot within the jurasic and triasic geogene samples from the area east of the Rhine rift, as expected. Galena from Bruchsal represents the immediate isotopy on site. The distribution of data points in the diagram indicates that the individuals of Stettfeld are indeed local and their isotopy seem to be representative for Southwestern Germany more specifically Schwarzwald region.

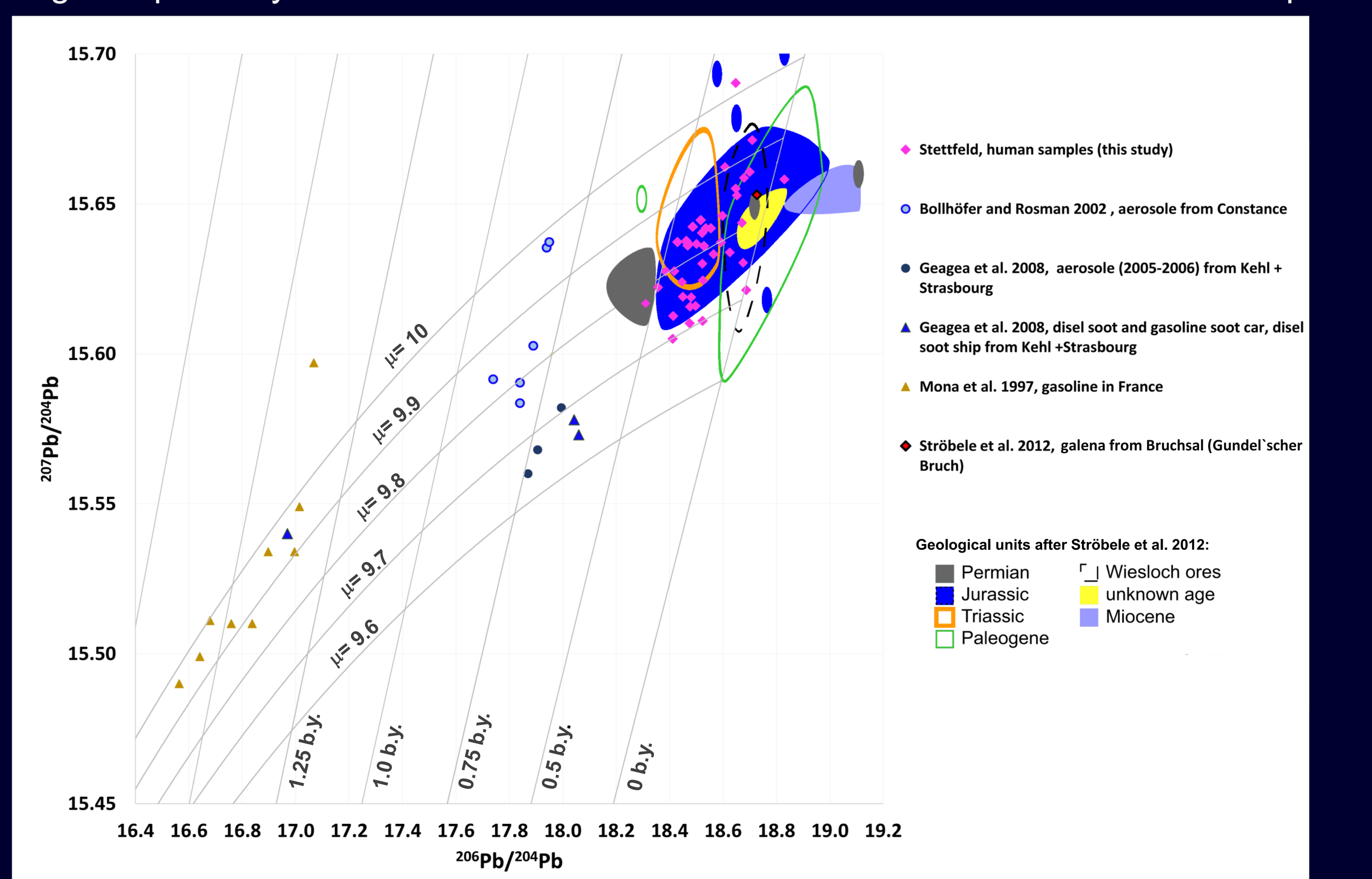

Fig. 3: $^{207}Pb/^{204}Pb$ to $^{206}Pb/^{204}Pb$ plot with all human samples from this study and comparative data of the surrounding geology and environment. Also shown are isotope evolution curves of a Pb isotope evolution model proposed by Stacey & Kramers (1975).

Tab. 4: Correlations between Sr and Pb isotope ratios and Sr and Pb concentrations

correlations		$^{87}Sr/^{86}Sr$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	Sr µg/g	Pb µg/g
$^{87}Sr/^{86}Sr$	Pearson correlation r	1	-.193	-.041	-.121	-.257	-.099	-.610**	-.081
	significance p (2-sided)		.227	.801	.450	.105	.539	.00002	.614
$^{208}Pb/^{204}Pb$	Pearson correlation r	-.193	1	.889**	.849**	.972**	.789**	.211	-.019
	significance p (2-sided)	.227		.00000	.00000	.00000	.00000	.192	.905
$^{207}Pb/^{204}Pb$	Pearson correlation r	-.041	.889**	1	.662**	.756**	.593**	-.021	-.119
	significance p (2-sided)	.801	.00000		.00000	.00000	.00004	.898	.465
$^{206}Pb/^{204}Pb$	Pearson correlation r	-.121	.849**	.662**	1	.874**	.985**	.200	-.192
	significance p (2-sided)	.450	.00000	.00000		.00000	.00000	.217	.234
$^{208}Pb/^{207}Pb$	Pearson correlation r	-.257	.972**	.756**	.874**	1	.825**	.312	.032
	significance p (2-sided)	.105	.00000	.00000	.00000		.00000	.050	.844
$^{206}Pb/^{207}Pb$	Pearson correlation r	-.099	.789**	.593**	.985**	.825**	1	.175	-.236
	significance p (2-sided)	.539	.00000	.00004	.00000	.00000		.281	.143
Sr µg/g	Pearson correlation r	-.610**	.211	-.021	.200	.312	.175	1	.229
	significance p (2-sided)	.00002	.192	.898	.217	.050	.281		.151
Pb µg/g	Pearson correlation r	-.081	-.019	-.119	-.192	.032	-.236	.229	1
	significance p (2-sided)	.614	.905	.465	.234	.844	.143	.151	

**. Correlation significant on the level of 0.01 (2-sided).

Tab. 5: Summary of Sr and Pb isotope ratios of the complete data set

	N	Mean	σ	Median	Min	Max	Span
$^{87}Sr/^{86}Sr$	42	0.70940	0.00062	0.70942	0.70782	0.71091	0.00309
$^{208}Pb/^{204}Pb$	41	38.492	0.123	38.471	38.243	38.803	0.560
$^{207}Pb/^{204}Pb$	41	15.636	0.018	15.636	15.605	15.690	0.085
$^{206}Pb/^{204}Pb$	41	18.538	0.111	18.523	18.310	18.830	0.520
$^{208}Pb/^{207}Pb$	41	2.4618	0.0055	2.4612	2.4489	2.4761	0.0272
$^{206}Pb/^{207}Pb$	41	1.1863	0.0064	1.1856	1.1725	1.2026	0.0301

Tab. 6: Local isotope range defined by Isoplot

	Isoplot σ	Mean	σ	Min	Max	Span
$^{87}Sr/^{86}Sr$	1.82	0.70938	0.0002	0.70901	0.70975	0.00074
$^{208}Pb/^{204}Pb$	2	38.460	0.066	38.351	38.605	0.066
$^{207}Pb/^{204}Pb$	1.9	15.631	0.012	15.610	15.655	0.045
$^{206}Pb/^{204}Pb$	2	18.536	0.095	18.353	18.710	0.353
$^{208}Pb/^{207}Pb$	2	2.4604	0.0031	2.4541	2.4673	0.0132
$^{206}Pb/^{207}Pb$	2	1.1862	0.0056	1.1750	1.1965	0.0215

5 Example of migration combining Sr and Pb Ratio

To find out if the Pb-system can be useful for provenance analyses and provide additional information supporting the Sr results a $^{87}Sr/^{86}Sr$ to $^{207}Pb/^{204}Pb$ plot was generated. In this diagram all 12 individuals and the local isotopy defined by Isoplot (blue lines) are depicted (Fig. 4).

The young female in grave 300, approximately 30 years old, did not adjust to the local isotope values of Sr and Pb (red arrow indicates the isotopic trend). Therefore she can clearly be identified as a non-local individual. During the morphological examination it was also noticed that her skull is clearly different in shape compared to the other women. Furthermore she was separtaley buried at the most south-eastern part of the graveyard.

The circa 30 year old man in grave 309 shows the local Pb and Sr isotopy in the bone samples. However his tooth 18 exhibits a higher radiogenic Pb signal, indicating his non-local origin. By only considering the Sr isotopic ratio of the tooth 18, his forgein provenance would have gone unnoticed.

The excavation of grave 348 revealed a man (B) and woman (A) buried one on top of the other. For this reason it is assumed that they were a couple or at least close relatives. This hypothesis can be supported by the results of the Pb and Sr isotope measurements, since they obviously spent their childhood in the same region.

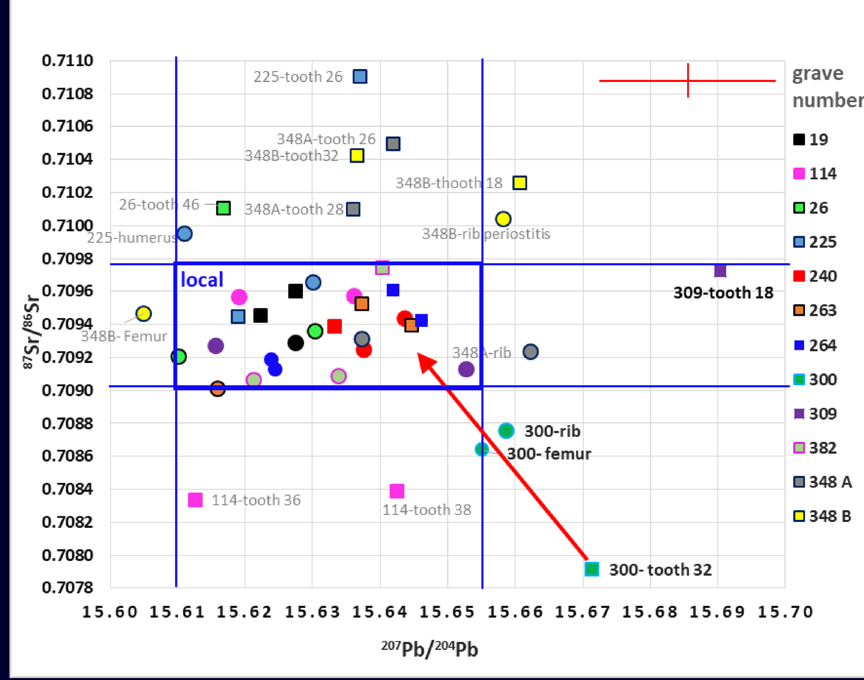

Fig. 4: $^{87}Sr/^{86}Sr$ to $^{207}Pb/^{204}Pb$ plot showing the twelve human individuals from this study. Circles represent bones, squares are tooth samples

6 Conclusion

The local Sr isotope ratio of Stettfeld (0.70938±0.0002) is in accordance with our expectations and is in good agreement with the results from other similar studies (Fig. 1).

There are no Pb isotope ratio data on historical bones available for comparison in this region, therefore geological samples were used (Fig. 3).

That we are able to demonstrate migration with Pb isotope ratios was shown in figure 4. Concentration measurements of Sr and Pb elements serve as first indicators for contamination.

It can be assumend that the original isotope ratios are preserved and migration can be determined. Although minor contaminations can not be excluded, they become negligible when the archaeological and anthropological investigations and hypotheses are in agreement with the obtained data.

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