



Tracking mobility using human hair: What can we learn from lead and strontium isotopes?



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ABSTRACT

The isotope ratios of strontium (Sr) and lead (Pb) in water derive from local geology and their isotopic signature can be linked to the age and type of underlying bedrocks and soils (if applicable), and are transferred up the food-chain. Both elements are transferred to human blood through diet and water, and some of it will ultimately be incorporated into the hair structure, making Sr and Pb isotopes interesting tools for tracing human mobility. In this study, we analyzed both the elemental concentration and isotope ratios of Sr and Pb from four different women of different ages to monitor their permanent relocation from central France to Eastern Canada during the summer 2012. For comparison, we also characterized bulk hair samples of sedentary individuals and local tap waters from their regions of origin and of settlement. Our results indicate that the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are significantly modified by the change of environment, but also confirm that human hair compositions are impacted by other external factors (such as dust). Sr and Pb isotope systematics demonstrate their added value for detecting human mobility, but require further studies to better constrain the main sources and processes controlling their respective budgets in human hair for provenancing purposes.

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1. Introduction

Strontium and lead are absorbed through the digestive system and are incorporated in the soft tissues of the body (i.e. hair, nails) through the bloodstream (Sr; [1]). Several sources contribute to the intake of Sr and Pb including endogenous sources as diet (foods, plants, water) and exogenous sources such as dust and aerosols. A study by the Agency for Toxic Substances and Disease Registry [2] suggested that humans ingested about 3.3 mg of strontium per day and in average up to 2 mg came from water. The absorption rate of Sr and Pb is an important factor to consider while determining the endogenous sources. While some vegetables may contain higher concentrations of Sr and Pb than water, if the human body cannot efficiently absorb these elements, the vegetable source remains insignificant compared to water. The same goes for any type of food. The isotope ratios of these elements have been used in numerous previous studies ranging from monitoring the lead contamination of a population [3] to tracing an individual's movement with strontium [4].

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from soil and water varies geographically, depending on the local geology, and is transmitted to plant and animals through nutrient intake and diet [4] with minimal or no fractionation [5]. The idea to use isotope ratios to trace an individual's movement derives from that very principle. Many studies have used the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio

in organic tissues, such as antlers, teeth, bones, leaves, feathers and hair [6–20] to link an individual to its environment, present or past.

The lead isotope system in the environment is similarly complex. Its isotope ratio depends on its geological sources, but also on anthropogenic inputs. An additional layer of complexity comes with the fact that globalization of markets reduced the isotope discrimination of commercial lead sources to a minimum because of worldwide distribution of metals of various geographical origins [21]. Anthropogenic sources of lead include soils, gasoline, incinerators, paints, smelters and historically, make-up compounds [3,21–26]. Lead is incorporated into the body in the same manner as strontium, with about 99% being stored in bones where they are substituting for the Ca positions in apatite ([1] and references therein).

Hair is mainly composed of a keratin protein, which can integrate several trace elements in its structure, including lead (Pb) and strontium (Sr). A study conducted by Rabinowitz et al. [27] shows a correlation between the ingested food and the lead concentration and its isotope ratio in hair. An ingested lead tracer allowed the authors to characterize the lead exchanges between blood, soft tissues and bone. Studies have also been conducted on strontium concentration and corresponding isotope ratio. In hair, Gellein et al. [28] found an increase in concentration along a single hair strand over a three-year period, the smaller concentrations being measured at the root. This tendency was explained by the individual formerly living in a region where high strontium concentrations were found in water. However, studies have demonstrated that the contribution from external sources of strontium and lead (e.g. dust) may need to be taken into account on top of the

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endogenous source [29]. More recently, Tipple et al. [30] have shown that the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in hair of an individual can vary lengthwise and along the cross-section indicating that the isotope ratio would not only represent the dietary intake, but would be a combination of both his diet and the local environment, which complicates the interpretation of Sr isotope data from hair [30]. The identification and quantification of the exogenous source would present a challenge. While the anthropogenic component of atmospheric dust can be easily measured, the terrigenous component may present large isotope variations following the local geology. Glacial till, for instance, is defined as a heterogeneous and unsorted material deposited by a glacier. The isotope ratio of such lithology, as is found in southern Quebec, could vary between that of carbonates, granite or even ultramafic rocks (these can have $^{87}\text{Sr}/^{86}\text{Sr}$ composition anywhere between 0.703 and 0.740).

Few studies have used the potential of combining Sr and Pb isotope ratios in both teeth and bones [31–33] for human provenancing. Font et al. [20] used the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in modern scalp hair to trace the movement of one woman from India to The Netherlands. They sub-divided the hair into temporal sections each corresponding to a geographical change. The results of the Pb isotopes show very little variation along the strand of hair, while they observe larger variation for the Sr isotopes. The oldest hair sections have more radiogenic ratios corresponding to the higher values observed in India. The more recent sections were interpreted as reflecting the street dust and tap water values from The Netherlands.

The purpose of the present study is to quantify the potential of a multi-isotope study ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) for human provenancing by measuring the effect (tracing) of the known migration of several individuals from two families between France and Canada. The study will focus on total hair analysis with no discrimination between the endogenous and exogenous sources of Sr and Pb, as both when combined in the hair will define a regional source and will be equally affected by the migration. Previous studies, based on $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios only, showed that significant isotope differences are expected between the drinking water of the two regions: the St Lawrence River (source of local tap water) in Quebec shows a low $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70937, reflecting the Paleozoic carbonates in its watershed; [34]) and a rather high $^{206}\text{Pb}/^{207}\text{Pb}$ (1.17–1.18; [35]) while the Loire River in France has a more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature and a lower $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{87}\text{Sr}/^{86}\text{Sr} = 0.711446$; $^{206}\text{Pb}/^{207}\text{Pb} = 1.12$ – 1.13 ; [36]). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of both rivers reflect the typical atmospheric Pb ratio of these regions, 1.167 for Canada and 1.105–1.142 for France [37]. Due to the lack of available ^{204}Pb -normalized isotopic data in older studies, only the $^{206}\text{Pb}/^{207}\text{Pb}$ was reported above.

2. Materials and methods

Three types of samples were collected: i) bulk hair from 7 individuals from France (Loiret region) and from Canada (Montreal), ii) hair strands, for temporal analysis, from 4 long-haired female individuals who moved from France to Canada during the summer of 2012 and iii) 8 water samples (tap and bottle water) from the two studied regions. Samples are described in Table 1. Individuals 1, 2 and 3 are from the same family from the Loiret region; 2 and 3 are siblings, number 1 is the mother of these children, while individual 4 is also a child but from a different family from the Paris region.

Each hair strand consisted of about 40 individual hairs. The amount of hair was adjusted in order to have a minimum of 15 ng of lead for the isotope ratio analysis. They were of the same length and taken from the same region of the head. The strands were cut into 4 cm sections, assumed to represent a 4-month time period (assuming an average growth rate of 1 cm month^{-1}). Each section was weighed (3.0 to 7.9 mg) and placed into separate aluminum foils for storage. The bulk hair samples (14.3 to 96.5 mg) were taken, using the same protocol, from sedentary people permanently living in Montreal (Canada), St Benoit and St Martin d'Abbat (two neighboring villages in the Loiret

region; France). Waters were sampled in pre-washed 15 ml polypropylene bottles.

Hair sections were washed using a solution of HPLC grade chloroform and methanol [2:1, v:v] (CHROMASOLV® Plus, CHROMASOLV®; Sigma-Aldrich) [38]. The results of Tipple et al. show that this wash, identified as “Treatment 2” in their study, cannot fully separate the exogenous component from the endogenous of strontium. Therefore the isotope ratios measured in our samples represent a combination of both components (i.e. endogenous and exogenous). Sections were placed in a paper filter and soaked in the solution for 3 min, then rinsed with Milli-Q water. This step was repeated 3 or 4 times. The samples were dried at room temperature in a clean room environment (better than class-1000). The same washing procedure was used for bulk hair samples.

The analytical procedure was adapted from Font et al. [18,20]. The dissolution procedure consists of a 3 step dissolution sequence in a sealed Teflon beaker: 1) 14 N HNO_3 + 8 N HCl, 2) 14 N HNO_3 , and 3) 14 N HNO_3 + ultrapure H_2O_2 (ULTREX®II, J.T. Baker). The water samples were pipetted into a Teflon beaker, set on a hotplate for complete evaporation in a class-100 hood. The amount of drinking water evaporated per sample was adjusted similarly to the hair sample (1.0 to 30.0 ml). The nitric acid was produced by sub-boiling distillation and the hydrochloric acid was obtained by dilutions from ultrapure concentrated HCl (Optima, Fisher Scientific) using Milli-Q™ deionized water.

The ion exchange columns were disposable bio-spin columns pre-soaked several days in diluted HCl and rinsed with deionized water. Two hundred microliters of new Sr-spec resin (50–100 μm , Eichrom) was deposited in each column. The cleaning of the resin was done first using 8 N HCl to remove any Pb traces, followed by Milli-Q water to eliminate strontium. The resin was then conditioned for Sr and Pb retention with 3 N HNO_3 before introducing the sample. All samples were taken up in 3 N HNO_3 and sonicated for 10 min prior to introduction into the column. A ca. 10% aliquot was kept for trace element content analysis. Resin was then washed using 3 N HNO_3 to fix Sr and remove matrix elements, including isobaric Rb. The strontium fraction was collected using Milli-Q water. A further elution step was done using 2.5 N HCl followed by the collection of the Pb fraction using 8 N HCl. Both elemental fractions were evaporated to dryness on a hotplate at 110 °C and stored dried in the Teflon beakers until mass spectrometry.

Trace elements were analyzed by a double-focusing plasma source mass spectrometer (Atom; Nu Instruments). Standard deviation when measuring Sr and Pb concentrations is better than 5%. Strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) was measured by Thermal Ionization Mass Spectrometry (TIMS) on a Thermo Triton plus. The Sr fraction was loaded on a Re filament using 1 μl of 8 N HNO_3 and a tantalum activator [39]. Mass bias was corrected by normalizing all ratios to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Analyses of NIST SRM-987 standard material gave an average $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71026 (± 0.00003 , 2σ , $n = 5$, during the course of this study).

The Pb fraction was taken in 1 ml of 2% HNO_3 containing TI (SRM997) for instrumental mass bias evaluation [40]. The isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) were measured by MC-ICP-MS on a NuPlasma II with an Aridus II desolvating membrane as the introduction system. Measurements of the standard NIST SRM-981 were interspersed between samples. We also repeatedly measured an in-house standard, yielding an average $^{208}\text{Pb}/^{206}\text{Pb}$ of 2.0425 ($2\sigma = 0.0003$; $n = 22$). Total chemistry procedural blanks for Sr and Pb were below 300 pg and 100 pg, respectively, which are negligible compared to the quantities of Sr and Pb analyzed in hair samples (57.6 ng and 38.5 ng on average).

3. Results and discussion

Concentrations of water samples vary between 0.1 and 343.9 ppb for Sr, and 0.1 and 10.8 ppb for Pb (Table 1). The highest Sr and Pb concentrations are measured in waters from Montreal, slightly exceeding the

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