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Published in:
Journal of Archaeological Science: Reports

DOI:
10.1016/j.jasrep.2020.102379

Publication date:
2020

Document Version
Peer reviewed version

Citation for published version (APA):
Toxvaerd, S. (2020). The strontium isotope ratio $^{87}Sr/^{86}Sr$ in archaeological organic matter conserved in acidic anaerobic environments is hard to interpret. *Journal of Archaeological Science: Reports*, *31*, Article 102379. https://doi.org/10.1016/j.jasrep.2020.102379

The strontium isotope ratio $^{87}Sr/^{86}Sr$ in archaeological biological materials conserved in acidic anaerobic environments is hard to interpret

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Abstract

The strontium isotope ratio $^{87}Sr/^{86}Sr$ is used to determine the provenance of archaeological biological materials. However, for biological materials in an acidic environment such as peat bogs and Bronze Age burial mounds, the interpretation of the ratio is not straightforward. The acidic environment in peat bogs and Bronze Age burial mounds dissolves parts of the biological materials so that the chemically bounded strontium in hair, nails, bones and teeth is released into the aqueous environment. This dissipation of strontium can change the local strontium isotope ratio and affect the possibility of a precise determination of the provenance of the biological materials.

The article provides a chemical and physicochemical analysis of the acidic effect on the isotope ratio in biological materials, and shows how to detect whether the diagenesis might have changed the original strontium isotope ratio.

Keywords:
Strontium isotope ratio $^{87}Sr/^{86}Sr$, Archaeological biological materials, Isotope diffusion

1. Introduction

Archaeological research uses strontium isotopes to determine the provenance of people who died thousands of years ago. The magnitude of the ratio R=$^{87}Sr/^{86}Sr$ of two strontium isotopes varies with the geographical location of soil substrates. Strontium is absorbed in biological materials, and the ratio of the isotopes is used to determine the location where the biological materials were created [1]. In archaeology, the determination of the ratio is used to determine the provenance of old biological materials, e.g. wood [2, 3, 4, 5, 6], hair, teeth and bones [7, 8, 9, 10].

The value of the isotope ratio in archaeological biological materials, compared to the ratio in the environment at the funeral place, has led to a series of spectacular conclusions: e.g. that a young Danish female from the Bronze Age (Egtvedgirl) came from Schwarzwald [8], and that an iron-age female, buried in a Danish peat bog, shortly before her death was on a long distance travel [9]. However, the investigations have not taken into account that an acidic environment can effect the strontium isotope ratio. The acidic environment in the Bronze Age burial mounds and in the peat bogs will release chemically bounded strontium in the biological materials, which can contaminate the archaeological materials [11]. Over long periods of time this diagenesis might have changed the ratio of the strontium isotopes.

Based on physicochemical and chemical properties for strontium, I shall in the following argue that an acidic environment can change the strontium isotope ratio in the biological materials and thereby complicate the interpretation of their provenance. A chemical analysis can, however, establish whether the strontium ratio in the archaeological materials has been affected by the acidic environment.

2. The chemistry of strontium isotopes

The geological abundance on Earth of two strontium isotopes is x(^{87}Sr)= 0.0700 and x(^{86}Sr)=0.0986 (x: mole fractions) [12], i.e. with a mean ratio R=0.7099, but with local variations. The geographical variations of R in the soil are a result of many interacting factors. Water-deposited geological settlements can have a value R in the lower end of the interval, and so have volcanic rocks from the mantel of the Earth, whereas older rocks from the crust of the Earth have a value in the upper end of the interval. There are several other interacting factors, e.g. weathering rates, surface water flows, and anthropogenic factors like fertilizer runoff and biomass burning. In the European soils, the ratio typically varies in the range of $[0.7025, 0.7300]$ [13].

The scientific basis for using the value of the R-ratio to investigate the origin of biological materials is based on the geographical variation of R and on the fact that the strontium in biological materials is obtained from the ground water and by the metabolism stored in the biosystems: for plants directly from water in the soil, and for the vertebrates directly (drinking water) as well as indirectly from their food. The geographical variation of R can, however, vary considerably locally, because water-deposited geological formations appear along with much older rocks from the crust, which have a significant higher value of R. See an example of R's geographical variation in a local area in Southwestern Sweden [14], where the value of R varies from 0.712 to 0.726 within a distance of $\approx$ 50 km. The ratio varies locally from 0.708 to 0.713 in a similar investigation from Eastern Ireland [15], and in England/Scotland the ratio varies from 0.707 to 0.722, with great local variations [16]. The ratio for surface water in the local environment within ten kilometers from the Egtved Bronze Age mound in Denmark, where the Egtved girl was buried, varies from R=0.7093 to R=0.7150 [17]. These facts affect previous conclusions about the provenance of the archaeological corpses.

2.1. The isotope ratio ^{87}Sr/^{86}Sr *in biological materials*

Plants and vertebrates absorb strontium from the strontium in the ground water, and for vertebrates also from their food. It is incorporated in the biomass by metabolic processes that take days. Strontium appears in bones, teeth, nails, hair, and in wood and plant fibres. Bones consist mainly of insoluble hydroxyapatite, $Ca_5(PO4)_3(OH)$ and the strontium appears as strontium hydroxyapatite, $Sr_5(PO4)_3(OH)$. Tooth enamel is an inert crystalline form of hydroxyapatite [18].

The strontium is adsorbed in hair and nails (10-100 μg/g) [19], and is bounded in another way than in bones and teeth. Hair and nails are peptides, which are polymers of amino acids. The polymers are created by negatively charged peptide bonds, and some of the amino acids in the polymers, aspartic- and glutamic acid, contain side chains with an additional carboxyl group: -COOH. A hair is a tubular protein chain with a marrow, and the marrow (medulla) peptides are very rich in glutamic acids [20]. The strontium ions, Sr^{2+}, in hair is not crystalline bounded as in the bones and teeth, but are bounded by ionic bonds to the negative charges in the peptides. The pH in vertebrates is in general neutral with pH$\approx$7, and the extra carboxyl group in peptide units of glutamic acid is negatively charged: -COO^-, at pH=7 and can adsorb Sr^{2+} by an ion-binding. So the high content in the peptides of glutamic acids units with the -COO^- group can cause the adsorption of trace elements in hair, as well as the release of the trace elements by low pH [21], where the carboxyl group, -COOH, appears without a negative charge.

The adsorption of strontium in plants is qualitatively due to the same mechanisms as the adsorption of strontium in peptides [22]. Plants consist mainly of polymers of carbohydrates, and the material in wood is typically cellulose. The cations are attached to negatively charged carboxylate ions at the cellulose surface and the release of the cations is pH dependent [23].

A significant percentage of biological materials is water. Plants (wood) contain typically ≈ 50 % water; teeth and the solid (material) parts of bones contain about 10% water [24] and tooth enamel about 2%. There is an ongoing ionic diffusion of the strontium ions in the aqueous part of the biological materials, inclusive the water in enamel and the material parts of bones [25].

2.2. Strontium deposits in acidic environments

Most places in the biosphere have a neutral pH. Exceptions are peat bogs with pH between 3.2 and 4.0 [26], and also some of the Danish Bronze Age burial mounds have an acidic environment with pH=4 [27]. The physico-chemical behaviour of the bio-strontium is strongly affected by the acidic environment. The hydroxyapatite in bones and teeth are dissolved by a low pH. An extreme example is the complete dissolution of bones in the Egtved girl's body, in which also the teeth were affected by the low pH.

The solubility of salts of phosphoric acids depends on pH. Phosphoric acids have three acidic hydrogen atoms and the three equilibrium acid constants are: pK_1=2.14, pK_2=7.20 and pK_3=12.37. The pH in peat bogs and Bronze Age mounds have a pH≈3-4. Since this pH is in between $pK_1 = 2.14$, and $pK_2 = 7.20$ for phosphoric acids, it implies that the phosphoric acid is mainly of the form $H_2PO_4^-$. The calcium and strontium salts, $Ca(H_2PO_4)_2$ and $Sr(H_2PO_4)_2$, are soluble, which explains why the bones of the Egtved girl are dissolved.

The ionic bounded strontium in the peptides is also affected by the acidic environment. The carboxylic acids in the glutamic units in hair peptides [20] are acetic acid-like and with pK values pK≈4.7. Since peat bogs and the Bronze Age burials have a pH, which is of the order one less than pK is means that 90% of the strontium in hair is no longer bounded, but free [21], and the ions will diffuse away in the aqueous environment.

The peat bogs and Bronze Age mounds contain sulfate ions, SO_4^{2+}, due to the decay of organic materials, and strontium sulfate Sr_2SO_4, is very slightly soluble. Strontium sulfate is not affected by the acidic environment in contrast to the calcium and strontium salts of phosphoric acid. Sulfuric acid is a very strong acid and so is hydrogensulfate (pK_2=1.2). So strontium sulfate remains unaffected by an acidic environment with pH≈4. However, this pH affects the concentration of strontium ions in the aqueous environment with sulfate ions, SO_4^{2-}, which over time will precipitate with the dissolved Sr^{2+}.

2.3. Diffusion of the strontium ions

After the death of a biosystem there is still a "passive" transport by diffusion of Sr^{2+} in the aqueous part of the biosystem. The diffusion of a molecule or ion is given by the Einstein diffusion formula [28]

$$l = \sqrt{\mathrm{D} \times \mathrm{t}}, \tag{1}$$

where l is the distance an ion or molecule has diffused in a time t, and D is the diffusion constant, which for Sr^{2+} in water is D≈ 1.34×10^{-9} m^2/sec [29]. The Egtved girl was buried 1370 BC and the barrow was excavated 1921, i.e. 1370+1921=3291 years after her funeral. A strontium cation in the aqueous environment in the grave, if not reprecipitated, had diffused a distance of

$$l = \sqrt{1.34 \times 10^{-9} \times 60 \times 60 \times 24 \times 365 \times 3291} = 11.8m \tag{2}$$

after she was buried.

Teeth consist primarily of micro crystalline hydroxyapatite, but contains of the order 2% H_2O (enamel)- 6% H_2O (dentin). The diffusion in the aqueous environments in bones and teeth are decades slower, for tooth enamel it is $D(Sr^{2+}) \approx D(Ca^{2+}) = 1.7 \times 10^{-12}$ m^2/sec [25], and a strontium ion dissolved from strontium apatite in the enamel has diffused a distance of at least 42 cm in 3291 years.

The Bronze Age mounds contained a plate of organic-bounded iron, which encapsulated a wet peat-like core with the oak-coffin [30]. It is this encapsulation, which have preserved the organic materials in the wet and oxygen-free environment for thousands of years. But because of this encapsulation, all the strontium originally in the peat, coffin, skin and the girl was still inside the core at the excavation. So the consequence of a diffusion distance of $\approx 12m$ means that all the released strontium ions, if not re-precipitated, have explored the hole aqueous environment within the encapsulated mound, and that the strontium isotopes from hair and dissolved bones have been mixed with strontium isotopes from the peat.

The aqueous environment in the mounds and in peat bogs contain other diffusing ions, and especially the diffusion of sulfate ions is important in the context with strontium. The diffusion constant of the sulfate ion is

$D(SO_4^{2-})=5\times10^{-10}$ m^2/sec [31], and since strontium ions bind strongly to the sulfate ions, the dissolved strontium will re-precipitate with sulfate ions anywhere in the aqueous environment, independent of the original location of strontium in the bio-material.

Another fact which affects the value of the isotope ratio is the difference in diffusion, caused by the mass difference of the isotopes. This will not play any role in the short-time deposition of strontium in wood, bones and hair of the living organism [11], but will affect the ratio in the long term. (This diffusion effect on the isotope ratio is different from the mass-dependent isotope fractionation by exchange of isotopes between two phases [32, 33]). The mass dependence is given by the ratio of the diffusion coefficients [34, 35]

$$D(^{87}Sr)/D(^{86}Sr) = \sqrt{86/87} = 0.9942, \tag{3}$$

i.e the light isotope diffuse faster than the heavy isotope. It will affect the ratio R at any *concentration gradient* of strontium. Such gradients exist in the water in hair, bones and tooth enamel at the acidic erosion. During a release of strontium by the acidic erosion of enamel and bones, the light isotope diffuse most quickly and with the result that the isotope ratio R for strontium ions in the enamel increases.

The increase of the value of R, due to a difference in the diffusion of the isotopes, can be obtained from the diffusion equation (Fick's second law). When some strontium hydroxyapatite is dissolved at a certain time (t=0) at an enamel surface (at $x = 0$) and diffuse away from the surface, then the concentration $[Sr(x,t)^{2+}]$ a distance x from where it was dissolved and after a diffusion time t, is [36]

$$[Sr(x,t)^{2+}] = [Sr(0,0)^{2+}](\pi Dt)^{-1/2}e^{-\frac{x^2}{4Dt}}. \tag{4}$$

The relation between the isotope ratio, R(x,t), and the ratio in the enamel

$$R_0 = [^{87}Sr(0,0)^{2+}]/[^{86}Sr(0,0)^{2+}] \tag{5}$$

is derived from equation No. 4. It is

$$R(x,t) = R_0\sqrt{\frac{D(^{86}Sr)}{D(^{87}Sr)}}e^{-\frac{x^2}{4D(^{87}Sr)t}+\frac{x^2}{4D(^{86}Sr)t}} \approx 1.0029R_0 \tag{6}$$

for small x. This fact can explain why one measures a higher value of R in old eroded bones and teeth than in the aqueous vicinity nearby. E. g.

the ratio for the Egtved girl's eroded molar was R=0.71187 [8]. If the main part of this strontium is desiccated strontium salts from the eroded part of the molar, the original ratio in the enamel was not 0.71187, but $R_0 \approx 0.71187/1.0029=0.70981$ and well inside the interval of local values of R at Egtved [17].

2.4. Diagenesis of strontium deposits in acidic environments

There is an extensive literature on the diagenesis of wood [37] and bones and teeth [38]. The present article only deals with matters that are important for the diagenesis of strontium deposits in acidic environments. And to be more precise, *in acidic anaerobic environments*, which have conserved biological materials at pH≈ 3-4. Strontium remains bounded in dry, or neutral and basic environments as strontium hydroxyapatite in teeth and bones, and in the peptides in hair, nails and skin by ionic bonds to negative charges in the peptides.

A general problem with applying the strontium isotope ratio on biological materials is that the materials might have been exposed to contamination of strontium from the external environment. This contamination is usually removed by washing it in an acidic liquid before determining the isotope ratio [39, 40, 41, 42]. In [41] the strontium contamination in the lipid layer at the surface of modern human hair is removed by washing it in an acidic liquid (pH=1). This cleaning procedure was also used before the isotope ratios in the hairs of the Bronze Age girls were determined [8, 10]. But when it comes to archaeological materials, which have been conserved in an acidic environment for thousands of years, this method is of course not only irrelevant, it can also affect the strontium isotope ratio in the archaeological materials. Because all which was left of the girls were their hair, nails and some bones, so all the rest of the bodies has disappeared over time in the acidic environment. This strontium is somewhere as a soluble or insoluble strontium salt and perhaps in the eroded part of the biological material. So the strontium one removes by this procedure might on one hand be some soluble strontium salt, which originate from the hair or enamel, and which is not a contamination, and which should not be removed. And on the other hand, there might be a contamination, e.g. as Sr_2SO_4 precipitated by SO_4^{2-} and diffusing strontium ions, which is not removed by this cleaning method.

An assessment of procedures to remove exogenous diagenetic strontium from archaeological wool is given by [43]. They concluded from the cleaning procedures that most of the diagenetic Sr deposited during burial was present as particulates. The strontium particulates were removed by high-pressure N_2 gas, and the authors noticed that although the strontium content in burial samples was highly variable, the $^{87}Sr/^{86}Sr$ ratios were generally higher than in unburied controls. The diagenetic Sr particulates could very well be strontium sulfate, and the higher ratios of the isotopes could be caused by the difference in isotope diffusion in the peptides given by equation No. 6.

3. Summary

Measurements of the strontium isotope ratio are an important and valuable method to determine the geographical origin of biological materials. In general, it is reliable provided that the biological materials have not been stored in aqueous acidic environments over a long time. The strontium in the biological materials most likely remains bounded, if the environment is alkaline or neutral, and the ratio is not affected over time. But over time the acidic environment releases strontium from teeth, bones, cellulose and peptides, and the released strontium ions, Sr^{2+}, diffuse, re-precipitate and can affect the local value of the isotope ratio.

The degree of erosion of the biological materials is important for the possibility of using the magnitude of the isotope ratio to a determination of their provenance. When a tooth is eroded in the acidic environment, the strontium ions diffuse away in the eroded part of the enamel, and the light isotope fastest. The result is that the value of isotope ratio increases. The Bronze Age Skrydstrup girl's hair and molar enamel were investigated, and only the end part of her long hair and the molar enamel had a value of the isotope ratio, which exceed the value of the aqueous environment outside the mound. The authors concluded from these results that the Skrydstrup girl came from a place outside Denmark [10]. But these biological materials, the molar enamel and the end part of a hair, are the most eroded parts of the material left, and the increase of the value can be explained by the difference in diffusion of the two isotopes given by equation No. 6.

In conclusion: The chemical composition of strontium in acidic anaerobic conserved biological materials must be determined before one can use the strontium isotope ratio to conclude from where the biological materials have obtained the strontium. Only if the strontium in the archaeological materials appears in the same manner as the metabolic obtained strontium can one use the method to determine the provenance of the biological materials. E.g.

only if the strontium in an eroded tooth appears as strontium hydroxyapatite is a determination of the strontium isotope ratio applicable.

4. Acknowledgment

Jeppe C Dyre is gratefully acknowledged. This work was supported by the VILLUM Foundations Matter project, grant No. 16515.

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