Journal of Archaeological Science: Reports 31 (2020) 102379

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

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

Søren Toxvaerd

Department of Science and Environment, Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark

ARTICLE INFO

Keyword:
Strontium isotope ratio $^{87}Sr/^{86}Sr$
Archaeological organic matter
Isotope diffusion

ABSTRACT

The strontium isotope ratio $^{87}Sr/^{86}Sr$ is used to determine the provenance of archaeological organic matter. However, for organic matter 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 organic matter 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 organic matter.

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

1. Introduction

Archaeological research uses strontium isotopes to determine the origin of organic matter and the provenance of people from their human remains in tombs. The magnitude of the ratio $R = ^{87}Sr/^{86}Sr$ of two strontium isotopes varies with different geological settings. Strontium is absorbed in organic matter, and the ratio of the isotopes is used to determine the location where the organic matter were created (Coelho et al., 2017). In archaeology, the determination of the ratio is used to determine the provenance of old organic matter, e.g. wood (English et al., 2001; Drouet et al., 2005; Rich et al., 2016; Hajj et al., 2017; Millon et al., 2018), hair, teeth and bones (Frei et al., 2009; Frei et al., 2015; Frei et al., 2015; Frei et al., 2017).

The value of the isotope ratio in archaeological organic matter, compared to the ratio in the environment at the funeral place, has led to a series of conclusions regarding the provenance of the human rests: e.g. that a young Danish female from the Bronze Age (Egtved Girl) came from Schwarzwald (Frei et al., 2015), and that an iron-age female, buried in a Danish peat bog, shortly before her death was on a long distance travel (Frei et al., 2015). 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 organic matter, which can contaminate the archaeological materials (von Carnap-Bornheim et al., 2007). Over long periods of time this diagenesis might have changed the ratio of the strontium isotopes.

The paper will use two specific cases in Denmark, the Egtved Girl (Frei et al., 2015) and the Skrydstrup Woman (Frei et al., 2017) to discuss the effects of acidic environment in biological remains such as teeth, hair and bones. 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 organic matter 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. Archaeological deposits in acidic anaerobic environments

An acidic anaerobic environment with organic matter appears when the organic material is deposited without access of oxygen. The incompleted decay of the organic materials creates humus acids and acidic polysacchadides (sphagnan), and the acidic anaerobic environment prevents the organic matter from a complete oxidating decay. The result of this incompleted oxidation can result in that e.g. bones, skin, nails and hair are preserved over long times.

There are many examples of acidic anaerobic environments with archaeological deposits. One example is peat bogs and Northern Europe has many peat bogs with archaeological deposits. The peat bogs have a pH between 3.2 and 4.0 (Clymo, 1984), and there are many finds where this acidic anaerobic environment with humus acids and sphagnan (Painter, 1991; Painter, 1991) have e.g. preserved hair, nails and skin of people buried in the bogs. The findings are typically from the Celtic Iron Age ca. 300 years BC.

Another example is some danish Bronze Age burial mounds. In some of the Danish Bronze Age burial mounds from East Jutland, the oak coffins were first covered by grass peat before the mounds were built by clay. The Bronze Age mounds contain a plate of organic-bounded iron,

https://doi.org/10.1016/j.jasrep.2020.102379
Received 18 October 2019; Received in revised form 3 March 2020; Accepted 22 April 2020

which encapsulates a wet peat-like core with the oak coffin (Breuning-Madsen and Holst, 1998). This construction results in an local acidic anaerobic environment at the oak coffin, and it is this encapsulation, which have preserved the organic materials in the wet and oxygen-free environment for thousands of years (Breuning-Madsen et al., 2003). The Danish Bronze Age burial mounds from East Jutland are constructed in the period 1300–1400 BC. The burial mounds have an acidic environment with pH = 4 (Breuning-Madsen et al., 2000).

An acidic environment with pH = 4 or less will release the chemical bounded Sr^{2+} and can affect the strontium isotope ratio $^{87}Sr/^{86}Sr$.

3. 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) (Holden et al., 2019), 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] (Hoogewerff et al., 2019).

The scientific basis for using the value of the R-ratio to investigate the origin of organic matter is based on the geographical variation of R and on the fact that the strontium in organic matter 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 (Blank et al., 2018), where the value of R varies from 0.712 to 0.726 within a distance of ≈50 km. The ratio varies locally from 0.708 to 0.713 in a similar investigation from Eastern Ireland (Ryan et al., 2018), and in England/Scotland the ratio varies from 0.707 to 0.722, with great local variations (Snoeck et al., 2018). 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 (Tomsen and Andreasen, 2019). These facts affect previous conclusions about the provenance of the archaeological corpses.

3.1. The isotope ratio $^{87}Sr/^{86}Sr$ in organic matter

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 (Ouladdiaf et al., 2015).

Strontium is absorbed in hair and nails (Rodushkin et al., 2000; Rosborg et al., 2003; Prejac et al., 2017) but is bounded in another way than in bones and teeth. Hair and nails consist of peptides, which are polymers of amino acids. The polymers are created by negatively charged peptide bonds. The hair contains 11–18 percent of sulfur-containing (-SH) amino acids, cysteine and the dimmers cystine (Dahiya and Yadav, 2013) 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 (Bencze, 1990). 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≈7, and the extra carboxyl group in peptide units of glutamic acid and sulphur in cysteine are negatively charged: $-COO^-$, $-S^-$, 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 (Bate, 1966), where the carboxyl group, -COOH, appears without a negative charge. This fact explains the observation of a higher concentration of strontium in hair from alkaline areas than from acidic areas (Rosborg et al., 2003).

The concentration of strontium in human depends not only on the concentration of strontium in food and drink water, but on several other factors. It also depends on age and gender. Whereas men in general absorb more strontium in bones than women, the opposite is the case with respect to absorption of strontium in hair, where women absorb most (Prejac et al., 2017). The reported values of concentration of strontium in human varies, however, greatly: 10–100 μg^{-1} (Rodushkin et al., 2000), 312–13200 μg^{-1} (Rosborg et al., 2003), and these facts have the consequence that the concentration of strontium in archaeological organic matter is not very informative.

The adsorption of strontium in plants is qualitatively due to the same mechanisms as the adsorption of strontium in peptides (Hubbe et al., 2011). 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 (Argun et al., 2007).

A significant percentage of organic matter is water. Plants (wood) contain typically ≈50 % water; teeth and the solid (material) parts of bones contain about 10% water (Figueiredo et al., 2010) and tooth enamel about 2%. There is an ongoing ionic diffusion of the strontium ions in the aqueous part of the organic matter, inclusive the water in enamel and the material parts of bones (van Duk et al., 1983).

3.2. Strontium deposits in acidic environments

The biosphere has in general a neutral pH, but there are as mentioned many exceptions such as rain forests, tundra, peat bogs and some Bronze Age burial mounds. The physicochemical 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 (Bencze, 1990) 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 (Bate, 1966), 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+}.

3.3. 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 (Einstein, 1905)

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

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 $D \approx 1.34 \times 10^{-9}$ m^2/s (Harned and Polestra, 1953). 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 re-precipitated, 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/s (van Duk et al., 1983), 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 (Breuning-Madsen and Holst, 1998). 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 $D(SO_4^{2-}) = 5 \times 10^{-10}$ m^2/s (Krom and Berner, 1980), 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 (von Carnap-Bornheim et al., 2007), 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 (Habfast, 1983; Young et al., 2002)). The mass dependence is given by the ratio of the diffusion coefficients (Toxvaerd, 1985; Nuevo et al., 1995)

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

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 (Atkins and de Paula, 2014)

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

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

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

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 (Frei et al., 2015). 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 (Tomsen and Andreasen, 2019).

3.4. Diagenesis of strontium deposits in acidic environments

There is an extensive literature on the diagenesis of wood (Kolavali et al., 2017) and bones and teeth (Kendall et al., 2018). 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 organic matter 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.

There is a general trend in the way strontium is absorbed in human bones and teeth, it is absorbed and mainly bounded near the surface (Dahl et al., 2001; Kamenov et al., 2018). This has two consequences. Firstly strontium is more quickly released by erosion and diffusion, and secondly strontium can be more easily replaced by other cations. If the replaced ion is not strontium, it does not affect the isotope ratio. But if the cation is another strontium ion from somewhere else, it can affect the isotope ratio. The diagenesis of strontium in teeth show, that archaeological enamel in general contains a smaller concentration of strontium than found in modern enamel (Kamenov et al., 2018). A corresponding diagenetic effect seems to be the case for bones (Nelson et al., 1986). So there is an ongoing change in the strontium concentration in teeth and bones and presumably also in hair, in the acidic environment with release and exchange of strontium ions.

A general problem with applying the strontium isotope ratio on organic matter 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 (Hoppe et al., 2003; Lee-Thorp et al., 2003; Tipple et al., 2013; Snoeck et al., 2015). In Tipple et al. (2013) 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 (Frei et al., 2015; Frei et al., 2017). 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 von Holstein et al. (2015). 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.

4. Summary

Measurements of the strontium isotope ratio are an important and valuable method to determine the geographical origin of organic matter. In general, it is reliable provided that the organic matter have not been stored in aqueous acidic environments over a long time. The strontium in the organic matter 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, ion-exchange with other cations, and this will affect the local value of the isotope ratio.

The degree of erosion of the organic matter 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 for strontium in the aqueous part of the eroded materials increases. The Bronze Age Skrydstrup Woman'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 Woman came from a place outside Denmark (Frei et al., 2017). But these organic matter, 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: An acidic environment with pH less than pH = 4–5 will release the ionic bounden strontium ions from there depositions in the organic matter. This will result in mixing of strontium, a fact which will affect the strontium isotope ratio for the reasons given above. A measurement of pH, and an investigation on whether the material is eroded can determine, if the strontium deposites have been affected by the acidic environment.

If the pH is below pH = 4–5, as is the case in e.g. peat bogs, a measurement of the strontium isotope ratio can still give a valuable information on the origin of the organic matter provided, that the acidic environment over time has not changed the ratio. Some tests regarding this possibility is possible. As mentioned the diagenesis of organic matter in an acidic environment will in general result in a lower concentration of strontium in bones, teeth and hair. A simple measurement of the concentration of strontium is help full, but unfortunately the concentration itself depends on several factors as stated above. But it is a sign of dissolution, if the concentration in the most eroded part of the material is less than in the more intact part of the materials. E.g. if the end tip of a hair contains less strontium than at the hair root.

The chemical composition of strontium in organic matter can be determined, and this will also give an indication of whether there have been an ion-exchange or re-precipitation of strontium. E.g. if the investigated enamel contains only strontium apatite and not strontium sulphate can one exclude a re-precipitation of strontium. Because 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 organic matter.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Jeppe C Dyre is gratefully acknowledged. This work was supported by the VILLUM Foundation's Matter project, Grant No. 16515.

References

Argun, M.E., Dursun, S., Ozdemir, C., Karatas, M., 2007. Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. J. Hazard Mater. 141, 77–85.
Atkins, P., de Paula, J., 2014. Athins' Physical Chemistry. Oxford University Press Chapter 28.
Bate, I.C., 1966. Adsorption and elution of trace elements on human hair. Int. J. Appl. Radiat. Isot. 17, 417–423.
Bencze, K., 1990. What contribution can be made to biological monitoring by hair analysis? Fresenius. J. Anal. Chem. 337, 867–876.
Blank, M., Sjögren, K.-G., Knipper, C., Frei, K.M., Storå, J., 2018. Isotope values of the bioavailable strontium in inland southwestern Sweeden – a baseline for mobility studies. PLoS ONE 13 (e0204649), 1–30.
Breuning-Madsen, H., Holst, M.K., 1998. Recent studies on the formation of iron pans around the oaken log coffins of the bronze age burial mounds of Denmark. J. Arch. Sci. 25, 1103–1110.
Breuning-Madsen, H., Holst, M.K., Rasmussen, M., 2000. The chemical environment in a burial mound shortly after construction- an archaeological-pedological experiment. J. Arch. Sci. 28, 691–697.
Breuning-Madsen, H., Holst, M.K., Rasmussen, M., Elberling, B., 2003. Preservation within log coffins before and after barrow construction. J. Arch. Sci. 30, 343–350.
Clymo, R.S., 1984. *Sphagnum*-dominated peat bog: a natural acid ecosystem. Phil. Trans. Soc. Lond. B 305, 487–499.
Coelho, I., Castanheira, I., Bordado, J.M., Donard, O., Silva, J.A.L., 2017. Recent developments and trends in the application of strontium and its isotopes in biological related fields. Trends Analyt Chem. 90, 45–61.
Dahiya, M.S., Yadav, S.K., 2013. Elemental composition of hair and its role in forensic identification. Open Access Sci. Reports 2 doi:10.41727.scientificreports.721.
Dahl, S.G., Allain, P., Marie, P.J., Mauras, Y., Boivin, G., Ammann, P., Tsouderos, Y., Delmas, P.D., Christiansen, C., 2001. Incorporation and distribution of strontium in bone. Bone 28, 446–453.
Drouet, T., Herbauts, J., Demaiffe, D., 2005. Long-term records of strontium isotopic composition in tree rings suggest changes in forest calcium sources in the early 20th century. Global Change Biol. 11, 1926–1940.
Einstein, A., 1905. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. Ann. Phys. 322, 549–560.
English, N.B., Betancourt, J.L., Dean, J.S., Quade, J., 2001. strontium isotopes reveal distant sources of architectural timber in Chaco Canyon, New Mexico. Proc. Nath. Acad. Sci. 98, 11891–11896.
Figueiredo, M., Fernando, A., Martins, G., Freitas, J., Judas, F., Figueiredo, H., 2010. Effect of the calcination temperature on the composition and microstructure of hydroxyapatite derived from human and animal bone. Ceram Int. 36, 2383–2393.
Frei, K.M., Skals, I., Gleba, G., Lyngstrøm, H., 2009. The Huldremose Iron Age textiles, Denmark: an attempt to define their provenance applying the strontium isotope system. J. Arch. Sci. 36, 1965–1971.
Frei, K.M., Mannering, U., Kristiansen, K., Allentoft, M.E., Wilson, A.S., Skals, I., Tridico, S., Nosch, M.L., Willerslev, E., Clarke, L., Frei, R., 2015. Tracing the dynamic life story of a Bronze Age Female. Sci. Rep. 5, 10431.
Frei, K.M., Mannering, U., Price, D., Iversen, R.B., 2015. strontium isotope investigations of the Haraldskær woman – a complex record of various tissues. ArchéoSciences V 39, 93–101.
Frei, K.M., Villa, C., Jørkov, M.L., Allentoft, M.E., Kaul, F., Ethelberg, P., Reiter, S.S., Wilson, A.S., Taube, M., Olsen, J., Lynnerup, N., Willerslev, E., Kristiansen, K., Frei, R., 2017. A matter of months: high precision migration chronology of a Bronze Age female. PLoS ONE 12 (e0178834), 1–20.
Habfast, K., 1983. Fractionation in the thermal ionization source. Int. J. Mass Spectrom. Ion Phys. 51, 165–189.
Hajj, F., Poszwa, A., Bouchez, J., Guérold, F., 2017. Radiogenic and stable strontium isotopes in provenance studies: a review and first results on archaeological wood from shipwrecks. J. Arch. Sci. 86, 24–49.
Harned, H.S., Polestra, F.M., 1953. The differential diffusion coefficient of strontium chloride in a diluted aqueous solution at 25. J. Am. Chem. Soc. 75, 4168–4169.
Holden, N.E., Coplen, T.B., Böhlke, J.K., Tarbox, L.V., Benefield, J., de Laeter, J.R.,

Mahaffv, P.G., O'Connor, G., Roth, E., Tepper, D.H., Walczyk, T., Wieser, M.E., Yoneada, S., 2019. IUPAC periodic table of the elements and isotopes (IPTEI) for the education community- update 2019 (IUPAC Technical Report). Pure Appl. Chem. 90, 1833–2092.
Hoogewerff, J.A., Reimann, C., Ueckermann, H., Frei, R., Frei, K.M., van Aswegen, T., Stirling, C., Reid, M., Clayton, A., Ladenberger, A., 2019. Bioavailable $^{87}Sr/^{86}Sr$ in European soils: a baseline for provenancing studies.
Hoppe, K.A., Koch, P.L., Furutani, T.T., 2003. Assessing the preservation of biogenic strontium in fossil bones and tooth enamel. Int. J. Osteoarchaeol. 13, 20–28.
Hubbe, M.E., Hasan, S.H., Ducoste, J.J., 2011. Cellulosic substrates for removal of pollutants from aqueous systems: a review. 1. Metals. Bioresources 6, 2161–2287.
Kamenov, G.D., Lofaro, E.M., Goad, G., Krigbaum, J., 2018. J. Arch. Sci. 99, 27–34.
Kendall, C., Eriksen, A.M.H., Kontopoulos, I., Collins, M.J., Turner-Walker, G., 2018. Diagonesis of archaeological bone and tooth. Palaeogeogr., Palaeoclimatol. Palaeoecol. 491, 21–37.
Kolavali, R., Hasani, M., Theliander, H., 2017. The sorption of monovalent cations onto norway spruce: model studies using wood flour and LiCl solution. J. Wood Chem. Technol. 37, 110–123.
Krom, M.D., Berner, R.A., 1980. The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments. Limnol. Oceanogr. 25, 327–337.
Lee-Thorp, J., Sponheimer, M., 2003. Three case studies used to reassess the reliability of fossil bone and enamel isotope signals for paleodietary studies. J. Antrop. Archaeol. 22, 208–216.
Millon, S., Eisenhaur, A., Billamboz, A., Rösch, M., Krausse, D., Nelle, O., 2018. Iron Age utilization of silver fir *(Abias alba)* wood around the Heuneburg – local origin or timber import? Quat. Int. 463, 363–375.
Nelson, B.K., DeNiro, M.J., Schoeninger, M.J., De Paulo, D.J., 1986. Geochim. Cosmochim. Acta 50, 1941–1949.
Nuevo, M.J., Morales, J.J., Hayes, D.M., 1995. Mass dependence of isotope self diffusion by molecular dynamics. Phys. Rev. E 51, 2026–2032.
Ouladdiaf, B., Rodriquez-Carvajal, J., Goutaudier, C., Ouladdiaf, S., Grosgogreat, B., Pradelle, N., Colon, P., 2015. Crystal structure of human tooth enamel studied by neutron diffraction. Mater. Res. Express 2, 025401.
Painter, T.J., 1991. Lindow Man, Tollund Man and other peat-bog bodies: the preservation and antimicrobial action of sphagnan, a reactive glycuronoglycan with tanning and sequestering properties. Carbohydr. Polym. 15, 123–142.
Painter, T.J., 1991. Preservation in peat. Chem. Ind. 17, 421–424.
Prejac, J., Vinjević, V., Skalny, A.A., Grabeklis, A.R., Mimica, N., Momilović, B., 2017. Hair for a long-term biological indicator tissue for assesing the strontium nutritional status of men and women. J. Trace Elem. Med. Bio. 42, 11–17.
Rich, S., Manning, S.W., Degryse, P., Vanhaecke, F., Latruwe, K., Van Lerberghe, K., 2016. Toput a cesar ship in a bottle: Dendroprovenancing three ancient East Mediterranean watercraft with the 87St/86St isotope ratio. J. Arch. Sci. Report 9, 514–521.
Rodushkin, I., Axelsson, M.D., 2000. Application of double focusing sector field ICP-MS for multielemental characterization of human hair and nails. Part II. A study of the inhabitants of northern Sweden. Sci. Total Environ. 262, 21–36.
Rosborg, I., Nihlgård, B., Gerhardson, L., 2003. Hair element concentrations in females in one acid and one alkaline area in southern Sweden. Ambio 32, 440–446.
Ryan, S.E., Snoeck, C., Crowley, Q.G., Babechuk, M.G., 2018. 87Sr/86Sr and trace mapping of geosphere-hydrosphere-biosphere interactions: a case study in Irland. Appl. Geochem. 92, 209–224.
Snoeck, C., Lee-Thorp, J., Schulting, R., de Jong, J., Debouge, W., Mattielli, N., 2015. Calcined bone provides a reliable substrate for strontium isotope ratios as shown by an enrichment experiment. Rapid Commun. Mass. Spectrom. 29, 107–114.
Snoeck, C., Pouncett, J., Clayes, P., Goderis, S., Matielli, N., Pearson, M.P., Willis, C., Zazzo, A., Lee-Thorp, J.A., Schulting, R.J., 2018. strontium isotope analysis on cremated human remains from Stonehenge support links with west Wales. Sci. Rep. 8 (10790), 1–8.
Thomsen, E., Andreasen, R., 2019. Agricultural lime disturbs natural strontium isotope variations: implications for provenance and migration studies. Sci. Adv. 5 (eaav8083), 1–11.
Tipple, B.J., Chau, T., Chesson, L.A., Fernandez, D.P., Ehleringer, J.R., 2013. Isolation of strontium pools and isotope ratios in modern human hair. Anal. Chim. Acta 798, 64–73.
Toxvaerd, S., 1985. Mass dependence of the self diffusion in a liquid. Mol. Phys. 56, 1017–1023.
van Duk, J.W.E., Borggreven, J.M.P.M., Driessens, F.C.M., 1983. Diffusion in mammalian tooth enamel in relation to the caries process. Archs. Oral. Biol. 28, 591–597.
von Carnap-Bornheim, C., Nosch, M-L., Grupe, G., Mekota, A.-M., Schweissing, M.M., 2007. Stable strontium isotopic ratios from archaeological organic remains from the Thorsberg peat bog. Rapid Ciommun. Mass Spectrom. 21, 1541–1545.
von Holstein, I.C.C., Font, L., Peacock, E.E., Collins, M.J., Davies, G.R., 2015. An assessment of procedures to remove exogenous Sr before $^{87}Sr/^{86}Sr$ analysis of wet archaeological wool textiles. J. Arch. Sci. 53, 84–93.
Young, E.D., Galy, A., Nagahara, H., 2002. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. Geochemica et Cosmochemica Acta 66, 1095–1104.