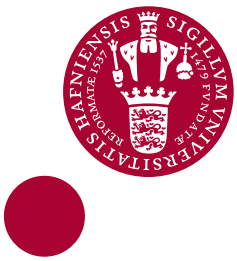

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Stable strontium isotopic ratios from archaeological organic remains from the Thorsberg peat bog

Claus von Carnap-Bornheim[1], Marie-Louise Nosch[2], Gisela Grupe[3,4]*, Anna-Maria Mekota[4] and Mike M. Schweissing[3]

[1]Archäologisches Landesmuseum, Stiftung Schleswig-Holsteinische Landesmuseen Schloß Gottorf, 24837 Schleswig, Germany
[2]The National Danish Research Foundation's Centre for Textile Research, The SAXO Institute, University of Copenhagen, Njalsgade 102, 2300 Copenhagen S, Denmark
[3]Staatssammlung für Anthropologie und Paläoanatomie, Karolinenplatz 2a, 80333 München, Germany
[4]Department I für Biologie, Bereich Biodiversitätsforschung/Anthropologie, LMU München, Grosshaderner Str. 2, 82152 Martinsried, Germany

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Stable strontium isotope ratios in archaeological finds have frequently been used to determine their place of origin, in order to reconstruct migration and trade. Peat bogs offer favourable burial conditions for the preservation of organic remains such as woollen textiles and leather by a natural tanning process. However, these finds are impregnated by peat substances including contaminant strontium which is likely to mask the original $^{87}Sr/^{86}Sr$ isotopic ratio of the specimens. In this paper, we present a pilot study analysing stable strontium isotopic ratios from Iron Age textile and leather finds from the Thorsberg peat bog, focusing on a sample processing method which permits the quantitative removal of contaminating strontium from the specimens. Copyright © 2007 John Wiley & Sons, Ltd.

The Thorsberg peat bog, located in Anglia, Schleswig-Holstein, Germany, is famous for its Iron Age archaeological finds which date to the second and third centuries AD. The material consists of hundreds of weapons and personal equipment of Germanic warriors which can be interpreted as votive offerings.[1] Since burial conditions in such sphagnum bogs are moist, oxygen-deficient, and characterised by an acidic pH, organic remains such as leather and textiles are usually very well preserved by way of a natural tanning process caused by plant polyphenols (tannins). Of the many scientific facets concerning such a sacred place, one question concerns the catchment area of those people who donated their valuables, or the geographical region where the artefacts had been manufactured.

The stable strontium (Sr) isotopic ratios of archaeological finds have frequently been used to determine their place of origin. In nature, Sr occurs mainly in the form of strontionate or coelestin. The chemical behaviour of Sr salts is similar to those of calcium (Ca) salts; however, the solubility products of the former are usually lower.[2] Sr occurs in the form of four stable isotopes (0.54% ^{84}Sr, 9.87% ^{86}Sr, 7.04% ^{87}Sr, 82.53% ^{88}Sr), where ^{87}Sr is a decay product of ^{87}Rb which has a half-life of 48.8×10^9 years.[3] Therefore, the $^{87}Sr/^{86}Sr$ isotope ratio in bedrock is a function of both its initial rubidium (Rb) content and the elapsed time, a relationship which allows geologists to utilise the stable Sr isotopic signature for the dating of rocks. $^{87}Sr/^{86}Sr$ ratios in rocks vary roughly from 0.700 to 0.750; rocks older than 100 million years exhibit isotopic ratios in the upper range, while younger ones (e.g. volcanic rocks) show the lowest ratios. The local, geochemically determined Sr isotopic signature enters the food chain via soil and groundwater. Due to the small mass difference, isotopic fractionations remain below measurement error. Consequently, individuals residing in a certain area preserve the local Sr isotopic signature specific for that area in their tissues. Provided that the area under study displays sufficient geochemical diversity or at least exhibits clearly defined geochemical boundaries, the detection of a non-local $^{87}Sr/^{86}Sr$ isotope ratio in an archaeological find indicates a different place of origin.

The archaeological material analysed is frequently bone or dental enamel, a substrate where Sr readily substitutes for Ca and becomes firmly incorporated into the apatite crystal lattice.[4–14] The elegant aspect of this approach is that although soil cations, including Sr, tend to contaminate archaeological finds, it is only local Sr from the immediate burial environment that is actually capable of doing so. As long as a find exhibits a non-local Sr isotopic signature, a different place of origin is ascertained. Therefore, sample preparation necessitates the thorough removal of contaminating Sr, the isotopic ratio of which will otherwise superimpose the indigenous biological signal and may obscure the measurement data.[15] Bulk bone and tooth specimens are usually robust enough structurally to allow separation of indigenous from contaminating Sr by acid leaching. Basketry and matting manufactured from plant material, which was preserved under favourable burial conditions, have also recently been studied successfully for a definition of their source area by the use of stable Sr isotope ratios.[16]

**Correspondence to*: G. Grupe, Department I für Biologie, Bereich Biodiversitätsforschung/Anthropologie, LMU München, Grosshaderner Str. 2, 82152 Martinsried, Germany.
E-mail: ASM.Grupe@extern.lrz-muenchen.de

To the authors' knowledge, stable Sr isotopic analyses have not yet been performed on organic remains from a bog environment. A stable Sr isotopic analysis of such finds is, however, complicated by several problems.

Because Sr is a non-essential trace element, its overall concentration in the vertebrate body is low (4.6 μg/g in humans).[17] Recent reference values for Sr concentrations obtained on large modern series are almost absent for vertebrates other than humans, and virtually no solid data exist, especially for skin. Data available for modern humans show that Sr concentrations in hair and skin only range from less than one ppm to a few ppm.[18–22] However, since hair functions as an excretory channel for trace elements, Sr should, in general, be more abundant in hair and wool (the raw material for textiles) than in skin (the raw material for leather). In contrast, a peat bog is made up of decaying plants. Since plants do not discriminate against Sr in favour of Ca in the way that vertebrates do, plants are enriched with this element relative to the majority of vertebrate tissues.[23,24] A recent evaluation of transfer factors for ^{90}Sr (T_f = ratio of the radioactivity in nutrients compared with the specific radioactivity in the soil) resulted in T_f values between 0.3 and 3 for plants and vegetables, which were higher than those for mushrooms, berries, and animal flesh.[2] As a result, the burial environment of organic finds recovered in a peat bog is characterised by the presence of potentially contaminant Sr,[25] whereby the acidic environment promotes the availability of this element in the form of free ions. Consequently, low-strontium organic specimens are likely to be contaminated with high-strontium burial substrates, which in turn may result in the masking of the original isotope ratio.

The basic *post mortem* processes of trace element contamination of organic remains have been known for many years: ionic migration from metal-enriched solutions to human hair increases as the differences in metal concentration between solution and hair become greater, and the enrichment of hair with cations is enhanced at higher pH.[26,27] In moist environments, the keratin fibres absorb water and swell up, a process in which fibre-bound water permits the intrusion of free metal ions from the soil into the hair, most probably promoted by attraction through charged functional groups of the polypeptides.[28,29] Organic tissues like hair and skin are largely made up of proteins, which consist of amino acids. At acidic pH, however, amino acids are positively charged and react as cations, while at higher pH they become negatively charged. Organic archaeological finds from a peat bog environment will therefore be characterised by two competing diagenetic mechanisms: The migration of exogenous Sr into the hair should be promoted by the presence of free Sr ions in an acidic, moist environment, while the contamination of hair and skin with Sr should be impeded by the positive charge of amino acids at low pH.

In this paper, we present a pilot study focusing on the sample preparation of textile and leather finds from the Thorsberg peat bog. The study is a prerequisite for the determination of the place of origin of the finds based on stable Sr isotope ratios. It is the result of a collaboration between the Landesmuseum Schloß Gottorf, the Staatssammlung für Anthropologie und Paläoanatomie in Munich, and the Danish National Research Foundation's Centre for Textile Research.

EXPERIMENTAL

Organic samples consisted of pieces of leather, woolen textiles, one piece of fur, and three soil samples from the Thorsberg bog. While the organic finds were recovered many decades ago, soil samples were taken in the year 2006 at depths of 30, 50, and 70 cm from cores drilled specifically for this study. Bulk soil samples and the pore fluid were measured in addition to the archaeological finds. The textile samples analysed consisted merely of a single thread only a few centimetres in length. These small sample sizes unfortunately prevented the measurement of intial $^{87}Sr/^{86}Sr$ ratios in nine out of thirteen untreated specimens (see Results section). Sample processing included a rehydration step, followed by a methanol/chloroform wash. All labware was made of Teflon or quartz glass that had undergone 4 h of thorough cleaning in a hot vapour of concentrated nitric acid. The chemicals were all of suprapure quality.

The rehydration solution, developed and successfully used in previous tests on mummified skin,[30] consists of 8 parts of a 0.2% commercial fabric softener in a 5% sodium carbonate solution, and 2 parts of aqueous formaldehyde (4%). The intention of this rehydration step was to leach exogenous substances originating from the bog, which had infiltrated the tissues composing the specimens. The samples were incubated in 5 mL of this rehydration solution and maintained in a constant state of gentle motion. As expected, the solutions turned yellowish to brown as the samples gradually rehydrated. Therefore, solutions were changed daily until they remained clear. This took up to 11 days for the textile samples, and 16 days for the fur. Stable Sr isotope ratios of the solutions at various steps of this rehydration process were measured to monitor any changes.

After rehydration was complete, the specimens were first washed in distilled water, and then in a methanol/chloroform (2:1) solution for 2 h.[31] Finally, they were rinsed twice in distilled water and then air-dried.

The textile and leather specimens, as well as the soil samples, were then processed as follows. In order to reduce the samples to their mineral content, they were ashed in a muffle furnace for 12 h at 500°C. The remaining inorganic phase was wet ashed under pressure for 6 h at 160°C in 1 mL concentrated nitric acid, together with 30 mg of a ^{84}Sr spike (NBS 988, National Bureau of Standards, Washington DC, USA). After the acid had cooled to room temperature, distilled water (4 mL) was added. This was the stock solution for the mass spectrometry.

Nitric acid from the stock solution was evaporated at 120°C in a clean air bench, and the remainder solubilised in 3 mL 6 N HCl for 24 h. The acid was evaporated once more, and the sample solubilised in another 3 mL HCl. A volume of 2 mL of each of the samples was centrifuged for 15 min at 9000 rpm. Sr was separated twice from interfering Rb by cation-exchange columns (Dowex AG 50Wx8, 200–400 mesh), with HCl as the mobile phase. $^{87}Sr/^{86}Sr$ isotopic ratios were determined by the double-filament technique

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with a Finnigan MAT 261 thermal ionisation mass spectrometer (Finnigan, San Jose, CA, USA). The samples were solubilised with HCl and 1 μL of the solution was put on tungsten filaments for examination by mass spectrometry. Quality control was achieved by the Standard Reference Material SRM 987 (National Bureau of Standards) for the $^{87}Sr/^{86}Sr$ ratios, and the Standard Reference Material SRM 1400 'Bone ash' (National Bureau of Standards) for the wet ashing and Rb-Sr separation. The measurement precision was ±0.00001.

RESULTS AND DISCUSSION

Three measurements of the NBS 987 standard (reference value: 0.710235) varied from 0.710233 to 0.710236, three measurements of the NBS 1400 'Bone ash' standard varied from 0.713021 to 0.713044 with regard to the Sr isotope ratio, and from 230 to 234 ppm with regard to its Sr content (Table 1).

Three soil samples from the Thorsberg bog, taken at depths of 30, 50 and 70 cm, had very similar $^{87}Sr/^{86}Sr$ isotopic ratios, ranging from 0.708985 to 0.709015, and thus differing by 0.00003 only. The pore fluid had a similar same isotopic ratio as expected (0.708935), but contained only 2 ppm of Sr as opposed to >350 ppm Sr in the bulk bog samples. The isotopic ratio of the peat bog burial environment is therefore in agreement with the overall geological signature of the North German Plain and the Jutland Peninsula, which is rather homogenous (e.g. 0.7078 at Kjølby/Denmark,[32] 0.7086 in the Emsland/Germany,[33] 0.7096 at Gorleben/Germany[34]). The rehydration solution is isotopically lighter ($^{87}Sr/^{86}Sr$ isotopic ratio of 0.708004) than the soil samples, where the difference of 0.00098 is significant. Any incomplete removal of this rehydration solution from the leather and textile specimens should therefore have skewed their Sr isotopic ratios to lower values. Isotopic signatures higher than those of the soil samples should accordingly indicate a non-local origin of the leather and textiles, or a non-local origin of the animals, fur and skin from which they have been manufactured.

Table 1. Measurement data from this pilot study. Probable non-local specimens are written in bold face

specimen	type	duration of rehydration	Sr (ppm)	$^{87}Sr/^{86}Sr$
P1	leather	16 days	22	0.709074
P3	leather	0 (untreated)	23	0.708994
P3	leather	10 days	21	0.708945
P4	leather	0 (untreated)	27	0.708844
P4	leather	10 days	29	0.708724
P5	leather	0 (untreated)	31	0.709804
P5	leather	10 days	**36**	**0.710246**
P7	leather	0 (untreated)	26	0.708874
P7	leather	16 days	24	0.708743
P8	fur	16 days	**26**	**0.709570**
P9	wool	5 days	**54**	**0.709542**
P10	wool	5 days	40	0.708999
P11	wool	5 days	**61**	**0.709647**
P12	wool	5 days	58	0.709047
P13	wool	5 days	94	0.708954
P14	wool	5 days	44	0.708856
P15	wool	11 days	**84**	**0.709957**
A1	rehydration solution		24	0.708004
TBM 30	peat	0	378	0.708994
TBM 50	peat	0	394	0.708985
TBM 70	peat	0	368	0.709015
PF	pore fluid	0	2	0.708935
NBS 987	standard			0.710236
NBS 987	standard			0.710233
NBS 987	standard			0.710235
NBS 1400	standard		234	0.713021
NBS 1400	standard		231	0.713044
NBS 1400	standard		230	0.713043

The results clearly show that some of the organic specimens (P5, P8, P9, P11, and P15) exhibited $^{87}Sr/^{86}Sr$ ratios higher than their burial environment (Table 1). This can only be due to an efficient leaching of impregnating peat substance from the finds, a procedure which, as mentioned previously, was also monitored visually by observing the tainting of the rehydration solutions. Unfortunately, only specimens P3, P4, P5 and P7 were large enough to save some material for the measurement of the initial Sr isotopic signature, prior to the rehydration step. Differences in $^{87}Sr/^{86}Sr$ ratios varied from 0.000049 (P3) to 0.000442 (P5) (Table 1). Since Sr is positively charged in its ionic state, it cannot firmly bind to the amino acids, which make up the keratin and collagen fibres of the textile and leather finds, because these are also positively charged in the acidic peat bog environment. The rehydration of the specimens in an aqueous solution with an alkaline pH served the purpose of both leaching the peat substance out of the specimens and simultaneously promoting the precipitation of exogenous cations.

The stepwise elution of infiltrating bog material from the specimens is shown in Fig. 1. After 24 h of rehydration, the Sr isotopic ratios remained indistinguishable from those of the soil, with the exception of sample P5, which still exhibited a Sr isotopic signature which is encountered in areas of the North German Plain.[34] Although the second rehydration solution of the fur sample (day 2) already had a Sr isotopic ratio close to the final ratio of the specimen itself, the infiltrating bog substances were leached from the two wool samples much more slowly. As early as within the first 24 h, the fur specimen began to show initial signs of disintegration, and small hair particles were recovered in the rehydration solution. This explains the early rise of the stable Sr isotopic signature from the first rehydration day to the second. Wool specimen P9 exhibited this sudden change after 5 days, while a steady rise of Sr isotopic ratios in the rehydration solutions from the sixth day onwards was observed for wool specimen P15. Since the soil samples had lower ratios, this increase is best explained by the small particles that progressively became detached from the sample. It is noteworthy that the Sr isotopic ratios in the leachates changed with the duration of the rehydration procedure all in the same direction, i.e. away from the Sr isotopic signature of the peat bog and its pore fluid to higher values. This holds also for the leather specimen P5, which already had a somewhat higher pretreatment signature, and the place of origin of which could be ascertained after the decontamination had been completed (see below).

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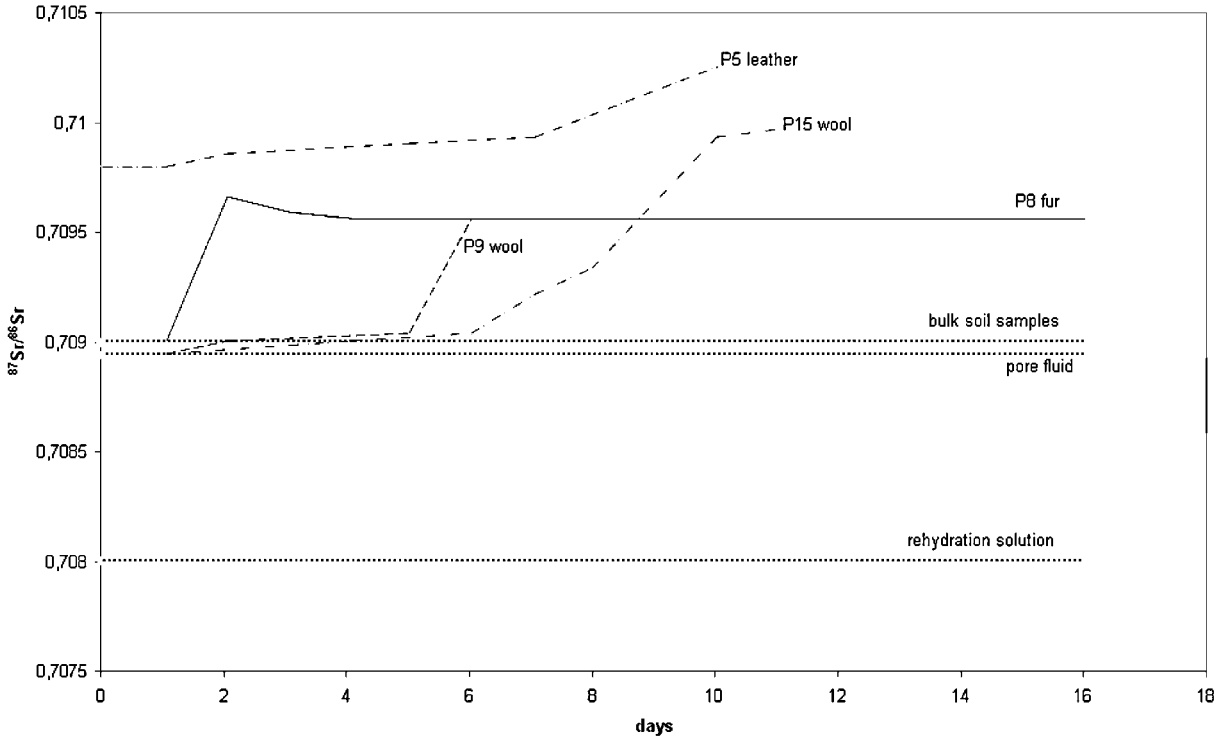

Figure 1. Examples for stable strontium isotopic ratios in rehydration solutions and purified specimens (endpoint of the curves).

While Sr isotopic signatures higher than those of the soil samples indicate that the specimens had been decontaminated (lower signatures might have been due to an incomplete removal of the rehydration solution), it is still difficult to define the appropriate cut-off value between local and non-local isotopic signatures. Norway and northern Scandinavia are dominated by crystalline rocks of pre-Cambrian and later periods, where stable Sr isotopic signatures >0.710 are characteristic.[35] Taking the archaeological record into account, which hypothesises trade contacts with countries to the north of the Thorsberg peat bog, leather specimen P5 could have originated from there, since it also revealed a final isotopic signature slightly higher than 0.710. Conservative calculations would support this assumption, since this signature both exceeds the median isotopic value of all specimens (which is 0.709047), and also exceeds their 75th percentile. Possibly, the textile sample P15 with a final isotopic signature of 0.709957 has also been introduced from or manufactured in the north. Both P5 and P15 differed in their final Sr isotopic ratios from the pore fluid – which should contain free contaminating Sr cations – by more than 0.001. However, such a definition of probable place of origin is restricted to gross geological differences in the region of interest, and cannot take small-scale variations into account. To achieve this, an isotopic mapping of archaeological strata in the Baltic region is a necessity. Such an evaluation is currently in progress: archaeological soil samples, artefacts, and archaeological bones from small residential animals are being collected within the framework of a project by the 'International Sachsensymposium', directed by the senior author (CvC-B).

At this point of our study, which primarily focused on the decontamination procedure of the organic specimens, it is, however, conspicuous that Sr isotopic ratios between 0.7091 and 0.7095 do not occur in our sample (Fig. 2). This might be due to random effects, but this 'optical gap' in Fig. 2 is in fairly good agreement with the small-scale geological differences existing in the North German Plain (cf. the variability between 0.7086 and 0.7096 in northern Germany[33,34]), and between north and south Scandinavia. Therefore, it is possible that the textile samples P9 and P11 and the leather specimen P8 are also of non-local origin and were brought into the area by trade or migration, possibly from a smaller distance. To tentatively define an appropriate internal cut-off value for the 'local' and 'non-local' specimens analysed in this pilot study, twice the standard deviation of the $^{87}Sr/^{86}Sr$ ratio of the 'local' samples (0.000264) is added to the highest one encountered in this group (0.709074, leather specimen P1). This results in a $^{87}Sr/^{86}Sr$ value of 0.709338, which means that the preliminary intrasample cut-off value may be defined as 0.7094.

Further research is certainly needed to positively identify organic finds from the Thorsberg peat bog as imported or of local origin. This will necessitate the acquisition of substantial numbers of archaeological soil samples to facilitate the evaluation of the small-scale variability exhibited by stable Sr isotopic ratios in this area, an effort which has already been started. Alternatively, the measurement of isotopic ratios of bone from small, sedentary mammals with a restricted home range, such as mice and rabbits, has also been suggested,[36] and this will also be performed in the near future. The primary aim of this study, however, was to test whether contaminating strontium from the burial environment can be successfully removed from organic samples after long inhumation periods. We conclude that this is indeed possible and therefore would encourage further

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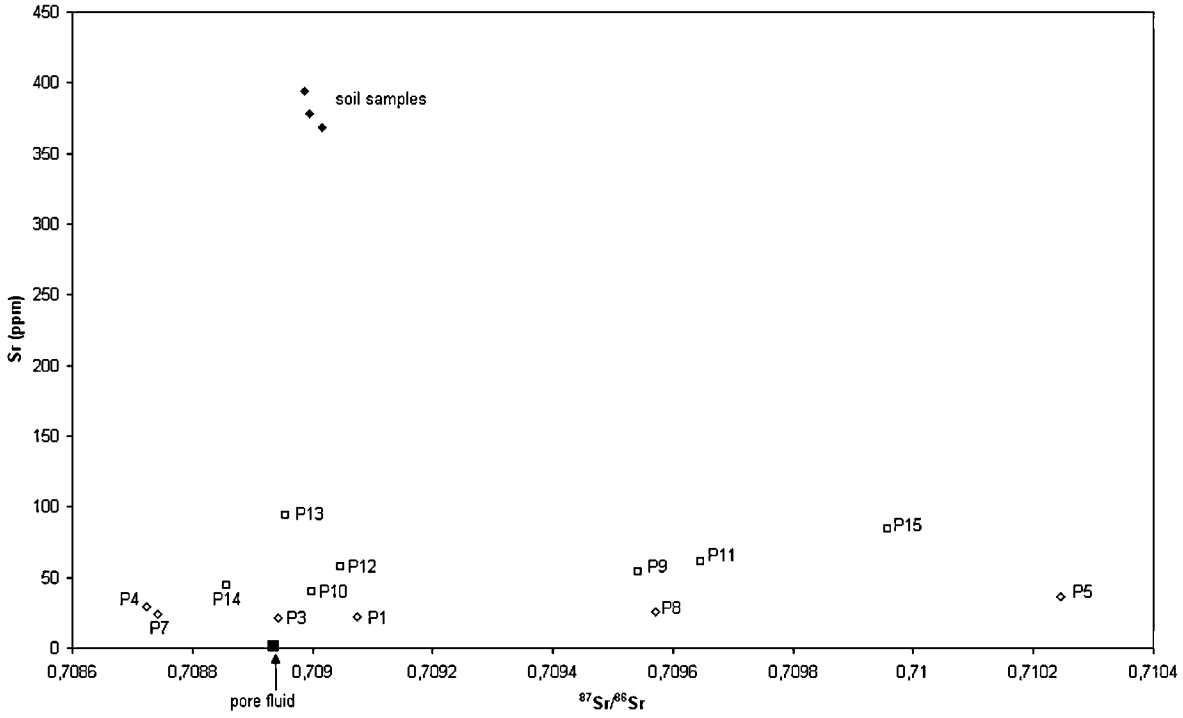

Figure 2. Stable strontium isotopic ratios in leather/fur (open diamonds) and wool (open squares) samples from the Thorsberg peat bog. The preliminary cut-off value between 'local' and 'non-local' finds is defined as 0.7094 (cf. text).

efforts in this direction for the purposes of increased efficiency and accuracy in future isotope studies.

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