Trace element ratios in tooth enamel as palaeodietary indicators of seaweed consumption and coastal grazing, and their broader applicability

Magdalena Blanz [a,b,c,*], Samuel Stewart [d,e], Ingrid Mainland [a], Philippa Ascough [f], Andrea Raab [g], Jörg Feldmann [g], Mark A. Taggart [d]

[a] Archaeology Institute, University of the Highlands and Islands, Orkney College UHI, Kirkwall, Orkney, KW15 1LX, Scotland, UK
[b] Vienna Institute for Archaeological Science (VIAS), University of Vienna, Franz Klein-Gasse 1/III, 1190, Wien, Austria
[c] Human Evolution and Archaeological Sciences (HEAS), University of Vienna, Austria
[d] Environmental Research Institute, University of the Highlands and Islands, Castle St, Thurso, Scotland, KW17 7JD, UK
[e] Université Paris-Saclay, CEA, List, F-91120 Palaiseau, France
[f] NEIF Radiocarbon Laboratory, Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, UK
[g] Institute for Chemistry, TESLA - Analytical Chemistry, University of Graz, Universitätsplatz 1/I, 8010, Graz, Austria

ARTICLE INFO

ABSTRACT

Ratios of barium and strontium concentrations in skeletal samples (e.g. in the logarithmic form lg(Ba/Sr)), are a possible alternative or supplementary marker to stable carbon isotope ratios (δ^{13}C) for identification of marine food consumption. Previous studies have compared lg(Ba/Sr) values between different species of animals with differing diets, but few studies have been performed where animals of the same species consumed known diets ranging from completely terrestrial to completely marine. Additionally, how seaweed consumption affects dental and bone Ba, Sr and other trace element concentrations has not yet been directly investigated.

In this study, tooth enamel from modern sheep (n = 15) that consumed known diets containing varying amounts of terrestrial grasses and seaweeds were analysed for their Sr, Ba, Ca, V, Mn, Co, Ni, As, and U concentrations. Additionally, δ^{13}C values were analysed to enable comparison of δ^{13}C and trace element ratios as markers of marine plant food consumption. The consumed vegetation types (grasses and seaweeds) were also analysed for trace element ratios, as were soils and sands from areas where the animals were pastured. To investigate how decay processes (i.e., diagenesis) may affect lg(Ba/Sr) in archaeological tooth enamel, teeth of 22 sheep from seven archaeological sites (ranging from ca. 5000 to 1000 years old) on the Orkney Islands, Scotland, were also analysed.

The results show that tooth enamel from seaweed-eating sheep had significantly different lg(Ba/Sr) (−2.4 to −1.6) and δ^{13}C values (−6.7‰ to −3.3‰) when compared to terrestrial-feeding sheep (lg(Ba/Sr) 0.6 to −0.5; δ^{13}C −15.5‰ to −14.7‰), with a linear correlation between lg(Ba/Sr) and δ^{13}C (R^2 = 0.94). Vegetation, soil and sand results confirmed the assumed dependence of enamel lg(Ba/Sr) values on the (bioaccessible) Ba and Sr concentrations of the consumed matter. The archaeological samples had elevated relative amounts of U, V, As, Mn, Co, and Ni, attributable to diagenesis. However, the lg(Ba/Sr) values of the archaeological enamel followed the trend established using the modern samples, indicating that diagenesis did not cause significant changes in lg(Ba/Sr) in these samples. In conclusion, lg(Ba/Sr) values in enamel appear to be a useful indicator of the relative amount of marine food consumed, including seaweeds. This may be particularly advantageous for samples and locations where δ^{13}C is unreliable or ambiguous as an indicator of marine food consumption.

1. Introduction

Particularly when considering complex omnivorous diets, interpretation of single palaeodietary markers faces issues of equifinality, whereby the same end-result can be achieved by many different dietary combinations. For example, stable carbon isotope ratios (δ^{13}C) of skeletal material are routinely used to identify the extent of marine dietary contributions and to study the relative contributions of C$_3$ and C$_4$ plants

---

to diets (Kelly, 2000; Schwarcz, 1991). However, a combination of terrestrial C3 plants ($\delta^{13}C$ generally between −32‰ and −23‰; Kohn, 2010) and marine foods ($\delta^{13}C$ around −15‰ to −20‰, Chisholm et al., 1982; Raven et al., 2002) can give rise to the same consumer $\delta^{13}C$ value as a completely terrestrial diet combining C3 and C4 plants ($\delta^{13}C$ around −10‰ to −16‰ in C4 plants; Basu et al., 2015; O'Leary, 1988). Here, combining multiple, independent markers can help to exclude significant dietary contributions of particular food types, and provide additional resolution (Madgwick et al., 2021). While other stable isotope ratios, including $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, $\delta^{34}S$ and $\delta^{66}Zn$, have been utilised in palaeodietary studies (Balasse et al., 2019; Jaouen et al., 2016; Makarewicz and Sealy, 2015; Richards et al., 2003; Schwarcz, 1991), the potential of trace element analysis has not yet been fully explored (Simpson et al., 2021).

Barium (Ba) and strontium (Sr) appear to be the most reliable trace elements for use as palaeodietary indicators, in part because of their lower susceptibility to diagenesis particularly in tooth enamel compared to other trace elements (Ezzo, 1994; Hollund et al., 2014; Sponheimer and Lee-Thorp, 2006). Both Sr and Ba may substitute for calcium (Ca) in geological systems and organisms due to their similar properties, and Sr/Ca and Ba/Ca vary with underlying geology in terrestrial systems. As part of the biopurification of Ca, organisms discriminate against Sr and Ba in favour of Ca, causing a decrease in bone Sr/Ca of around 70%, and Ba/Ca of around 84% with each trophic step (Peek and Clementz, 2012a). In marine systems, these biopurification steps also take place, but marine Ba/Sr ratios tend to be lower on average than in terrestrial systems (Burton and Price, 1990; Peek and Clementz, 2012a), because sulphates (SO_4^{2-}) in seawater bind large amounts of barium into insoluble barium sulphate ($BaSO_4$), depleting surface waters of dissolved barium (Peek and Clementz, 2012a). It has been shown that the proportion of marine food in diets can therefore be studied using skeletal Ba/Sr ratios (usually as lg(Ba/Sr), the decadic logarithm; Burton and Price, 1990; Knudson et al., 2012). Since enamel $\delta^{13}C$ values are measured on carbonates (CO_3^{2-}), they are not inherently coupled to Ca, Ba, and Sr. Enamel trace element ratios thus provide a separate, independent means of assessing diets, which may be particularly useful when $\delta^{13}C$ and other dietary indicators are ambiguous due to natural inter-individual variability and/or face issues of equifinality, or when $\delta^{13}C$ cannot be studied (e.g., potentially in burnt material).

However, there is currently no detailed understanding yet of how skeletal lg(Ba/Sr) values change with marine food consumption. Comparisons of how specific diets affect skeletal lg(Ba/Sr) compositions have so far primarily been made based on animals of different species consuming differing diets (e.g. Kohn et al., 2013). Because of this, differences in how elements are absorbed (e.g., ruminants vs monogastric animals) are frequently neglected, so it can be difficult to distinguish if the cause of differences observed in skeletal composition are the result of differences in the dietary composition or are instead due to differing consumer species. These two factors can be disentangled by studying how different diets affect the skeletal composition of a single animal species.

The consumption of seaweed and terrestrial C3 vegetation by sheep, i.e., a simple herbivorous diet with varying amounts of marine food intake and constant dietary trophic level, provides an ideal opportunity for further study of the uptake and transfer of Ba, Sr and Ca and other trace elements into tooth enamel. The development of As concentrations in teeth as a marker of exposure to As is also particularly well-suited to be investigated using seaweed- and grass-eating sheep, since many seaweeds contain significantly higher As concentrations than most terrestrial vegetation (Caumette et al., 2007; Hansen et al., 2003b). The consumption of seaweed by terrestrial mammals is common today on several Scottish islands including North Ronaldsay (Paterson and Coleman, 1982) and Rum (Conradt, 2000), but has also been observed in Norway (Hansen and Aanes, 2012), Iceland (Hersteinsson and Macdonald, 1996), and the USA among many other countries (reviewed in

Carlton and Hodder, 2003). The consumption of seaweed by sheep in particular is archaeologically and historically well-attested to in Britain (e.g. Balasse et al., 2019, 2005; Martin, 1716). Here, stable carbon isotope ratios can be used as a quantitative indicator of seaweed consumption, because C4 plants were virtually absent from Britain in prehistory (Britton et al., 2008; Still et al., 2003). Comparison to enamel $\delta^{13}C$ values thus helps evaluate how ratios of Sr, Ba and Ca vary with differing amounts of seaweed-consumption, even when the exact amount of seaweed consumed (for example by semi-feral modern, or archaeological sheep) was not observed. The results of this study may then be transferred to contexts where $\delta^{13}C$ alone is not sufficient as an indicator of marine food consumption.

The aim of this study was to assess how tooth enamel lg(Ba/Sr) values vary with seaweed consumption, and to what extent the inadvertent consumption of soil and sand by grazers may influence lg(Ba/Sr) values. To achieve this, tooth enamel from modern and archaeological seaweed-eating sheep and grass-eating sheep, terrestrial vegetation, seaweed, soils, and sand were analysed to study variations in trace elemental composition (Ba, Sr and Ca for dietary study, and Mn, Co, Ni, V and U for diagenetic monitoring). These data were compared to $\delta^{13}C$ data from the same animals. Additionally, the potential of using dental As concentration as a marker of seaweed consumption, and of As exposure more generally, was evaluated. The results of this study improve the identification of seaweed consumption in herbivores and help extend current knowledge of how trace element ratios may be used for palaeodietary studies around the world.

2. Materials and methods

2.1. Mandibles, enamel sampling and analysis

Modern sheep mandibles were collected in 2004 on the islands of Rousay, Holm of Aikerness (near Westray) and North Ronaldsay within the Orkney archipelago, Scotland. The sheep on Rousay were pastured on indigenous grassland and reseeded grassland (n = 6), while the sheep from the Holm of Aikerness had access to virtually no grass, and primarily consumed seaweed (n = 3). Sheep on North Ronaldsay had access to unimproved maritime heath, indigenous grassland and cultivated grassland, but mainly consumed seaweed (n = 7; Hansen et al., 2003a, 2003b). Further detail on these sheep is available in previous publications (Balasse et al., 2009; Blanz et al., 2020). Archaeological mandibles and loose teeth were acquired from seven archaeological sites on the Orkney Islands, shown in Table 1 and Supplementary File 1. This material was selected for trace elemental analysis with the aim of including as wide a range of $\delta^{13}C$ values as possible (previously published in Balasse et al., 2009; Blanz et al., 2020), to enable better comparison between $\delta^{13}C$ and lg(Ba/Sr) values.

The outer surfaces of the molars were removed using diamond coated drill bits (NTI-Kahla) to reveal a clean layer of enamel, from which at least 0.17 g of powdered enamel (per tooth) was obtained by drilling along the entire surface length of the enamel on the buccal side. To remove diagenetic material, e.g., Sr incorporated into diagenetic apatite, the archaeological samples (except for the samples from Bu Sands) were washed in 0.1 M acetic acid and rinsed with distilled water. The pretreated archaeological samples and untreated modern samples were dissolved in concentrated HNO_3 and H_2O_2 in an open vessel microwave digestion system (CEM Mars 5 Microwave Technology). The digests were diluted with bidistilled water and measured using inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) for Ba, Co, Mn, Ni, Sr and As, and by hydride generation inductively coupled plasma tandem mass spectrometry (HG-ICP-MS/MS) for As in the modern samples for higher sensitivity. Microwave induced plasma atomic emission spectrometry (MP-AES) was used to measure Ca, Ba and Sr concentrations, enabling an additional check on the quality of analysis by measuring Ba and Sr using two independent methods. Additional details regarding sample pre-treatment, instrumental setup and

Table 1

List of sheep teeth sampled for trace element analysis.

sample prefix	archaeological site	Orkney Island	approximate age	observed diet[1]	sampled teeth for trace elements	no. samples	δ13C analysis material
ROU	*N/A*	Rousay	recent[1]	terrestrial grasses	lower 3rd molars	5	collagen[1], enamel[9,10]
NR	*N/A*	North Ronaldsay	recent[1]	grasses, seaweeds	lower 3rd molars	7	collagen[1], enamel[9,10]
HAW	*N/A*	Holm of Aikerness	recent[1]	seaweeds	lower 3rd molars	3	collagen[1], enamel[9,10]
BV	Beachview	Mainland	Late Norse period[2]	*N/A*	lower 2nd molars	2	collagen[10]
SG	Snusgar	Mainland	Late Norse period[3]	*N/A*	lower 2nd molars	2	collagen[10]
BS	Bu Sands	Burray	Iron Age/Viking/medieval[4]	*N/A*	various molars*	3	enamel[10]
SWR	Swandro	Rousay	Late Iron Age[5]	*N/A*	lower 2nd molars	2	collagen[10]
MH	Mine Howe	Mainland	Iron Age[6]	*N/A*	lower 3rd molars	3	collagen[1], enamel[9,10]
NOB	Ness of Brodgar	Mainland	Neolithic[7]	*N/A*	lower 3rd molars	8	collagen[1], enamel[9,10]
POC	Point of Cott	Westray	Neolithic[8]	*N/A*	lower 2nd molars	3	collagen[1], enamel[9,10]

*teeth from Bu Sands are two lower 1st or 2nd molars and an upper 3rd molar; [1]see Blanz et al. (2020);[2]Morris (1986);[3]Griffiths et al. (2019);[4]Brend (2010);[5]Bond and Dockrill (2019);[6]Mainland et al. (2016);[7]Card et al. (2018);[8]Barber (1997);[9]Balasse et al. (2009);[10]this study.

additional reagents used are given in Supplementary File 1. Certified reference materials NIST1400 (bone ash) and NIST 1486 (bone meal) were also analysed in triplicate and element recoveries of generally between 94 and 109% for As, Sr, Ba and Ca were obtained. Compared to the differences between samples, the analytical error was negligible (see Supplementary File 2 for further details).

For analysis of δ13C and δ18O in the modern samples and the archaeological samples from Bu Sands, aliquots of the same enamel samples were analysed using an automated cryogenic distillation system (Kiel IV carbonate device, ThermoFisher Scientific) coupled to an isotope ratio mass spectrometer (DELTA V Advantage, ThermoFisher Scientific). Repeated measurements of the laboratory carbonate standard Marbre LM (normalised to NBS19) and also of one of the enamel samples, showed standard deviations of below 0.03‰ for δ13C, and below 0.06‰ for δ18O. The sheep mandibles from Snusgar, Beachview and Swandro were analysed for collagen δ13C following collagen extraction (using a modified Longin (1971) method described in Dunbar et al., 2016) according to Sayle et al. (2013). Results are reported with 1σ precisions of ±0.2‰ for δ13C and ±0.3‰ for δ15N. The dataset collected by the experimental analyses above was expanded with previously published bone collagen δ13C and δ15N data from the mandibles the teeth in this study were extracted from, reported in Blanz et al. (2020), and sequential enamel δ13C results for the modern and selected archaeological samples (Balasse et al., 2009; Blanz et al. forthcoming).

2.2. Modern vegetation, soil, and sand samples

Since ruminants (e.g. sheep, cattle) are known to ingest significant amounts of soil both deliberately and inadvertently (Abrahams and Steigmajer, 2003; Smith et al., 2009; Thornton and Abrahams, 1983), their contribution to a sheep's elemental uptake also needs to be considered. For this reason, grasses, seaweeds, soil and sand were obtained in summer 2019 from North Ronaldsay and Rousay from the same areas that the sheep were pastured in. Multiple areas on the islands were sampled in triplicate at distances of around 50–100 m from each other. Each of these triplicates comprised pooled terrestrial vegetation (at least 2 g dry weight; n = 25), seaweed (at least 2.5 g dry weight, n = 27), soil or sand samples (at least 30 g dry weight; n = 40) from three locations around 5 m from each other (see Supplementary File 1). Seaweed sampling was focussed on the kelps *Laminaria digitata* and *Laminaria hyperborea,* and dulse (*Palmaria palmata*), as these are the species primarily consumed by the sheep on North Ronaldsay (Hansen et al., 2003a; 2003b). Both fresh and stranded seaweeds were sampled, and these were also subsampled to stipe, meristem and blade fractions. Soils were broadly categorised by visual inspection as either predominantly sandy (defined here as >50% sand), or not predominantly sandy.

2.2.1. Vegetation analysis

Vegetation samples were dried at 50 °C and comminuted in a grinder (Cuisinart SG20U). Sample aliquots and the certified reference materials

BCR-129 (Hay Powder) and DC73348 (Bushes, Branches and Leaves) were microwave digested (Anton Paar, Multiwave PRO) at 180 °C in concentrated nitric acid and hydrogen peroxide. The diluted digests were measured by ICP optical emission spectroscopy (ICP-OES; Varian 720-ES) for concentrations of Ba, Sr, Ca, Co, Mn, and As (see Supplementary File 1 for further details).

2.2.2. Soil and sand bioaccessibility simulation

The non-bioaccessible fraction of Sr, Ba and Ca is considerably larger in sand and soil than in the vegetation samples (Abbasi et al., 2016; Shock et al., 2007; Tamponnet et al., 2008). Therefore, the sheep digestive process needs to be simulated to gain relevant data for sands and soils. Soil and sand samples were dried at 105 °C for 24 h and then sieved to <2 mm for 30 min with a sieve shaker (AS200 Basic, Retsch, Germany). To estimate bioaccessibility for selected elements in the sand and soil, an amended version of the physiologically-based extraction test (PBET) described by Bruce et al. (2007) was used. A detailed description of the employed bioaccessibility test and reagents is available in Supplementary File 1. Following the bioaccessibility simulation, an aliquot of each sample was diluted with 8% nitric acid solution and analysed for Ba, Sr, Ca, Co, Mn, Ni and As by ICP-OES (Varian 720-ES).

2.3. Data treatment

Ratios of Ba, Sr, As, V, U and Ca were calculated from concentrations in mg/kg. Values are reported as averages ± 1σ, whereby averages for lg (Ba/Sr) were calculated here as the arithmetic mean of the calculated lg (Ba/Sr) values, resulting in a geometric mean of the original concentration ratio data (as per Burton and Price, 1990; similarly for other ratios, e.g., lg(Ba/Ca) and lg(Sr/Ca)). Standard deviations were calculated using the logarithmically transformed values unless noted otherwise. When comparing between archaeological and modern material, δ13C values must be adjusted for the lowered δ13C values in modern atmospheric CO_2 (affecting entire ecosystems) caused by the burning of fossil fuels (also called the Suess effect; Keeling, 1979; McCarroll et al., 2009). Therefore, where comparisons to modern data are made, archaeological δ13C data were corrected for the fossil fuel effect by subtracting 1.6‰ (Keeling, 1979; McCarroll et al., 2009). To assess differences in the elemental composition between sample groups (e.g., soils, grasses or enamel of differing origin), two-sample two-tailed t-tests or one-way ANOVA followed by post-hoc Tukey tests were performed using Minitab software (Minitab 18, Minitab Inc., USA). The statistical significance threshold was set at α = 0.05.

3. Results

3.1. Modern material

3.1.1. Enamel from modern sheep

Clear differences in enamel composition based on dietary grouping

are apparent (Table 2): Grass-eating sheep had lg(Ba/Sr) values of −0.6 to −0.5 and enamel $\delta^{13}C$ values of −15.5‰ to −14.7‰ whereas seaweed-eating sheep had lg(Ba/Sr) values of −2.4 to −1.6 and $\delta^{13}C$ values of −6.7‰ to −3.3‰ (Fig. 1). Enamel lg(Sr/Ca), lg(As/Ca), lg(V/Ca), lg(U/Ca) and $\delta^{13}C$ were statistically significantly elevated (all p < 0.001; Figs. 2 and 3) in sheep that ate at least some seaweed compared to solely grass-eating sheep, while lg(Ba/Ca) and lg(Ba/Sr) ratios were both significantly lower (p < 0.001; Fig. 3) in seaweed eaters when compared to grass-eating sheep. Concentrations of V in the modern enamel ranged from 18 to 2169 µg/kg, of U from 5 to 58 µg/kg, and of As from 6 to 427 µg/kg. Individual values, Co, Mn, Ni and $\delta^{18}O$ data, and the results of the replicate and CRM analyses are given in the Supplementary File 2.

3.1.2. Modern vegetation, soil and sand samples

Three of the soil samples from North Ronaldsay contained significant amounts (over ca. 50%) of sand, while the soils sampled on Rousay and soils from two other sampled sites on North Ronaldsay were not predominantly sandy (see Supplementary File 2). Grass lg(Ba/Sr) values generally overlapped with bioaccessible values (to ungulates) in the soil they were growing on (Figs. 1 and 3). The highest lg(Ba/Sr) values were observed for soil and grass from Rousay (−0.2 ± 0.2; mean of soil and grass data ± 1σ), whereas North Ronaldsay soil and grass had lower values (−1.2 ± 0.4). The lowest lg(Sr/Ba) values were measured for sands and seaweeds (−2.1 ± 0.2). Concentrations of As varied significantly between sample types, with ≤2 mg/kg in grasses, 48.1 ± 5.2 mg/kg in seaweeds and 5.2 ± 4.2 mg/kg bioaccessible in soils and sands (all dry weights; see Supplementary File 2).

3.2. Archaeological material

Linear correlations were observed between lg(Ba/Sr) and enamel $\delta^{13}C$ for Ness of Brodgar ($R^2 = 0.94$) and Mine Howe ($R^2 = 0.91$), but the samples from Point of Cott varied in lg(Ba/Sr) by only 0.04 while enamel $\delta^{13}C$ varied by −3.2‰ (Fig. 4, left). No clear overall trends were observed between collagen $\delta^{13}C$ and lg(Ba/Sr) data (Fig. 4, right), or between lg(As/Ca), lg(V/Ca), lg(U/Ca) and $\delta^{13}C$ data (see Supplementary File 2). For all archaeological enamel samples, lg(Sr/Ca) values were between −3.2 and −2.3, and lg(Ba/Ca) values were between −3.9 and −3.2 (Fig. 5). Values ranged from −6.4 to −4.5 for lg(V/Ca), and from −7.4 to −5.9 for lg(U/Ca) in the archaeological enamel samples (Fig. 6).

4. Discussion

4.1. Modern samples

4.1.1. Effects of diet on enamel lg(Ba/Sr) and $\delta^{13}C$

The $\delta^{13}C$ results are similar to previously published data for enamel of modern sheep consuming seaweed and C_3 plants (Balasse et al., 2009), and follow the same trend between dietary groups as the collagen $\delta^{13}C$ values from the same animals (Blanz et al., 2020). The lg(Ba/Sr) results show the opposite trend to the $\delta^{13}C$ data, with higher lg(Ba/Sr) values (averaging −0.55 ± 0.07) for grass-eating sheep, and lower values (averaging −2.10 ± 0.14) for seaweed-eating sheep. The results therefore indicate that by consuming seaweed, sheep enamel can attain anomalously low lg(Ba/Sr) values, more similar to those of marine animal bones (averaging −1.6 ± 0.4; Gilbert et al., 1994; Peek and Clementz, 2012a; Ramirez et al., 2019; Zumholz et al., 2006) than to terrestrial animal bones (averaging −0.4 ± 0.7 with a minimum of −1.6, excluding humans, in Burton et al., 1999; Elias et al., 1982; (Gilbert et al., 1994); compare Fig. 7). These results are supported by the composition of the animals' dietary input, with low lg(Ba/Sr) values of −2.1 ± 0.2 for seaweed and sand compared to the higher lg(Ba/Sr) values of −0.2 ± 0.2 for grass and soil on Rousay (Fig. 1). A decrease in Sr/Ca of 77%, and 87% in Ba/Ca was observed between grass from Rousay and the enamel of sheep from Rousay, which is largely similar to previous reports for bone (Peek and Clementz, 2012a). This shows the potential of lg(Ba/Sr) as a dietary marker.

However, despite consuming the most seaweed and having the highest enamel $\delta^{13}C$ values, the enamel of sheep from the Holm of Aikerness unexpectedly did not have the lowest lg(Ba/Sr) values (Fig. 1). This may be due to differing relative proportions of the different seaweeds consumed on Holm of Aikerness and North Ronaldsay, as both $\delta^{13}C$ and Ba and Sr concentrations vary between seaweed species (Raven et al., 2002 and Supplementary File 2). It is also important to consider that with differing proportions of seaweed and grass the relationship between dietary $\delta^{13}C$ and lg(Ba/Sr) does not scale linearly: For example, a theoretical diet composed of 50% grass with 10 mg Ba/kg and 20 mg Sr/kg (i.e., lg(Ba/Sr) = −0.3) and 50% seaweed with 5 mg Ba/kg and 1000 mg Sr/kg (i.e., lg(Ba/Sr) = −2.3), would result in an overall dietary composition of 7.5 mg Ba/kg and 510 mg Sr/kg (i.e., lg(Ba/Sr) = −1.8). This resulting lg(Ba/Sr) value (of −1.8) is much closer to the seaweed value of −2.3 than to that of grass (−0.3); therefore, in this example a bias towards seaweed consumption is present due to its higher Sr concentrations. In contrast, variations in carbon concentration are not as drastic between grasses and seaweeds, and so this mixing effect is less dramatic (e.g., 41% C in grasses and 36% C in seaweeds with $\delta^{13}C$ values of −30.1 and −17.2‰, respectively, would result in an overall dietary

Table 2

Mean concentrations of selected elements and $\delta^{13}C$ isotope ratios, all ± 1σ. Terrestrial vegetation is abbreviated as terr. veg.

sample type	origin	known diet	$\delta^{13}C$ (‰)	Ca (mg/kg)	Sr (mg/kg)	Ba (mg/kg)	As (mg/kg)	V (µg/kg)	U (µg/kg)	n
tooth enamel	Rousay	terr. veg.	−15.0 ± 0.3	321774 ± 23950	420 ± 86	118 ± 20	0.014 ± 0.007	37 ± 15	9.9 ± 3.8	5
tooth enamel	North Ronaldsay	terr. veg., seaweed	−5.5 ± 0.7	305843 ± 17001	1203 ± 356	9.4 ± 4.1	0.117 ± 0.083	375 ± 70	32 ± 12	7
tooth enamel	Holm of Aikerness	seaweed	−3.6 ± 0.2	346550 ± 19980	1057 ± 129	8.5 ± 2.4	0.225 ± 0.175	1570 ± 523	45 ± 12	3
tooth enamel	archaeological sites		−12.1 ± 0.4*	296193 ± 43885	720 ± 331	90 ± 52	0.163 ± 0.205	1867 ± 1977	125 ± 124	23
terr. veg.	Rousay			4110 ± 882	23.4 ± 8.5	11.1 ± 4.1	≤0.5			10
terr. veg.	North Ronaldsay			5819 ± 1830	92 ± 46	7.1 ± 3.7	≤2			15
seaweeds	North Ronaldsay			12635 ± 5533	1120 ± 816	6.3 ± 3.2	48 ± 22			26
soil**	Rousay			883 ± 331	7.3 ± 2.0	5.7 ± 1.7	4.5 ± 2.1			9
soil**	North Ronaldsay			2218 ± 2183	25 ± 17	4.5 ± 2.0	9.0 ± 6.0			6
sandy soil**	North Ronaldsay			31376 ± 12928	293 ± 135	7.7 ± 3.0	6.2 ± 4.6			9
sand**	North Ronaldsay			30891 ± 11031	213 ± 74	2.1 ± 0.9	3.3 ± 2.9			13

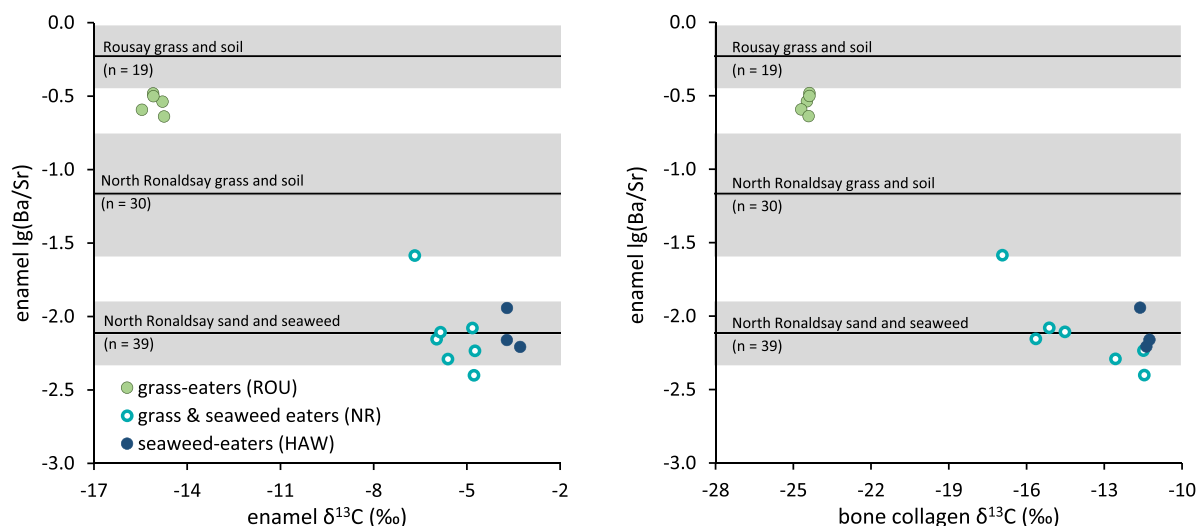*excludes 6 teeth without $\delta^{13}C$ data, **bioaccessible fraction.

Fig. 1. Modern sheep tooth enamel lg(Ba/Sr) and tooth enamel (left) and bone collagen (right) δ^{13}C data, indicated by circular markers. Horizontal lines indicate the mean lg(Ba/Sr) values for grass, soil, sand, and seaweeds $\pm 1\sigma$ (areas shaded grey). The abbreviations in the legend indicate sheep origin: ROU – Rousay, NR – North Ronaldsay, HAW – Holm of Aikerness, Westray. The collagen δ^{13}C data were previously published in Blanz et al., (2020).
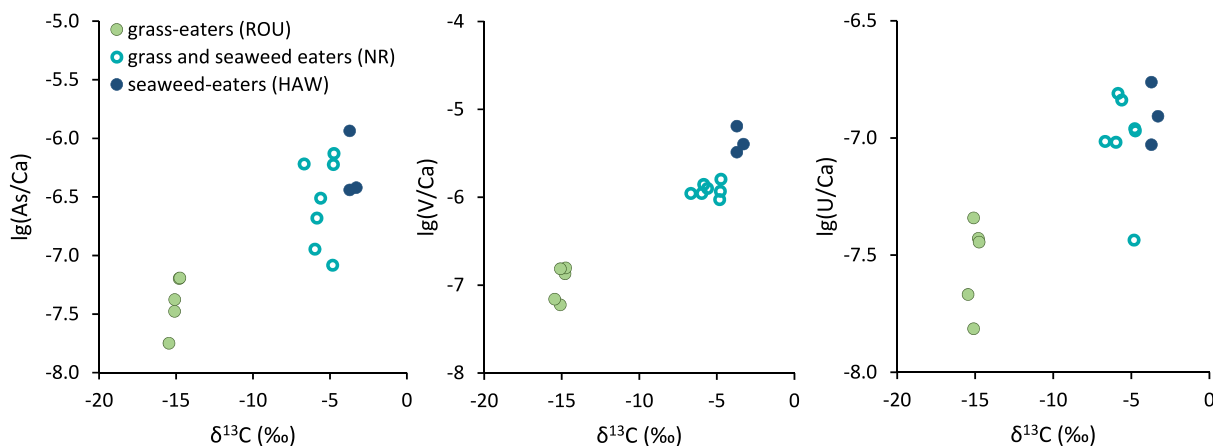

Fig. 2. Modern sheep tooth enamel lg(As/Ca), lg(V/Ca), lg(U/Ca) and enamel δ^{13}C values.

composition of −24.1‰ instead of the arithmetic mean of −23.7‰; data from Blanz et al., 2020). While potentially misleading if not fully considered, this bias towards Sr-rich seaweeds for enamel lg(Ba/Sr) values in mixed grass-seaweed diets may be turned to an advantage, potentially allowing for the identification of minor amounts of seaweed in the diet using this tracer, which may not be clearly identifiable by δ^{13}C alone.

4.1.2. Origin of lower lg(Ba/Sr) ratios in North Ronaldsay soil and terrestrial vegetation

Literature values for lg(Ba/Sr) in topsoil in areas of North America and Europe have been reported to be around 0.4 ± 0.4 (Balter et al., 2002; Burton et al., 1999; Elias et al., 1982; Hamilton et al., 2002; Smith et al., 2005). This is similar to the data from Rousay, where soil lg(Ba/Sr) values ranged from −0.4 to +0.1. However, soil lg(Ba/Sr) values on North Ronaldsay ranged from only −1.8 to −0.6. Sand from North Ronaldsay had even lower lg(Ba/Sr) values (ranging from to −2.4 to −1.6; Fig. 3), and sandy soils on North Ronaldsay had lower lg(Ba/Ca) values compared to the clay/loamy soils on North Ronaldsay (mean of −1.6 compared to −0.7, p < 0.001). Marine sand consists in part of marine shells, which have lg(Ba/Sr) ratios of around −2.5 (Bowen, 1956; Burton and Price, 1990; Pearce and Mann, 2006). Therefore, the

cause of the lower lg(Ba/Sr) ratios in the soil samples from North Ronaldsay is likely the large amount of marine sand, and this lowering of lg(Ba/Sr) may be expected for soils with substantial amounts of marine derived sand/shell material. These results suggest that there is potential for coastal grazing of terrestrial vegetation on shell-rich sandy soils to be identifiable by a combination of lg(Ba/Sr), δ^{13}C and possibly other dietary markers, but further study is necessary.

4.1.3. Exposure to arsenic, and its incorporation into enamel

To assess the significance of elevated As concentrations in tooth enamel of seaweed-eating sheep (mean 149 µg/kg, range 26–427 µg/kg; data from both North Ronaldsay and Holm of Aikerness sheep) compared to grass-eating sheep (range <10–22 µg/kg, p = 0.03) it is necessary to consider the extent of As exposure in both dietary groups. North Ronaldsay sheep consume around 0.5 kg of seaweed (dry weight) per day (Hansen et al., 2003a), and sheep of similar bodyweight can be estimated to consume around 0.6 kg of grass (dry weight) per day (Penning et al., 1995), leading to estimated average daily dietary As burdens of around 25 mg and ≤1 mg, respectively, based on the results of this study. Contributions from drinking water and seawater in the study area are likely negligible (Smedley and Kinniburgh, 2002), whereas soil and sand consumption by the sheep may contribute up to
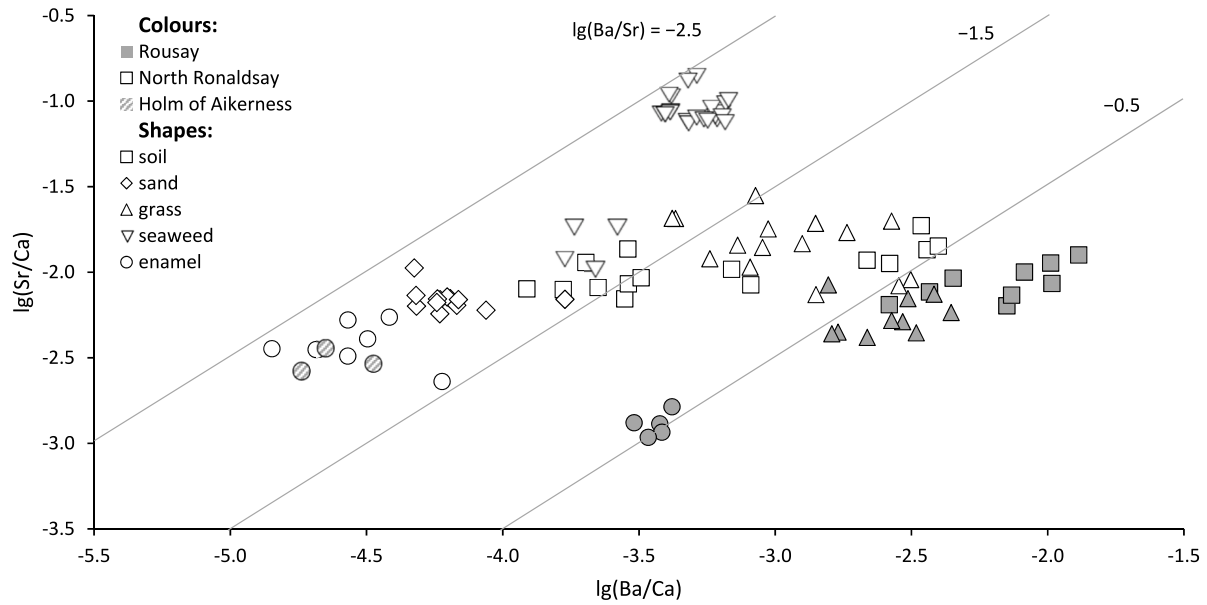
Fig. 3. Measured lg(Sr/Ca) and lg(Ba/Ca) in tooth enamel of seaweed-eating (North Ronaldsay and Holm of Aikerness) and grass-eating (Rousay) modern sheep, and in grasses, seaweeds, and bioaccessible fractions of soils and sands (bioaccessibility assessed for ungulates, not plants). Symbol colour indicates island sampled, while the shapes indicate sample types (NB: Only three samples are from Holm of Aikerness). Diagonal grid lines indicate lg(Ba/Sr) values, calculated as lg(Ba/Ca) − lg(Sr/Ca) = lg(Ba/Sr).
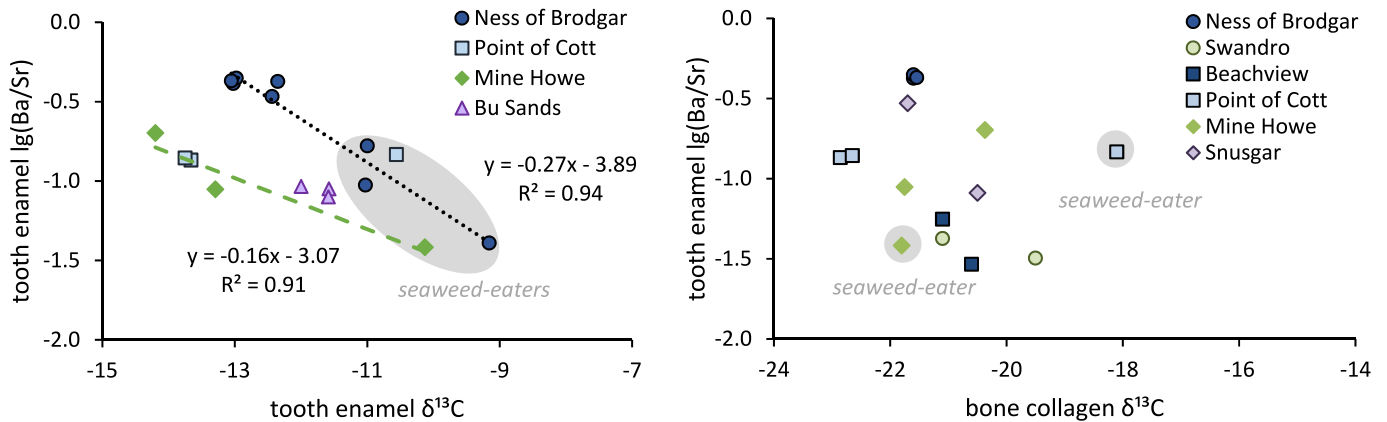
Fig. 4. Archaeological sheep tooth enamel lg(Ba/Sr) plotted against δ^{13}C data (shown here without adjusting for the fossil fuel effect) of enamel shown on the left, and mandible bone collagen δ^{13}C on the right. The linear trendlines are for data from Mine Howe (dashed), and Ness of Brodgar (dotted). The shaded areas indicate sheep interpreted to have been consuming seaweed (particularly in winter) based on sequential enamel δ^{13}C and δ^{18}O results from the same teeth (Balasse et al., 2009 and Blanz et al. forthcoming); such data was unavailable for sheep from Bu Sands, Swandro, Beachview and Snusgar.

ca. 2 mg per day, assuming a soil/sand intake of generally <30% (as a dry weight proportion of diet; Abrahams and Steigmajer, 2003; Smith et al., 2009) based on the measured As concentrations in the sampled soils and sand. Therefore, in this study, exposure to As is estimated as 1–2 orders of magnitude higher in seaweed-eating sheep than in grass-eating sheep. Together with the enamel results (Fig. 2), this indicates that increased As exposure leads to elevated As concentrations in tooth enamel, and thereby also elevated lg(As/Ca) values (modern grass-eaters range −7.7 to −7.2; seaweed-eaters range −7.1 to −5.9). Previous work on dentine indicated uptake during life directly from the diet due to surface and saliva contact as a strong possibility (Blanz et al., 2018), which might also be the case here, but is less likely for enamel than dentine.

4.2. Archaeological material

4.2.1. Diagenetic effects on Ba, Sr, As, V and U

Since all recent and archaeological sheep in this study were from areas with underlying Rousay or Stromness flagstone geology (Astin, 1990; Supplementary File 1), geological differences are unlikely to account for large differences in trace element ratios between archaeological and modern samples with similar δ^{13}C values, and these are thus more likely due to differences in diet or diagenesis. Diagenetic changes in trace element concentrations can greatly affect trace element ratios since the elements have different chemical properties (e.g., different solubilities). In contrast, enamel carbonate stable carbon isotope ratios are relatively robust against diagenetic alterations (Lee-Thorp and Sponheimer, 2003; Lee-Thorp and van der Merwe, 1991) since the loss of a relatively small amount of carbon from the sample is unlikely to greatly affect the isotope ratio in the remaining sample. Assessing the
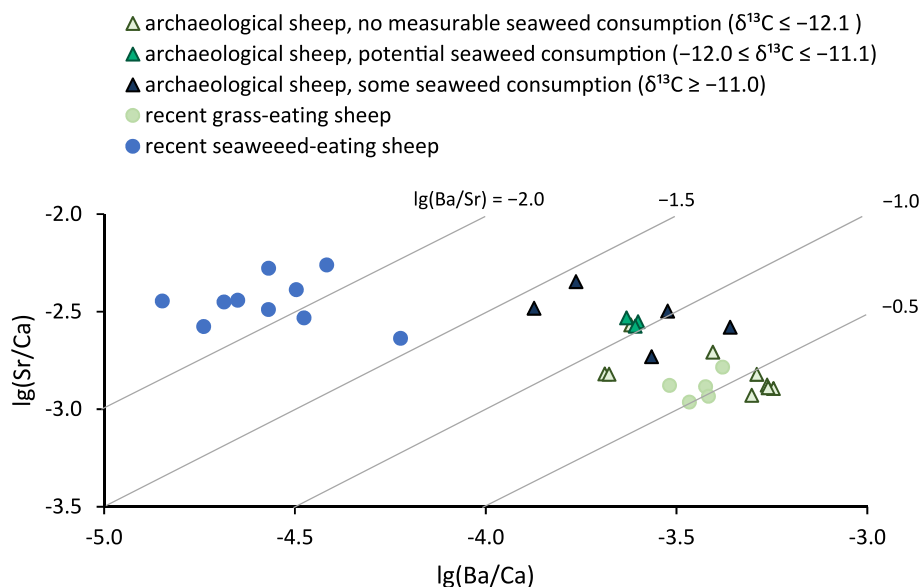
Fig. 5. Graph of lg(Ba/Ca) plotted against lg(Sr/Ca) for archaeological and modern sheep teeth. The $\delta^{13}C$ values in the legend are for the same enamel sample, without adjusting for the fossil fuel effect. Interpretations of seaweed consumption also take into account sequential enamel $\delta^{13}C$ data (from Balasse et al., 2009 and Blanz et al. forthcoming). The three sheep with potential seaweed consumption were not sampled sequentially and are from Bu Sands.
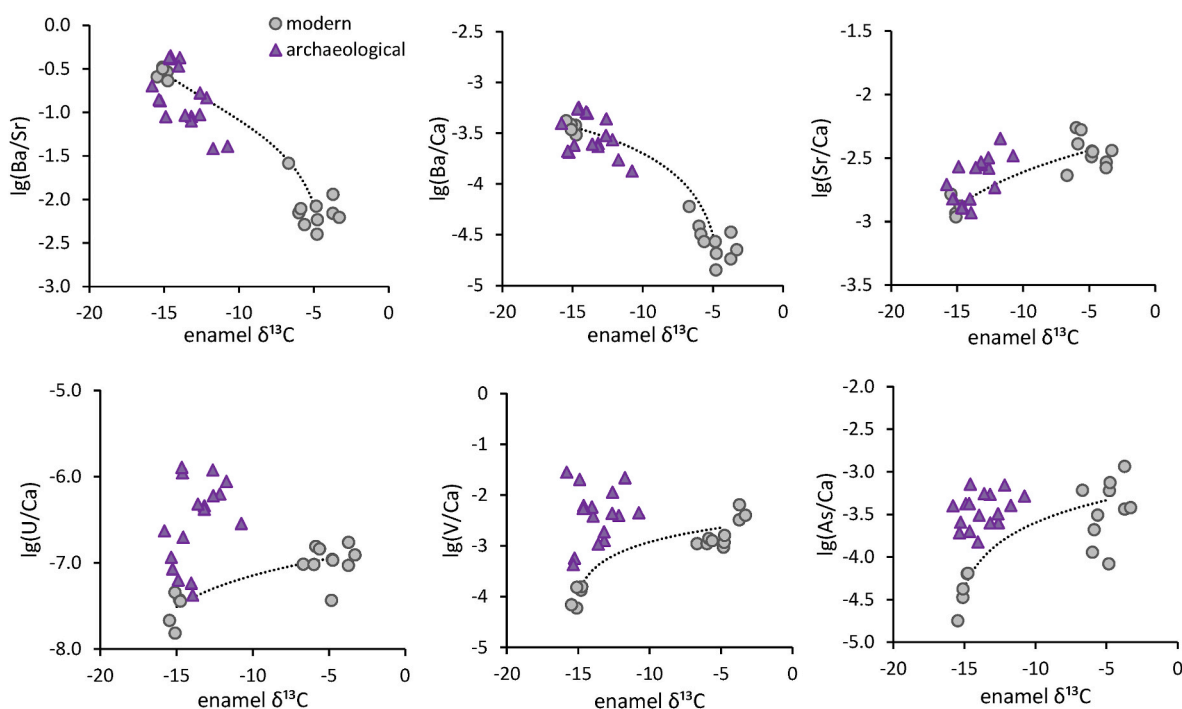

Fig. 6. Recent and archaeological sheep tooth enamel lg(Ba/Sr), lg(Ba/Ca), lg(Sr/Ca), lg(U/Ca), lg(V/Ca) and lg(As/Ca) values plotted against $\delta^{13}C$ enamel data. For the archaeological sheep data, 1.6‰ were subtracted from the enamel $\delta^{13}C$ data to account for the fossil fuel effect. Dotted black lines show a simple linear mixing model (see Supplementary File 1) for varying amounts of seaweed-consumption using the averages for the modern sheep as endpoints. These theoretical mixing lines are non-linear because the y-axes display concentration ratios of two elements whose endpoint concentrations differ.

viability of using Ba/Sr ratios for palaeodietary inferences may therefore be possible by comparison of the relationship between $\delta^{13}C$ values and trace element ratios for modern and archaeological material. Fig. 6 shows a collation of the modern and archaeological data, including a mixing model for the modern enamel which shows the expected enamel composition with varying amounts of seaweed consumption. Where trace element results deviate significantly from the mixing line, diagenesis is likely to have significantly affected the trace element ratio. The archaeological enamel lg(Ba/Sr), lg(Ba/Ca) and lg(Sr/Ca) values

largely fit the mixing line created from the modern data. Therefore, the correlation between the trace element ratios and $\delta^{13}C$ values in both archaeological and modern material suggests that the archaeological lg(Ba/Sr), lg(Ba/Ca) and lg(Sr/Ca) values were not significantly affected by diagenesis, and reflect dietary inputs. In contrast, the archaeological enamel lg(U/Ca), lg(V/Ca) and lg(As/Ca) values deviate from the calculated mixing lines. Both V and U have been suggested for use as indicators of diagenesis (Grimstead et al., 2017; Lambert et al., 1985), and the results of this study indicate that these elements are indeed
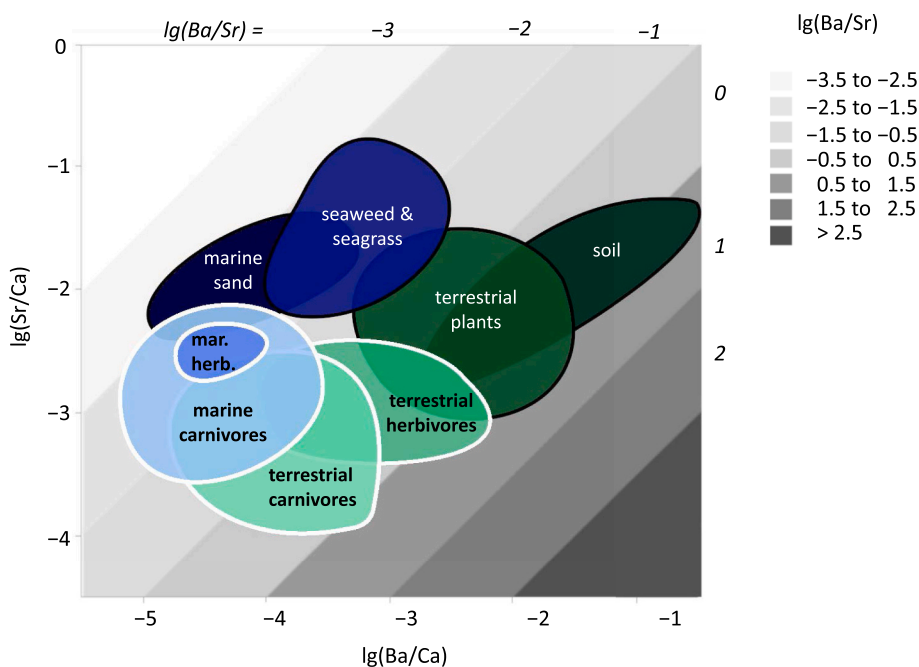
Fig. 7. Approximate illustration of the relationship between lg(Ba/Ca) and lg(Sr/Ca) in marine and terrestrial ecosystems based on data for modern bone, vegetation, soil and sand. The different shades of grey indicate lg(Ba/Sr) values, calculated as lg(Ba/Ca) − lg (Sr/Ca) = lg(Ba/Sr). Insufficient enamel datapoints were available to construct a similar plot for modern tooth enamel instead of bone, but largely similar trends are to be expected. Due to a scarcity of data, the area shown for marine sand also includes data for marine shells and corals. The range for marine herbivores (abbreviated as mar. herb.) is likely drastically underestimated due to lack of data. Data for deserts (see Burton and Price, 1990), the sandy soils from this study, and omnivores and invertebrates were omitted for clarity. Data shown are from Balter et al. (2002), 2001; Bowen (1956); Burton et al. (1999); Drouet and Herbauts (2008); Elias et al. (1982); Hamilton et al. (2002); Li et al. (2005); Mauchline and Templeton (1966); Patterson and Settle (1977); Peek and Clementz (2012a), 2012b; Ramirez et al. (2019); Shacklette, 1980; Smith et al. (2005); Sponheimer and Lee-Thorp (2006) and this study. See Supplementary File 1 Fig. S4 for a more detailed, statistical display of the same data.

significantly more concentrated in some of the archaeological samples than in modern samples of terrestrial feeding sheep (Fig. 6). However, due to differing uptake mechanisms, skeletal material may disproportionately accumulate certain trace elements with a strong affinity for the inorganic phase of teeth (Simpson et al., 2021). Therefore, diagenetic alteration is only of concern when the analytes in question are significantly affected by the alteration. While U/Ca and V/Ca appear to have been significantly affected by diagenesis, this does not appear to be the case for Ba/Sr, Ba/Ca and Sr/Ca. In contrast, the elevated As/Ca ratios in archaeological samples compared to modern grass-eating sheep shown in Fig. 6 indicates that As accumulates diagenetically in enamel. Arsenic has also previously been shown to accumulate significantly in archaeological bones due to diagenesis (Pike and Richards, 2002). Therefore, while *in vivo* concentrations of As in enamel do appear to reflect exposure to As (and may thus be useful to identify As exposure in modern samples), their use as palaeodietary indicators remains limited in most contexts due to diagenetic issues.

4.2.2. Interpretation of Ba, Sr and Ca data

The correlations between lg(Ba/Sr) and enamel δ^{13}C for sheep from Ness of Brodgar and Mine Howe indicate that lg(Ba/Sr) values can track marine contributions to the diet in archaeological samples despite the potential for diagenesis. The archaeological lg(Ba/Sr) results are overall consistent with the enamel δ^{13}C results, indicating that the extent of seaweed consumption by modern sheep on North Ronaldsay today was not present in the archaeological sheep in this study. However, there appear to be some site-specific differences (Fig. 4, left) which could be due to differences in underlying geology, differing (extent of) diagenetic processes, or may not be site-specific after all (as the sample sizes are low). This complicates setting threshold values of lg(Ba/Sr) (or lg(Sr/Ca) and lg(Ba/Ca)), below/above which seaweed-consumption can be interpreted to have taken place, and this likely needs to be assessed on a site-by-site basis. However, if the cause for these differences between sites is site-specific, but non-diagenetic, lg(Ba/Sr) may also present an opportunity to further investigate animal movement at a high resolution if local variability is well-known, particularly when combined with other markers (e.g. lg(Sr/Ba), δ^{13}C, and ^{87}Sr/^{86}Sr). More data are needed to investigate the source of site-specific differences.

In contrast to the modern samples, the archaeological collagen δ^{13}C results do not show a correlation with the lg(Ba/Sr) data (Fig. 4, right).

This might be in part because of the difference in sampled tissue, as bone collagen reflects a different time period than tooth enamel. Similar (but smaller) discrepancies have also been found between enamel δ^{13}C and bone collagen δ^{13}C of seaweed-eating sheep (Blanz et al., 2020). Additionally, the spread of the archaeological collagen δ^{13}C data is comparatively narrow and indicates a primary reliance on terrestrial C$_3$ vegetation by most of these sheep, which corresponds with the absence of low lg(Ba/Sr) values.

4.3. General implications for archaeological and palaeoecological studies

While soil Sr/Ca and Ba/Ca values vary, which affects the rest of the foodweb geographically, general global trends are still identifiable (Fig. 7). By comparing measured Sr/Ca and Ba/Ca values to reference data for the ecosystem and area in question, more precise dietary information may be gained than by relying on isotope ratios alone. However, Ba, Ca and Sr concentrations in animal meat, bones, terrestrial plants, seaweeds, and soils vary considerably and so introduce biases towards foods and other ingested material with higher concentrations. For example, carnivorous, meat-based diets are generally poorer in Sr and Ba (Burton et al., 1999; as also reflected in the bones of carnivores compared to herbivores, Fig. 7), and ingested soil and dust (e.g. from unclean food or felines licking their fur) has been suggested to lead to misleading lg(Sr/Ca) and lg(Ba/Ca) patterns indicating a lower trophic level (i.e., plant consumption; Kohn et al., 2013).

Nevertheless, biases towards certain food groups may also be taken advantage of. For example, seaweeds and seagrasses have among the highest lg(Sr/Ca) values (Fig. 7) and have high concentrations of Sr and Ca (1120 ± 800 mg Sr/kg, and 12634 ± 5425 mg Ca/kg in seaweeds, cf. in grasses around 62 ± 4 mg Sr/kg, and 5082 ± 1704 mg Ca/kg; data from this study). These higher concentrations create a bias in consumer lg(Ba/Sr) and lg(Sr/Ca) toward seaweed (and seaweed-fertilised terrestrial plants; Blanz et al., 2019). In contrast, δ^{13}C$_{collagen}$ data are biased toward dietary protein (Krueger and Sullivan, 1984; Webb et al., 2017). Therefore, combining lg(Sr/Ca) and δ^{13}C measurements may enable the identification of small amounts of seaweed consumption in otherwise terrestrial diets, and distinguishing between the consumption of Sr-rich seaweeds and the consumption of C$_4$ plants. However, this requires a thorough understanding of the limitations and biases of each of these markers, and a knowledge of the local soil composition (and its

variability) and foodweb for the interpretation of ratios of Ba, Sr and Ca.

Given this area-specific knowledge, more detailed interpretations of mobility and grazing areas are then likely possible in herbivores. For example, on Orkney, it might be feasible to use variations in enamel lg(Ba/Ca) to identify whether grazing was concentrated in areas with particularly sandy soil of marine origin. Ingestion of sandy, Ba-poor soils and the Ba-poor grasses growing on them would lead to low consumer lg(Ba/Ca) values, while $\delta^{13}C$ would be virtually unchanged by sandy soil ingestion (due to the higher concentrations of carbon in the diet) and the consumption of grass growing on sandy soil (see vegetation data in Blanz et al., 2020). This combination of low $\delta^{13}C$ and low lg(Ba/Ca) values with high lg(Sr/Ca) values would thus indicate grazing in areas with marine sandy soil, potentially enabling differentiation between animals from different grazing areas. By employing laser ablation ICP-MS on teeth, it may even be possible to gain information on seasonal differences in soil and sand ingestion and the diet, although this would need to be separated out from the background variability in Sr/Ca and Ba/Ca ratios (de Winter et al., 2016; Peek and Clementz, 2012b), and changes due to sampling depth (de Winter et al., 2019). Combination with other isotope ratios, e.g. $^{87}Sr/^{86}Sr$ and $\delta^{18}O$, should also be explored.

Values of lg(Ba/Sr) may also be useful in the study of burnt remains. Due to the variable loss of carbon isotopes during the burning process, $\delta^{13}C$ values are unreliable as dietary indicators in burnt bones (DeNiro et al., 1985). Sr and Ba concentrations and their ratio are also affected by burning (Grupe and Hummel, 1991). However, if cremation temperatures were below 800 °C, and the sample still contains residues of primary carbon, it may be possible to estimate *in vivo* concentrations of Ba and Sr (Grupe and Hummel, 1991). The analysis of Ba and Sr concentrations may therefore allow previously unattainable dietary information to be gained from burnt skeletal remains. If possible, this would be particularly useful to screen samples for significant marine dietary input when selecting burnt material for carbon dating, since accurate dating of burnt material that contains significant amounts of marine carbon is impossible if the local reservoir effect has not been accurately determined (Zazzo et al., 2012).

Finally, the elevated Sr concentrations in enamel of seaweed-eating sheep (Table 2) confirm previous hypotheses that seaweed consumption can lead to elevated Sr concentrations in the consumers skeletal material (Evans et al., 2012). While the strontium stable isotope ratio $^{87}Sr/^{86}Sr$ was not measured directly in this study, this elevated Sr concentration also indicates that the stable isotope ratio $^{87}Sr/^{86}Sr$ may be significantly affected by seaweed consumption, which needs to be considered in studies of past mobility.

5. Conclusion

This study has shown that tooth enamel ratios of Sr, As, U, and V to Ca are elevated in seaweed-eating compared to terrestrially grazing sheep, whereas lg(Ba/Sr) is lower in seaweed-eating sheep. Due to diagenetic processes, As, U and V are not reliable as palaeodietary indicators in most contexts even in tooth enamel, but enamel lg(Ba/Sr) ratios can add information to current conventional analyses in an integrated dental approach. For example, when concentrations of Sr are determined in preparation for $^{87}Sr/^{86}Sr$ measurements, Ba concentrations may also be analysed at the same time at little extra cost to enable additional study of lg(Ba/Sr).

As a sole, independent marker, sequential enamel $\delta^{13}C$ data remain the more precise method of identifying marine food intake if C_4 plants are absent. Nevertheless, trace element analysis offers an independent method to $\delta^{13}C$ that is particularly sensitive to seaweed consumption, and further work with laser ablation ICP-MS on enamel may enable detailed seasonal information to be gained from trace element ratios. Therefore, the use of lg(Ba/Sr) as a secondary marker can be particularly valuable in $\delta^{13}C$ studies with potentially complex diets involving marine foods and C_3 and C_4 plants, and merits further research.

Further fundamental research is required to enable more routine use

of lg(Ba/Sr) ratios also in other contexts, including the study of modern reference material with known dietary histories. Since lg(Ba/Sr) ratios appear to vary between bone and enamel, and between different teeth of the same individual (Peek and Clementz, 2012b), comparisons between datasets need to be made with caution. For application of enamel lg(Ba/Sr) as a marker in archaeology, palaeontology and geobiology more widely, knowledge of the approximate concentrations of Ba and Sr in the potential foods and soils consumed is required, including an assessment of how local and regional geology may differ from literature values, as well as an understanding of how lg(Ba/Sr) values transfer between the different trophic levels (discussed e.g. in Peek and Clementz, 2012a). The study of lg(Ba/Sr) in archaeological bones is generally to be discouraged due to diagenetic effects, and enamel should be targeted instead. This study has shown that the potential uses of Ba and Sr ratios in enamel are not yet fully explored, and hold potential for future palaeodietary research.

Author contributions

Literature review: MB. Sampling and sample preparation: MB, SS. MP-AES, ICP-MS, HG-ICP-MS and ICP-OES measurements: AR, MB, SS, MT. Data evaluation and figure preparation: MB, SS. MB wrote the manuscript in consultation with all authors. All authors read and approved the final draft prior to submission.

Declaration of competing interest

None.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jas.2022.105551.

References

Abbasi, S., Lamb, D.T., Palanisami, T., Kader, M., Matanitobua, V., Megharaj, M., Naidu, R., 2016. Bioaccessibility of barium from barite contaminated soils based on gastric phase in vitro data and plant uptake. Chemosphere 144, 1421–1427. https://doi.org/10.1016/j.chemosphere.2015.10.031.

Abrahams, P.W., Steigmajer, J., 2003. Soil ingestion by sheep grazing the metal enriched floodplain soils of Mid-Wales. Environ. Geochem. Health 25, 17–24.

Astin, T.R., 1990. The Devonian lacustrine sediments of Orkney, Scotland; implications for climate cyclicity, basin structure and maturation history. J. Geol. Soc. London. 147, 141–151. https://doi.org/10.1144/gsjgs.147.1.0141.

Balasse, M., Mainland, I., Richards, M.P., 2009. Stable isotope evidence for seasonal consumption of marine seaweed by modern and archaeological sheep in the Orkney archipelago (Scotland). Environ. Archaeol. 14, 1–14. https://doi.org/10.1179/174963109X400637.

Balasse, M., Tresset, A., Dobney, K., Ambrose, S.H., 2005. The use of isotope ratios to test for seaweed eating in sheep. J. Zool. 266, 283–291. https://doi.org/10.1017/S0952836905006916.

Balasse, M., Tresset, A., Obein, G., Fiorillo, D., Gandois, H., 2019. Seaweed-eating sheep and the adaptation of husbandry in Neolithic Orkney: new insights from Skara Brae. Antiquity 370, 919–932.

Balter, V., Bocherens, H., Person, A., Labourdette, N., Renard, M., Vandermeersch, B., 2002. Ecological and physiological variability of Sr/Ca and Ba/Ca in mammals of West European mid-Würmian food webs. Palaeogeogr. Palaeoclimatol. Palaeoecol. 186, 127–143. https://doi.org/10.1016/S0031-0182(02)00448-0.

Balter, V., Person, A., Labourdette, N., Drucker, D., Renard, M., Vandermeersch, B., 2001. Were Neandertalians essentially carnivores? Sr and Ba preliminary results of the mammalian palaeobiocoenosis of Saint-Cesaire. Comptes Rendus l'Academie Sci. - Ser. IIa Sci. la Terre des Planetes 332, 59–65. https://doi.org/10.1016/S1251-8050(00)01490-7.

Barber, J., 1997. The Excavation of a Stalled Cairn at the Point of Cott, Westray, Orkney. Scottish Trust for Archaeological Research, Edinburgh. Monograph 1).

Basu, S., Agrawal, S., Sanyal, P., Mahato, P., Kumar, S., Sarkar, A., 2015. Carbon isotopic ratios of modern C3-C4 plants from the Gangetic Plain, India and its implications to paleovegetational reconstruction. Palaeogeogr. Palaeoclimatol. Palaeoecol. 440, 22–32. https://doi.org/10.1016/j.palaeo.2015.08.012.

Blanz, M., Ascough, P., Mainland, I., Martin, P., Taggart, M.A., Dieterich, B., Wishart, J., Sayle, K.L., Raab, A., Feldmann, J., 2019. Seaweed fertilisation impacts the chemical and isotopic composition of barley: implications for analyses of archaeological skeletal remains. J. Archaeol. Sci. 104, 34–44. https://doi.org/10.1016/j.jas.2019.02.003.

Blanz, M., Britton, K., Grant, K., Feldmann, J., 2018. Potential dietary, non-metabolic accumulation of arsenic (As) in seaweed-eating sheep's teeth: implications for archaeological analyses. J. Archaeol. Sci. 94, 21–31. https://doi.org/10.1016/j.jas.2018.03.008.

Blanz, M., Mainland, I., Richards, M., Balasse, M., Ascough, P., Wolfhagen, J., Taggart, M.A., Feldmann, J., 2020. Identifying seaweed consumption by sheep using isotope analysis of their bones and teeth: modern reference δ13C and δ15N values and their archaeological implications. J. Archaeol. Sci. 118 https://doi.org/10.1016/j.jas.2020.105140.

Bond, J.M., Dockrill, S.J., 2019. The Knowe of Swandro, Data Structure Report: 2018 Field Season. University of Bradford.

Bowen, H.J.M., 1956. Strontium and barium in sea water and marine organisms. J. Mar. Biol. Assoc. U. K. 35, 451–460. https://doi.org/10.1017/S0025315400010298.

Brend, A., 2010. Bu sands, burray, Orkney (South Ronaldsay parish), survey. In: Milburn, P. (Ed.), Discovery and Excavation in Scotland, New Series, ume 11. Cathedral Communications Limited, Tisbury, Wiltshire, p. 126.

Britton, K., Müldner, G., Bell, M., 2008. Stable isotope evidence for salt-marsh grazing in the Bronze Age Severn Estuary, UK: implications for palaeodietary analysis at coastal sites. J. Archaeol. Sci. 35, 2111–2118. https://doi.org/10.1016/j.jas.2008.01.012.

Bruce, S., Noller, B., Matanitobua, V., Ng, J., 2007. In vitro physiologically based extraction test (PBET) and bioaccessibility of arsenic and lead from various mine waste materials. J. Toxicol. Environ. Health Part A Curr. Issues 70, 1700–1711. https://doi.org/10.1080/15287390701434901.

Burton, J.H., Price, T.D., 1990. The ratio of barium to strontium as a paleodietary indicator of consumption of marine resources. J. Archaeol. Sci. 17, 547–557. https://doi.org/10.1016/0305-4403(90)90035-4.

Burton, J.H., Price, T.D., Middleton, W.D., 1999. Correlation of bone Ba/Ca and Sr/Ca due to biological purification of calcium. J. Archaeol. Sci. 26, 609–616. https://doi.org/10.1006/jasc.1998.0378.

Card, N., Mainland, I., Timpany, S., Towers, R., Batt, C., Ramsey, C.B., Dunbar, E., Reimer, P., Bayliss, A., Marshall, P., Whittle, A., 2018. To cut a long story short: formal chronological modelling for the late neolithic site of ness of Brodgar, Orkney. Eur. J. Archaeol. 21, 217–263. https://doi.org/10.1017/eaa.2016.29.

Carlton, J.T., Hodder, J., 2003. Maritime mammals: terrestrial mammals as consumers in marine intertidal communities. Mar. Ecol. Prog. Ser. 256, 271–286.

Caumette, G., Ouypornkochagorn, S., Scrimgeour, C.M., Raab, A., Feldmann, J., 2007. Monitoring the arsenic and iodine exposure of seaweed-eating North Ronaldsay sheep from the gestational and suckling periods to adulthood by using horns as a dietary archive. Environ. Sci. Technol. 2673–2679.

Chisholm, B.S., Nelson, D.E., Schwarcz, H.P., 1982. Stable-carbon isotope ratios as a measure of marine versus terrestrial protein in ancient diets. Science 216 (80), 1131–1132. https://doi.org/10.1126/science.216.4550.1131.

Conradt, L., 2000. Use of a seaweed habitat by red deer (Cervus elaphus L.). J. Zool. Soc. London 250, 541–549.

de Winter, N.J., Snoeck, C., Claeys, P., 2016. Seasonal cyclicity in trace elements and stable isotopes of modern horse enamel. PLoS One 11, 1–29. https://doi.org/10.1371/journal.pone.0166678.

de Winter, N.J., Snoeck, C., Schulting, R., Fernández-Crespo, T., Claeys, P., 2019. High-resolution trace element distributions and models of trace element diffusion in enamel of Late Neolithic/Early Chalcolithic human molars from the Rioja Alavesa region (north-central Spain) help to separate biogenic from diagenetic trends. Palaeogeogr. Palaeoclimatol. Palaeoecol. 532, 109260. https://doi.org/10.1016/j.palaeo.2019.109260.

DeNiro, M.J., Schoeninger, J., Hastorf, C.A., 1985. Effect of heating on stable isotopes. J. Archaeol. Sci. 0–6.

Drouet, T., Herbauts, J., 2008. Evaluation of the mobility and discrimination of Ca, Sr and Ba in forest ecosystems: consequence on the use of alkaline-earth element ratios as tracers of Ca. Plant Soil 302, 105–124. https://doi.org/10.1007/s11104-007-9459-2.

Dunbar, E., Cook, G.T., Naysmith, P., Tripney, B.G., Xu, S., 2016. AMS 14C dating at the scottish universities environmental research centre (SUERC) radiocarbon dating laboratory. Radiocarbon 58, 9–23. https://doi.org/10.1017/RDC.2015.2.

Elias, R.W., Hirao, Y., Patterson, C.C., 1982. The circumvention of the natural biopurification of calcium along nutrient pathways by atmospheric inputs of industrial lead. Geochem. Cosmochim. Acta 46, 2561–2580.

Evans, J.A., Chenery, C.A., Montgomery, J., 2012. A summary of strontium and oxygen isotope variation in archaeological human tooth enamel excavated from Britain. J. Anal. At. Spectrom. 27, 754–764. https://doi.org/10.1039/c2ja10362a.

Ezzo, J.A., 1994. Putting the "Chemistry" back into archaeological bone chemistry analysis: modeling potential paleodietary indicators. J. Anthropol. Archaeol. https://doi.org/10.1006/jaar.1994.1002.

Gilbert, C., Sealy, J., Sillen, A., 1994. An Investigation of Barium, Calcium and Strontium as Palaeodietary Indicators in the Southwestern Cape, South Africa. J. Archaeol. Sci. 173–184. https://doi.org/10.1006/jasc.1994.1020.

Griffiths, D., Harrison, J., Athanson, M., 2019. Beside the Ocean: Coastal Landscapes at the Bay of Skaill, Marwick and Birsay Bay, Orkney. Archaeological Research 2003-17. Oxbow, Oxford.

Grimstead, D.N., Clark, A.E., Rezac, A., 2017. Uranium and vanadium concentrations as a trace element method for identifying diagenetically altered bone in the inorganic phase. J. Archaeol. Method Theor 1–16. https://doi.org/10.1007/s10816-017-9353-z.

Grupe, G., Hummel, S., 1991. Trace element studies on experimentally cremated bone. I. Alteration of the chemical composition at high temperatures. J. Archaeol. Sci. 18, 177–186. https://doi.org/10.1016/0305-4403(91)90046-R.

Hamilton, S., Buhl, K.J., Lamothe, P., 2002. Selenium and other trace elements in water, sediment, aquatic plants, aquatic invertebrates, and fish from streams in southeastern Idaho near phosphate mining operations. Environ. Res.

Hansen, B.B., Aanes, R., 2012. Kelp and seaweed feeding by High-Arctic wild reindeer under extreme winter conditions. Polar Res. 31, 1–6. https://doi.org/10.3402/polar.v31i0.17258.

Hansen, H.R., Hector, B.L., Feldmann, J., 2003a. A qualitative and quantitative evaluation of the seaweed diet of North Ronaldsay sheep. Anim. Feed Sci. Technol. 105, 21–28. https://doi.org/10.1016/S0377-8401(03)00053-1.

Hansen, H.R., Raab, A., Francesconi, K.A., Feldmann, J., 2003b. Metabolism of arsenic by sheep chronically exposed to arsenosugars as a normal part of their diet. 1. Quantitative intake, uptake, and excretion. Environ. Sci. Technol. 37, 845–851. https://doi.org/10.1021/es026074n.

Hersteinsson, P., Macdonald, D.W., 1996. Diet of arctic foxes (Alopex lagopus) in Iceland. J. Zool. 240, 457–474. https://doi.org/10.1111/j.1469-7998.1996.tb05298.x.

Hollund, H.I., Jans, M.M.E., Kars, H., 2014. How Are Teeth Better than Bone? an Investigation of Dental Tissue Diagenesis and State of Preservation at a Histological Scale (With Photo Catalogue). Internet Archaeol. https://doi.org/10.11141/ia.36.7.

Jaouen, K., Szpak, P., Richards, M.P., 2016. Zinc isotope ratios as indicators of diet and trophic level in arctic marine mammals. PLoS One 11, 1–13. https://doi.org/10.1371/journal.pone.0152299.

Keeling, C.D., 1979. The Suess effect: 13carbon-14carbon interrelations. Environ. Int. 2, 229–300. https://doi.org/10.1016/0160-4120(79)90005-9.

Kelly, J.F., 2000. Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. Can. J. Zool. 78, 1–27. https://doi.org/10.1139/z99-165.

Knudson, K., O'Donnabhain, B., Carver, C., Cleland, R., Price, T.D., 2012. Migration and Viking Dublin: paleomobility and paleodiet through isotopic analyses. J. Archaeol. Sci. 39 (2), 308–320. https://doi.org/10.1016/j.jas.2011.09.014.

Kohn, M.J., 2010. Carbon isotope compositions of terrestrial C3 plants as indicators of (paleo)ecology and (paleo)climate. Proc. Natl. Acad. Sci. 107, 19691–19695. https://doi.org/10.1073/pnas.1004933107.

Kohn, M.J., Morris, J., Olin, P., 2013. Trace element concentrations in teeth - a modern Idaho baseline with implications for archeometry, forensics, and palaeontology. J. Archaeol. Sci. 40, 1689–1699. https://doi.org/10.1016/j.jas.2012.11.012.

Krueger, H.W., Sullivan, C.H., 1984. Models for carbon isotope fractionation between diet and bone. In: Stable Isot. Nutr. ACS Symp. Ser. No.258, pp. 205–220. https://doi.org/10.1021/bk-1984-0258.ch014.

Lambert, J.B., Simpson, Vlasak S., Szpunar, C.B., Buikstra, J.E., 1985. Bone diagenesis and dietary analysis. J. Hum. Evol. 14, 477–482. https://doi.org/10.1016/S0047-2484(85)80026-9.

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. Anthropol. Archaeol. 22, 208–216. https://doi.org/10.1016/S0278-4165(03)00035-7.

Lee-Thorp, J.A., van der Merwe, N.J., 1991. Aspects of the chemistry of modern and fossil biological apatites. J. Archaeol. Sci. 18, 343–354. https://doi.org/10.1016/0305-4403(91)90070-6.

Li, H.C., Ku, T.L., You, C.F., Cheng, H., Edwards, R.L., Ma, Z.B., Tsai, W.S., Li, M.D., 2005. 87Sr/86Sr and Sr/Ca in speleothems for paleoclimate reconstruction in Central China between 70 and 280 kyr ago. Geochem. Cosmochim. Acta 69, 3933–3947. https://doi.org/10.1016/j.gca.2005.01.009.

Longin, R., 1971. New method of collagen extraction for radiocarbon dating. Nature 230, 241–242. https://doi.org/10.1038/230241a0.

Madgwick, R., Lamb, A., Sloane, H., Nederbragt, A., Albarella, U., Pearson, M.P., Evans, J., Madgwick, R., Lamb, A., Sloane, H., Albarella, U., Pearson, M.P., A, J.E.,

2021. A veritable confusion: use and abuse of isotope analysis in archaeology. Archaeol. J. 1–25. https://doi.org/10.1080/00665983.2021.1911099, 00.

Mainland, I., Towers, J., Ewens, V., Davis, G., Montgomery, J., Batey, C., Card, N., Downes, J., 2016. Toiling with teeth: an integrated dental analysis of sheep and cattle dentition in Iron Age and Viking-Late Norse Orkney. J. Archaeol. Sci. Rep. 6, 837–855. https://doi.org/10.1016/j.jasrep.2015.12.002.

Makarewicz, C.A., Sealy, J., 2015. Dietary reconstruction, mobility, and the analysis of ancient skeletal tissues: expanding the prospects of stable isotope research in archaeology. J. Archaeol. Sci. 56, 146–158. https://doi.org/10.1016/j.jas.2015.02.035.

Martin, M., 1716. A Description of the Western Islands of Scotland, second ed. A. Bell, London, UK.

Mauchline, J., Templeton, W.L., 1966. Strontium, calcium and barium in marine organisms from the Irish sea. ICES J. Mar. Sci. 30, 161–170. https://doi.org/10.1093/icesjms/30.2.161.

McCarroll, D., Gagen, M.H., Loader, N.J., Robertson, I., Anchukaitis, K.J., Los, S., Young, G.H.F., Jalkanen, R., Kirchhefer, A., Waterhouse, J.S., 2009. Correction of tree ring stable carbon isotope chronologies for changes in the carbon dioxide content of the atmosphere. Geochem. Cosmochim. Acta 73, 1539–1547. https://doi.org/10.1016/j.gca.2008.11.041.

Morris, C.D., 1986. The Birsay Bay Project Vol 2. Sites in Birsay Village and on the Brough of Birsay, Orkney. Sutton Publishing, Stroud.

O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Bioscience 38, 328–336. https://doi.org/10.2307/1310735.

Paterson, I.W., Coleman, C.D., 1982. Activity patterns of seaweed-eating sheep on North Ronaldsay, Orkney. Appl. Anim. Ethol. 8, 137–146. https://doi.org/10.1016/0304-3762(82)90139-0.

Patterson, C., Settle, D., 1977. Comparative distributions of alkalies, alkaline earths and lead among major tissues of the tuna thunnus alalunga. Mar. Biol. 39, 289–295. https://doi.org/10.1007/BF00391003.

Pearce, N.J.G., Mann, V.L., 2006. Trace metal variations in the shells of Ensis siliqua record pollution and environmental conditions in the sea to the west of mainland Britain. Mar. Pollut. Bull. 52, 739–755. https://doi.org/10.1016/j.marpolbul.2005.11.003.

Peek, S., Clementz, M.T., 2012a. Sr/Ca and Ba/Ca variations in environmental and biological sources: a survey of marine and terrestrial systems. Geochem. Cosmochim. Acta 95, 36–52. https://doi.org/10.1016/j.gca.2012.07.026.

Peek, S., Clementz, M.T., 2012b. Ontogenetic variations in Sr/Ca and Ba/Ca ratios of dental bioapatites from Bos taurus and Odocoileus virginianus. J. Trace Elem. Med. Biol. 26, 248–254. https://doi.org/10.1016/j.jtemb.2012.04.001.

Penning, P.D., Parsons, A.J., Orr, R.J., Harvey, A., Champion, R.A., 1995. Intake and behaviour responses by sheep, in different physiological states, when grazing monocultures of grass or white clover. Appl. Anim. Behav. Sci. 45, 63–78. https://doi.org/10.1016/0168-1591(95)00602-O.

Pike, A.W.G., Richards, M.P., 2002. Diagenetic arsenic uptake in archaeological bone. Can we really identify copper smelters? J. Archaeol. Sci. 29, 607–611. https://doi.org/10.1006/jasc.2001.0754.

Ramirez, M.D., Miller, J.A., Parks, E., Avens, L., Goshe, L.R., Seminoff, J.A., Snover, M.L., Heppell, S.S., 2019. Reconstructing sea turtle ontogenetic habitat shifts through trace element analysis of bone tissue. Mar. Ecol. Prog. Ser. 608, 247–262. https://doi.org/10.3354/meps12796.

Raven, J.A., Johnston, A.M., Kübler, J.E., Korb, R., McInroy, S.G., Handley, L.L., Scrimgeour, C.M., Walker, D.I., 2002. Mechanistic interpretation of carbon isotope discrimination by marine macroalgae and seagrasses. Funct. Plant Biol. 29, 335–378. https://doi.org/10.1071/PP01201.

Richards, M.P., Fuller, B.T., Sponheimer, M., Robinson, T., Ayliffe, L., 2003. Sulphur isotopes in palaeodietary studies: a review and results from a controlled feeding experiment. Int. J. Osteoarchaeol. 13, 37–45. https://doi.org/10.1002/oa.654.

Sayle, K.L., Cook, G.T., Ascough, P.L., Hastie, H.R., Einarsson, Á., McGovern, T.H., Hicks, M.T., Edwald, Á., Fririksson, A., 2013. Application of 34S analysis for elucidating terrestrial, marine and freshwater ecosystems: evidence of animal movement/husbandry practices in an early Viking community around Lake Mývatn, Iceland. Geochem. Cosmochim. Acta 120, 531–544. https://doi.org/10.1016/j.gca.2013.07.008.

Schwarcz, H.P., 1991. Some theoretical aspects of isotope paleodiet studies. J. Archaeol. Sci. 18, 261–275. https://doi.org/10.1016/0305-4403(91)90065-W.

Shacklette, H.T., 1980. Elements in fruits, and vegetable from areas of commercial production in the Conterminous United States. U. S. Geol. Surv. Prof. Pap. 1178, 149.

Shock, S.S., Bessinger, B.A., Lowney, Y.W., Clark, J.L., 2007. Assessment of the solubility and bioaccessibility of barium and aluminum in soils affected by mine dust deposition. Environ. Sci. Technol. 41, 4813–4820. https://doi.org/10.1021/es0703574.

Simpson, R., Cooper, D.M.L., Swanston, T., Coulthard, I., Varney, T.L., 2021. Historical overview and new directions in bioarchaeological trace element analysis: a review. Archaeol. Anthropol. Sci. 13 https://doi.org/10.1007/s12520-020-01262-4.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568. https://doi.org/10.1016/S0883-2927(02)00018-5.

Smith, D.B., Cannon, W.F., Woodruff, L.G., Garrett, R.G., Klassen, R., Kilburn, J.E., Horton, J.D., King, H.D., Goldhaber, M.B., Morrison, J.M., 2005. Major- and Trace-Element Concentrations in Soils from Two Continental-Scale Transects of the United States and Canada. Open-File Rep. 2005–1253. US Dep. Inter. US, p. 20.

Smith, K.M., Abrahams, P.W., Dagleish, M.P., Steigmajer, J., 2009. The intake of lead and associated metals by sheep grazing mining-contaminated floodplain pastures in mid-Wales, UK: I. Soil ingestion, soil-metal partitioning and potential availability to pasture herbage and livestock. Sci. Total Environ. 407, 3731–3739. https://doi.org/10.1016/j.scitotenv.2009.02.032.

Sponheimer, M., Lee-Thorp, J.A., 2006. Enamel diagenesis at South African Australopith sites: implications for paleoecological reconstruction with trace elements. Geochem. Cosmochim. Acta 70, 1644–1654. https://doi.org/10.1016/j.gca.2005.12.022.

Still, C.J., Berry, J.A., Collatz, G.J., DeFries, R.S., 2003. Global distribution of C 3 and C 4 vegetation: carbon cycle implications. Global Biogeochem. Cycles 17. https://doi.org/10.1029/2001gb001807, 6-1-6–14.

Tamponnet, C., Martin-Garin, A., Gonze, M.A., Parekh, N., Vallejo, R., Sauras-Yera, T., Casadesus, J., Plassard, C., Staunton, S., Norden, M., Avila, R., Shaw, G., 2008. An overview of BORIS: bioavailability of radionuclides in soils. J. Environ. Radioact. 99, 820–830. https://doi.org/10.1016/j.jenvrad.2007.10.011.

Thornton, I., Abrahams, P., 1983. Soil ingestion - a major pathway of heavy metals into livestock grazing contaminated land. Sci. Total Environ. 28, 287–294. https://doi.org/10.1016/S0048-9697(83)80026-6.

Webb, E.C., Lewis, J., Shain, A., Kastrisianaki-guyton, E., Honch, V., Stewart, A., Miller, B., Tarlton, J., Evershed, R.P., Webb, E.C., Lewis, J., Shain, A., Kastrisianaki-guyton, E., Honch, V., Stewart, A., Miller, B., Tarlton, J., Evershed, R.P., 2017. The influence of varying proportions of terrestrial and marine dietary protein on the stable carbon- isotope compositions of pig tissues from a controlled feeding experiment. STAR Sci. Technol. Archaeol. Res. 3, 28–44. https://doi.org/10.1080/20548923.2016.1275477.

Zazzo, A., Saliège, J.F., Lebon, M., Lepetz, S., Moreau, C., 2012. Radiocarbon dating of calcined bones: insights from combustion experiments under natural conditions. Radiocarbon 54, 855–866. https://doi.org/10.1017/s0033822200047500.

Zumholz, K., Hansteen, T., Klügel, A., Piatkowski, U., 2006. Food effects on statolith composition of the common cuttlefish (Sepia officinalis). Mar. Biol. 237–244. https://doi.org/10.1007/s00227-006-0342-0.