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The effect of seaweed fertilisation on sulfur isotope ratios ($\delta^{34}S$) and grain size in barley: implications for agronomy and archaeological research

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Introduction: Stable sulfur isotope ratios ($\delta^{34}S$) in bone collagen are often employed to study the consumption of marine and freshwater fish, wetland grazing, marine foraging patterns, and the possible geographic origins of food sources. However, a recent small-scale crop experiment showed that biofertilisation with seaweed can elevate $\delta^{34}S$ in Celtic beans by ca. 10 ‰. Consumption of this food could erroneously suggest a marine diet and therefore has important implications for the reconstruction of past diets and dietary origins. However, limited research has so far been undertaken on cereals.

Methods: To address this issue, a large-scale field trial was undertaken on the Orkney Islands, whereby bere barley (a Scottish landrace, *Hordeum vulgare* L.) was biofertilised with seaweed at different dosages (25 t/ha, 50 t/ha), with a mineral NPK fertiliser, and left unfertilised as a control.

Results: The total barley biomass yield was higher and barley grains were enlarged following all fertilisation treatments compared to the control barley. Barley grain and straw from seaweed-fertilised crops had more elevated $\delta^{34}S$ values by around 2–3 ‰ compared to unfertilised plants, while the NPK-fertilised grains and plants had $\delta^{34}S$ values 1 ‰ lower.

Discussion: These results confirm previous hypotheses that seaweed fertilisation can elevate cereal $\delta^{34}S$ values. The comparatively small $\delta^{34}S$ difference between control and seaweed fertilised crops in this field trial is likely due to background elevated $\delta^{34}S$ values in the soil (+12.7 ‰), which in turn may be due to long-term exposure to oceanic-influenced rain and sea spray and/or possible historical application of seaweed, or the underlying bedrock composition. The results of this study show that seaweed fertilisation can increase barley grain sizes and $\delta^{34}S$ values, and thus should be considered when reconstructing land management and dietary practices in the archaeological record.

KEYWORDS
sulfur stable isotope ratios ($\delta^{34}S$), seaweed, fertilisation, barley, archaeobotany, SDG: life on land, thousand grain weight (TGW)

1 Introduction

The analysis of stable isotope ratios of archaeological plant material and skeletal remains has proven to be a valuable tool to study past plant husbandry practises, and to reconstruct past human and animal diets. The analysis of stable isotope ratios of carbon (δ^{13}C) and nitrogen (δ^{15}N) are frequently used to study past plant irrigation and fertilisation practises, and the extent of marine food and meat consumption by humans and animals (Bogaard et al., 2007; Makarewicz and Sealy, 2015; Schoeninger and Moore, 1992). Additionally, sulfur isotope ratio (δ^{34}S) analyses of bone collagen enable the study of freshwater and marine fish consumption, wetland habitat use by grazing animals, marine animal foraging patterns, and the estimation of possible geographic origins of food sources, among other uses (e.g., Guiry et al., 2024, 2022; Lamb et al., 2023; Nehlich, 2015; Sayle et al., 2019; Szpak and Buckley, 2020; Vika, 2009).

These palaeodietary reconstructions make use of collagen δ^{34}S, δ^{13}C, and δ^{15}N values to model dietary stable isotope ratios based on predictable offsets. However, plant carbon, nitrogen and sulfur isotope ratios can vary considerably, even within a single plant or leaf due to plant metabolism, and many environmental variables, such as climate and nutrient status, sea spray effects and oceanic influenced rain, amongst other factors (see Craine et al., 2015; Gröcke, 2020; Nehlich, 2015; Szpak, 2014; Tcherkez and Tea, 2013). Understanding this baseline variability is crucial for accurate dietary reconstructions, which can be achieved (at least in principle) through the stable isotope analysis of preserved plant material from the same site and time period, and/or by estimating the plant stable isotope ratio using modern reference data (if no suitable material is preserved). When plant remains are preserved in archaeological contexts, this usually occurs due to carbonisation, which may alter the original isotopic values in the plant (Beuning and Scott, 2002; Fraser et al., 2013; Nitsch et al., 2019). A greater understanding of agricultural-management practises that affect the isotopic composition of crop plants prior to carbonisation is required in order to produce more accurate palaeodietary reconstructions, especially in humans (Gröcke et al., 2021).

Factors affecting crop stable isotope ratios include manuring and other soil amendment strategies. For example, cereal δ^{15}N values are generally elevated following fertilisation with terrestrial animal dung (Bogaard et al., 2007; Fraser et al., 2011; Kanstrup et al., 2011), seaweed, fish, and seabird guano (Blanz et al., 2019; Gröcke et al., 2021; Szpak et al., 2019; though other factors can also affect δ^{15}N; Craine et al., 2015; Szpak, 2014). Where archaeological plant remains are preserved, commonly through charring, fertilisation-induced changes in the isotopic composition of crops can be assessed to study past fertilisation practises, including the investigation of when fertilisation first became an established part of agriculture (Bogaard and Outram, 2013). This also has important implications for the reconstruction of past diets, as consumption of biofertilised grain may lead to elevated consumer δ^{15}N values that could be interpreted as the consumption of more meat and dairy. If the possibility of biofertilisation is not taken into account (and plant remains are not analysed directly), the amount of meat/dairy consumption is in danger of being overestimated (see Gröcke et al., 2021).

While the effects of fertilisation on δ^{15}N are well-studied today, there has been considerably less work on crop sulfur isotope ratios. Archaeological grains are rarely analysed for δ^{34}S, possibly in part because the factors affecting δ^{34}S values in crops are not fully understood (e.g., Nitsch et al., 2019). Field studies have shown that synthetic and organic fertilisers may affect δ^{34}S values of crops (Georgi et al., 2005; Gröcke et al., 2021; Mizota and Sasaki, 1996; Szpak et al., 2019), particularly when these are marine-derived, such as seabird guano, marine fish, and seaweed (Gröcke et al., 2021; Szpak et al., 2019). Historical accounts describe the frequent use of seaweed as a fertiliser particularly in coastal areas of the British Isles, in north-western France and Denmark, among others (e.g., Fenton, 1997; Hendrick, 1898; Neill, 1970; Russell, 1910; Sauvageau, 1920; Stephenson, 1968). Initial experimental work on Celtic beans showed an increase in stable sulfur isotope ratios (δ^{34}S) due to fertilisation with seaweed, as well as when fertilising with marine fish (at an experimental site at a distance of ~10 km from the ocean; Gröcke et al., 2021). However, no such experimental research has been undertaken on δ^{34}S in cereals.

δ^{34}S values are often employed to study the consumption of marine and freshwater fish and to study the proximity of food sources to the coast (with higher collagen δ^{34}S values generally indicating a marine influence; seawater $\delta^{34}S \approx +22$ ‰ ± 1 ‰; Bottrell and Newton, 2006). Consumption of marine-fertilised (e.g., with seaweed, fish, shellfish) terrestrial crops may therefore lead to systematic overestimations of the consumption of marine foods if archaeobotanical remains are not analysed from the site. This also affects sites further inland due to transport of seaweed-fertilised crops and dried seaweed to be used as fertiliser. Thus, to enable more robust interpretations of plant δ^{34}S values, further research is required.

In addition to the effects of seaweed-fertilisation on the crop's stable isotope ratios, the effects of seaweed fertilisation may include variation in the number, size and mass of individual grains (as previously indicated in the study on Celtic beans; Gröcke et al., 2021). The most common cereal macrofossils recovered from archaeological sites are grain, and simple measurements (length, width, depth, mass) have been used to infer agricultural innovation, crop development and productivity from the past 10,000 years across the world (cf. Bishop et al., 2022; Fuller et al., 2017; Larsson and Bergman, 2023). Therefore, the overall aim of this study is to determine the effects of seaweed-fertilisation on barley δ^{34}S values and cereal grain sizes in an experimental field trial. The results of this work will help to interpret δ^{34}S data from archaeological crops (e.g., to identify marine biofertilisation), as well as to refine modelling of human and animal diets and archaeological cereal grain weights.

2 Materials and methods

2.1 Field trial

In order to assess the effect of seaweed-fertilisation on barley δ^{34}S values, a field trial was conducted. As the aim of this field trial was to gain information relevant to the reconstruction of past diets and farming practises, the field trial was designed to follow historically documented traditional farming practises as far as possible and practicable (rather than using e.g., present-day seaweed-extracts as fertiliser). The trial was undertaken with barley, as this was one of the earliest crops to be domesticated and has been of particular importance for both human and animal consumption until today (Fuller and Weisskopf, 2020), and historical evidence indicates it was frequently fertilised with seaweed (Fenton, 1997; Martin, 1716; Russell, 1910; Sauvageau, 1920). The traditional barley variety "bere barley" (*Hordeum vulgare* L.), a hulled lax-eared six-row landrace of barley (Martin et al., 2008), was chosen for this field trial rather than a modern barley variety, making greater similarity to barley varieties from archaeological sites more likely. A review of the historical literature on seaweed-fertilisation practises, and more detailed reasoning behind the field trial design choices are given in a previous publication on the same field trial (Blanz et al., 2019).

The field trial was conducted in 2017 on the Orkney islands (Scotland) at an agronomic experimental site ca. 100 m north of Orkney College and ca. 250 m south of the nearest coastline (58° 59′ N and 2° 57′ W; grid reference HY 456 114; Figure 1). This coastal site was exposed to oceanic-influenced rain and sea spray in windy weathers, which, with an $\delta^{34}S$ value of ca. +20 ‰, can elevate $\delta^{34}S$ (Richards et al., 2001; Zazzo et al., 2011). As seaweed-fertilisation is also expected to elevate $\delta^{34}S$ values in the barley (cf. Gröcke et al., 2021; Szpak et al., 2019), this might obscure fertilisation effects on $\delta^{34}S$. However, proximity to the ocean was likely frequently the case when fertilising crops with seaweed (cf. Fenton, 1997), so that this coastal site location offers a realistic perspective on the extent of the effects of seaweed fertilisation on $\delta^{34}S$. The trial site was used for growing bere barley from 2002 and was likely mainly used for grazing through most of the twentieth century as part of Weyland Farm. The earliest mention of this farm dates back to 1595 (Peterkin, 1820), so that it is likely that the trial site has a long history of being used for grazing and also growing bere barley. The field consisted of an acidic clay loam soil that was previously cultivated and fertilised with a low-level NPK mineral fertiliser (50 kg N/ha). It had not been subjected to other fertilisation-based agronomic field trials before, ensuring soil homogeneity throughout the trial area. A randomised block design was chosen with five replicate plots per fertilisation treatment, each measuring 3 m × 3 m (9 m^2) and spaced 1 m apart.

Stranded seaweed of various species (including *Laminaria* spp., *Fucus* spp., and *Ascophyllum nodosum;* all with evidence for historical use as a fertiliser: Fenton, 1997; Hendrick, 1898; Neill, 1970; Russell, 1910; Sauvageau, 1920) was collected from the shore at Newark Bay, Mainland, Orkney (Grid reference: HY 567 041). As historical documents indicate that seaweed was frequently applied composted at the time of seeding (Fenton, 1997; Sauvageau, 1920), the seaweed in this trial was composted for 1.5 months in

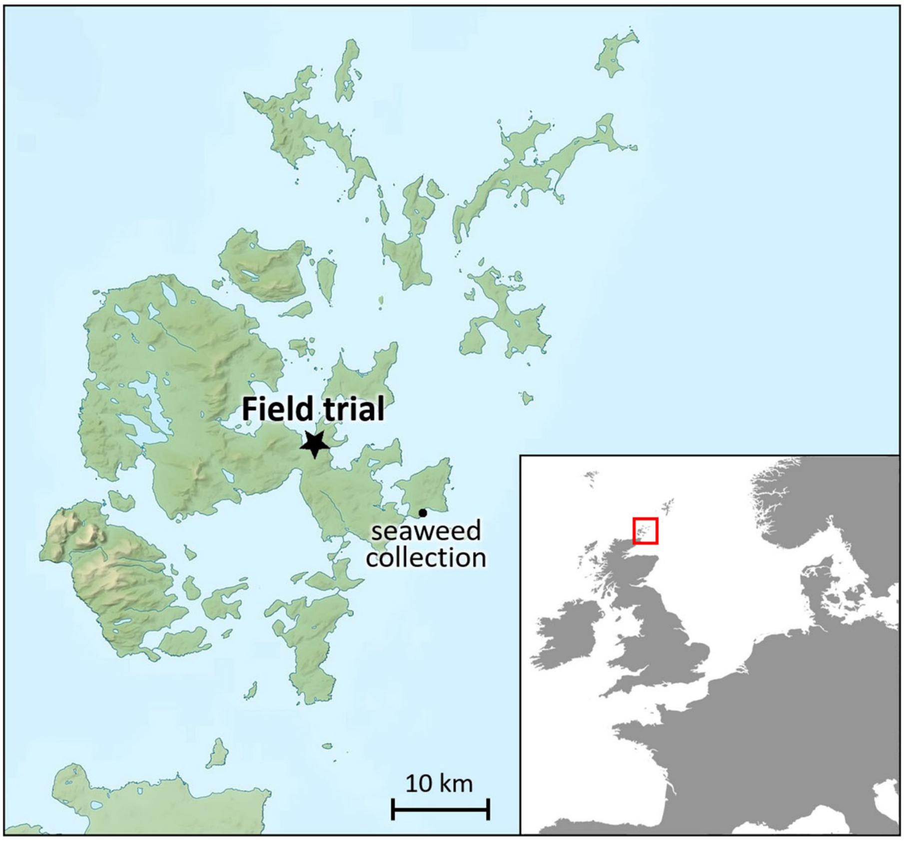

FIGURE 1
Location of field trial and seaweed collection on the Orkney Islands, Scotland, United Kingdom. Image contains Ordnance Survey data, licenced under UK Open Government Licence v3.0, and map data from Natural Earth II from www.NaturalEarthData.com (public domain).

10.3389/fearc.2024.1465082

FIGURE 2
The seaweed-fertilisation trial site north of Orkney College. **(Left)** at time of sowing - early May 2017; **(Right)** at time of harvest - September 2017.

aerated plastic bags. After ploughing and power-harrowing, the seaweed was applied to the seaweed-treated plots at two rates: 25 t seaweed/ha and 50 t seaweed/ha (wet weight; Figure 2). A third set of plots was fertilised with a conventional mineral 14-14-21 NPK fertiliser (YaraMila MAINCROP 14-14-21; Yara UK Ltd, Belfast, UK) at a rate of 50 kg N/ha. A fourth set of plots (control plots) was left unfertilised. This gave a total of 20 plots: 5 unfertilised, 5 with 25 t seaweed/ha, 5 with 50 t seaweed/ha, and 5 NPK-fertilised. The fertilisers in each plot were mixed into the soil by power-harrowing. The following day (early May 2017), bere barley was sown at a rate of ∼16 g/m^2 with a thousand grain weight of 30.3 g, using a tractor drawn seeder (width 3 m). A Cambridge roller was then used to flatten the soil surface. In early June 2017, an herbicide mixture was applied to all plots. Additional information on the field trial is available in Blanz et al. (2019) and Brown et al. (2020).

2.2 Sampling, yield, grain size measurements, and sulfur isotope analysis

In early September 2017 (i.e., after 4 months of growth), the bere barley was harvested from a 1 m × 1 m square at the centre of each 3 m × 3 m plot (to avoid edge effects, fertiliser run-off, and effects from tractor wheels). The barley was dried at 30 °C for 48 h (until constant weight) and weighed for yield evaluation (previously published in Brown et al., 2020). Thousand grain weights (TGWs) were estimated using 20 g grain subsamples using a MARVIN grain analyser (GTA Sensorik GmbH, Germany; i.e., 20 g grain was weighed, and then counted by the analyser). In archaeological contexts, there are frequently only few grains available, and whole grains need to be selected manually. Therefore, archaeological grains are usually weighed individually and measured for their size, but in much smaller numbers. To mirror these measurement conditions, this more detailed, small-scale approach was therefore also imitated in this study in parallel to the present-day agricultural yield evaluation. Fifteen bere barley plants were subsampled from each plot's central 1 m × 1 m square from which 10 individual grains per plot were randomly sub-sampled and archived. Five of these grains were randomly sub-sampled for this study, using random.org (Haahr, 2010). Each grain selected had a large proportion of the inner glume material (lemma and palea, ca. 90%) removed by scalpel, prior to biomass and isotopic measurements. This was undertaken as most hulled barley carbonised plant macrofossils found in the archaeological record in Atlantic Scotland have had the lemma and palea burnt off by the carbonisation process (except in rare circumstances such as the low temperature, reducing thermal environments in some parts of conflagrations; Church, 2002). The length, width and depth of each grain was then measured to the nearest 0.1 mm using the internal graticule of a Leica M80 stereomicroscope under × 7.5–60 magnification and the mass of each grain was measured to the nearest 0.001 g using a Mettler PM480 Delta Range balance. Two of the measured grains were then randomly sub-sampled for isotope analysis, ground individually using an agate mortar and pestle and weighed into tin capsules.

Additionally, 10 g of straw, including both stems and leaves, were taken from the 15 bere barley plants that were subsampled from each plot's central 1 m × 1 m square, homogenised using a spice and nut grinder (Model SG20U, Cuisinart Corp., Greenwich, USA), and sieved to 1 mm using a plastic mesh. The stems and leaves likely had different δ^{34}S values (Tcherkez and Tea, 2013), but were homogenised to gain an overview—future studies should ideally analyse these separately.

For the analysis of the fertilisers, a pooled sample (120 g dry weight) of the composted seaweed as it was at the time of application in May was dried, ground and sieved as described for the straw samples. An aliquot of 1.5 g of the conventional NPK fertiliser was homogenised to a fine powder using a mortar and pestle. The top 0–25 cm of soil were sampled in three random spots in each plot using an augur, both before fertilisation, and after the trial, and pooled within each treatment group. The material was then sieved through a metal 1 mm mesh sieve.

Sulfur stable isotope ratio measurements were undertaken on the ground individual grains (2 grains per plot, equalling 10 grains per treatment), the homogenised straw (one sample each per replicate plot), the soils (before and after the trial),

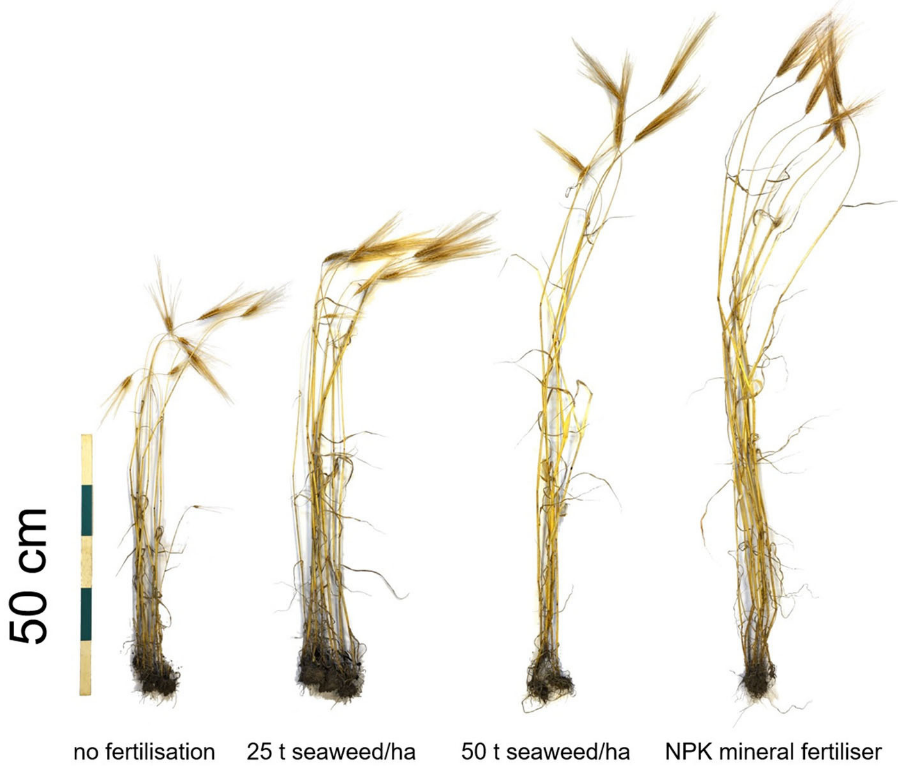

FIGURE 3
Harvested bere barley after the fertilisation trial. Image modified using GIMP software.

and fertilisers (two replicates each). Sulfur isotope analysis of the samples were performed using a Thermo Scientific™ EA IsoLink IRMS Delta V instrument in the Stable Isotope Biogeochemistry Laboratory (SIBL) at Durham University. Isotopic accuracy was monitored through repeated analysis of in-house standards (e.g., sulfanilamide) and international standards (e.g., IAEA-SO-5, IAEA-SO-6, NBS-127). These analytical standards provided an isotopic range from −31 ‰ to +20.3 ‰ in δ^{34}S. Analytical uncertainty in δ^{34}S for replicate analyses of the international standards was ± 0.2 ‰ (2 σ) and ± 0.3 ‰ (2 σ) for in-house standards and replicate sample analysis. Total sulfur concentrations were obtained as part of the isotopic analysis using sulfanilamide (sulfur = 18.62 wt %).

The results of this study were assessed by one-way ANOVA followed by *post-hoc* Tukey using RStudio software (R Core Team, 2021). The statistical significance threshold was set at $\alpha = 0.05$. In a previous study, δ^{13}C and δ^{15}N of crop material from this field trial had already been measured (Blanz et al., 2019), the results of which are also discussed in this study with relation to the newly measured δ^{34}S values.

3 Results

3.1 Yield and grain measurements

Total biomass yields (both straw and grains) were highest for barley grown with 50 t seaweed/ha, and lowest for the unfertilised plants, as exemplified in Figure 3. The individual fertilised grains were heavier on average than the unfertilised grains by 10% following 25 t/ha seaweed fertilisation, 15% heavier with 50 t/ha seaweed, and 9% heavier using the NPK mineral fertiliser (based on thousand grain weights measured with present-day agronomic measurement methods using 20 g subsamples; previously published in Brown et al., 2020). Additional yield results (including straw yields) from this trial are reported in detail in Brown et al. (2020).

The grain measurements of randomly selected grains in this study, meant to simulate grain measurements on small numbers of preserved archaeological grains, matched this pattern (see Table 1; Figure 4): all three fertilised sets of grains were demonstrably larger in length, width and depth measurements and heavier than the unfertilised grains. ANOVA followed by *post-hoc* Tukey indicated significant differences in grain length [$F_{(3,96)} = 16.7$, $p < 0.001$], width [$F_{(3,96)} = 13.1$, $p < 0.001$], depth [$F_{(3,96)} = 16.8$, $p<0.001$], and mass [$F_{(3,96)} = 13.1$, $p < 0.001$] for all comparisons of fertilised grain with unfertilised grain.

3.2 Stable sulfur isotope ratios

Sulfur isotope ratios of straw and grains from the seaweed-fertilised barley plants ranged between +13.2 ‰ and +16.0 ‰, with the 50 t/ha seaweed fertilised plants having on average slightly higher δ^{34}S values compared to those fertilised with 25 t/ha seaweed (by 0.3 ‰ for grains, and 0.8 ‰ for straw). These δ^{34}S values

TABLE 1 Summary of the biomass measurements of the grains from all four treatments, reported as minimum, maximum, mean and standard deviation (σ).

Soil condition	*n*	Length (mm)	Width (mm)	Depth (mm)	Mass (mg)	Equivalent TGW (g)
		Min–max, mean ± 1σ	Min–max, mean ± 1σ	Min–max, mean ± 1σ	Min–max, mean ± 1σ	
Unfertilised	25	5.6–6.7, 6.0 ± 0.3	2.5–3.5, 3.0 ± 0.2	2.0–2.8, 2.4 ± 0.2	19–41, 28 ± 6	28
25 t/ha seaweed	25	5.7–7.3, 6.5 ± 0.4	2.9–3.6, 3.3 ± 0.2	2.4–2.8, 2.6 ± 0.1	24–43, 34 ± 5	34
50 t/ha seaweed	25	6.2–7.4, 6.7 ± 0.3	3.0–3.6, 3.3 ± 0.2	2.5–2.9, 2.6 ± 0.1	29–47, 36 ± 5	36
NPK	25	5.8–7.4, 6.5 ± 0.4	2.7–3.6, 3.3 ± 0.2	2.2–2.8, 2.6 ± 0.2	24–46, 35 ± 5	35

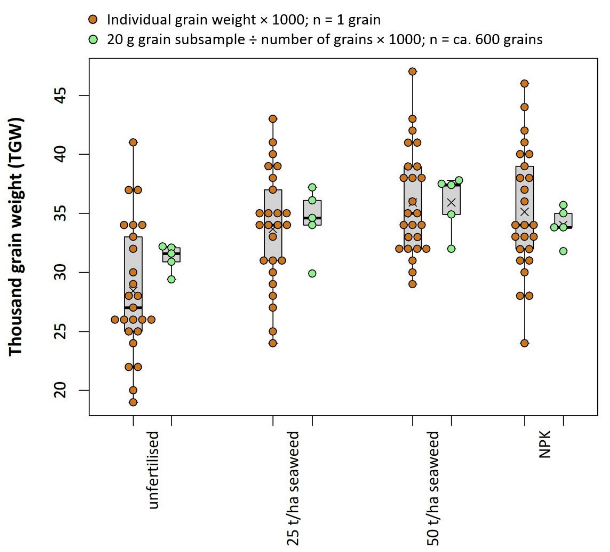

FIGURE 4
Comparison of thousand grain weight estimates using typical archaeobotanical methods (brown—individual grains weights) and present-day agronomic methods (green—20 g grain aliquot counted using a MARVIN grain analyser). Means are indicated by crosses. All grain originated from the same field trial; data from this study and Brown et al. (2020).

are higher than for both unfertilised and NPK-fertilised barley (range +10.8 ‰ to +13.4 ‰; Figure 5 and Table 2; all results are provided in the Supplementary material). For grains, ANOVA followed by *post-hoc* Tukey indicated the $\delta^{34}S$ differences to be significant [$F_{(3,36)} = 87.5$, $p < 0.001$, $n = 10$ per treatment] for all comparisons of seaweed-fertilised grain with unfertilised or NPK fertilised grain (all $p < 0.001$), whereas differences between the two seaweed-treatments were not found to be significant ($p = 0.69$), and neither were differences in $\delta^{34}S$ between NPK fertilised and unfertilised grains ($p = 0.09$). Similar results were found for straw following a separate ANOVA followed by *post-hoc* Tukey [$F_{(3,16)} = 25.1$, $p < 0.001$, $n = 5$ per treatment], with all comparisons of seaweed-fertilised straw with unfertilised or NPK fertilised grain being significantly different (all $p < 0.001$). Differences between the two seaweed-treatments were not found to be significant ($p = 0.29$), and neither were differences in $\delta^{34}S$ values between NPK fertilised and unfertilised straw ($p = 0.37$).

On average, straw tended to have higher $\delta^{34}S$ values than grains, except for the 25 t/ha seaweed treatment, where the straw results were variable. The NPK fertiliser had the lowest $\delta^{34}S$ value (+7.0 ‰) in this study, and the seaweed used as fertiliser had the most positive (+18.4 ‰). Soils had $\delta^{34}S$ values between +12.1 ‰ and +13.2 ‰. By comparison, seaweed-fertilised grain and straw had higher $\delta^{34}S$ values than the soil after the field trial (an increase of +2.4 ‰ on average), whereas NPK-fertilised and unfertilised grains had lower $\delta^{34}S$ values than the soil (a decrease of −0.8 ‰ on average), and unfertilised straw and NPK-fertilised straw had similar values to the soil after the field trial. A comparison to $\delta^{13}C$ and $\delta^{15}N$ values of bere barley grains from the same field trial (previously published in Blanz et al., 2019) is shown in Figure 6, and indicates a moderate correlation between $\delta^{34}S$ and $\delta^{15}N$ [statistically significant with $r_{(18)} = 0.67$, $p = 0.001$], but no correlation with $\delta^{13}C$ [$r_{(18)} = 0.06$, $p = 0.8$].

4 Discussion

4.1 Grain measurements

In this field trial, fertilisation with seaweed and NPK fertiliser both led to an increase in grain size. However, increased grain size is not in itself diagnostic of fertilisation: increased fertilisation frequently leads to larger number of tillers and ears, which may then result in a larger overall yield, but smaller individual grain sizes (see Bingham et al., 2007; Shah et al., 2017). Additionally, droughts, for example, can also lead to small grain sizes despite fertilisation, whereas a low seeding density (including growth on edges of fields) can lead to larger amounts of nutrients being available per plant and thus, larger grains despite a lack of fertilisation. Therefore, grain size itself is not sufficient to determine the nutritional status of a plant.

Nevertheless, these results show that fertilisation can increase size and mass of hulled bere barley grains and that an equivalent thousand grain weight (TGW) can be estimated based on the average mass of 25 individual grains multiplied by 1,000 (see Table 1). This estimate compares very well to the TGWs estimated using 20 g grain samples from each plot in this field trial using present-day agronomic standard methods (see Figure 4; Brown et al., 2020). These results indicate that in archaeological contexts, where it is frequently impossible to recover, identify, weigh and count similarly large amounts of complete grains, it should

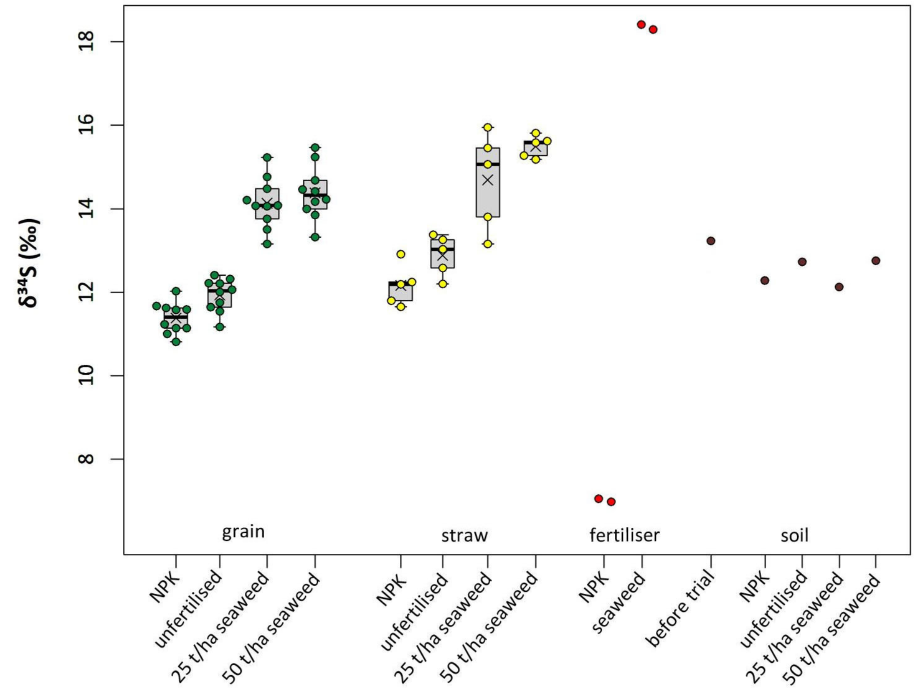

FIGURE 5
Stable sulfur isotope ratios of bere barley, fertiliser and soil from this field trial. Means are indicated by crosses. The five soil values are from pooled samples taken before **(Left)** and after the trial (four values on the **Right**).

TABLE 2 Summary of the stable sulfur isotope ratios and concentration sulfur in bere barley, fertilisers and soil from this field trial.

		*n**	Before trial	NPK	Unfertilised	25 t/ha seaweed	50 t/ha seaweed
				Mean ± 1σ	Mean ± 1σ	Mean ± 1σ	Mean ± 1σ
Grain	δ^{34}S (‰)	10		+11.38 ± 0.37	+11.93 ± 0.40	+14.13 ± 0.60	+14.38 ± 0.64
	%S			0.10 ± 0.02	0.11 ± 0.02	0.13 ± 0.02	0.13 ± 0.02
Straw	δ^{34}S (‰)	5		+12.16 ± 0.49	+12.88 ± 0.49	+14.68 ± 1.17	+15.49 ± 0.26
	%S			0.08 ± 0.01	0.10 ± 0.02	0.10 ± 0.01	0.09 ± 0.01
Fertiliser	δ^{34}S (‰)	2		+7.01 ± 0.05		+18.36 ± 0.08	+18.36 ± 0.08
	%S			1.28 ± 0.18		3.14 ± 0.08	3.14 ± 0.08
Soil	δ^{34}S (‰)	1	+13.23	+12.28	+12.73	+12.12	+12.75
	%S		0.08	0.12	0.08	0.17	0.18

Values indicate mean ± standard deviation (σ).
*n denotes the number of samples per treatment.

still be possible to arrive at reasonable estimations of TGW using smaller sample sizes (here $n = 25$), albeit with larger associated uncertainties.

Ferrio et al. (2004) have outlined a method to estimate individual grain weights from carbonised archaeological cereal grains, based on furnace experimentation of modern grains of wheat and barley. By combining the estimated individual weights of carbonised cereal grain assemblages, it is therefore possible to convert the averages of the grain weights of the individual archaeological cereal grains into TGW estimations, allowing direct comparison to the modern agronomic metric of TGW to the archaeological assemblages. This has clear research implications for understanding long-term trajectories of cereal productivity over thousands of years in different parts of the world (cf. Gron et al., 2021).

4.2 Sulfur stable isotope ratios

The δ^{34}S values of the seaweed-fertilised barley were elevated by ~2 ‰ compared to unfertilised barley. This was most likely caused by the elevated δ^{34}S value of the seaweed fertiliser (+18.4 ‰) compared to the soil prior to the trial (+12.7 ‰), as sulfur from decaying seaweed is incorporated into the growing bere barley.

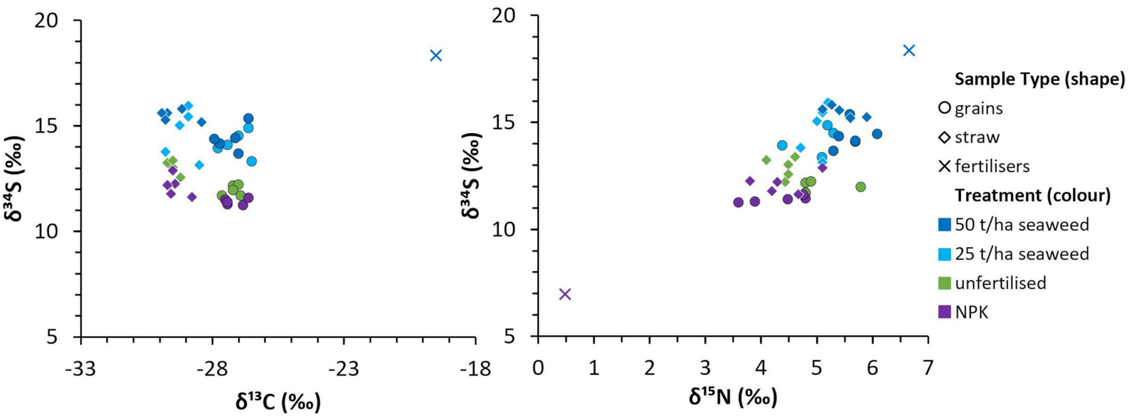

FIGURE 6
Comparison of δ^{34}S with δ^{13}C and δ^{15}N values from the same trial; δ^{13}C and δ^{15}N data from Blanz et al. (2019).

The absence of a statistically significant difference between the two seaweed treatments is likely due to the barley only taking up a limited amount of sulfur, and thus more available sulfur did not directly lead to a greater increase in δ^{34}S.

For the NPK fertilised barley, the opposite effect, i.e., a lowering of δ^{34}S compared to the unfertilised barley, was expected due to the low δ^{34}S value of the NPK fertiliser (+7.0 ‰); however, this difference was found to be less pronounced than for the seaweed fertilised barley (see Figure 5). This is likely because the NPK fertiliser application introduced less sulfur to the soil owing to the lower application rate and sulfur content of the mineral fertiliser (ca. 5 kg sulfur ha^{-1}) compared to seaweed fertilisation (ca. 785 kg sulfur ha^{-1} and 1,570 kg sulfur ha^{-1} for the treatments of 25 t/ha seaweed and 50 t/ha seaweed, respectively—although we hypothesise that not all of this sulfur would have been bioavailable during the course of this field trial).

The results of this study are similar to those previously reported for Celtic beans (Gröcke et al., 2021), where seaweed fertilisation led to ~10 ‰ higher δ^{34}S values compared to unfertilised beans (i.e., +16.2 ‰ in seaweed-fertilised beans and +6.6 ‰ in unfertilised beans in 2017). The much smaller difference in δ^{34}S between seaweed-fertilised and unfertilised barley in the present study is likely in part due to the comparatively high initial soil δ^{34}S value in the present study of +12.7 ‰. As the soil for the field trial in this study already had relatively high δ^{34}S values, the fertilisation of barley with seaweed likely had a smaller effect on δ^{34}S than it would have had in a soil with low δ^{34}S values. Additionally, the soil had a higher wt% sulfur concentration after the trial compared to Gröcke et al. (2021). Thus, when a sulfur-rich biofertiliser is added to a soil with low background sulfur concentrations (a macronutrient) a plant will more effectively incorporate and fractionate sulfur.

The origin of the higher soil δ^{34}S values in the field trial on Orkney is most likely its close proximity to the ocean, with its turbulent weather causing the frequent occurrence of sea spray and oceanic-influenced rain. This is supported by a δ^{34}S isoscape of Northern Ireland showing areas sheltered from oceanic influence to have lower δ^{34}S values than more exposed areas, and elevated δ^{34}S values in sheep from the Orkney Island of North Ronaldsay (Guiry and Szpak, 2020). Historical seaweed-fertilisation in the field trial area may have also elevated soil δ^{34}S values, as ethnographic and historical descriptions from the sixteenth to early twentieth century indicate seaweed fertilisation was common on Orkney (Fenton, 1997). Past elevated sulfur isotope ratios might have been preserved to some extent in the acidic clay loam soil (see work on clayey peat in Bottrell and Coulson, 2003). If seaweed-fertilisation does indeed increase soil δ^{34}S values in the long-term, this might be useful as a marker for seaweed-fertilisation in non-coastal areas (possibly together with elevated soil δ^{15}N values; Blanz et al., 2019; Commisso and Nelson, 2010, 2007, 2006; Gröcke et al., 2021). Although we show in this study seaweed-fertilisation can elevate soil δ^{34}S, detecting such a difference in practise might prove difficult. Additional sulfur isotope research on modern coastal environments and islands is required in order to develop more robust interpretations from δ^{34}S of archaeological grains and soils.

5 Conclusion: implications for archaeological studies and future directions

Fertilisation with seaweed and NPK fertiliser both led to increased grain sizes and the individual measurements of grain sizes corresponded to the TGW for each treatment. It is therefore possible to convert the averages of the estimated grain weights of the individual archaeological cereal grains (following the methodology of Ferrio et al., 2004) into TGW estimations, allowing direct comparison to the modern agronomic metric of TGW to archaeological assemblages. This has important implications for estimating long-term trajectories of cereal productivity over thousands of years in different parts of the world.

Furthermore, this study showed that seaweed fertilisation can increase δ^{34}S values of cereal crops. Where archaeological crops are sufficiently well-preserved to measure δ^{34}S (as described in Nitsch et al., 2019), the use of seaweed [and/or fish (Gröcke et al., 2021) and/or guano (Szpak et al., 2019)] as a biofertiliser as opposed to terrestrial animal manure may therefore be identified by elevated (i.e., marine) $\delta^{34}S$ values. However, in a cautionary tale, Guiry and Szpak (2020) reported elevated bone collagen $\delta^{34}S$ values from present-day sheep from (Orkney) and thus, $\delta^{34}S$ could not be used to discriminate seaweed-consumption. Other studies are also showing the complexity of modern coastal environments and its impact on not only sulfur, but also nitrogen and carbon (e.g., Göhring et al., 2023). More isotopic research on water, soils, plants and animals from island environments is required. This work has shown that archaeological studies relying on $\delta^{34}S$ values, for example in palaeodietary studies to identify marine and freshwater wetland grazing (e.g., Guiry et al., 2021, 2022; Lamb et al., 2023), to quantify consumption of freshwater and/or marine fish (e.g., Nehlich et al., 2011), or to study geographic origin (e.g., Vika, 2009), need to take into account the possibility of seaweed fertilisation and/or consumption.

Additional field experimental studies on different soils will provide more information on the impact of seaweed and/or fish (i.e., marine) biofertilisation on $\delta^{34}S$ in plants, and how long the input of seaweed remains in the soil. Other aquatic biofertilisers (e.g., shells, fish, and seawater) and their impact on $\delta^{34}S$ in wild plants and crops also need to be investigated. While seaweed was likely the most common marine biofertiliser in the European North Atlantic area in the last few centuries (cf. Blanz et al., 2019), historical sources from the nineteenth and twentieth centuries also attest to the use of seagrasses (which differ from seaweeds by having true roots, stems, and the ability to produce flowers and seeds) and freshwater plants (Fernández et al., 2022; Sharma, 1971; Wyllie-Echeverria and Cox, 1999). In some cases, these plants have much lower $\delta^{34}S$ values—e.g., eelgrass (*Zostera marina*) leaves are reported to have $\delta^{34}S$ values around +4 ‰ (likely due to uptake of sulfide; Holmer and Hasler-Sheetal, 2014): other studies have shown benthic organisms in tidal flats can produce low and even negative $\delta^{34}S$ values (e.g., Yamanaka et al., 2003). Biofertilisation with such plants, and/or growing crops in coastal regions where sulfide processes occur, can be expected to produce low or negative crop $\delta^{34}S$ values. Similarly, biofertiliser mixtures of seaweed (sulfate-influenced) and seagrass (sulfide-influenced) may counteract each other and have very limited impact on crop $\delta^{34}S$ values: this will primarily depend on the original soil $\delta^{34}S$ value.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary material, further inquiries can be directed to the corresponding authors.

Author contributions

MB: Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualisation, Writing – original draft, Writing – review & editing. DRG: Conceptualisation, Data curation, Funding acquisition, Investigation, Methodology, Resources, Validation, Writing – review & editing. PM: Investigation, Methodology, Resources, Writing – review & editing, Conceptualisation, Funding acquisition. MJC: Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fearc.2024.1465082/full#supplementary-material

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