REVISITING THE POTENTIAL OF CARBONISED GRAIN TO PRESERVE BIOGENIC $^{87}SR/^{86}SR$ SIGNATURES WITHIN THE BURIAL ENVIRONMENT

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Strontium isotope analysis of archaeological crops is a potential method of provenancing and identifying the movement of crops in the past but there remains uncertainty as to whether original $^{87}Sr/^{86}Sr$ values can be obtained from carbonized buried grains. We have determined that HCl leaching removes some, but not all, exogenous strontium from carbonised cereal grains buried in soil for up to one year. We conclude that while further work could refine the leaching method, strontium isotope analysis of archaeological cereal grains can distinguish crops sourced outside a particular (e.g. local) zone if it can be shown that leaching changes grain $^{87}Sr/^{86}Sr$ values significantly from the expected strontium signature.

Keywords: strontium; cereal grains; carbonisation; leaching; contamination; burial experiment

INTRODUCTION

Mobility studies in archaeology routinely use the strontium (Sr) isotope composition (specifically the ratio of $^{87}Sr/^{86}Sr$) of human and faunal tooth enamel to identify where individuals originated, whether they moved during the period of tooth formation, and therefore whether they were local to the area in which their remains were deposited (e.g. Bentley et al., 2012; Bogaard et al., 2014). Such studies enable reconstruction of the interactions between people—and their animals—in the past and can contribute to wider understanding of how mobility related to, and impacted on, concepts of cultural identity that are inferred in other ways from the archaeological record.

Strontium in biological systems stems from a combination of *in situ* weathering of bedrock during soil formation and input of Sr from precipitation and air-borne particles (Bentley, 2006). Strontium-87 is the product of radioactive decay of rubidium-87 (^{87}Rb) and so the $^{87}Sr/^{86}Sr$ value of bedrock depends on its initial $^{87}Sr/^{86}Sr$ value, Rb/Sr ratio and age. Old rocks with high Rb/Sr ratios, such as granites, therefore tend to be enriched in ^{87}Sr and have high $^{87}Sr/^{86}Sr$ values, whereas younger rocks with lower Rb/Sr ratios, such as basalts, tend to have lower $^{87}Sr/^{86}Sr$ values (Faure and Powell, 1972). Plants take up Sr from the soil in which they grow and thus have $^{87}Sr/^{86}Sr$ values that reflect their geographical origin. When ingested, these values are preserved in the tissues of the consumer (Ericson, 1985). Tooth enamel is the most commonly sampled material in Sr isotope studies, since it has been shown to preserve its original $^{87}Sr/^{86}Sr$ value during burial (Budd et al., 2000).

Strontium in archaeological crop remains

The $^{87}Sr/^{86}Sr$ values of modern plants growing in the locality of an archaeological site are often determined in studies into past mobility to establish the variation in the $^{87}Sr/^{86}Sr$ values of the locally bioavailable Sr, but there are also good reasons for determining the $^{87}Sr/^{86}Sr$ values of archaeological crops. Strontium isotope analysis of archaeological crop remains presents a potential method of provenancing and identifying the movement of crops in the past as well as establishing the bioavailable Sr isotope composition of plant foods available to humans during their lifetime. This in turn may provide a means of reconstructing ancient trade networks and identifying the redistribution of crop surpluses from producer to consumer sites. Strontium isotope analysis of archaeological crop remains has not been routinely employed, however, due to concerns about contamination with Sr from the burial environment and uncertainty about whether biogenic $^{87}Sr/^{86}Sr$ values are retained in botanical remains that have been buried for long periods of time.

Strontium has been found—in order of decreasing concentration—in the straw, bran and endosperm of cereal plants (Runia, 1987). While little work has focussed on Sr specifically, its similarity in chemical behaviour to calcium (Ca) means that inferences can be made about Sr based on studies into Ca in plants (Isermann, 1981). Chemical imaging by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has shown that Ca and other metals tend to be concentrated in the seed coat and aleurone layers of mature wheat grains (Wu et al., 2013), an observation that is consistent with the theory that metal cations (like Sr^{2+}) are readily bound by chelation to phytic acid (Reddy et al., 1982), which is concentrated in aleurone cells (Regvar 2011). In general, cereal grains contain a relatively low amount of Sr (c. 2

ppm; Laursen et al., 2011) which means that any contamination with Sr from the burial environment is likely to swamp the biogenic $^{87}Sr/^{86}Sr$ values of cereal grains.

Moreover, cereal grains have an amorphous and fairly open structure once carbonised (Charles et al., 2015) that could permit ready absorption of exogenous Sr. Carbonised cereal grains are essentially a type of biochar, whose high internal surface area and negative charge means that it has a high adsorption capacity for heavy metals. As a result, the use of biochars—formed from a range of organic materials—in the remediation of contaminated soils has been the subject of much research (reviewed by Beesley et al., 2011). The surface of biochars produced by pyrolysis at temperatures between 200 and 400˚C (cf. archaeological preserved cereal grains; Charles et al., 2015) are rich in oxygen-containing functional groups, which enable the creation of surface complexes between cations (like Sr^{2+}) and the biochar surface (Uchimiya et al., 2011). Biochars formed at higher temperatures tend to have higher carbon/oxygen ratios and a more electronegative surface. As a result, metal sorption occurs via electrostatic interaction between the metal cations and the negative charge associated with delocalised electrons in aromatic structures (Harvey et al., 2011). Given the high aromaticity of archaeological carbonised grains compared to their modern carbonised counterparts (Styring et al., 2013), it is possible that the relative importance of these two sorption mechanisms (complex formation versus electrostatic interaction) changes during burial of carbonised cereal grains. What remains unclear is whether the high affinity of biochars for metal cations is an advantage for the use of archaeological crop remains as geographical tracers, since biogenic Sr will also be strongly bound, or whether it is a disadvantage, since exogenous Sr that has been adsorbed from the burial environment will be difficult to remove.

Few studies have investigated the potential of using archaeological crop remains as geographical tracers. Larry V. Benson and colleagues have investigated the reliability of maize kernel $^{87}Sr/^{86}Sr$ values (as well as trace metal concentrations and lead isotope values) in determining the location of agricultural fields in the Americas (reviewed in Benson, 2012). They used a procedure employed by palynologists to remove minerals from sediment samples in order to clean carbonised and uncarbonised maize cobs. This involved leaching in c. 3 M hydrochloric acid (HCl) to dissolve carbonate minerals, followed by leaching in hydrofluoric acid (HF) to dissolve silicate minerals (Benson et al., 2010). They suggested that low aluminium and Sr concentrations (≤ 4.2 ppm Sr) could indicate the removal of soil mineral contamination (Benson et al., 2010; Benson, 2012). They also found, however, that this leaching removed much of the biogenic Sr (and other metals) from uncarbonised maize cobs, raising the question of whether any biogenic Sr would be retained after leaching (Benson et al., 2010). They did not test this on carbonised cobs, however, which might have a better retention capacity for metals.

Heier et al. (2009) investigated: i) the effect of charring on the concentration and $^{87}Sr/^{86}Sr$ value of hulled barley grains; ii) the adsorption of Sr by carbonised and uncarbonised barley grains soaked in a chalk solution; and iii) the effectiveness of several leaching methods in removing the adsorbed Sr. They found that charring decreased the $^{87}Sr/^{86}Sr$ value of cereal grains by 0.0001 and they posited that this could be due to inherent variability in the $^{87}Sr/^{86}Sr$ values of different grains, or contamination during the charring process. They also found that both carbonised and uncarbonised grains absorbed Sr from the chalk solution in which they were soaked,

but that leaching in 6M HCl for 24 h removed > 95% of the exogenous Sr from carbonised grains, but not from uncarbonised grains. Leaching of uncontaminated carbonised grains in 6 M HCl for 24 h was found to reduce the biogenic Sr concentration by 60%, and reduce the $^{87}Sr/^{86}Sr$ value by 0.0001 (Heier et al. 2009). This demonstrated the risk of using harsh leaching methods to remove exogenous Sr.

While the Heier et al. (2009) study has demonstrated the potential for biogenic $^{87}Sr/^{86}Sr$ values to be preserved and recovered in carbonised cereal grains found on archaeological sites, since this study was published only one study by Bogaard et al. (2014) has employed Sr isotope analysis of archaeological crop remains to identify the location of ancient crop fields. Moreover, there remained some uncertainty in the study's conclusions as to where the archaeological plants were grown. While the behaviour of archaeological charred plant $^{87}Sr/^{86}Sr$ values under leaching in 6 M HCl for 24 h suggested that their cultivation in one particular landscape zone could be ruled out, it remained uncertain whether or not all of the exogenous Sr had been removed. It is clear, then, that further work is required to address these outstanding concerns.

Given that both Benson (2012) and Heier et al. (2009) found that carbonised plant material retained biogenic Sr better than uncarbonised, and since the majority of archaeological crop material is found in a carbonised state, we focussed our investigations on carbonised cereal grains only. We also investigated the potential of using cereal rachis (the 'stem' within the cereal ear, constituting lignin-rich 'chaff') that is often preserved on archaeological sites as a geographical tracer. The relatively

high Sr content of wheat straw compared to grains (Runia 1987) suggests that rachis may be a good material for Sr isotope analysis.

The aim of this study is to address some of the outstanding questions from the Heier et al. (2009) study, in the hope of establishing whether or not archaeological crop remains can be used as reliable geographical tracers. Is the effect of charring on cereal grain $^{87}Sr/^{86}Sr$ values still significant when more samples are compared? Do carbonised cereal grains adsorb Sr to the same extent when they are buried in soil compared to being soaked in a chalk solution? And can this exogenous Sr be removed by leaching to yield the biogenic Sr isotope signature? Finally, given the difficulty in digesting carbonised grains by conventional methods, we share a protocol for the successful digestion of carbonised grains and separation of Sr for isotopic analysis.

METHODS AND SAMPLES

Effect of charring on cereal grain $^{87}Sr/^{86}Sr$ values

Bread wheat (*Triticum aestivum* L.) grains grown without manure were sampled in 2002 from the long-term agricultural experiment at Bad Lauchstädt, Germany (51.50 N, 11.99 E). Grains were placed in porcelain crucibles, which were buried in individual beakers of sand to exclude oxygen, before heating in a Gallenkamp Plus II electric oven. The oven was preheated, and when the oven reached 230˚C the grains were placed in the oven and removed after 24 hours. These conditions have been found to produce carbonised grains that are morphologically similar to well preserved, undistorted grains found on archaeological sites (Charles et al. 2015). After

cooling, grains were removed from the crucibles and crushed in an agate mortar and pestle before digestion. Five samples of 10 grains each were carbonised and another five samples of 10 grains each were kept uncarbonised for comparison (Table 1).

Burial experiment

Bread wheat (*T. aestivum* L.) grains and rachis grown without manure were sampled in 2004 from the long-term agricultural experiment at Rothamsted, UK (51.81 N, -0.37 E). Grains and rachis were charred according to the protocol above. The carbonised cereal grains and rachis were buried in soil collected from between 0-15 cm depth in Achnasheen, northwest Scotland (57.58 N, -5.07 E). Sub-samples of 50 carbonised grains or rachis were placed in open-gauze fabric bags, soil was added and mixed with the carbonised crop material and then the bags were tied up and buried 10 cm deep in a large plastic pot. Deionized (DI) water was added throughout the duration of burial to keep the soil damp. Crop material remained buried for 3, 9 and 12 months. On retrieval, crop material was recovered by dry-sieving, washed in DI water to remove adhering soil and freeze-dried.

These cereal grains and rachis and soil were selected because the biosphere $^{87}Sr/^{86}Sr$ map created by Evans et al. (2010) allowed us to predict that the crop material and soil would have significantly different $^{87}Sr/^{86}Sr$ values, so that even low levels of Sr contamination could be detected. The $^{87}Sr/^{86}Sr$ values of a DI water leach of the soil and of the unburied carbonised cereal grains and rachis from the same plot as the crop material used in the burial experiment are given in Table 1.

Long-term burial

Bread wheat (*T. aestivum* L.) grains grown without manure and irrigated between two and four times a year were sampled in 2007 from a field in Borja, Spain (41.83 N, -1.53 E). Grains were charred according to the protocol above. The carbonised cereal grains were placed in bags of agricultural soil and then buried 30 cm under common garden soil in Birmingham, UK, as described in Fraser et al. (2013). On retrieval, grains were recovered by wet sieving, washed in DI water and air-dried at c. 40˚C. The grains analysed in this study were buried for 36 months.

The Sr concentrations and $^{87}Sr/^{86}Sr$ values of carbonised naked barley (*Hordeum vulgare* var. *nudum* L.) grains retrieved from the archaeological site of Çatalhöyük, Turkey (37.67 N, 32.83 E), were also determined in this study. While three samples were comprised of grains carbonised *in situ* in a clay bin, preventing the grains from mixing directly with the soil matrix, another three samples were comprised of grains that had spilled from the bin and mixed with the surrounding soil. The grains carbonised *in situ* were expected to have adsorbed a lower concentration of exogenous Sr than the grains that had direct contact with the soil.

Leaching experiments

Three samples of the carbonised grains and rachis that had been buried for 12 months, each comprising 15 grains or 20 rachis internode segments, were selected for leaching experiments. Each sample was crushed using an agate mortar and pestle and then

divided into three sub-samples, which were subjected to one of the following protocols:

(1) No leaching

(2) Leaching in 10 mL 6 M HCl for 24 h at room temperature

(3) Leaching in 10 mL 6 M HCl and HF for 24 h at room temperature

A fourth sample of carbonised grains (n = 25), that had been buried for 12 months, was selected for additional leaching experiments. This sample was also crushed using an agate mortar and pestle and then divided into five sub-samples, which were subjected to one of the following protocols:

(1) No leaching

(2) Leaching in 10 mL 1 M ammonium acetate (NH_4OAc) for 24 h at room temperature

(3) Leaching in 10 mL 6 M HCl for 36 h at room temperature

(4) Leaching in 10 mL 6 M HCl for 48 h at room temperature

(5) Leaching in 10 mL 6 M HCl for 72 h at room temperature

In order to test whether the leaching procedures remove biogenic Sr, we took a sample of 30 bread wheat grains also harvested from the long-term agricultural experiment at Rothamsted in 2004, but from a different plot that had received 35 t/ha/yr cattle manure since 1852. There was insufficient crop material remaining from the unmanured field at Rothamsted to use in these experiments. These grains were carbonised under the same conditions as grains used in the burial experiment and were crushed using an agate mortar and pestle and then divided into six sub-samples, which were subjected to one of the following protocols:

(1) No leaching

(2) Leaching in 10 mL 1 M ammonium acetate (NH_4OAc) for 24 h at room temperature

(3) Leaching in 10 mL 6 M HCl for 24 h at room temperature

(4) Leaching in 10 mL 6 M HCl for 36 h at room temperature

(5) Leaching in 10 mL 6 M HCl for 48 h at room temperature

(6) Leaching in 10 mL 6 M HCl for 72 h at room temperature

Crushing ensured that the samples were homogenised and that the leaching treatment was therefore the cause of any differences in the $^{87}Sr/^{86}Sr$ values of sub-samples, rather than natural differences in $^{87}Sr/^{86}Sr$ values among grains/rachis. After leaching, the sub-samples of leached crop material were centrifuged, the supernatant leachates collected in clean Teflon beakers and the leached crop material rinsed in DI water three times. The DI water from each rinse was added to the leachate. Sr isotope analysis of both leached crop material and the leachates was carried out in order to fully characterise the $^{87}Sr/^{86}Sr$ values of the Sr that was removed during leaching.

Digestion and determination of $^{87}Sr/^{86}Sr$ values

Prior to digestion, all crop samples were crushed using an agate mortar and pestle. Some of the samples were digested and their $^{87}Sr/^{86}Sr$ values determined in the Earth Science department, University of Oxford, UK. Other samples were digested and their $^{87}Sr/^{86}Sr$ values determined at the NERC Isotope Geoscience Laboratory (NIGL), Keyworth, UK (marked in Supplementary Table).

At Oxford, crop samples were digested with 4.5 ml 15.4 M nitric acid (HNO_3) and 3 ml 30% H_2O_2 at 210 °C, 250 psi for 90 min using a MARS Microwave Digestion System (CEM Corp., UK) with XP-1500 Plus™ (PTFE) vessels. Digests were dried and dissolved in 500 µL 2 M HNO_3. An aliquot of 100 µL was taken to determine the concentration of Sr in each sample using inductively coupled plasma-mass spectrometry (ICP-MS). The remaining 400 µL of solution was centrifuged and Sr separated using Eichrom Sr-spec pure resin (50-100 µm). Prior to isotopic analysis, the samples were dissolved in an appropriate volume of 0.1 M HNO_3 and Sr isotopic measurements were performed with a Nu Instruments NuPlasma multi collector ICP-MS instrument at the University of Oxford. All samples were run to an internal precision of ± 0.00005 (2 SE) or better. The samples were run at a time when the international standard for $^{87}Sr/^{86}Sr$, NBS987, gave a value of 0.710261 ± 0.00003 (n = 107, 2σ). Data are corrected to the NBS 987 $^{87}Sr/^{86}Sr$ value of 0.710255. Procedural Sr blanks contributed <1% of the ^{88}Sr signal and are therefore considered negligible.

Out of five carbonised grain samples, two did not yield sufficient Sr for isotopic analysis. This is despite the fact that the Sr concentrations of these two samples before separation on the Sr-spec resin (as determined by ICP-MS) were the same as the other samples (Appendix 1). The key difference was the colour of the digested solutions: they were more yellow than their counterparts. An additional test, whereby 100 charred cereal grains were homogenised by crushing and split into ten sub-samples before digesting, also found that two out of nine sub-samples (one was excluded from the analysis due to spillage) yielded insufficient Sr for isotopic analysis after the separation step (Appendix 1). Again, these two samples were the most yellow in solution. Since these samples were homogenised, differences in the yield of Sr after

separation using Sr-spec resin must be dependent upon the efficiency of digestion, rather than differences in composition between cereal grain samples. It is posited that the low yield of Sr after separation with Sr-spec resin is due to incomplete digestion of organic compounds using the microwave method, meaning that these organic compounds interfere with the efficiency of the separation procedure. This is supported by the fact that all of the uncarbonised grain samples yielded sufficient Sr for isotope analysis (Appendix 1). For this reason, it was decided to separate Sr using Dowex® AG50 X8 resin (200-400 mesh) for the remaining samples in this study, because the larger volume of resin used is expected to make it less susceptible to interference by undigested organics. The remaining Sr isotope analyses were therefore carried out at NIGL, Keyworth, UK.

At NIGL, crop samples were weighed into Teflon beakers and ^{84}Sr-enriched tracer solution was added (this allows determination of Sr concentration at the same time as $^{87}Sr/^{86}Sr$ values). Crop samples were digested with 8 M HNO_3 and 30% H_2O_2 on a hot plate at c. 100 °C, until solutions were pale orange-yellow. Digests were dried and converted into their chloride form by addition of 6 M HCl. This solution was then dried down and the residues dissolved in 1 mL 2.5 M HCl. Strontium was separated using Dowex® AG50 X8 resin (200-400 mesh). Strontium was loaded onto a single rhenium filament with tantalum fluoride, following the method of Birck (1986) and the Sr isotope composition and concentration were determined by thermal ionization mass spectroscopy (TIMS), using a Thermo Triton multi-collector mass spectrometer. All samples were run to an internal precision of ± 0.00005 (2 SE) or better. The samples were run at a time when the international standard for $^{87}Sr/^{86}Sr$, NBS987, gave a value of 0.710255 ± 0.00001 (n = 34, 2σ). Procedural Sr blanks were ~80 pg.

RESULTS

Intra-grain variability

Two of the carbonised bread wheat grain samples comprised grains whose embryo and apical (non-embryo) ends had been separated. Thus one sample contained 20 embryo ends (CHBWem) and the other sample contained 20 apical ends (CHBWno). The aim was to determine whether bread wheat grain embryos (with their higher concentration of Ca detected by LA-ICP-MS; Wu et al. 2013) contain higher concentrations of Sr. The Sr concentrations and $^{87}Sr/^{86}Sr$ values of these samples are given in Appendix 2. The concentration of Sr in the embryo end sample (4.8 ppm) was not markedly greater than the concentration of Sr in the non-embryo end sample (4.4 ppm), and so no subsequent separation of cereal grains was carried out in this study.

Intra-field variability and the effect of charring

Table 1 and Figure 1 show the Sr concentrations and $^{87}Sr/^{86}Sr$ values of uncarbonised and carbonised bread wheat grains grown in the same field at Bad Lauchstädt agricultural station, Germany. Uncarbonised grains have a Sr concentration of 2.8 ± 0.2 ppm and $^{87}Sr/^{86}Sr$ value of 0.70955 ± 0.00010 (1σ, n = 5). Carbonised grains have a Sr concentration of 4.4 ± 0.8 ppm and $^{87}Sr/^{86}Sr$ value of 0.70983 ± 0.00031 (1σ, n = 5). The higher Sr concentration in carbonised cereal grains was earlier noted by Heier et al. (2009). It is due to the loss of non Sr-containing volatiles during charring

(Styring et al., 2013), which reduces the mass of the grains but not the Sr content. A Welch two sample t-test shows that there is no significant difference between the $^{87}Sr/^{86}Sr$ values of uncarbonised and carbonised bread wheat grains ($t(4.87) = -1.85$, $p = 0.125$). This is due to the relatively high variability in the $^{87}Sr/^{86}Sr$ values of different grain samples from a single field and particularly carbonised cereal grains. Such variability is highly relevant, since it demonstrates that even cereal grains grown in the same field (in the same year) can have $^{87}Sr/^{86}Sr$ values that differ by up to 0.00077. This variability is likely to be determined by the distinct geology of a region and it is therefore not possible to predict a universal value for the variability in $^{87}Sr/^{86}Sr$ value within a field, but similar differences are likely to be expected in different contexts. It is also likely that homogenization of multiple grains in each sample had already reduced some of the inter-grain variability in $^{87}Sr/^{86}Sr$ values. The reason for the larger variability in $^{87}Sr/^{86}Sr$ values of carbonised grains is unclear.

Adsorption of Sr from the burial environment – short-term burial

Table 1 and Figure 2 show the Sr concentrations and $^{87}Sr/^{86}Sr$ values of carbonised bread wheat grains grown in the same field at Rothamsted agricultural station, UK, and buried for different durations in soil with a $^{87}Sr/^{86}Sr$ value of 0.71478. Unburied grains have a Sr concentration of 2.2 ± 0.1 ppm and $^{87}Sr/^{86}Sr$ value of 0.70805 ± 0.00003 (1σ, n = 3). Grains buried for 3 months have a Sr concentration of 5.4 ± 0.5 ppm and $^{87}Sr/^{86}Sr$ value of 0.71281 ± 0.00002 (1σ, n = 2). Grains buried for 9 months have a higher Sr concentration of 8.7 ± 0.6 ppm and $^{87}Sr/^{86}Sr$ value of 0.71343 ± 0.00002 (1σ, n = 2). Grains buried for 12 months have a Sr concentration of 8.3 ± 0.4 ppm and $^{87}Sr/^{86}Sr$ value of 0.71352 ± 0.00007 (1σ, n = 4).

Table 1 and Figure 2 also show the Sr concentrations and $^{87}Sr/^{86}Sr$ values of carbonised bread wheat rachis grown in the same field at Rothamsted agricultural station, UK, and buried for different durations in soil with a $^{87}Sr/^{86}Sr$ value of 0.71478. The unburied rachis sample has a Sr concentration of 4.6 ppm and $^{87}Sr/^{86}Sr$ value of 0.70890 (n = 1). Rachis samples buried for 3 months have a markedly higher Sr concentration of 95.3 ± 0.6 ppm and $^{87}Sr/^{86}Sr$ value of 0.71453 ± 0.00002 (1σ, n = 2). Rachis samples buried for 9 months have a Sr concentration of 102.1 ± 1.6 ppm and $^{87}Sr/^{86}Sr$ value of 0.71455 ± 0.00001 (1σ, n = 2). Rachis samples buried for 12 months have a Sr concentration of 92.5 ± 11.6 ppm and $^{87}Sr/^{86}Sr$ value of 0.71451 ± 0.00010 (1σ, n = 3).

Adsorption of Sr from the burial environment – long-term burial

Table 1 and Figure 3 show the Sr concentrations and $^{87}Sr/^{86}Sr$ values of carbonised bread wheat grains sampled from a single field in Borja, Spain, and buried for three years in soil with a $^{87}Sr/^{86}Sr$ value of 0.70930. Unburied grains have a Sr concentration of 38.5 ± 7.4 ppm and $^{87}Sr/^{86}Sr$ value of 0.70835 ± 0.00003 (1σ, n = 3). Grains buried for 3 years have a Sr concentration of 25.4 ± 1.0 ppm and $^{87}Sr/^{86}Sr$ value of 0.70831 ± 0.00017 (1σ, n = 3). A Welch two sample t-test shows that there is no significant difference between the Sr concentrations or $^{87}Sr/^{86}Sr$ values of unburied and buried bread wheat grains ($t(2.08) = 3.03$, $p = 0.090$ and $t(2.09) = 0.18$, $p = 0.874$, respectively).

Table 1 and Figure 3 also show the Sr concentrations and $^{87}Sr/^{86}Sr$ values of carbonised naked barley grains retrieved from the archaeological site of Çatalhöyük, Turkey. The soil that surrounded the clay bin from which they were recovered has a $^{87}Sr/^{86}Sr$ value of 0.70800. The carbonised naked barley grains have a Sr concentration of 292.2 ± 12.3 ppm and $^{87}Sr/^{86}Sr$ value of 0.70800 ± 0.00008 (1σ, n = 6). A Welch two sample t-test shows that there is no significant difference between the Sr concentrations or $^{87}Sr/^{86}Sr$ values of naked barley grains that were recovered from within a clay bin—with no contact with soil—and those that had not (t(2.89) = 0.09, p = 0.933 and t(3.13) = 0.90, p = 0.431, respectively).

Leaching experiments – removing exogenous Sr from buried grains

Figure 4a shows that the Sr concentrations of carbonised bread wheat grains that had been buried for 12 months decreased from 8.3 ± 0.4 ppm (1σ, n = 4) to 0.7 ± 0.1 ppm (1σ, n = 5) after leaching in 6 M HCl for up to 72 h at room temperature. The buried grains leached in 6 M HCl for 48 h failed to yield a Sr concentration or $^{87}Sr/^{86}Sr$ value and are therefore not included in our analysis. The $^{87}Sr/^{86}Sr$ values of the leached grains also decreased (in the direction of the $^{87}Sr/^{86}Sr$ value of unburied grains from the same field) from 0.71352 ± 0.00007 (1σ, n = 4) to 0.71089 ± 0.00036 (1σ, n = 5). There is no decrease in Sr concentration or $^{87}Sr/^{86}Sr$ value with increased leaching time in 6 M HCl—all leachable Sr seems to have been removed after 24 h. Leaching in 6 M HCl and HF or 1 M NH_4OAc for 24 h at room temperature also decreased the Sr concentrations and $^{87}Sr/^{86}Sr$ values of the buried carbonised bread wheat grain samples, but not to the same extent as leaching in 6 M HCl only. Leaching in 6 M HCl and HF decreased the Sr concentrations and $^{87}Sr/^{86}Sr$ values to 1.8 ± 0.3 ppm and

0.71173 ± 0.00025 (1σ, n = 3), respectively and leaching in 1 M NH_4OAc decreased the Sr concentration and $^{87}Sr/^{86}Sr$ value to 4.3 ppm and 0.71279 (n = 1), respectively (Figure 4a).

The $^{87}Sr/^{86}Sr$ values of the material removed from buried grains leached in 6 M HCl and HF are similar to that of the soil (0.71445 ± 0.00012; 1σ, n = 3; Figure 4a and Table 1), but the $^{87}Sr/^{86}Sr$ values of the material removed from buried grains leached in 6 M HCl for 24 h and over are lower (0.71373 ± 0.00008; 1σ, n = 5; Figure 4a and Table 1), which could indicate removal of biogenic Sr from the grain themselves. The $^{87}Sr/^{86}Sr$ value of the material removed from buried grains leached in 1 M NH_4OAc for 24 h falls between the two (0.71406, n = 1; Figure 4a and Table 1).

Figure 4b shows that the mean Sr concentration of carbonised bread wheat rachis that had been buried for 12 months decreased from 92.5 ± 11.6 ppm (1σ, n = 3) to 1.6 ± 0.2 ppm (1σ, n = 3) after leaching in 6 M HCl for 24 h at room temperature. Their mean $^{87}Sr/^{86}Sr$ value did not decrease, but actually increased slightly from 0.71451 ± 0.00010 to 0.71501 ± 0.00067. Figure 4b also shows that leaching in 6 M HCl and HF for 24 h at room temperature did not markedly decrease the $^{87}Sr/^{86}Sr$ value of these carbonised bread wheat rachis samples (0.71359; n = 1). The $^{87}Sr/^{86}Sr$ values of the material removed from buried rachis leached in 6 M HCl are similar to that of the soil (0.71451 ± 0.00009; 1σ, n = 3; Figure 4b and Table 1), as are the $^{87}Sr/^{86}Sr$ values of the material removed from buried grains leached in 6 M HCl and HF (0.71493 ± 0.00014; 1σ, n = 3; Figure 4b and Table 1).

Leaching experiments – quantifying the removal of biogenic Sr

Figure 5 shows that after leaching in 6 M HCl for between 24 and 72 h at room temperature, the Sr concentrations of carbonised bread wheat grains that had not been buried decreased from 6.5 ppm (n = 1) to 1.2 ± 0.2 ppm (1σ, n = 4). There is no correlation between leaching duration and Sr concentration; 5.3 ppm or 82% biogenic Sr is removed during leaching in 6 M HCl for 24 h or longer. The $^{87}Sr/^{86}Sr$ values of the leached grains are slightly higher than the un-leached grain sample (0.71037 ± 0.00001; 1σ, n = 4 compared to 0.71031; Figure 5), whereas the $^{87}Sr/^{86}Sr$ values of material leached out of the leached grains are slightly lower than the $^{87}Sr/^{86}Sr$ value of the un-leached grains (0.71027 ± 0.00001; 1σ, n = 4 compared to 0.71031; Figure 5). The difference in $^{87}Sr/^{86}Sr$ values are at the fifth decimal place, however, which suggests that the biogenic Sr that is removed during leaching is not from a distinct isotopic pool. The carbonised grains leached in 1 M NH_4OAc for 24 h failed to yield a Sr concentration or $^{87}Sr/^{86}Sr$ value and are therefore not included in our analysis.

DISCUSSION

Strontium is found at a similar concentration in both embryo and apical ends of carbonised cereal grains, despite imaging that indicates that calcium and other metal cations are concentrated in the embryo of cereal grains (Wu et al. 2013). This makes sample selection easier since any part of the grain can be used for Sr isotope analysis. Strontium concentration of carbonised cereal grains is low (c. 4.4 ppm), however, compared to that of fresh leaves and twigs of ligneous plants (c. 200-700 ppm; Hartman and Richards, 2014) that are usually used in establishing local Sr isotopic

baselines. This means that small quantities of exogenous Sr from the soil are likely to alter the $^{87}Sr/^{86}Sr$ values of archaeological cereal grains.

This study has revealed high variability in $^{87}Sr/^{86}Sr$ values of cereal grain samples grown in the same field and during the same year. This highlights the need to characterise the full range in $^{87}Sr/^{86}Sr$ values within the local area (however 'local' is defined) in order to determine whether crops could have been grown locally or not. This high variability in crop $^{87}Sr/^{86}Sr$ values also underlines the importance of taking multiple archaeological crop samples from the same context, since a relatively small standard deviation of 0.00031 (based on five samples) disguises a range in $^{87}Sr/^{86}Sr$ values of 0.00077, despite homogenization of 10 grains per sample. Unfortunately, this degree of variability is likely to change depending on the local environment—geological units, soil types, atmospheric deposition of Sr—although it is worth noting that similar variability in the $^{87}Sr/^{86}Sr$ values of multiple (n = 3) plant samples from within a 50 m radius of one another was observed in northern Israel and the Golan regions (average $\sigma = 0.00025$; Hartman and Richards, 2014).

Our extended investigation into the effect of carbonisation on cereal grain $^{87}Sr/^{86}Sr$ values has revealed that there is no change in $^{87}Sr/^{86}Sr$ value associated with the carbonisation process. It is likely that the difference observed between the $^{87}Sr/^{86}Sr$ values of carbonised and uncarbonised cereal grain samples by Heier et al. (2009) was due to biogenic variability between samples, as suggested by the authors. The larger variability in $^{87}Sr/^{86}Sr$ values of carbonised compared to uncarbonised grains is difficult to explain, but could be due to the greater potential for contamination.

More surprising is the difference in the $^{87}Sr/^{86}Sr$ values of cereal grains and rachis from the same field (mean difference = 0.00085). While this difference could be accounted for by the natural variability between samples (as seen in cereal grain samples from the same field), the difference in $^{87}Sr/^{86}Sr$ values of cereal grains and rachis could reflect partitioning of Sr into these parts of the cereal plant at different times of the year, when the relative contribution of Sr from i.e. bedrock and atmospheric sources is different. Since grain filling is restricted to a particular portion of the total growth period of the plant (Sofield et al., 1977), cereal grain $^{87}Sr/^{86}Sr$ values may differ from those of the rest of the plant if the Sr assimilated during this period derives from a different source. For example, when rainfall is higher there could be a higher input of Sr from atmospheric sources (cf. Hartman and Richards, 2014).

It is clear from the burial experiments that cereal grains and rachis adsorb exogenous Sr and that this adsorption of Sr is significant after less than 3 months of burial in soil. Rachis shows a much greater susceptibility to adsorb exogenous Sr than grain and seemed to reach saturation after 3 months of burial. This is likely to be due to the greater surface area of rachis fragments compared to grains, permitting faster and greater adsorption of Sr. In contrast, the carbonised cereal grains that were buried in garden soil for three years show little evidence for adsorption of exogenous Sr, which demonstrates that the degree of exogenous Sr adsorption is dependent on soil type. The garden soil in which the grains were buried comprised large pieces of plant material and few fine particles compared to the soil from Achnasheen in which the short-term burial experiment was carried out.

The high Sr concentration and consistent $^{87}Sr/^{86}Sr$ values (close to the $^{87}Sr/^{86}Sr$ value of the soil) of the cereal grain samples from the archaeological site of Çatalhöyük demonstrates that all of the cereal grains had adsorbed exogenous Sr. In addition, the cereal grains that had remained physically separate from the surrounding soil matrix (recovered *in situ* from a clay storage bin) contain as much Sr as those that were recovered from the soil itself. It therefore seems that adsorption of exogenous Sr occurs through movement of water soluble Sr, rather than physical contamination of cereal grains with soil *per se*. The $^{87}Sr/^{86}Sr$ values of these cereal grain samples were very close to those determined in 24 h 6 M HCl leaches of other plant material (almonds, naked barley grain, clubrush nutlets, wild mustard seeds, pea seeds; mean $^{87}Sr/^{86}Sr$ value = 0.70802) recovered from Çatalhöyük, presumed to reflect the $^{87}Sr/^{86}Sr$ value of the soil in which they were buried (Bogaard et al., 2014).

Leaching in 6 M hydrochloric acid, 6 M hydrochloric acid and hydrofluoric acid, or 1 M ammonium acetate for 24 h or longer succeeded in removing some of the exogenous Sr from carbonised cereal grains, but none of these leaching protocols resulted in buried grains yielding a $^{87}Sr/^{86}Sr$ value similar to unburied grains. It should be noted, however, that the short-term burial experiment deliberately used soil and carbonised cereal grains with very different $^{87}Sr/^{86}Sr$ values, so even a very small contribution of exogenous Sr changes the $^{87}Sr/^{86}Sr$ value of the buried cereal grains significantly. Since leaching of carbonised grains in 6 M HCl for 24 h or longer removes biogenic as well as exogenous Sr, it is not possible to use the concentration of Sr in leached buried grains as an indicator of the amount of exogenous Sr remaining after leaching.

Leaching in 6M HCl + HF was less successful at yielding cereal grains with $^{87}Sr/^{86}Sr$ values close to those of their unburied counterparts than leaching in 6 M HCl only. This might be because the HF dissolved some recalcitrant mineral particles still adhering to the buried grains, which contributed additional Sr compared to grains that were leaching in HCl only. Benson et al. (2010) also observed that cleaning in HF resulted in higher concentrations of aluminium in carbonised archaeological corn cobs. They suggest that HF was dissolving residual aluminosilicate minerals that originated from the burial environment. Similarly, leaching in 1 M ammonium acetate was also less effective at removing exogenous Sr than leaching in 6 M HCl. Ammonium acetate is commonly used to extract exchangeable cations from soil (Ure et al., 1993), making it a gentler treatment compared to HCl, which also extracts Sr bound to Fe-Mn oxides, adsorbed to clays, and bound in carbonates (Négrel et al., 2000). The $^{87}Sr/^{86}Sr$ values of buried carbonised rachis leached in 6 M HCl and 6 M HCl and HF did not change compared to unleached rachis, suggesting that the leaching procedures failed to remove exogenous Sr. This is despite the reduction in Sr concentration of leached rachis and indicates that biogenic Sr was preferentially removed during leaching.

CONCLUSIONS

This study has shown that carbonised cereal grains adsorb exogenous Sr from the soil in which they are buried and that though leaching in 6 M HCl for 24 h was found to be the most successful method, it does not remove all of this exogenous Sr. Furthermore, leaching of carbonised cereal grains removes biogenic Sr as well as exogenous Sr, and so it is not possible to use the Sr concentration of leached cereal

grains as a means of determining when all exogenous Sr has been removed. Rather, if the $^{87}Sr/^{86}Sr$ value of a cereal grain sample after leaching differs from the range of $^{87}Sr/^{86}Sr$ values determined within a defined region (e.g. within a 2 km radius of the site), it is possible to say that the cereal grains were not grown in that region. In the case of the short-term burial experiment, for example, if the cereal grains grown at Rothamsted were recovered in northwest Scotland, it would not be possible to identify their growing location as southeast England (based on their post-burial, post-leaching $^{87}Sr/^{86}Sr$ value of 0.711), but it would be clear that the grains did not grow in soil with a similar $^{87}Sr/^{86}Sr$ value to that in which they were buried, or indeed in soil with a $^{87}Sr/^{86}Sr$ value of greater than 0.711. The incomplete removal of exogenous Sr contamination by leaching therefore only results in an *underestimation* of the likelihood that cereals were grown outside the local area.

Strontium isotope analysis of carbonised cereal grains preserved on archaeological sites can therefore be used to elucidate whether or not staple crops were produced locally, or in some other defined region, provided that the $^{87}Sr/^{86}Sr$ value range for this potential growing region is well characterised through systematic determination of modern plant $^{87}Sr/^{86}Sr$ values (cf. Hartman & Richards 2014). It is also desirable that $^{87}Sr/^{86}Sr$ values of multiple cereal grains samples from the same archaeological context are determined, given the large variation in cereal grain $^{87}Sr/^{86}Sr$ values from the same field. Unfortunately rachis is not a suitable material for Sr isotope analysis, despite its higher initial concentration of Sr compared to grain.

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FIGURE CAPTIONS

Figure 1. The effect of carbonisation (heating at 230˚C for 24 h) on: a) the Sr concentration, and b) the $^{87}Sr/^{86}Sr$ values of cereal grain samples.

Figure 2. The change in Sr concentration (note the logarithmic scale) and $^{87}Sr/^{86}Sr$ values of carbonised cereal grain and rachis samples after burial in soil (whose $^{87}Sr/^{86}Sr$ value is marked with a dashed line) for 3, 9 and 12 months.

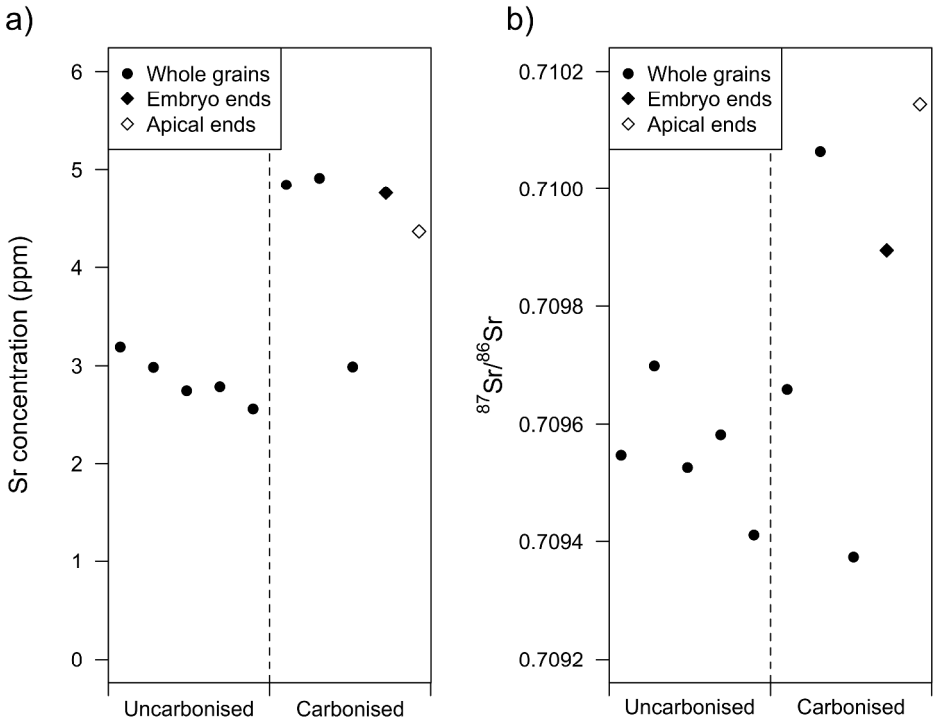
Figure 3. The: a) Sr concentration (note the logarithmic scale) and b) $^{87}Sr/^{86}Sr$ values of carbonised cereal grain samples from Borja, Spain (buried in garden soil in Birmingham for 3 years) and Çatalhöyük (dated to c. 6000 cal BC). The $^{87}Sr/^{86}Sr$ values of the soil in which the grain samples were buried are marked with dashed lines.

Figure 4. The effect of leaching in 6 M HCl, 6 M HCl + HF, or 1 M NH_4OAc for between 24 and 72 hours on the Sr concentration and $^{87}Sr/^{86}Sr$ values of: a) carbonised cereal grain and b) carbonised rachis samples that had been buried in soil (whose $^{87}Sr/^{86}Sr$ value is marked with a dashed line) for 12 months.

Figure 5. The effect of leaching in 6 M HCl for between 24 and 72 hours on the Sr concentration and $^{87}Sr/^{86}Sr$ values of unburied carbonised cereal grain samples.

Table 1. Summary of crop sample and soil Sr concentrations and $^{87}Sr/^{86}Sr$ values determined in this study. The Sr concentration of leachates are calculated by

subtracting the Sr concentration of the leached sample from the Sr concentration of the unleached sample.



The effect of carbonisation (heating at 230°C for 24 h) on: a) the Sr concentration, and b) the 87Sr/86Sr values of cereal grain samples.

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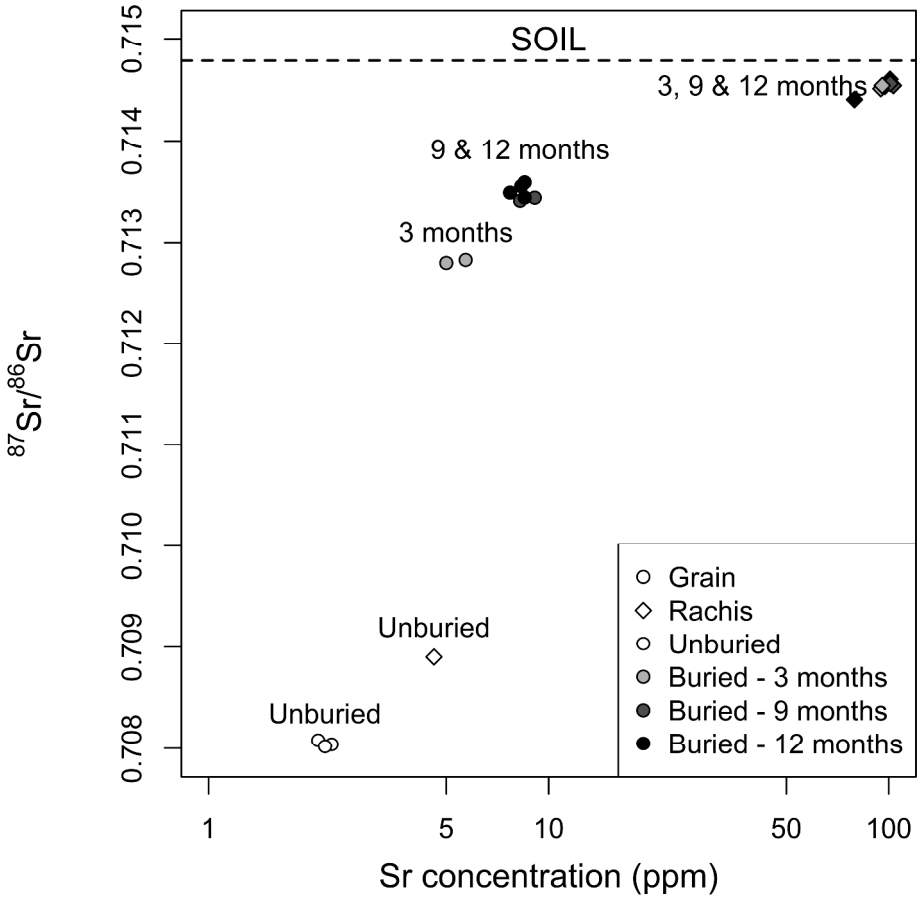

The change in Sr concentration (note the logarithmic scale) and 87Sr/86Sr values of carbonised cereal grain and rachis samples after burial in soil (whose 87Sr/86Sr value is marked with a dashed line) for 3, 9 and 12 months.

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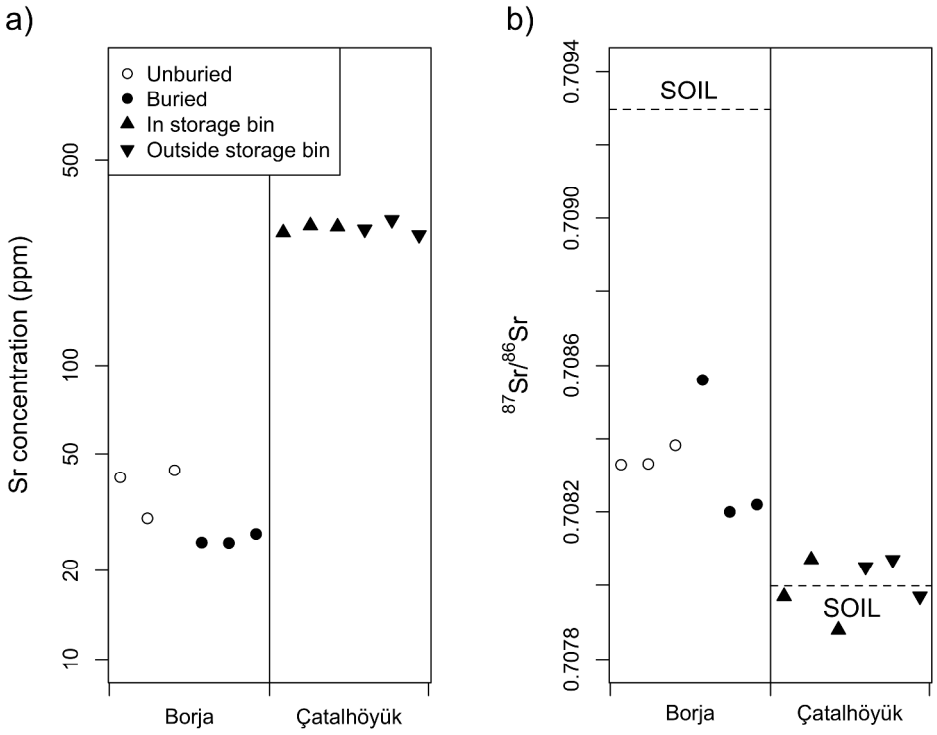
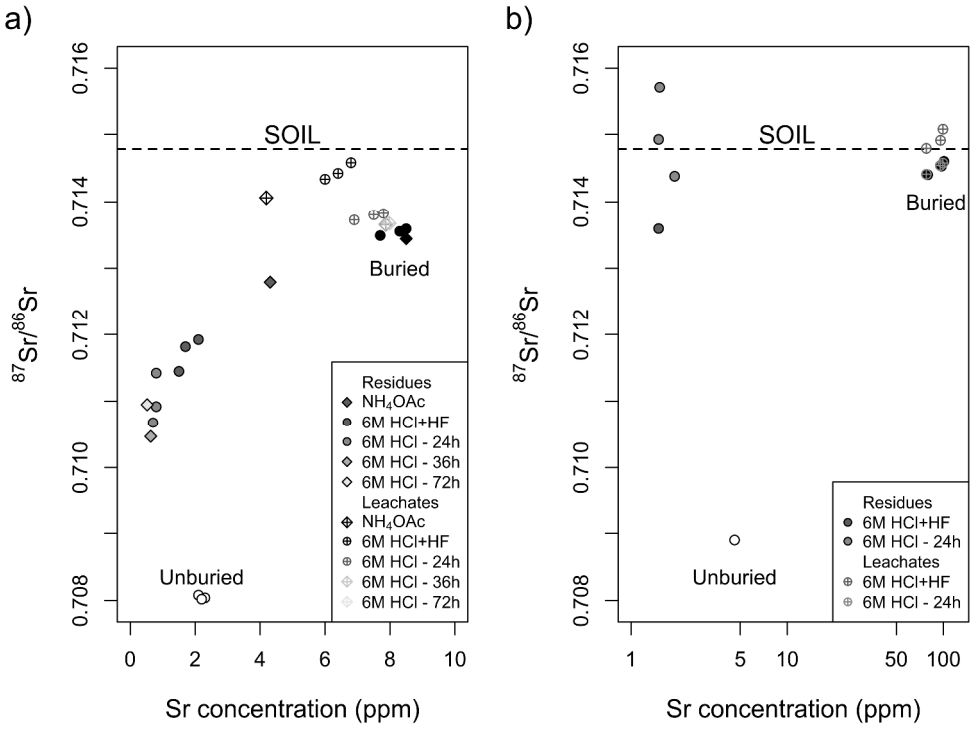


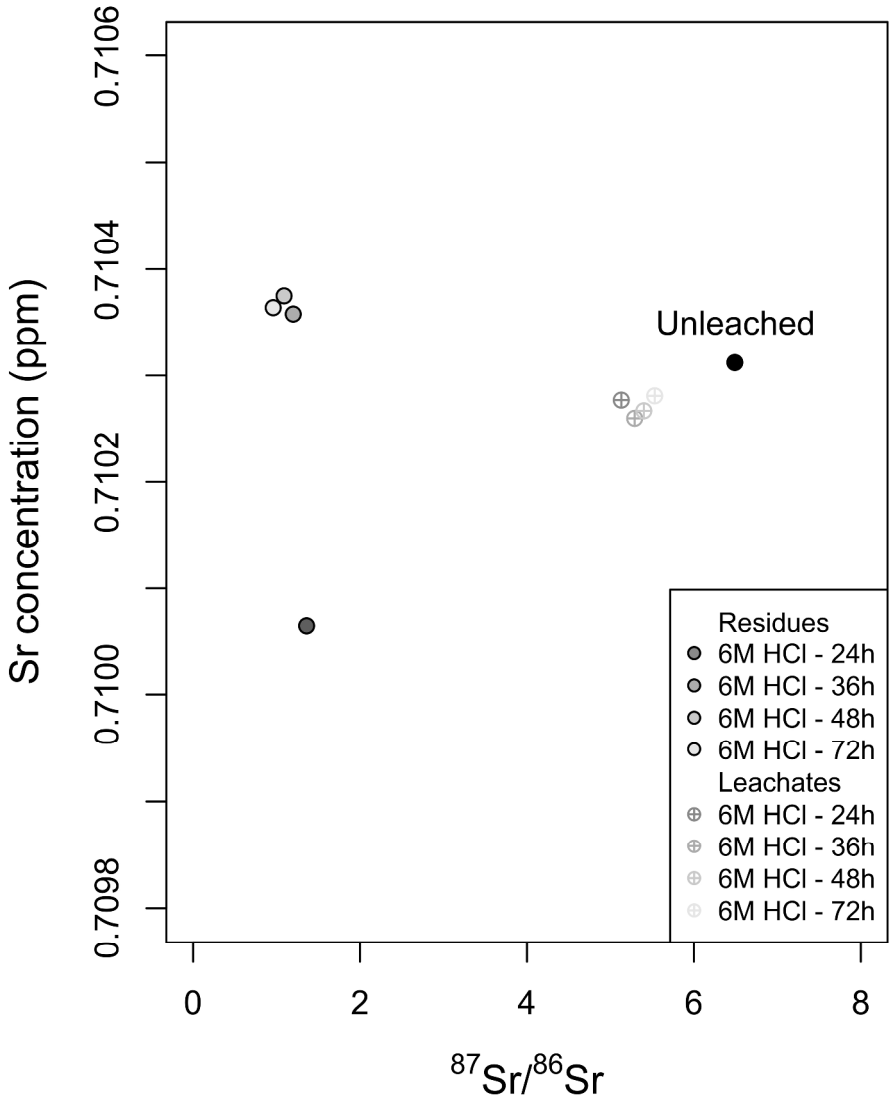
The: a) Sr concentration (note the logarithmic scale) and b) 87Sr/86Sr values of carbonised cereal grain samples from Borja, Spain (buried in garden soil in Birmingham for 3 years) and Çatalhöyük (dated to c. 6000 cal BC). The 87Sr/86Sr values of the soil in which the grain samples were buried are marked with dashed lines.

2222x1693mm (72 x 72 DPI)



The effect of leaching in 6 M HCl, 6 M HCl + HF, or 1 M NH4OAc for between 24 and 72 hours on the Sr concentration and 87Sr/86Sr values of: a) carbonised cereal grain and b) carbonised rachis samples that had been buried in soil (whose 87Sr/86Sr value is marked with a dashed line) for 12 months.

2257x1693mm (72 x 72 DPI)



The effect of leaching in 6 M HCl for between 24 and 72 hours on the Sr concentration and 87Sr/86Sr values of unburied carbonised cereal grain samples.

1411x1693mm (72 x 72 DPI)

Sample	Replicates	No. grains/rachis in each sample	Treatment
Effect of charring			
Modern uncarbonised grains (Bad Lauchstädt)	5	10	None
Modern carbonised grains (Bad Lauchstädt)	5	10	Carbonised
Burial experiment			
Modern carbonised grains (Rothamsted)	3	10	Carbonised
	2	10	Carbonised
	2	10	Carbonised
Modern carbonised rachis (Rothamsted)	1	4	Carbonised
	2	10	Carbonised
	2	10	Carbonised
Soil used in burial experiment	1	NA	
Long-term burial			
Modern carbonised grains (Borja)	3	10	Carbonised
	3	10	Carbonised
Soil used in burial experiment	1	NA	
Archaeological carbonised grains (Çatalhöyük) - in storage bin	3	10	Carbonised
Archaeological carbonised grains (Çatalhöyük) - outside storage bin	3	10	Carbonised
Soil surrounding grains at Çatalhöyük	1	NA	
Leaching experiments - buried grains			
Modern carbonised grains (Rothamsted)	3	15	Carbonised
	3		
	3		
Leachates from buried grains	3	NA	NA
	3		
Modern carbonised grains (Rothamsted)	1	25	Carbonised
	1		
	1		
	1		
	1		
Leachates from buried grains	1	NA	NA
	1		

	1		
	1		
Leaching experiments - buried rachis			
Modern carbonised rachis (Rothamsted)	3	20	Carbonised
	3		
	1		
Leachates from buried rachis	3	NA	NA
	3		
Leaching experiments - unburied grains			
Modern carbonised grains (Rothamsted)	1	30	Carbonised
	1		
	1		
	1		
	1		
	1		
Leachates from grains	1	NA	NA
	1		
	1		
	1		
	1		

Burial duration	Leaching	$^{87}Sr/^{86}Sr$	Sr (ppm)	Lab
None	None	0.70955 ± 0.00010	2.8 ± 0.2	Oxford
None	None	0.70983 ± 0.00031	4.4 ± 0.8	Oxford
None	None	0.70805 ± 0.00003	2.2 ± 0.1	NIGL
3 months	None	0.71281 ± 0.00002	5.4 ± 0.5	NIGL
9 months	None	0.71343 ± 0.00002	8.7 ± 0.6	NIGL
None	None	0.70890	4.6	NIGL
3 months	None	0.71453 ± 0.00002	95.3 ± 0.6	NIGL
9 months	None	0.71455 ± 0.00001	102.1 ± 1.6	NIGL
	Water	0.71478		NIGL
None	None	0.70835 ± 0.00003	38.5 ± 7.4	Oxford/NIGL
36 months	None	0.70833 ± 0.00020	25.4 ± 1.0	NIGL
	Water	0.7093		NIGL
c. 8000 years	None	0.70797 ± 0.00009	291.7 ± 8.5	NIGL
c. 8000 years	None	0.70803 ± 0.00005	292.7 ± 17.5	NIGL
	Water	0.70800		NIGL
12 months	None	0.71354 ± 0.00005	8.2 ± 0.4	NIGL
	10 mL 6 M HCl 24 h	0.71101 ± 0.00038	0.8 ± 0.1	NIGL
	10 mL 6 M HCl + HF 24 h	0.71173 ± 0.00025	1.8 ± 0.3	NIGL
NA	10 mL 6 M HCl 24 h	0.71378 ± 0.00005	7.4 ± 0.5	NIGL
	10 mL 6 M HCl + HF 24 h	0.71445 ± 0.00012	6.4 ± 0.4	NIGL
12 months	None	0.71344	8.5	NIGL
	10 mL 6 M HCl 36 h	0.71046	0.6	NIGL
	10 mL 6 M HCl 48 h	no result	no result	NIGL
	10 mL 6 M HCl 72 h	0.71095	0.5	NIGL
	10 mL 1 M NH_4OAc 24 h	0.71279	4.3	NIGL
NA	10 mL 6 M HCl 36 h	0.71366	7.9	NIGL
	10 mL 6 M HCl 48 h	0.71365	NA	NIGL

	10 mL 6 M HCl 72 h	0.71367	8.0	NIGL
	10 mL 1 M NH_4OAc 24 h	0.71406	4.2	NIGL
12 months	None	0.71451 ± 0.00010	92.5 ± 11.6	NIGL
	10 mL 6 M HCl 24 h	0.71501 ± 0.00067	1.6 ± 0.2	NIGL
	10 mL 6 M HCl + HF 24 h	0.71359	1.5	NIGL
NA	10 mL 6 M HCl 24 h	0.71451 ± 0.00009	90.9 ± 11.5	NIGL
	10 mL 6 M HCl + HF 24 h	0.71493 ± 0.00014	91.0 ± 11.6	NIGL
None	None	0.71031	6.5	NIGL
	10 mL 6 M HCl 24 h	0.71007	1.4	NIGL
	10 mL 6 M HCl 36 h	0.71036	1.2	NIGL
	10 mL 6 M HCl 48 h	0.71038	1.1	NIGL
	10 mL 6 M HCl 72 h	0.71036	1.0	NIGL
	10 mL 1 M NH_4OAc 24 h	no result	no result	NIGL
NA	10 mL 6 M HCl 24 h	0.71028	5.1	NIGL
	10 mL 6 M HCl 36 h	0.71026	5.3	NIGL
	10 mL 6 M HCl 48 h	0.71027	5.4	NIGL
	10 mL 6 M HCl 72 h	0.71028	5.5	NIGL
	10 mL 1 M NH_4OAc 24 h	0.71024	NA	NIGL