APPENDIX A

METHODS

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I Preparation of G-BASE vegetation samples

The vegetation samples provided by the British Geological Survey's (BGS) Geochemical Baseline Survey of the Environment (G-BASE) consist of the thin terminal branches (twigs) of mature woody shrubs, and occasionally also include leaf material. These samples are air-dried and stored under ambient conditions within the Kraft paper sample bags in which they were collected. The purpose of the two methods outlined below is to produce a batch of homogenous plant powders suitable for digestion following the microwave-assisted method detailed in Section II of this document. Unless otherwise stated, only Milli-Q™ deionised water and ultrapure reagents were used.

I.i Initial preparation

The purpose of the method described below is to separate any leaf material from the sample so that it can be used for future analysis, remove the exposed outer surfaces from woody material and prepare a suitable quantity of fine woodchips (ca. 2 g) that can be subjected to cryogenic milling (see Section I.ii). In this study, these processes were divided into five sequential tasks, undertaken at separate workstations:

A: Sample inspection
B: Removal and storage of leaf material
C: Removal of outer bark
D: Chipping and storage of woody material
E: Tool cleaning

Before undertaking sample preparation labelled and pre-weighed sample containers were prepared to receive chipped wood material (77 ml PP Securitainer™), and any available plant foliage (10 × 15 cm LDPE zip-lock specimen bag). Appropriate working practices were adopted to avoid sample cross-contamination, and the transfer of material between progressively clean workstations: Only one sample was prepared at a time; work surfaces, trays and tools were cleaned and bench-lining paper prepared at each workstation before commencing preparation. Each process was undertaken wearing powder-free examination gloves. The gloves were changed when moving between progressively clean workstations and lab-coat inspected for adhering debris.

Work station A: Sample inspection

1. Remove vegetation from Kraft sample bag and transfer any leaves to workstation B.
2. Return any fine twigs from which it would not be possible to remove the outer bark to the Kraft sample bag and discard discoloured/diseased material.
3. Select sufficient woody material to produce a total of 2 g of chips from up to five separate twigs, returning unused material to the Kraft sample bag.
4. Use carbon steel knife to remove any substantial loose material (e.g. moss, bark, sediment) from the selected twigs.
5. Place knife at workstation E.

Work station B: Removal and storage of leaf material

1. Inspect leaf sample and discard any obviously discoloured/diseased leaves.
2. Transfer remaining leaf material to labelled and pre-weighed zip-lock plastic bag; double-bag the sample of leaf material to avoid cross-contamination.
3. Record of sample weight.
4. Work leaf material within bag to achieve a flaky texture (resembling broken-leaf tea leaves) such that the majority of fragments are < 3 mm in diameter*.

*This step can be postponed to avoid cross-contamination and minimise additional glove changes between stations.

Work station C: Removal of outer bark

1. Transfer selected twig sample to workstation B.
2. Using disposable scalpel, shave outer bark (periderm and cork) away from selected twig until cork cambium and wood are exposed (cut from where twig is held, and away from body to avoid contaminating exposed surface).
3. Continue until all outer bark is stripped from the twig, minimising contact with stripped surface; discard any obviously discoloured/diseased material.
4. Cut small notch below where twig is held and use this to snap stripped portion of twig off onto clean weighing paper placed beyond immediate working area.
5. Prepare approximately ≥ 2 g of bark-free wood; if necessary transfer weighing paper to balance to check weight.
6. Transfer residual material back into Kraft sample bag.
7. Place scalpel at workstation E.

Work station D: Chipping and storage of woody material

1. Transfer stripped wood from workstation C to workstation station D.
2. Use new disposable scalpel to split wood into strips of a diameter suitable for cutting into chips.
3. Use steel hand-shears to cut strips of wood into 2–3 mm chips (hold strip at one end, allow chips to fall onto weighing paper).
4. Transfer chipped material to clean, pre-weighed and labelled Securitainer™.
5. Record sample weight.
6. Place hand-shears at workstation E.

Work station E: Tool cleaning

1. Wipe down tools above lining paper to remove any loose debris using a dry, lint-free tissue.
2. Discard any loose debris and disposable tools
3. Wipe down each piece of equipment with acetone to remove any adhering material (use new lint-free tissue for each piece).
4. Prepare workstations with appropriate tools.

I.ii Homogenisation using cryogenic mill

Both the woodchips and flaked leaf material (Section I) provided by samples collected by the British Geological Survey's (BGS) Geochemical Baseline Survey of the Environment (G-BASE) were homogenised prior to microwave-assisted digestion (Section III), using a bench-top cryogenic mill (SPEX™ SamplePrep 6850 Freezer/Mill). This piece of equipment can accommodate up to four separate grinding vials (6751 Small Grinding Vial)

capable of milling up to ca. 2 g of plant material. In the system used within this study each grinding vial consists of a polycarbonate cylinder with two steel end-plugs, and an internal steel impactor; the impactor is driven by an external electro-magnetic coil while the sealed vials are immersed in liquid nitrogen. A milling cycle consists of two grinding periods each of two minutes duration, with a cooling period of four minutes before and between grinds.

The closed grinding vials minimise cross-contamination and are easy to clean. Before use, the mill components were rinsed in RO water then scrubbed with a soft brush, using a warm dilute detergent solution (Decon^{TM}). The separate components were then rinsed three times in a large volume of deionised water, placed in an ultrasonic bath in deionised water for five minutes, and rinsed again three times in deionised water. Prior to use, the dry mill components were wiped down with methanol using lint-free tissue and assembled to avoid the accumulating airborne dust. The method used to mill wood chips and leaf material are detailed in the step-wise method below.

Stage 1: Load grinding vials

1. Label all grinding vials with appropriate sample details.
2. Prepare a clean workstation with a sheet of bench-lining paper and put on a pair of powder-free examination gloves.
3. Before opening any containers use anti-static gun to minimise dust transfer.
4. Transfer the sample into a grinding vial (gently shake vial to allow sample to be distributed around steel impactor).
5. Replace vial cap and sample lid, retaining pre-contaminated sample container to store milled sample.
6. Clean up any residual sample material from workstation.
7. Remove and dispose of gloves.
8. Repeat steps 2–7 for remaining samples.

Stage 2: Load cryogenic mill

1. Following established laboratory health and safety guidelines, fill mill reservoir with liquid nitrogen.
2. Load grinding vials into mill and secure retaining mechanism.
3. Slowly lower samples into reservoir, allowing gas to escape and
4. Start mill program.
5. Once milling cycle has completed, remove grinding vials from mill and place in rack to allow samples to achieve room temperature*.
6. Repeat steps 2–5 for remaining samples.

*Before the milled sample can be transferred back to their original (pre-contaminated) containers they must be allowed to reach room temperature to avoid accumulating condensation or ice. This may take several hours.

Stage 3: Transfer milled samples back to original, pre-contaminated sample containers

1. Prepare a clean workstation with a sheet of bench-lining paper and put on a pair of powder-free examination gloves.
2. Before opening any containers use anti-static gun to minimise dust transfer.
3. Open sample container and place at workstation and prepare clean weighing paper.
4. Remove one end-plug from milling vessel and dislodge any adhering powder onto weighing-paper, then tip steel impactor from grinding vessel onto weighing paper and gently dislodge any residual plant powder.

5. Place impactor and grinding vessel cap into waste container to avoid cross-contamination.
6. Tip sample from weighting-paper into sample container.
7. Tip remaining plant powder from the grinding vessel into sample container (gently knock/tap milling vessel to dislodge sample).
8. Seal sample container.
9. Place dirty milling equipment into waste container to avoid cross-contamination.
10. Clean up workstation, remove and dispose of examination gloves.
11. Repeat steps 1–11 for remaining samples.

II Extraction of strontium from vegetation samples

The methods detailed below refer to the use of a MARS-Xpress™ microwave system manufactured by CEM, and can be applied to a batch of up to 24 samples at a time. Although more sophisticated, higher-pressure systems are available, the simple construction of digestion vessels used in this system simplifies the cleaning process, which means that low procedural blanks can be achieved routinely. The 55 ml digestion vessels are constructed from PFA Teflon with a simple pressure control mechanism in the lid assembly consisting of a TFM Teflon stopper, which fits inside a vented screw-top cap. The vessels are loaded into reinforced fibreglass cells housed within a microwave carousel and have an operating temperature of 220°C, and operating pressure of 20 Bar (290 PSI). During the microwaving procedure, the temperature of each vessel is monitored by an infrared sensor within the microwave chamber. All chemical treatments were undertaken under clean conditions within laminar-flow hoods and acid leached Savilex™ beakers. Unless otherwise stated Milli-Q™ deionised water and purity reagents were used throughout.

II.i Cleaning digestion vessels

The step-wise procedure detailed below is a complete procedure (Version 2), but was developed iteratively. Version 1 of the cleaning procedure did not include the use of methanol to dissolve plant residues and facilitate the physical cleaning of the digestion vessels prior to leaching (Stage 1), the use of an overnight analar-grade HNO_3 (50 % w/w) leach in a full-hight hot block (Stage 2), or the large-volume leach in deionised water (Stage 3). These steps, which complete version 2 of the method, are highlighted in open boxes; Version 1 of the cleaning process was completed without these steps. The microwave parameters used in the microwave-assisted leaches (Stages 2 and 4) are detailed in Table A 01.

Table A 01: Parameters used in microwave-assisted vessel leaching program.

Stage	Microwave power		Temp	Ramp	Hold
	Max	%			
1	800 W	100 %	150 °C	10 min	20 min
2	0 W	0 %	—	—	1 hr

Stage 1: Physical cleaning

1. Remove labels from vessel using methanol and lint-free tissue.
2. Rinse vessel and lid assembly thoroughly with deionised water.
3. Use roll of lint-free tissue to wipe out vessel and lid assembly.
4. Dispense ca. 1 ml of methanol to vessel and agitate gently to release organic residues.

5. Use roll of lint-free tissue moistened with methanol to wipe out vessel, and clean the rim and thread at top of vessel.
6. Rinse vessel with deionised water.
7. Remove stopper from cap.
8. Wipe cap out thoroughly, using lint-free tissue moistened with methanol and rinse with deionised water.
9. Rinse stopper with deionised water and wipe thoroughly, using lint-free tissue moistened with methanol.
10. Place stopper within cap and thoroughly flush lid assembly through with deionised water.
11. Replace lid assembly on digestion vessel.
12. Repeat steps 1–11 for remaining vessels.

Stage 2: Microwave-assisted analytical grade HNO_3 leach

1. Dispense ca. 5 ml of deionised water into digestion vessel and carefully add ca. 5 ml HNO_3 (50 wt. %), then replace lid assembly; take to finger-tightness then give additional $^1/_4$ turn.
2. Place vessel in rack and repeat step 1 for remaining vessels.
3. Transfer digestion vessels to microwave carousel and place within microwave compartment.
4. Start microwave program.
5. Remove carousel from microwave compartment and place under fume hood.
6. Vent each vessel in turn without fully opening:
    - Tip vessel away from body at approx 45°.
    - Hold knurled rim of cap and ensure that vent is not obstructed.
    - Rotate vessel rather than cap to release seal.
7. Place digestion vessel in rack.
8. Transfer microwave-leached vessels to clean suite.
9. Remove lid assembly from vessel and decant acid from vessel into waste beaker.
10. Rinse vessel three times with deionised water.
11. Rinse lid assembly three times with deionised water.
12. Dispense ca. 10 ml of deionised water into digestion vessel, then replace lid assembly; take to finger-tightness then give additional $^1/_4$ turn.
13. Place vessel to rack and repeat steps 8–11 for remaining vessels.
14. Repeat steps 3–10 as for microwave-assisted acid leach.
15. Dispense ca. 1 ml HNO_3 (50 wt. %) into digestion vessel then replace lid assembly; take to finger-tightness then give additional $^1/_4$ turn.
16. Place vessel in tall heating block on hotplate (105°C).
17. Repeat steps 14 and 15 for remaining vessels and leave on hotplate overnight.

Stage 3: Large volume leach in deionised water

1. Turn hotplate off.
2. Decant acid from vessel into waste beaker.
3. Place digestion vessel into one large Teflon beaker and lid assembly into another.

4. Repeat steps 2 and 3 for remaining vessels.
5. Fill beakers with deionised water, then decant and re-fill.
6. Place beakers on hotplate (105°C) covered by a watch glass and leave on hotplate overnight.

Stage 4: Microwave assisted HCl leach

1. Turn hotplate off.
2. Decant water from Teflon beakers, refill with deionised water and decant.
3. Assemble all lids with cap and stopper.
4. Re-assemble vessels and lids.
5. Dispense ca. 10 ml of HCl (6 M) into digestion vessel; then replace lid assembly; take to finger-tightness the give additional $^1/_4$ turn.
6. Place vessel in rack.
7. Repeat steps 5 and 6 for remaining vessels.
8. Repeat steps 3–10 as for Stage 2.

Stage 5: Final HCl leach

1. Add ca. 1 ml of 6 M HCl to vessel, then replace lid assembly; take to finger-tightness the give additional $^1/_4$ turn.
2. Place vessels in tall heating block on hotplate (105°C).
3. Repeat steps 1 and 2 for remaining vessels and leave on hotplate overnight.

Stage 6: Preparation for drying

1. Turn hotplate off.
2. Decant acid from vessel into waste beaker.
3. Rinse vessel three times wih deionised water.
4. Rinse lid assembly three times with deionised water.
5. Replace lid assembly; take to finger tightness the give additional $^1/_4$ turn
6. Place vessel in tall heating block on hotplate (105°C).
7. Repeat steps 2–6 for remaining vessels and allow to come to temperature.

Stage 7: Dry vessels

1. Turn hotplate off.
2. Remove lid assembly from warm vessel, retaining stopper within cap.
3. Carefully shake out remaining water into waste beaker.
4. Place warm digestion vessel and lid assembly on tray.
5. Repeat steps 2–5 for remaining vessels.
6. Place tray in drying box while vessels are still warm and leave until dry before replacing lids.

II.ii Microwave-assisted digestion

The single acid (HNO_3) microwave-assisted digestion method detailed below is a complete method (Version 3), but was developed iteratively. In Version 1, the microwaved plant material was dried down with 0.5 ml of H_2O_2 (30%) and then converted to chloride using 1 ml of 6 M HCl before being subjected to column chemistry (Section VI). Version 2 included a step in which the dried-down, microwaved sample was re-dissolved and oxidised in a small volume of HNO_3 (8 M) and H_2O_2 (30 %) in a 1:10 (v/v) mixture (Stage 5). In the final iteration of the method (Version 3), a small quantity (0.1 ml) of H_2O_2 (30%) was added

to the digestion vessels prior to microwaving (Stage 2); this quantity of H_2O_2 is not intended to oxidise the sample directly, but to reduce the vapour pressure of the digest and maintain acid concentrations within the digestion vessels. The additional steps from Version 2 are highlighted in open boxes, and the additional steps comprising Version 3 are highlighted on a grey background. The microwave parameters detailed in Table 2 were selected to avoid rapid overheating and allow a high temperature to be sustained for the allotted time.

Table A 02: Parameters used in microwave-assisted digestion program

Stage	Microwave power		Temp	Ramp	Hold
	Max	%			
1	800 W	80 %	150 °C	15 min	0 min
2	800 W	100 %	175 °C	10 min	20 min
3	0 W	0 %	—	—	1 hr

Stage 1: First addition of HNO_3 for pre-digestion

1. Select digestion vessel containing weighed sample; use anti-static gun to minimise material adhering to sides of digestion vessel.
2. Remove lid, retaining stopper within screw-cap to avoid touching stopper.
3. Dispense 1 ml HNO_3 (8 M) into digestion vessel:
4. Tip vessel away from body at ca. 45° angle.
    - Gently pour in a thin stream of acid, allowing the liquid to rinse sides by carefully rotating vessel
5. Replace lid assembly, but do not over tighten lid; take to finger-tightness only.
6. Repeat steps 1–4 for remaining samples.
7. Transfer vessels to weighing room to add known quantity of ^{84}Sr-enriched spike (Oak Ridge Dilute Strontium).
8. Allow samples to pre-digest overnight at room temperature.

Stage 2: Addition of nitric acid

1. Select digestion vessel and remove lid, retaining stopper within screw-cap to avoid touching stopper.
2. Dispense 4 ml of HNO_3 (8 M) into digestion vessel:
3. Tip vessel away from body at ca. 45° angle.
4. Gently pour in a thin stream of acid, allowing the liquid to rinse sides by carefully rotating vessel.
5. Replace lid, but do not tighten; take to finger-tightness only.
6. Repeat steps 1–3 for remaining vessels.
7. Inspect digestion vessels; if samples and acid are not well mixed, or deposits of sample material sit above the level of the acid, swirl the vessel gently, but avoid splashing further sample material up the sides of the digestion vessel.
8. Allow to vessels stand for ca. 30 min.
9. Select digestion vessel and remove lid, retaining stopper within screw-cap to avoid touching stopper.
10. Dispense 0.1 ml of H_2O_2 (30%) into vessel and re-seal lids; take to finger tightness then give additional $^1/_4$ turn.
11. Inspect digestion vessels; if samples and acid are not well mixed, or deposits of sample material sit above the level of the acid, swirl the vessel

gently, but avoid splashing further sample material up the sides of the digestion vessel

12. Repeat steps 7 and 8 for remaining vessels.

Stage 3: Microwave assisted digestion

1. Transfer digestion vessels to microwave carousel and place within microwave compartment.
2. Start microwave program.
3. While microwave program in sunning prepare a set of beakers to collect microwave-digested plant material
4. Select appropriate number of acid-leached beakers and mark vessels and lids with sample ID
5. Add ca. 1 ml of HCl (6 M) to each beaker, replace lids and place on hotplate (105°C).
6. Rinse beakers and lids three times with deionised water before use, and dry in heating-block on hotplate (105°C).
7. Remove carousel from microwave compartment and place under fume hood*.
    - Vent each vessel in turn without fully opening:
    - Tip vessel away from body at approx 45°.
    - Hold knurled rim of cap and ensure that vent is not obstructed.
    - Rotate vessel rather than cap to release seal.
8. Place digestion vessel in rack.
9. Transfer microwave-leached vessels to clean suite.
10. Allow NOx fumes to disperse from digestion tubes (ca. 1 hr).

*On removal from the microwave the samples should appear as a clear blue-green solution. Colour will gradually change to pale straw-like yellow as NOx fumes are vented.

Stage 4: Initial dry down and secondary oxidation

1. Select digestion vessel and remove lid, retaining stopper within screw-cap to avoid touching stopper.
2. Version 1 and 2: Dispense 0.5 ml of H_2O_2 (30 %) into vessel.

2.	Version 3:	Dispense 0.4 µl of H_2O_2 (30 %) into vessel.

3. Swirl the sample gently to mix, but avoid splashing further sample material up the sides of the digestion vessel.
4. Repeat steps 1–3 for remaining samples.
5. Allow samples to stand for ca. 30 min.
6. Transfer samples to pre-prepared beakers (see Stage 3) and place in heating-block on cold hotplate with lids loosely in place.
7. Turn on hotplate and allow to come to temperature (50°C).
8. Slowly increase hotplate temperature to achieve 105°C over the course of ca. 2 hrs*.
9. Remove lids from beakers to allow samples to dry down; remove beaker lids and allow samples to evaporate to dryness.

*Monitor progress of dry down, adjusting temperature as necessary to avoid spitting as O_2 is evolved from peroxide during heating.

Stage 5: Additional chemical oxidation

1. Turn hotplate off and remove samples from heating-block.
2. Dispense 2 ml of HNO_3 (8 M) into each sample.
3. Replace lids and return the beakers to the hotplate (50°C).
4. Once temperature is achieved inspect the beakers to confirm dissolution of the samples; swirl each beaker gently to ensure proper mixture.
5. Turn hotplate off and remove samples from heating block and allow the beakers to cool.
6. Dispense 0.2 ml of H_2O_2 (30%) into each sample; swirl each beaker gently to ensure proper mixture.
7. Replace lids loosely and return the beakers to the hotplate (50°C).
8. Slowly increase hotplate temperature to achieve 105°C over the course of 2 hrs*.
9. Remove lids from beakers to allow samples to dry down.

*Monitor progress of dry down, adjusting temperature as necessary to avoid spitting as O_2 is evolved from peroxide during heating.

Stage 6: Conversion to chloride

1. Turn hotplate off and remove samples from heating-block.
2. Dispense 1 ml of HCl (6 M) into each sample in turn and replace caps on each beaker: swirl each beaker gently to ensure proper mixture.
3. Replace lids and return the beakers to the hotplate (50°C).
4. Inspect the beakers to confirm dissolution of the samples; swirl each beaker gently to ensure proper mixture.
5. Remove lids from beakers and allow samples to evaporate to dryness (105°C).

III Soil leach

Within this study a deionised water leach (Milli-Q™) was used to extract labile strontium form soil samples provided by the G-BASE project (Chapter 2), which had been prepared for the analysis of loss-on-ignition (referred to as the 'LOI split'). This material had been dried, sieved (2 mm mesh), and disaggregated in an agate planetary ball mill. Ten millilitres of deionised water was used to leach 1 g of prepared soil, over a 24-hour period under constant agitation at room temperature. Following centrifugation measured aliquot of the supernatant fluid (< 10 ml) was transferred to an acid-leached Savilex™ beaker using a pipette and mixed with a known quantity of a ^{84}Sr-enriched tracer solution (Oak Ridge Diluter Strontium) to allow determination of strontium concentrations by ID-TIMS.

Stage 1: Weighing

1. Thoroughly mix soil samples by rotating/rolling the sample container; allow the contents to settle for ca. 1 min before weighing.
2. Place fresh weighing paper on balance, allow balance to stabilise and re-set tare.
3. Use anti-static gun to minimise cross-contamination between containers.
4. Weigh out 1 g soil onto fresh weighing paper and re-seal sample container, placing it away from working area
5. Rerecord weighed mass of soil.
6. Transfer sample to centrifuge tube.
7. Place soil in centrifuge tube and replace lid.

8. Perform any necessary clean-up before proceeding with next sample or completing weighing exercise.

Stage 2: Leaching

1. Dispense 10 ml of deionised water into each centrifuge tube opening one tube at a time closing each tube in turn.
2. Once deionised water has been added to all tubes seal the cap and neck of each tube with a strip of Parafilm^{TM}, wrapping the strip tightly around the neck and cap of the tube.
3. Once all tubes are sealed, agitate each tube in turn to ensure that the soil and deionised water are thoroughly mixed.
4. Place the tubes in a rack and place rack in large zip-lock PE specimen bag before removing from the clean-suite.
5. Place the samples on a shaker-table and allow the samples to leach at room temperature for 24 hrs.

Stage 3: Centrifugation

1. During centrifuging process, prepare labelled set of pre-cleaned beakers to collect supernatant:
2. Select appropriate number of acid-leached beakers and mark vessels and lids with sample ID
3. Add ca. 1 ml of HCl (6 M) to each beaker, replace lids and place on hotplate (105°C).
4. Rinse beakers and lids three times with deionised water before use, and dry in heating-block on hotplate (105°C).
5. Transfer sample tubes to centrifuge and run each batch at 4000 rpm for 20 min to remove particulates from suspension
6. Decant liquid to clean centrifuge tubes to avoid transferring particulates to pipette (see step 4) and centrifuge again at 4000 rpm for 20 min.
7. Spike prepared beakers with known quantity of ^{84}Sr enriched tracer solution (Oak Ridge dilute Strontium).
8. Draw off and record measured volume (< 10 ml) of supernatant fluid from each centrifuge tube in turn, using a clean pipette tip.
9. Dispense 1 ml HCl (6 M) into each beaker; swirl gently to ensure proper mixture.
10. Place samples into heating block on hotplate (105°C); remove beaker lids and allow samples to evaporate to dryness.

IV Water samples

Due to the low concentrations of strontium in stream water and rainwater all pre-cleaned Savilex^{TM} lab-ware was subjected to additional leaching before use. Pipette tips were rinsed three times in HCl (6 M) and then three times in deionised water before use. When it was necessary to determine strontium concentrations, the appropriate beakers were spiked with 10 µl of the ^{87}Sr-enriched tracer solution (Oak Ridge Dilute Strontium) under clean conditions.

Stage 1: Assemble samples and prepare beakers

1. Remove water samples from cold-storage
2. Wipe down containers to avoid transferring material to clean-suite

3. Transfer samples to clean-suite and allow to equilibrate at room temperature.
4. Prepare labelled set of pre-cleaned beakers:
5. Select appropriate number of acid-leached beakers and mark vessels and lids with sample ID.
6. Add < 1 ml of HCl (6 M) to each beaker, replace lids and place on hotplate (105°C).
7. Rinse beakers and lids three times with deionised water before use, and dry in heating-block on hotplate (105°C).

Stage 2: Measure out alliquot of water

1. Assemble necessary containers, dispensing and transfer equipment.
2. Select prepared beaker
3. Rinse pipette tip and transfer appropriate volume of water into beaker (5 ml of stream water, 20 ml of rainwater)
4. Dispose of pipette tip and replace lids on beaker and water bottle.
5. Repeat steps 2–4 for remaining samples
6. Dispense 2 ml of HCl (6 M) into each measured aliquot of water and replace lids; swirl gently to ensure proper mixture.
7. Place samples into heating block on hotplate (105°C); remove beaker lids and allow samples to evaporate to dryness.

V Preparation of archaeological samples

Sample preparation procedures were based on the recommendations of Montgomery (2002). In order to obtain samples of archaeological enamel that can provide reliable endogenous $^{87}Sr/^{86}Sr$ values, it is necessary to remove the outer surfaces of the crown to a depth of at least 100 µm and remove all dentine (Budd *et al.* 2000). Once excised from the tooth, all exposed enamel surfaces – including the edges of any new breaks that propagated during sample preparation – were abraded using a diamond impregnated dental burr, under a low-power binocular microscope. Additional preparatory steps were carried out under clean conditions; unless otherwise stated, all work was undertaken within laminar-flow hoods using high purity reagents and acid leached Savilex™ beakers. The same laboratory procedures were applied to enamel and dentine samples.

V.i Preparation of workspace and dental tools.

To avoid gross cross-contamination the work area was cleaned between handling each tooth, powder free examination gloves were changed and lab coat carefully inspected for adhering debris. Clean dental tools were used to prepare samples from each tooth. Tools were cleaned as necessary as follows:

1. Wipe dust away from smooth tool parts using lint-free issue
2. Rinse tool three times in deionised water.
3. Clean tools ultrasonically for 5 min in dilute Decon™ solution (deionised water) and rinse three times in deionised water.
4. Clean tools ultrasonically for 5 min in deionised water and dampen sparingly with methanol to enhance drying.

V.ii Faunal material

1. Where necessary, extract tooth from alveolar bone; clean tooth with a soft brush in deionised water to remove loose material, and allow to dry.
2. Remove cementum from selected buccal lobe using tungsten carbide dental burr.
3. Record maximum height of crown, with respect to the cervical margin, measured along the growth axis of tooth (long-axis of tooth approximately perpendicular to circumferential striae).
4. Abrade outer surface of selected crown lobe, using a variety of dental burrs to polish the exposed enamel and allow assessment of condition.
5. Mark-up each sample location (*ca.* 2 mm high circumferential band) using a soft graphite pencil and measure distance (top and bottom) from cervical margin (avoid areas of crown where enamel is cracked, opaque or discoloured).
6. Using flexible dental saw, excise strip of enamel (ca. 4 mm wide) from full height of crown, encompassing all sample locations (where possible exploit any pre-existing longitudinal cracks).
7. Divide enamel strip into sections according to measured sample locations; transfer samples to labelled microtubes.
8. Remove all dentine from each sample (retain) where possible.
9. Using a variety of dental burrs, heavily abrade the exposed surfaces of each enamel sample (including the surfaces of any beaks that propagate during this process); use low power binocular microscope confirm removal of all dentine and any enamel that appears to be pitted, opaque or discoloured.
10. Transfer prepared enamel to clean labelled microtubes.

V.iii Human material

1. Teeth were removed from the alveolar bone, rinsed in deionised water to remove any loosely adhering material and allowed to dry.
2. A region of each crown was selected for sampling, on the basis of apparent condition and with the aim of maximising the worn crown height.
3. The outer enamel of the selected cusp was abraded to a depth of at least 100 µm using a tungsten carbide dental burr.
4. A slice of enamel was excised, representing the entire available crown height using a flexible, diamond edged rotary dental saw.
5. Where possible the majority of the adhering dentine was cut away as one piece, or collected as powder from a tungsten burr. Any remaining dentine was removed using a variety of dental burs. A low power binocular microscope was used to confirm removal of all dentine and any enamel that appeared to be pitted, opaque or discoloured.
6. Transfer prepared enamel to clean labelled microtubes.

V.iv Sample pre-treatment

Additional cleaning, chemical preparation and analyses were carried out in clean laboratory facilities at the NERC Isotope Geosciences Laboratory (NIGL). Chemical procedures were undertaken within laminar flow hoods using high purity reagents and acid leached vessels.

1. Each sample was transferred to a small, labelled glass beaker.
2. Acetone was added and gently agitated to remove grease.
3. After ca 10 minutes the acetone was decanted and the sample was rinsed three times in deionised water.
4. Each sample was covered with Parafilm^{TM} and cleaned ultrasonically for ca 10 minutes to remove any adhering particles.
5. The water was decanted and the samples were rinsed three times in deionised water.
6. The samples were placed on a hotplate for ca. 30 min at 50 °C in deionised water.
7. The warm water was gently agitated, decanted and the samples were rinsed three times in deionised water.
8. The samples were places on the hotplate to dry
9. Clean dry samples sealed in beaker with Parafilm^{TM} until further processing undertaken.

V.v Dissolution of dental tissues

Samples were processed in 4 batches (P534, P540, P545, P548) following established methods. Each batch of up to 26 samples included at least three procedural blanks.

1. Dry samples were weighed into pre-cleaned Savilex Teflon vessels.
2. A ^{84}Sr enriched spike (Oak Ridge Dilute Sr) of known weight was added to each sample to allow concentrations to be calculated by isotope dilution.
3. Under a laminar flow hood 2 ml of Teflon-distilled 8M HNO_3 was added to each sample and the beakers left, with the lids off and allowed to dry down at 105 °C.
4. To convert the Sr to the chloride form suitable for extraction 2 ml of quartz distilled 6 M HCL was added to each sample and the beakers left, with the lids off to dry down at 105 °C.

Strontium was extracted from the samples using cation exchange resin columns (Dowex AG 50W-X12) following standard laboratory methods (Section VI). These procedures result in the production of a dried-down, purified strontium chloride salt.

VI Column Chemistry

Strontium is separated from the sample solutions for TIMS analysis, using a appropriately calibrated cation exchange resin columns (Dowex AG 50W-X12). Before undertaking column chemistry, pre-treated and dried-down samples are re-dissolved in 2.5M HCl in order to satisfy the conditions for chromatographic separation. Samples are left at room temperature for at least 1 hr to equilibrate before being applied to the columns. Where appropriate, the samples are transferred to labelled centrifuged tubes and centrifuged at 4000 rpm for 20 min to separate any residual precipitate. The strontium eluted from the columns is collected within a set of clean Savilex beakers, prepared by adding 2mls of 6M HCl to up to 26 acid-leached beakers and placing them on a hotplate at 110°C. These are then are rinsed three times in Milli-Q deionised water before use. Under normal circumstances, the columns will be left stored in Milli-Q deionised water (at stage 2 below): cue-cards are provided to record the current cleaning step

Stage 1: **Prepare columns**

1. Wash columns with 50 ml of (HCl 6M).
2. Wash with 50 ml of deionised water.
3. Clean columns and racks.
4. Wash with 50 ml of HCl (6 M).
5. Condition with 15 ml of HCl (2.5 M).

Stage 2: **Separation**

1. Pipette 1 ml of the samples from the centrifuge tubes onto the column.
2. Wash in with 1 ml 2.5M HCl.
3. Discard 45 ml 2.5M HCl (containing Ca and Rb).
4. Collect 12 ml 2.5M HCl containing.
5. Evaporate Sr eluate to dryness.
6. Initiate stage 1.