A light stable isotope (C, N, H, O) approach to identifying movement of medieval textiles in North West Europe

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PhD thesis

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September 2012

Abstract

This thesis examined how light stable isotopic analysis could be used to examine the provenance of archaeological wool textiles preserved by anoxic waterlogging.

Preliminary studies in modern sheep wool samples showed that their carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), un-exchangeable hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) composition varied systematically with geographical location in British Isles and Iceland, but were significantly influenced by farming practice (fodder provision, fertilizer use). Keratin and collagen isotope values within a single sheep were shown to be systematically related. Experimental characterisation of the isotopic effects of wool degradation by elemental, amino acid and isotopic composition showed that changes in experimentally buried samples were minimal compared to samples treated under high-temperature hydrous conditions, which showed significant hydrolysis, oxidation and racemisation.

These results were used to interpret data from 101 archaeological textiles from contexts dated between AD 700–1600 from excavations at Reykholt, Iceland; York and Newcastle, Britain; Hessens, Germany; and Birka, Sweden. Local isotope range for each location was defined by assemblage median ± maximum variation derived from a modern flock. Isotopic identifications of local/non-local wool did not always correspond to typical/atypical interpretations of textile origin based on features of textile construction, fibre type and dye use. Thus distinctions could be made between the movement of textiles (atypical construction, non-local composition), movement of textile techniques (atypical construction, local composition) and movement of raw wool (typical construction, non-local composition). The most significant limitation of the technique was insufficient isotopic difference between regions of origin and deposition. The results made a significant contribution to understanding the origin of a number of specific textile types, including the much-discussed ‘Frisian cloth’.

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Acknowledgements

I am grateful to the following organisations for providing funding and access to equipment for the work included in this thesis: The Natural Environment Research Council, EuroPlanet TNA and the Vrije Universiteit Amsterdam, The University of York, The Anglo-Saxon Laboratory, The Catherine Mackichan Trust and the York Archaeological Trust.

I also thank the following people:

For research supervision, advice, expertise and guidance: Matthew Collins, Allan Hall, Oliver Craig, Penelope Walton Rogers, Kirsty Penkman and Steve Ashby.

For technical training and support: Richard Allen (S-block laboratories, York), Jason Newton ($\delta^{13}C/\delta^{15}N$ and $\delta^{2}H/\delta^{18}O$ analysis, NERC Life Sciences Mass Spectrometry Facility, East Kilbride), Gareth Davies, Laura Font Morales, Martijn Klaver, Jason Laffoon ($^{87}Sr/^{86}Sr$ analysis, Department of Petrology, Vrije Universiteit Amsterdam), Nienke van Doorn and Mike Buckley (ZooMS, York), Beatrice Demarchi, John Stewart, Becky Claypole, Kirsty Penkman (neAAR, York), Matt Pickering and Brendan Keely (elemental analysis, York), David Sherlock (Biology/D0 equipment, York), Marco Biazzo (collagen preparation, York), Hannah Koon (Spex mill, York), and Ian Panter (freeze dryer, York Archaeological Trust).

For samples: Cluny Johnstone, Mike Sandison and other contacts in the Shetland Sheep Society, Emma Eyþórsdóttir (Landbúnaðarháskóli Íslands), Escrick Abbatoir; Julie Hamilton (University of Oxford) and Polydora Baker (English Heritage); Penelope Walton Rogers (Anglo-Saxon Laboratory), Guðrún Sveinbjarnardóttir (Þjóðminjasafn Íslands), Christine McDonnell (York Archaeological Trust), Andrew Parkin (Great North Museum), Mari-Louise Franzen (Statens historiska museum), Klaus Tidow (formerly Neumünster Textilmuseum), Anette Siegmüller (Niedersächsisches Institut für Historische Küstenforschung); Maura Pellegrini (University of Bradford/University of Oxford) and Auli Tourunen (University of Turku); Howell Edwards (University of Bradford) and Grant Zazula (Government of Yukon Department of Tourism and Culture); Elizabeth Peacock (Göteborgs universitet) and Gordon Turner-Walker (National Yunlin University of Science & Technology).

For administrative support: Alizon Holland and all in the King's Manor Office.

For clues, cheer, cunning and commiseration, as required: everybody in G65 and S-block.

For non-archaeology- or -science-related professional expertise: Lesley Murphy, Rob Leadley, Parv Pye, Cerys at Yearsley Pool.

For hugs: Mum, Dad, Anna, Val, and Tony. Jude and family, Laura, Ellie, Helen, Lisa, Ashley, Beatrice, Gavin, Zoë and all in the York City Levy.

Declaration

This thesis is the result of the author's original work except where acknowledged or specifically stated in the text. It has not been submitted for any other degree or examination at any other university or academic institution.

Isabella Christina Charlottie von Holstein, September 2012

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1. Introduction

The purpose of this section is to provide a context for the research chapters that follow, by (1) introducing the study of medieval textiles, focusing particularly on (2) how assessments of origin have been made; (3) explaining the basis of studies of isotopic composition, with particular reference to the biochemical structure of hair; and (4) exploring how these two methods of understanding archaeological medieval textiles can be combined to understand their origin.

1.1. Research into medieval textiles

Wool textiles are among the most complex artefacts found in medieval archaeological deposits in Europe. Their technology of manufacture and some aspects of their use are largely reconstructable from the artefacts themselves, even where the tools do not survive (Walton Rogers 2011b). These objects are the products of multi-stage and multi-tool manufacturing processes (Jenkins 2003; Table 1.1), leading to a very wide range of possible textile types, which varied across Europe. Wool textiles were bulky, non-fragile, varied and valuable, and constituted the most important class of manufactured object in long-distance trade in the later Middle Ages, and possibly well before this (Munro 2003, 181).

Non-mechanised textile production is a highly labour-intensive process. Andersson (1999, 11-13) calculated that using a drop spindle to spin enough yarn for the clothing of two people requires nearly 2,000 hours, or for a single sail, 3 person-years. Textile manufacture is also characterised by its potential for high specialisation. From the beginning of the medieval period (5th century onwards) and in rural settlements, all manufacturing steps (Table 1.1) were probably carried out by the same group of people within a community; however towards the end of the period (13th century onwards), and in urban settlements, each stage is likely to have been practised by a different group of specialised craftspeople (Munro 2003; Andersson 2007). Such industry, whether on a domestic or workshop scale, was therefore a significant investment in time for a society, and its organisation was socially meaningful (Barber 1991; Costin 2001). Medieval textile manufacture is therefore of great importance for understanding contemporaneous society.

The raw material for many of these artefacts and activity, wool, was produced across Europe throughout the Middle Ages (Ryder 1984; Costin 2001). Sheep could be kept successfully on land where arable cultivation or cattle farming would be more difficult (e.g. McGovern *et al.* 2007), and hence were an important feature of farming on poor soils e.g. in upland environments. Indeed it is speculated that the finest (i.e. narrowest) fibres were produced then, as today, from animals raised on poor grazing (Munro 2003, 186-9). However, in areas of good soil, sheep could also be important adjuncts to arable farming, with their manure

Table 1.1. Medieval wool textile manufacturing processes (see e.g. De Poerck 1951; Hoffmann 1964; Walton 1989; Hoffmann 1991; Walton 1991; Walton Rogers 1997; Cardon 1999; Jenkins 2003; Walton Rogers 2007c).

Element	Process	Objective
Fibre	Farming and shearing/rooing	Produce raw fibre and remove from sheep either by cutting or plucking
	Selection*	Select wool of desired fibre diameter range, length and crimp (waviness); ensure uniformity of fibre
	Scouring, washing†	Remove lanolin and dirt
	Combing, carding, bowing	Align fibres to desired degree and remove particulates
	Scouring, washing†	Remove lanolin and dirt
	Dyeing†	Produce desired colour
Yarn	Spinning, plying	Produce yarn of desired twist, thickness, uniformity and strength; combine single yarns into cord or plied yarns
	Scouring, washing†	Remove lanolin and dirt
	Dyeing†	Produce desired colour
Textile	Preparing warp for loom	Measure out lengths required, (depending on loom type) create starting border, attach to loom,
	Weaving	Interlock warp and weft to create textile. The warp is tied to the loom under tension; the weft is drawn through the warp yarns at right angles. Add finishing border
Finishing	Fulling	Remove dirt and shrink cloth to strengthen
	Tentering	Stretch shrunken cloth to desired weight
	Teaselling, shearing	Brush surface to raise nap, cut nap to desired length and evenness
	Dyeing†	Produce desired colour
Use/Reuse	Cutting, sewing	Produce desired shape

*Selection of wool is not likely to have been universal.

†Scouring, washing and dyeing may be carried out at several stages during textile preparation, but need not necessarily be carried out more than once.

used as fertilizer (e.g. Biddick 1989, 103). The importance of wool production in sheep-keeping however depended on a complex interaction between the genetic potential for wool quality of local sheep, the nature of agricultural land, workforce availability and prices for agrarian products of all types (Stone 2003). Medieval wool textiles therefore lie at the intersection of technology, society and environment (Andersson Strand *et al.* 2010). The archaeological remains of these spheres of activity are objects of wide application to understanding the medieval past.

Note that in the following sections, a 'wool textile' denotes a textile made of wool, as the term 'woollen' is reserved for a specific preparation technique in a medieval textile context (Table 1.2). Discussion includes finds from 7th-16th centuries from across northern Europe, from Greenland to Finland, and from Norway to Italy.

1.1.1 Sources of evidence for medieval textile research

The modern study of textiles from the Middle Ages employs evidence from archaeological, documentary, iconographic, ethnographic, experimental and scientific fields. Archaeological textiles are the most important source of evidence for the earlier part of the period (to the 12th century, approximately), while documentary records dominate understanding of later medieval textiles: compare the following representative bibliographies: Coatsworth and Owen-Crocker (2007) for the earlier period and Munro (2011) for the latter.

Archaeological textiles have been recovered from northern European graves of the 5th century onwards, mostly in the form of mineralised pseudomorphs (e.g. Bender Jørgensen 1986; Bender Jørgensen 1992; Médard *et al.* 2007; Walton Rogers 2007c) or as material preserved by anoxic waterlogging (e.g. Geijer 1938; Hägg 1991; Christensen and Nockert 2006). Material preserved by anoxic waterlogging predominates in settlement deposits in the 7th century and later. A number of very large assemblages of this type have been recovered (e.g. Hägg *et al.* 1984; Walton 1989; Hägg 1991; Maik 1991; Crowfoot *et al.* 2001; Østergård 2004; Brandenburgh 2010). In addition to the textiles themselves, archaeological finds of the tools used in textile manufacture have been investigated to explore the nature of production (e.g. Walton Rogers 1997; Andersson 1999; Walton Rogers 2001; Walton Rogers 2007b; Mårtensson *et al.* 2009).

Analysis of this material has included collaboration with craft weavers (Hoffmann 1964; Hammarlund and Vestergaard Pedersen 2007; Hammarlund *et al.* 2008) and experimental archaeologists (Pfarr 1999; Goldmann 2007; Reurink and Pedersen 2009), and has incorporated a number of ethnographic parallels (Hoffmann 1964; Weir 1970; Grenander Nyberg 1974; Ling Roth 1981; Schneider and Weiner 1986; Schneider 1987; Hurcombe 2007, 136-7, 140-1). Archaeobotanical and zooarchaeological data have been used to explore dyeing (Hall 1996) and sheep management practices (Crabtree 1996; Loveluck 2007, 96-8). The history of sheep farming has also been of interest (Malden 1915; Trow-Smith 1957; Donkin 1958; Ryder 1983; Stone 2003). Finally, collaboration with natural

Table 1.2. Glossary: relationships of technical terms and tools in medieval textile manufacture. For further details see e.g. Walton (1991), Coatsworth and Owen-Crocker (2007) or Munro (2003).

Element	Process	Tools	Features
Fibre	Combing, carding, bowing	Wool combs	Of several types: (1) short-toothed wool combs used as later cards until their introduction (see below); (2) long-toothed wool combs used for longer, straighter fibres: aligns them tightly, for spinning into smooth, dense, shiny yarn ('worsted' type) , from 13th-14th century; (3) tog combs used in Nordic countries to divide coarse hairs from undercoat in double-coated fleeces
		Wool cards	Introduced 14th century. Best suited for shorter, crimpier fibres: aligns them loosely for spinning into soft fluffy yarns ('woollen' type)
		Wool bow (rare)	As for carding (Chorley 1987)
Yarn	Spinning, plying	(Drop) spindle with whorl, or thigh-rolling with a spindle	Oldest spinning tool: weight and diameter of whorl affect diameter and degree of twist of yarn spun, but this is very dependent on the spinner's skill. Spinning and winding on (winding up the yarn produced) are two separate processes.
		Spindle wheel, also called 'great wheel' or 'walk wheel'	Introduced late 12th/early 13th century. Approximately three times as efficient as spindle with whorl but some differences in quality. Spinning and winding on are separate processes.
		Spinning wheel, also called Saxony wheel	Introduced late 15th century. Has U-shaped flyer which allows simultaneous spinning and winding on: twice as fast as spindle wheel.
		Distaff (optional)	Tool to hold combed/carded/bowed wool fibres as they are spun
	General remarks on spinning directions		Clockwise spinning is denoted Z; anti-clockwise S.
Fabric	Weaving	Warp-weighted loom	Warp is tensioned with weights. Weaving proceeds downwards from top of loom. Weft yarns are beaten into place using a weaving sword. The heddles, which are bar and loop systems producing the temporary separation of warp yarns (shed) to allow the weft to pass, are moved by hand.

Table 1.2 continued.

Element	Process	Tools	Features
Fabric	Weaving	Upright, two-beam loom	Warp is tensioned between two beams in an upright frame. Weaving proceeds upwards from bottom of loom. Weft yarns are packed into place using a toothed beater. The heddles are moved by hand.
		Horizontal, treadle loom	Introduced c. 10th-13th century. Warp is tensioned between two beams in a horizontal frame. Weaving proceeds forwards, away from the weaver. Weft yarns are packed into place using a reed, a slotted wooden frame attached to the loom. The heddles are moved using a lever and pulley system operated by the foot (hence 'treadle'). Faster to operate than other loom types but more costly to set up.
	General remarks on loom-woven textile types		All three looms can produce the two basic ways of combining warp and weft: tabby (over-one-under-one) and twill (over-more-than-one-under-one-or-more), with an offset between each successive weft, producing a diagonal rib (the wale) on the surface of the cloth. Tabby requires only one shed per loom. 2/1 twill (over-two-under-one) requires three and 2/2 twill (over-two-under-two) four. The number of heddles required per loom for each of these options differs: tabby requires one on warp-weighted looms but two on upright and treadle looms; 2/2 twill requires three plus the natural shed on warp-weighted looms, and four on upright and treadle looms; 2/1 twill requires three on warp-weighted and upright looms, but a variety of systems are possible on treadle looms. Twills can be made in plain, chevron, diamond or broken variants, where the direction of the wale is reversed at regular or irregular intervals to create a pattern. Such patterned fabrics are typically made of combed wool, and are not fulled or napped, so that the pattern is visible, but this is not invariably the case. In diamond and chevron variants, the pattern repeat, that is, the number of yarns before the wale is reversed to form the chevron or diamond, is an important variable.
	Narrow-weaving	Weaving tablets or no special tools	A variety of methods of producing tapes and cords: tablet-weaving, finger-looping, braids (Walton Rogers 2007c, 35-6)

Table 1.2 continued.

Element	Process	Tools	Features
Fabric	Non loom-woven textiles	Frame or needles	A variety of methods of producing textiles using a warp yarns in a frame (*sprang*), a single needle and warp yarn (*nålebinding*) or two needles and warp yarn (knitting). Sprang existed before the medieval period and was largely superseded by knitting from the 14th-15th centuries (Buckland 1979; Turnau 1983).
	Non-woven textiles: felt	No special tools	Production of cloth from carded wool by pressure and friction (no spinning or weaving)
Finishing	Fulling and tentering	Tank/trough; (if mechanised) fulling mill with tilt hammers; hooks, frame	Cleans cloth, strengthens cloth by shrinkage, slight matting of surface, stretch cloth afterwards to standard size
	Teaselling, shearing	Teasel frame, shears	Brush surface to raise nap, cut nap to desired length and evenness, repeat until desired quality reached. Typically carried out on textiles made from carded yarn, as their fluffy short fibres make a better surface.
Use/Reuse	Cutting, sewing	Shears, needles	Cutting and re-cutting clothing; joining sections, decorative stitching

scientists has developed methods to identify dyes (Walton and Taylor 1991; Ferreira *et al.* 2004; Clementi *et al.* 2007), date finds (Arneborg *et al.* 1999; Araki and Moini 2011) and analyse fleece quality (Ryder 1968; Walton Rogers 1995; Rast-Eicher 2008; Gleba 2012b). Understanding the nature of decay in archaeological wool textiles is also an important field of study (Needles and Regazzi 1987; Peacock 1996; Chen *et al.* 1998; Peacock 2001).

The manufacture of wool textiles was of central economic importance to a number of European countries during the later Middle Ages, with both raw materials and finished products being traded considerable distances. The documentary records of this industry and trade have generated a very substantial literature (e.g. Salzman 1923; Power 1941; De Poerck 1951; Carus-Wilson 1952; Salzman 1964; Chorley 1987, 1988; Biddick 1989; Munro 1994; Cardon 1999; Munro 2003; Spufford 2006, 232-41, 326-9; Bell *et al.* 2007; Jahnke 2009). The sparse documents referring to wool or wool textiles before the 12th century have also been examined, as have contemporaneous iconographic sources, such as manuscript illustration, painting and sculpture (Owen-Crocker 2004; Walton Rogers 2007c). Iconographic sources are also of use in the later medieval period (Scott 1986; Monnas 2008). Linking documentary references to textiles to specific find types is however difficult and relatively rarely attempted (e.g. Carus-Wilson 1969; Nahlik 1976; Hägg 1994; Walton Rogers 2002, 2882-3; Pritchard 2003; Pedersen and Nosch 2009; Walton Rogers 2011a). Exceptional finds of cloth samples attached to associated contracts are therefore of great interest (Wolff 1983; Cardon 1991).

1.1.2 Foci of medieval archaeological textile research

Archaeological data relating to textiles in the Middle Ages have been used to investigate a range of questions. Most are primarily textile-related, such as the adoption of new weaving technologies (Walton Rogers 2001), the use of textile technical features as markers of culture groups (Bender Jørgensen 1992; Walton Rogers 2007c, 229-52), reconstruction of costume (Hägg 1983; Walton Rogers 2007c, 139-228; Fransen *et al.* 2011), organisation of textile production (Henry 1999; Crummy 2002; Andersson 2007; Walton Rogers 2007a) and identification of trade and cultural links between sites or areas (e.g. Geijer 1980; Ingstad 1982; Bender Jørgensen 1986; Walton 1989; Maik 1990; Bender Jørgensen 1992; Tidow 1995; Rammo 2009). These topics have wider implications for questions of economic and social development in the European Middle Ages, such as the interrelationship between organisation of craft production and gender identity (Härke 2003; Speed and Walton Rogers 2004), or settlement character (e.g. Walton Rogers 1997; Andersson 2003; Walton Rogers 2007a).

Understanding these patterns is however complicated by chronological imbalances of sources of evidence. For example there are no data on the prices of specific textiles from the 8th century, as contemporaneous documents do not record this, and it cannot be measured in archaeological finds; however in the 15th century there are abundant documents referring

to prices of textiles (e.g. Chorley 1987) and raw wool (Munro 1978). Conversely, there is little data on rural textile consumption in the 15th century, as contemporary documents focus on urban concerns, and waterlogged textiles are almost universally found in towns; but rural textile consumption of the early medieval period has been reconstructed from grave good remains (Walton Rogers 2007c). Thus the relative abundance of historical data in the later Middle Ages, and of archaeological data from the earlier period, has meant that different questions have been asked about textile manufacture, distribution and consumption in each period.

Historical thinking about the range and volume of movements of raw wool and wool textiles during the medieval period developed significantly during the 20th century. Writing in 1975, Postan devoted 8 out of 12 pages in a summary of Britain's international trade in the later Middle Ages to a discussion of the wool trade (Postan 1975, 208-21). This is indicative of the dominance of this activity in discussions of later medieval economic development at the mid 20th century (Power 1941; Carus-Wilson 1952). For the earlier medieval period, scholars have suggested or implied that it:

- was close to nil (Grierson 1959; de Roover 1965, 42; Riu 1983; Maik 1983),
- showed continuity with Roman patterns (Ponting 1961, 1; Munro 2003, 216),
- foreshadowed 13th century trade patterns (Sawyer 1965; Lloyd 1977, 1-6),
- was primarily associated with the major trade fairs from the 7th century onwards (Verlinden 1965, 121),

though none of these suggestions claimed mutual exclusivity. By the early 21st century, however, a different historical picture of early medieval economic development had emerged, in which scholars specifically focused on shorter-term fluctuations and regional patterns of economic activity (Hodges 1982; McCormick 2001; Verhulst 2002; Wickham 2008; Barrett 2008; Sindbæk 2011). Thus the historical understanding of medieval wool textile trades can be shown to have shifted its perspective considerably over the last 60 years.

One of the drivers of this change has been the rapid accumulation of archaeological data from excavations in European medieval towns from the 1970s onwards (e.g. Clarke and Ambrosiani 1991; Schofield and Vince 1994; Arnold 1997; Swanson 1999; Richards 2000), which has included significant quantities of textiles. Their analysis has consistently been carried out with reference to historical data and its terms (e.g. Geijer 1938, 40-7; Crowfoot *et al.* 2001; Pedersen and Nosch 2009). Recently there has been an increase in work which is primarily archaeological, focusing on the earlier part of the Middle Ages (Walton Rogers 2007c, a; Siegmüller and Peek 2008).

1.1.3 Established methods of analysis

Modern analysis of an archaeological wool textile assemblage is likely to include: (1) description of all finds in the assemblage in terms of technical features of structure and evidence for subsequent use; and possibly (2) examination of a subset of samples for fleece types and/or dye use. The established core group of variables and their modes of measurement are listed in Table 1.3. Some of these features have functional dependence, e.g. the uniformity of fibre diameter in a sample of fleece can limit the regularity of yarn that can be spun from it. Most features do not have functional dependence, such as spin direction with selvedge type, or yarncount with weave type. However in archaeological assemblages, strong associations between such technical variables are often discernible, and may show strong geographical or temporal variation.

1.2 Identifying the provenance of archaeological textiles

Distinguishing local from non-local artefacts in an archaeological assemblage from a site is an essential step towards understanding the economic, technological, social and cultural links between that site and others, and to establish the range of craft processes occurring there. Textile specialists acknowledge that identifying non-local textiles in an assemblage using analysis of technical features, even combined with dye and fibre characterisation, is 'difficult if not impossible' (Gleba 2012a). Instead the focus has been on distinguishing typical from atypical textiles in an assemblage, with an awareness that this is not the same as distinguishing local from non-local material. However the bases for such identifications are often similar (e.g. Olausson 1988), incorporating assessments of the frequency of specific technical features in objects from similar sites, overall spatial distribution of similar objects, and the identification of raw materials which could not have a local origin.

Arguments for and against the identification of an atypical textile as non-local are highly specific to region and time period, and typically incorporate evidence from other sources (section 1.1.1). This section examines a number of examples where provenance has been suggested, showing how these ideas have been contextualised.

1.2.1 Interpreting atypical/typical technical features

Table 1.4 lists a number of examples of atypical textiles found in medieval contexts, showing the other sources of information which have been used to support a suggestion of non-local origin; examples considered typical of local production are listed in Table 1.5. For the later medieval period documentary sources of evidence are used to support these identifications, but this is more difficult earlier than c. AD 1200, when most arguments are based on frequency and quality. It is clear that analysts are aware of a number of potential confounding factors in these identifications, which include:

Table 1.3. Variables measured in medieval archaeological wool textile analysis (Walton and Eastwood 1984). *denotes not recorded by all researchers. †denotes typically carried out on a subset of textiles in an assemblage.

Element	Feature	Measurement	Measurement type
Overall	Size of find	Maximum width and height parallel to weave systems	Quantitative
	Present colour*	Visual impression	Qualitative
	Dye†	Identification of dye source(s), sometimes mordant or other special conditions of dye bath (Walton and Taylor 1991)	Qualitative
Fibre	Fleece type†	Diameter range and distribution of 100 fibres	Quantitative and qualitative
Yarn	Yarn spin/ply direction	Z or S	Qualitative
	Yarn spin/ply tightness*	Angle to direction of yarn	Quantitative
	Yarn diameter*	Maximum and minimum	Quantitative
Textile	Yarncount	Average per cm in both warp and weft	Quantitative
	Construction (weave type)	Typically tabby, 2/1 twill, 2/2 twill, tablet weaving, braid techniques. Twill subtypes: chevron (regular reverses in either warp or weft), diamond (regular reverses in both systems) or broken (irregular reverses in one system). The nature of the reverse and the regularity of the patterns are also recorded.	Qualitative
	Structural features	Nature of selvedges, starting borders, pile, weaving faults (if present), number of wefts in use	Qualitative
Finishing	Napped surface, pile	Density, evenness (if present)	Qualitative
Use/Reuse	Cutting, sewing	Folds and fold marks (hems or seams), sewing (structural or decorative), fastenings, cut edges, items joined together, stitching holes, knots, etc.	Qualitative
	Wear	Worn patches, matting (if present), presence of paint, tar or resin	Qualitative
	Context	Deposit type (cess pit, midden, land reclamation dump, ritual deposit, etc). In graves: location on body, relationship to other textiles in grave	Qualitative

Table 1.4. Interpreting atypical textiles from medieval assemblages. Sample ID refers to analyses in Chapters 7–8.

Textile description	Region/site	Period	Suggested interpretation	Other data used	Reference	Sample ID
Plain 2/2 ZZ twills ('Haraldskjær' type)	Norway	3rd century onwards	Local: spread of the warp-weighted loom and abandonment of the upright loom	Widespread earlier in DK; associated with finds of loom weights	(Bender Jørgensen 2003b, 93-6)	
Diamond twill with Z-spun warp and S-spun weft, mostly 20/18 pattern unit ('Virring' type)	Scandinavia	3rd–4th centuries	Non-local	Usually in more developed (finer) wool types than Haraldskjær and Huldremose types (both widespread)	(Bender Jørgensen 2003b, 93-6)	
Textiles with tubular selvedges, 2/1 twills, and textiles with soft finishing found at same sites	East Anglia	5th–7th century	Local: survivals of Romano-British textile cultures within Anglian dominated area	Toponymic evidence of geographic/political boundaries; grave goods in local cemeteries; earlier archaeology of wider region; documentary sources	(Walton Rogers 2012a)	
Madder-dyed 2/1 twill	Hessens, North Germany	7th–8th century	Possibly non-local	Both 2/1 twills and madder dye are rare in textile collections from this region at this date	(Tidow 1995; Walton Rogers 1995)	4329
2/1 twills	Urban deposits in England	10th century onwards	Local: re-introduction of the upright loom	Iconographic evidence; historical evidence; absence of loom weights; change of tool types to those associated with upright loom; nature of 2/1 twill textile construction	(Walton Rogers 2001)	4081-3
Tabby textiles, heavily fulled and napped, mostly in SS yarns	Reykholt, Iceland	*c*. AD 1400–1600	Non-local	Technical features (individually and in combination) are rare in Scandinavia but widespread in mainland Europe, where manufacture is supported by historical, archaeological and iconographic data	(Walton Rogers 2012b)	2903, 3966, 3967

Table 1.4 continued.

Textile description	Region/site	Period	Suggested interpretation	Other data used	Reference	Sample ID
Fulled, dyed textiles in Fine-type wool	Tartu, Estonia	14th–15th century	Non-local	Wool type rare in region; cloth types resemble those from more western regions of Europe, where local manufacture is supported by historical, archaeological and iconographic data	(Rammo 2009)	
Knitting fragment, kermes dyed, in Fine-type fleece	Newcastle upon Tyne	Early 15th century	Non-local	Unusual fleece type; unusual and very costly dye; unusual technique for region and period	(Walton 1981, 200)	3944
Knitted caps	Newcastle upon Tyne	Early 16th century	Local: introduction of technique	Fleece types resemble other local material; documentary evidence for arrival of technique; contemporaneous finds of knitting at other sites in Britain	(Walton 1981, 200)	3950, 3951

Table 1.5. Interpreting typical textiles from medieval assemblages. Sample ID refers to analyses in Chapters 7–8.

Textile description	Region/site	Period	Interpretation	Other data used	Reference	Sample ID
Spin-patterned tabby, normally striped but occasionally checked ('Gudmingegaard' type)	South eastern Germany	5th–8th century	Typical	Predominant in this area, infrequent in other areas	(Bender Jørgensen 2003a)	
ZS tabbies	North Germany	7th–10th centuries	Typical	Ubiquitous in this region and period	(Hägg *et al.* 1984, 111)	4331
ZS tabbies and 2/2 twills	York, North East England	9th–11th centuries	Typical	Common types; unremarkable quality	(Walton 1989; Walton 1990)	4060a, 4064, 4066-70, 4073, etc
ZS 2/2 twills with pigmented hard-spun warp in Hairy fleece and pale, loosely-spun weft in Hairy Medium fleece (*waðmál*)	Reykholt, Iceland	*c*. AD 1000–1600	Typical	Abundant in Greenland and across Scandinavia in the later medieval period (Walton 1989, 340-1; Østergård 2004)	(Walton Rogers 2012b)	2895-9, 3962-4, 2902, 4120
Fulled woollen SS tabbies and plain twills	Newcastle upon Tyne	15th–16th century	Typical	Widespread in contemporaneous urban assemblages; documentary evidence for local production of woollens	(Walton 1981, 194, 204-5)	3946-8, 3952-7

- rarity due to low volumes of production, either because of high cost (in materials or time), or low demand, e.g. considering an item appropriate for only a small number of uses or occasions (Schneider 1987).
- movement of technology or of textile style rather than movement of textiles. The processes of development, adoption and competition of technologies depend on their functional, political, economic and social contexts (Pfaffenberger 1992; Dobres and Hoffman 1994). Geographical spread of technology need not proceed at the same rate or involve the same places as the spread of goods.

1.2.2 Exotic raw materials

For a number of the interpretations included in Tables 1.4 and 1.5, arguments for local/non-local origin have been supported by analyses of the range of fibre diameters in a wool textile. Sheep were farmed across northern Europe in the medieval period, but the type and quality of fleece they produced varied (Munro 1978; Ryder 1984). Fleece quality refers to both fibre diameter and uniformity, and reflects genetic inheritance, environmental conditions and farming practice (e.g. Short 1955; Brown and Crook 2005; Safari *et al.* 2005; Geenty *et al.* 2009). A single fleece contains wool of several different qualities, being finest around the neck and roughest in the britch, and these can be separated by sorting and the initial fibre preparation step of combing, carding or bowing. Systems for analysing fibre characteristics in archaeological wool samples and relating them to breed groups (e.g. mountain, hill, downland, longwool) have been developed by Ryder (1968, 1981, 1991) and Rast-Eicher (2008). However relatively few examples of non-local textiles have been identified in this way, as fleece type analysis is laborious and not universally applied.

There is an obvious qualification to using non-local fleece types as evidence of non-local origin: a non-local raw material is not the same as non-local textile, and identification of movement of raw materials is not a direct marker of movement of textiles, but could mark independent movements of raw materials. Large international markets in raw wool existed by the 13th century, and for dyes even at the beginning of the 10th century (e.g. madder in McCormick 2001, 651), and it is not clear how far back either of these trade flows existed. Therefore archaeological identifications of non-local textiles on the basis of their raw materials are typically combined with other non-local indicators.

1.2.3 Competing interpretations

The debate over the identity of ‘Frisian cloth’ provides an example of how textile interpretation can change depending on the interpretation and importance placed on different types of auxiliary data. This historical term, used in the 8th–10th century, mostly in the Frankish Empire (references in Ingstad 1979; van Uytven 1983; Walton 1989, 416; Hägg 1994), clearly refers to cloths that were moved long distances.

Geijer first associated this term with the finest 2/1 and 2/2 ZZ diamond and chevron twills from 9th–10th century Birka, Sweden (1938, 25) because of their very high quality which was

almost without parallel at the time. She considered that they must have been imports to Viking Age Sweden, possibly by Frisian merchants, and that the most plausible interpretation of the available documentary evidence was that they were mostly made in Frisia in specialist workshops (Geijer 1938, 40-7). Alternative suggestions for the origins of these finds were: the Levant, because of technical similarities to finds from Palmyra (Hoffmann 1964, 227-57; Nockert 1988); Western Norway, because of technical similarities to finds in graves there (Bender Jørgensen 1992, 138); or the British Isles, because these textiles were frequently found in graves with Anglo-Irish metalwork (Ingstad 1979). More recently however, Andersson Strand has demonstrated that the fine yarns and weave patterns in these textiles could have been made with the spinning and weaving equipment found at the settlement of Birka (Andersson 2003).

An alternative identification of 'Frisian cloth' was made by Bender Jørgensen, who suggested that the term probably referred to 2/2 ZS chevron and diamond twills with a 20Z/18S pattern repeat (Bender Jørgensen 1992, 142-3) because these types are common at sites in Frisia (Tidow 1995). A further suggestion by Hägg argued that plain fulled 2/2 ZS twills should be so considered, because this textile type was used for cloaks or coats in earlier men's costume in Northern Germany (identified from grave goods), and historical references suggest the use of 'Frisian cloths' as coat/cloak materials (Hägg 1994). This position was seconded by Siegmüller and Peek (2008) who stressed the waterproof nature of fabrics made in this way from relatively primitive wool types, which are common at coastal sites in northern Germany and the Netherlands (Walton Rogers 1995).

At present therefore, there is no consensus on which of the above mutually exclusive hypotheses may be correct, nor on which set of data should have precedence. Without the trial of new methodologies or new ways of interpreting the data already gathered, there can be no resolution to these inquiries. In particular, the null hypotheses that the above-discussed works have sought to disprove would themselves be interesting to explore in more detail, for example that:

1. the meaning of 'Frisian cloth' changed significantly over the period of its attestation, either in the nature of the cloth made or the location(s) of its manufacture;
2. the term may have been a portmanteau word for a range of textiles made in Frisia or made elsewhere but traded by Frisian merchants. This range may itself may have changed over time.
3. the methods employed currently by textile archaeologists do not record the features which distinguished 'Frisian cloths' from other cloths to contemporaneous observers.

These alternative hypotheses all point to a more variable, less structured conception of early medieval textile movements than has so far been considered, but which is not inherently unlikely. It is possible to suggest methods of inquiry which could explore them, particularly if provenancing methods could be developed which are independent of textile structure.

1.2.4 Summary

This discussion has illustrated the willingness of textile researchers to incorporate data from other disciplines into assessments of textile origin. Information on the nature of construction of a textile has been combined with: assessments of find frequency and distribution; associated archaeological finds of clothing accessories and textile tools; ethnographic and experimental explorations of textile manufacturing processes; understanding of the relationship between wool type and sheep breed group; and multiple interpretations of historical documents. This section has also explored an example where this flexibility has led to competing assessments of textile origin. Continuing to improve our understanding of movements of textiles and their raw materials throughout the Middle Ages is important because of the economic significance of these commodities, and the social significance of how their manufacture was organised. An independent method of establishing the origin of a sample of archaeological wool would be very useful in this context.

1.3 Isotopic provenancing of organic materials

1.3.1 Previous applications

Most isotopic investigations of provenance of organic materials in archaeology have used a combination of oxygen ($\delta^{18}O$) and strontium ($^{87}Sr/^{86}Sr$) isotopes (e.g. Turner *et al.* 2009; Viner *et al.* 2010; Evans *et al.* 2012; Sjögren and Price 2013). Strontium is a trace element, found in relatively-to-very low concentrations, where it derives principally from soils and bedrock in any location (Sealy 2001). In contrast, oxygen is much more abundant in organic materials, and its isotopic composition is related to temperature, altitude, precipitation and distance from a coast, i.e. local climate (Pollard and Willson 2001). Combining these two independent measures allows tighter resolution of provenancing. The first investigations into isotopic provenancing in wool textiles focused on the strontium isotopic system (von Carnap-Bornheim *et al.* 2007; Frei *et al.* 2009a; Frei *et al.* 2009b; Frei *et al.* 2010). However concern has been raised regarding the robustness of $^{87}Sr/^{86}Sr$ measurements to diagenesis in organic materials (Budd *et al.* 2000; Trickett *et al.* 2003), which is at least in part due to the fact that it is a trace element.

The elements carbon, nitrogen, hydrogen and sulfur, are like oxygen, abundant in organic materials: it is of these atoms that the overwhelming majority of the soft tissues of organisms are built. Their isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{34}S$, respectively) have only occasionally been used in archaeology to explore geographic origin (Arnay-de-la-Rosa *et al.* 2010; Barrett *et al.* 2008; Schroeder *et al.* 2009; Pollard *et al.* 2011), but have instead been widely employed to investigate diet (e.g. Sealy 2001; Craig *et al.* 2006; Reynard and Hedges 2008; Nehlich *et al.* 2012). However, there is extensive evidence of these isotopes' geographic variation from analysis of keratin in studies of modern human hair (Ehleringer *et al.* 2008; Valenzuela *et al.*

2011; Valenzuela *et al.* 2012) and bird feathers (Hebert and Wassenaar 2005; Brattström *et al.* 2010) and from food traceability studies (Hedges *et al.* 2005; Camin *et al.* 2007; Camin *et al.* 2009; Schellenberg *et al.* 2010). They are therefore also good candidates for exploring the geographical origin of archaeological material artefacts made from organic raw materials.

1.3.2 Isotope basics

All isotopic tracing techniques (Wassenaar and Hobson 2008) examine the chemical composition of a tissue, focusing on the number of neutrons in the nuclei of the atoms of a particular element. Some nuclei with additional neutrons are unstable (such as carbon-14) and these are not studied using this technique. However carbon, nitrogen, hydrogen, oxygen and sulfur all have stable versions of their atoms with different numbers of neutrons: carbon-12 *vs.* carbon-13, nitrogen-14 *vs.* nitrogen-15, hydrogen-1 *vs.* hydrogen-2, oxygen-16 *vs.* oxygen-18, and sulfur-34 *vs*. sulfur-32. For all these elements, the fewer-neutron, lighter version (or isotope) is far more abundant (>94%) than the heavier. Isotopic analysis measures the proportion of the two versions of an element, compared to an external standard.

All the atoms in the body of an organism are derived from the organism's food, water and air. The isotopic composition of their body tissues therefore depends on the isotopic composition of diet, drinking water and air (this last affects oxygen isotope composition only). Different organisms (e.g. bacteria, algae, fungi, plants, birds, reptiles, mammals, etc.) concentrate the heavier isotopes to a greater or lesser extent in each of their tissues, depending on the nature of the sequences of reactions needed in the organism's body to synthesise the tissue from its precursors absorbed from the environment. The isotope value of a sample of organic tissue therefore provides information about the diet and metabolism of the organism that grew it, which are dependent on the environment, and hence the location in space and time, of the organism. These relationships are the basis of many applications of isotope measurements to questions of ecology, climatology, and oceanography, as well as palaeo-applications of all these fields (Hoefs 1997). The relationships between isotopic composition and geographic location is a recognised subfield within isotopic bio- and geo-chemistry (Bowen 2010).

1.3.3 Specific application to sheep wool samples

In the case of sheep wool, its isotopic composition indicates the sheep's dietary, drinking and respiratory consumption. Sheep diet consists of local plants and groundwater. The isotope values of the plants depend on plant species and growing conditions (Sealy 2001), and on rainwater isotope values (Wassenaar and Hobson 2008). Plants and rainfall isotope values vary across Europe with climate, reflecting the various influences of latitude, longitude, altitude, continentality and season (Bowen and Revenaugh 2003; Darling and Talbot 2003; Darling *et al.* 2003; Martin and Martin 2003; e.g. Camin *et al.* 2009). The

isotope values of sheep tissues therefore reflect the location and nature of the pasture(s) they graze (Piasentier *et al.* 2003; Hedges *et al.* 2005; Camin *et al.* 2007; Perini *et al.* 2009), with additional contributions reflecting the tissue under study and metabolic variations between individual sheep. Therefore the isotopic composition of a sample of sheep wool will vary systematically with geographic location, and can be used as an indicator of origin if geographic patterns of isotopic variation are known or can be predicted (compare Chesson *et al.* 2010; Valenzuela *et al.* 2011). The resolution of the technique for provenancing is limited by the inherent variability in isotope composition between tissues from individual sheep in the same flock, e.g. due to differences of age, sex, fleece colour and health status.

Complicating this analysis are the effects of differences in farming practice. The types of plants consumed by domesticated sheep are controlled by humans (Figure 1.1) , either by designating grazing location or providing fodder (compare the effects of cultural dietary practices on human hair isotopic composition: Valenzuela *et al.* 2012). The 'natural' local isotope values for any location may therefore be affected by practices such as transhumance to altitude, intensive *vs.* extensive stock keeping, and provision of fodder during seasons of low plant growth (winter in cold areas and summer in hot). Unusual past foddering practices, such as the use of fish meal (Kosiba *et al.* 2007) and seaweed (Balasse *et al.* 2006), are discernible isotopically. Therefore the isotopic composition of a sample of sheep wool must be interpreted not only with reference to its location but also to its method of rearing.

In summary, we expect that the isotope values of sheep wool from a single flock will cluster (but they will not be identical), and that the values of wool from flocks kept in different vegetation zones/climates and/or under different farming conditions will differ. These hypotheses were tested in chapters 2 and 3 respectively.

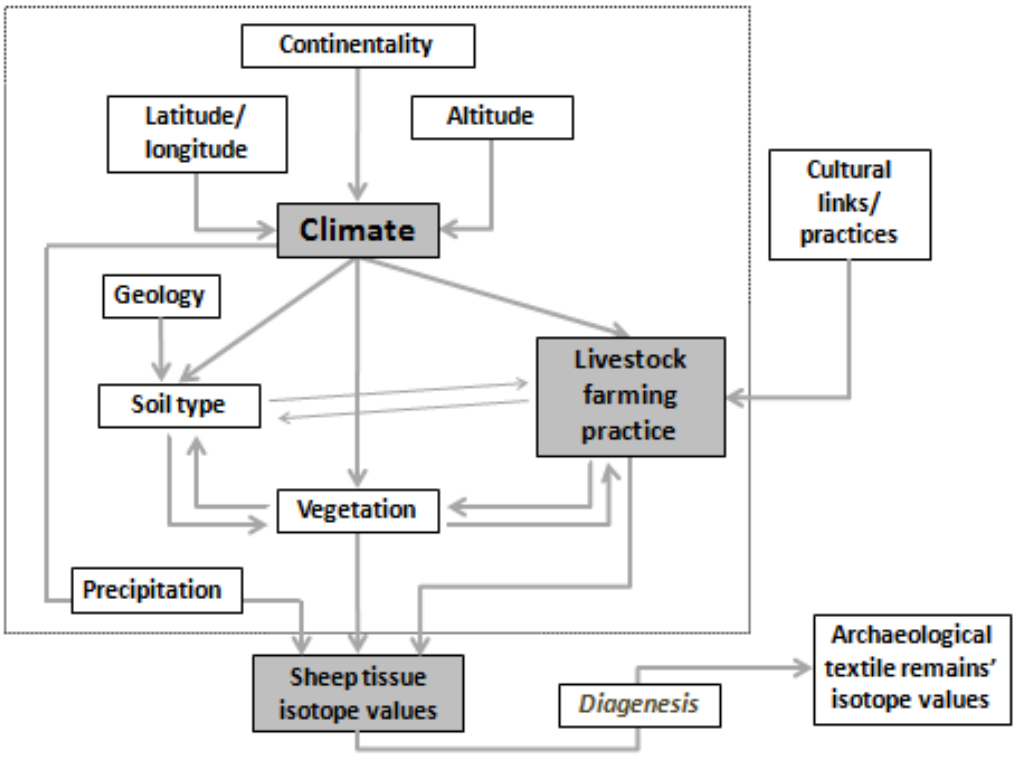

Figure 1.1. Schematic interrelationship of environmental and husbandry practices and their influence on sheep tissue isotope values.

1.3.3 Significance of taphonomic decay in archaeological wool samples

Wool is composed largely of proteins called keratins (Popescu and Wortmann 2010). There are several hundred types, which are combined to form the various structures of the wool fibre (Plowman 2003; Figure 1.2).

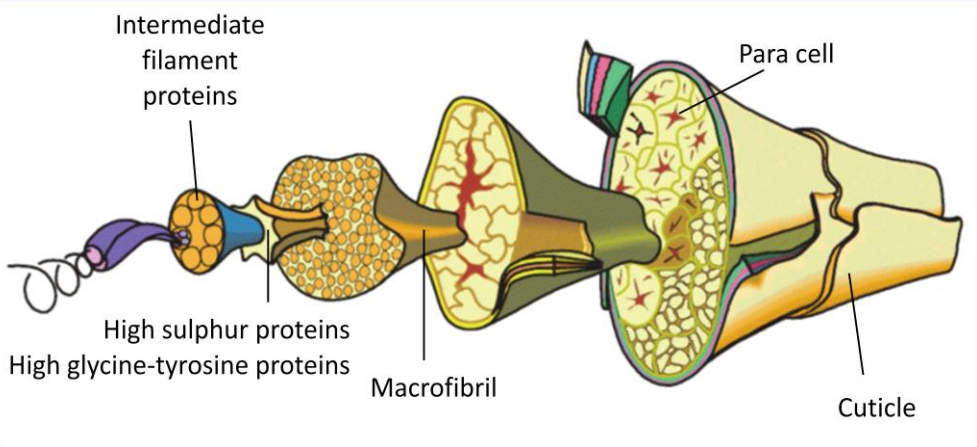

Figure 1.2. Structure of a mammalian hair fibre.

Proteins are composed of long chains of amino acids (AAs; Figure 1.3). Twenty different types occur in mammalian proteins, and they show a range of isotope values due to the fact that they are synthesised in the body in a variety of ways, and from different components of diet (McCullagh *et al.* 2005; Styring *et al.* 2010; Fogel *et al.* 2010; cited in Boecklen *et al.* 2011). The bulk isotopic composition of a hair fibre is therefore an average of those the AAs which make it up. Other minor components of a hair fibre, such as lipids and melanin, also make small contributions to overall isotope values.

The proportions of the different types of keratin proteins differ little between wool from different sheep breeds (Flanagan *et al.* 2002), but do vary significantly as hair fibres decay during burial (Wilson *et al.* 2007). Pre-burial treatments of the fibres, such as exposure to light during use, mechanical stress during manufacture, and chemical change caused by mordanting or washing, may also directly affect protein proportions and additionally may promote or retard decay during burial. Therefore it is possible that the changes which have occurred in archaeological wool samples during burial may have affected their isotope composition. These effects were examined in samples of modern wool which had been experimentally buried (Chapters 4 and 5) or degraded in water at high temperature (Chapter 4). The state of degradation of the residual decayed wool fibres was also assessed by:

- elemental analysis, quantifying the proportions of carbon, nitrogen, hydrogen, oxygen and sulfur present, and
- AA analysis, quantifying the proportions of AAs present, to indicate the degree of (long chain) protein breakdown into smaller units (peptides and/or individual AAs).

The aim of these analyses was to gain additional information on the nature of the changes occurring in the hair fibre during decay, and thus gain insight into the mechanisms of any isotopic change.

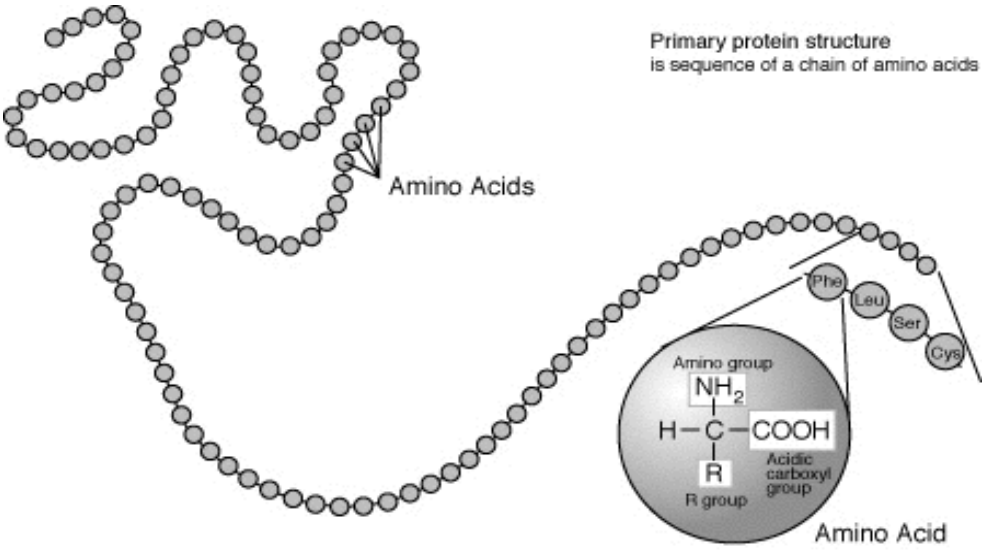

Figure 1.3. The primary structure of proteins. Image from Wikimedia commons.

1.3.4 Synthesis

Chapters 2–5 of this thesis, which focused entirely on modern samples of sheep wool, established the scientific context in which isotopic data obtained from archaeological wool samples can be interpreted. They established the degree of resolution of this provenancing technique in samples from modern flocks (Chapter 3) and how much this was affected by flock composition and husbandry practice (Chapters 2 and 3), and diagenesis (Chapters 4 and 5). At a single archaeological site, wool imported from areas of different climates and/or different farming practice are expected to show isotope composition which are outlying from site median, established by analysis of local-type textiles, but confirmed by analysis of raw wool and bone collagen isotope values from the same site. Suspected imported material is therefore not identified in isolation, but by comparison to local textiles' and bone samples' isotope compositions.

1.4 Integrating isotopic data with established artefact approaches

Identifying the origin of the raw material in an archaeological object is only one part of understanding that object. The isotopic composition of a sample of wool can only indicate the environment, and hence location, of the sheep that grew the sample, which need not correspond to the location of manufacture of a textile, or of is subsequent use(s). At rural sites, and in the early medieval period, it is likely that most textiles were made domestically from local wool (Walton Rogers 2007c, 41-8), but in the later period, and at urban sites, this is much less likely (Munro 2003). For a fuller understanding of an artefact's biography, features of construction, wear and deposition must be considered with the analytical data.

This thesis (Chapters 7 and 8) therefore considered isotopic composition data in the context of artefactual understandings of the textiles and the assemblages from which they were drawn, to attempt to distinguish between the movement of

- raw wool (typical construction, non-local composition)
- finished textiles (atypical construction, non-local composition) and
- textile techniques (atypical construction, local composition).

These three commodities (textiles, raw wool and textile craft knowledge) were unlikely to be under the same pressures of economic or social selection, and could therefore in theory move independently. In practice, this is not universally likely, because the nature of the finished textile is often closely related to the technical affordance of its raw materials (Knappett 2005; cited in Hodder 2011), though this can be mediated by craft knowledge. This integration therefore offered an opportunity to examine the underlying hypotheses of established methods of textile provenancing, which have rarely been explicitly articulated or debated (Chapter 6).

1.5 Summary and research questions

This research applied stable isotope analysis to wool textiles in order to explore their origin. The study focused on textiles from AD 700-1600 from sites bordering the North Sea, a period and region for which there is historical evidence for textile movement which cannot always be closely related to extant archaeological wool samples.

Research questions were as follows:

1. *Can light stable isotopic analysis identify the origin of samples of archaeological wool?* To answer this, the analytical method was applied to modern wool samples from the region in question (environmental context) and to wool samples which had been experimentally decayed (taphonomic context) before being applied to archaeological samples.
2. *How can isotopic data can be understood in textile artefactual context?* Isotopic data, indicating local/non-local raw material, was considered in the light of analyses of structural and stylistic features of textiles, indicating typical or atypical manufacturing for the site in question. Agreements and disagreements between isotopic and established provenancing methods (by dye, fibre and textile construction) were considered in detail.

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2. Isotopic relationships between bone collagen and wool keratin in domesticated sheep

Abstract

A variety of metabolic, dietary and climatic influences on isotopic variation have been established in mammalian hair. The relevance of these factors to collagen isotopic composition is unknown, but would be of great interest to zooarchaeological analyses of faunal skeletal tissue.

The relationships between carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), non-exchangeable hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) values of defatted, demineralised and gelatinised bone collagen and defatted wool keratin from two sheep flocks (n=20,5) in the UK were investigated, including testing for the effects of nutritional plane, sex, pregnancy and season of slaughter. Sulfur ($\delta^{34}S$) composition was also investigated for tissues from the smaller flock. Single amino acid (AA) $\delta^{13}C$ composition were examined by liquid chromatography-isotope ratio mass spectrometry (LC–IRMS) (n=2), which resolved 19 of 22 constituent AAs.

Bulk collagen was enriched over bulk keratin in $\delta^{13}C$ by 2.0–2.7‰ and in $\delta^{2}H$ by 29–40‰ but depleted relative to keratin in $\delta^{18}O$ by 1.8‰. Differences in $\delta^{15}N$ were within experimental error. Collagen samples were generally more enriched in $\delta^{34}S$ than keratin, but this was vary variable (range -0.1–3.3‰). Both collagen and keratin bulk $\delta^{13}C$ showed seasonal variation. Collagen $\delta^{13}C$ and $\delta^{15}N$ were depleted in pregnant compared to empty ewes; $\delta^{15}N$ in keratin showed the same pattern. For collagen, $\delta^{15}N$ and $\delta^{18}O$ were depleted and $\delta^{2}H$ was enriched in males compared to females. The difference in $\delta^{2}H$ between keratin and collagen was significantly greater in males than females. Nutritional plane did not significantly affect isotope values. Single AA $\delta^{13}C$ values were almost universally slightly enriched in collagen over keratin (median 0.7–0.9 ± 0.1–0.5‰ per AA), but serine and glycine showed greater enrichment (2.7–6.4 ± 0.5‰).

This study established isotopic offsets between bulk sheep bone collagen and hair keratin for $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$. Pregnancy, sex and season of slaughter significantly affected isotope values but did not change overall keratin-collagen relationships. Inter-tissue offsets were due to differences in composition, AA routing and probably turnover time. This dataset forms a baseline for isotopic investigations into archaeological sheep tissues.

Keywords: protein, amino acid, collagen, keratin, metabolism, environment, sheep, wool, light stable isotopes

2.1 Introduction

Isotope ecology studies of domesticated mammals typically focus on tissues which can be sampled non-invasively, such as hair, blood, or breath (e.g. Ayliffe *et al.* 2004; Cryan *et al.* 2004; Männel *et al.* 2007; Wassenaar and Hobson 2008; Wittmer *et al.* 2010; Longinelli and Selmo 2011; Zazzo *et al.* 2011), or those which are of agricultural interest, such as milk (e.g. Kornexl *et al.* 1997; Chesson *et al.* 2010; Bontempo *et al.* 2012) or muscle tissue (e.g. González-Martín *et al.* 2001; Schmidt *et al.* 2005; Camin *et al.* 2007; Bahar *et al.* 2008). These tissues are however found rarely or not at all in archaeological deposits (Karsten *et al.* 2012). Zooarchaeological isotope analysis has instead focused on bone and tooth tissues, as they are more resistant to degradation and are widely preserved (e.g. Copley *et al.* 2004; Balasse *et al.* 2006; Henton *et al.* 2009; Viner *et al.* 2010; Towers *et al.* 2011; Makarewicz and Tuross 2012). Here, analysis of skeletal elements of domesticate species for size, stage of development and markers of damage are used to examine herd/flock age, sex structures, pathology, and hence animal management practices (e.g. Greenfield *et al.* 1988; Crabtree 1996; Thomas 2005). Being able to apply the isotopic features of animal metabolism and management identified in modern studies to archaeological tissues is of great interest and would add significantly to understanding of past husbandry practices.

This study therefore focused on hair keratin and bone collagen, probably the most widely used tissues in domesticate mammalian ecological and archaeological research respectively. The relationships between bulk hair keratin and bone collagen isotope values have been examined in a number of species (Table 2.1; to the authors' knowledge there is no such $\delta^{24}S$ data). Both collagen and keratin are typically enriched over diet in both $\delta^{13}C$ and $\delta^{15}N$, with a greater enrichment for collagen than keratin in both isotopes. Patterns are less clear for $\delta^{2}H$ and $\delta^{18}O$ where very little collagen data has been obtained. For these isotopes, inputs from drinking water and atmospheric O_2 are significant in addition to dietary inputs. However for organisms consuming both food and water of local origin, both values should show a systematic relationship, and both should be strongly related to local precipitation values (Bowen *et al.* 2009).

Tissue is ultimately derived from that of an organism's dietary, drinking water and respiratory intake over the period of tissue formation. The isotopic composition of the tissues are therefore related to the compositions of intake. These relationships can be extremely complex (Caut *et al.* 2009 and commenting articles). The various tissues within an organism differ in: (1) composition, (2) rate of growth, (3) rate of turnover, and (4) routing of nutrients (Boecklen *et al.* 2011). In addition to dietary inputs, their isotopic compositions therefore reflect: (1) molecular and elemental composition, (2) catabolic and anabolic pathways to tissue formation and breakdown, (3) different exposure times to the various metabolic pools of nutrients in the body, and (4) differences in routing to tissue from these pools. As collagen and keratin are both proteins, comparison between them focuses on amino acid (AA) metabolism, period of growth and turnover, and routing of nutrients.

Table 2.1. Previously published relationships between keratin and collagen isotope values in mammals.

	Contributions	Species	Relative positions	Reference
$\delta^{13}C$	Dietary carbohydrate, protein, lipid	Humans	Collagen enriched 0–1‰ over keratin, high degree of individual variability	(O'Connell and Hedges 1999; O'Connell *et al.* 2001)
		Mammoths	Collagen enriched 1.3‰ over keratin	(Iacumin *et al.* 2005)
		Mice	Collagen enriched *c*. 1.8‰ over keratin	(DeNiro and Epstein 1978)
		Mice	Collagen enriched by 1–4‰ over (non-defatted) hair samples on adequate-nutrient diets, larger offset with low protein diet (7‰), smaller with high protein diet (1%)	(Tieszen and Fagre 1993)
		Pigs (juvenile)	Collagen enriched 0–4‰ over keratin, high degree of variability with growth rate	(Warinner and Tuross 2010)
		Greater kudu, springbok, warthog, oryx, blue wildebeest	Collagen enriched 0–2‰ over keratin	(Codron *et al.* 2012)
		Blesbok, red hartebeest	Collagen enriched 2–3‰ over keratin	(Codron *et al.* 2012)
$\delta^{15}N$	Dietary protein	Humans	Collagen enriched 0–2‰ over keratin, high degree of individual variability	(O'Connell and Hedges 1999; O'Connell et al. 2001)
		Mammoths	Collagen enriched 1.7‰ over keratin	(Iacumin *et al.* 2005),
		Mice	Collagen enriched -0.4–+0.7‰ over keratin	(DeNiro and Epstein 1978)
		Pigs (juvenile)	No clear pattern: all collagen and keratin within ±1‰	(Warinner and Tuross 2010)

Table 2.1 continued.

	Contributions	Species	Relative positions	Reference
$\delta^{15}N$	Dietary protein	Greater kudu, warthog, blue wildebeest, blesbok, red hartebeest	Collagen and keratin within ±1‰	(Codron *et al.* 2012)
		Springbok	Keratin enriched 3–4‰ over bone collagen	(Codron *et al.* 2012)
$\delta^{2}H$	Dietary carbohydrate, protein, lipid; drinking water	Rats	Collagen enriched 32–44‰ over keratin	(Kirsanow and Tuross 2011)
		Pigs	Collagen enriched 10–20‰ over keratin	(Tuross *et al.* 2008)
		Pigs (juvenile)	Collagen enriched 25–40‰ over keratin	(Warinner and Tuross 2010)
$\delta^{18}O$	Dietary carbohydrate, protein, lipid; drinking water; air	Rats	No difference between tissues	(Kirsanow and Tuross 2011)
		Pigs	Collagen depleted 2–3‰ relative to keratin	(Tuross *et al.* 2008)
		Pigs (juvenile)	Collagen enriched 1.5–3.0‰ over keratin	(Warinner and Tuross 2010)
$\delta^{34}S$	Dietary protein	-	-	-

2.1.1 Tissue composition

Keratin proteins make up more than 90% of the dry hair fibre by mass (Washburn *et al.* 1958; Popescu and Höcker 2007), and collagen makes up 25–50% of dry bone mass (Rogers *et al.* 1952). The individual AAs in both collagen and keratin have been shown to differ strongly in $\delta^{13}C$ (e.g. Hare *et al.* 1991; Fogel *et al.* 1997; Howland *et al.* 2003; McCullagh *et al.* 2005; Honch *et al.* 2012) and $\delta^{15}N$ (Hare *et al.* 1991; Fogel *et al.* 1997; Styring *et al.* 2010) values, because of differences in their synthetic and metabolic pathways within the body. Single AA $\delta^{13}C$ analysis in both collagen and keratin from a number of human individuals showed that different bulk compositions of collagen and keratin were largely due to their different AA compositions (Raghavan *et al.* 2010), but suggested that seasonal variation in diet and/or differences in routing of nutrients to the two tissues were not negligible factors.

2.1.2 Tissue turnover rate

Collagen, a storage tissue, is continually laid down and remobilised over an organism's lifetime. Rate of total turnover however varies greatly by age, health status, and skeletal element (e.g. Delmas 1995; Babraj *et al.* 2002) and also by species. Rates as low as 1.5–4% per year have been measured for human cortical bone in adulthood, or up to 15% per year in adolescence (Hedges *et al.* 2007), and as high as 135% per year in beagle trabecular bone (Kimmel and Jee 1982). At present therefore it is not clear whether turnover rates in domesticate mammalian species should be measured in terms of months or years. Keratin proteins, in contrast, are not remodelled after formation (Popescu and Höcker 2007), and their composition therefore reflects a shorter period of dietary intake and remobilised material, measured in weeks (e.g. Schwertl *et al.* 2003; Zazzo *et al.* 2008; Cerling *et al.* 2009; Auerswald *et al.* 2011; Zazzo *et al.* 2011). Comparison between hair keratin and bone collagen isotope values ($\Delta_{keratin\text{-}collagen}$) may therefore discern both shorter and longer term dietary inputs.

Isotopically significant short-term changes in diet in domesticated animals can be either environmental or anthropogenic. Sources of environmental variation include seasonal changes in forage type availability (Kohn *et al.* 1998; Wittmer *et al.* 2010), forage isotopic composition (Kohn 1996; Heaton 1999; Dawson *et al.* 2002), and drinking water isotopic composition (Kirsanow *et al.* 2008). Anthropogenic effects include provision of fodder during non-plant-growth seasons (Ayliffe *et al.* 2004; Makarewicz and Tuross 2006; Schnyder *et al.* 2006), and transhumance to alternative pastures, whether horizontal (Zazzo *et al.* 2011) or vertical (Männel *et al.* 2007). In addition, weathering of keratin tissues can affect keratin $\delta^{34}S$, which is affected by stalling practices (Auerswald *et al.* 2011). It is therefore likely that bone collagen and hair keratin in domesticate mammals integrate different periods of dietary, climatic and metabolic input, and that this contributes to the difference in isotope values between these tissues.

2.1.3 Factors affecting nutrient routing to tissue

Isotopic offsets between keratin and collagen ($\Delta_{keratin\text{-}collagen}$) can be considered a compound of the offsets between each tissue and diet, *i.e*. $\Delta_{diet\text{-}keratin}$ - $\Delta_{diet\text{-}collagen}$. These trophic relationships have been much more extensively studied than $\Delta_{keratin\text{-}collagen}$ (Boecklen *et al.* 2011) and are not constant for a particular tissue within a species even within a given environment. Both changes in diet (Codron *et al.* 2012) and changes in metabolism over the life of an organism can be significant here.

The central concept in understanding dietary effects on $\Delta_{diet\text{-}tissue}$ is nutritional status, that is diet quality and quantity relative to organism requirements. Isotopic composition of tissues has been shown to be related to adequacy of overall dietary intake (Fuller *et al.* 2005; Mekota *et al.* 2006; Warinner and Tuross 2010) for $\delta^{13}C$ and $\delta^{15}N$, and quantity of protein in diet for $\delta^{15}N$ (Hobson and Clark 1992; McCutchan Jr *et al.* 2003; Cherel *et al.* 2005; Podlesak and McWilliams 2006) and $\delta^{2}H$ (Birchall *et al.* 2005). In addition to catabolic states of nutritional stress, the anabolic state of pregnancy (Fuller *et al.* 2004) has also been shown to have measureable isotopic effects.

These changes are thought to be related to the remobilisation of endogenous reserves as precursors during protein synthesis. The effects of this can be complex, for example in $\delta^{15}N$, causing either enrichment of high-turnover tissues by a pseudo trophic level effect (Cherel *et al.* 2005) or conversely depletion of tissues by the rerouting of depleted metabolic waste to tissue synthesis (Fuller *et al.* 2004; Zazzo *et al.* 2010). Similarly, a switch from a C_3 silage to a C_4 concentrate diet caused a depletion in sheep tooth enamel $\delta^{13}C$, the converse of that expected from the composition of dietary input, which was attributed to an decrease in (highly depleted) digestive methane production on the lower roughage concentrate diet (Zazzo *et al.* 2010).

Nutrient routing to tissue is also related to age, as tissue growth and turnover rates vary over an organism's lifetime. A number of studies have examined how isotopic variables differ between animals of different growth rates (Zazzo *et al.* 2008; Warinner and Tuross 2010; Kirsanow and Tuross 2011; Harrison *et al.* 2011). Tissues laid down during periods of high growth typically reflect diet more strongly than during periods of slower growth, as the contribution from endogenous reserves is less important. Trophic enrichment is therefore lower, the inverse of the pattern with nutritional stress. An additional factor is that the diet during a high growth period will make a disproportionate contribution to storage tissues used for endogenous remobilisation later in life (Hedges *et al.* 2007).

In summary, isotopic offsets between collagen and keratin tissues in domesticated animals are expected to reflect animals' environment and metabolism over differing timescales. A considerable quantity of evidence has been gathered for understanding the behaviour of $\delta^{13}C$ and $\delta^{15}N$ in both keratin and collagen in response to these factors. Less data is

available to understand inputs to $\delta^{2}H$, $\delta^{18}O$ and $\delta^{34}S$ in domesticates, particularly for collagen.

2.1.4 This study

This study examined bulk $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, and $\delta^{18}O$ values in bone collagen and hair keratin in two groups of sheep (*Ovis aries*) from the UK. $\delta^{34}S$ data was also obtained for the smaller of these groups of animals. Single AA $\delta^{13}C$ was used to investigate the role of differences in composition in bulk isotopic differences between tissues.

The aims of the study were to: (1) compare the isotopic relationships between these tissues in sheep to those in other species; (2) relate single AA $\delta^{13}C$ to bulk $\delta^{13}C$ for both tissues and compare the results to those of Raghavan *et al*. (2010); and (3) explore contributory factors to these relationships by examining the effects of differences in nutritional plane, sex, breeding history and season of sample collection on isotope values.

Specific hypotheses were that:

- as in species previously tested (Table 2.1), sheep bone collagen show higher values of $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ than sheep wool keratin. A variety of behaviours for $\Delta^{18}O_{keratin\text{-}collagen}$ have been recorded so no hypothesis was made for $\delta^{18}O$ behaviour. Similarly, due to the lack of previously published evidence, no hypothesis was made for $\delta^{34}S$ behaviour;
- individuals on a higher nutritional plane will show more depleted values of $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ in both tissues than those on a lower nutritional plane, i.e. $\Delta_{diet\text{-}tissue}$ will be smaller, for both tissues;
- sex will make no difference to isotope value in either tissue;
- as early bred ewes were empty but lactating in the half-year before slaughter they will show more depleted $\delta^{15}N$ values than unbred ewes, but no differences in any other isotope;
- keratin isotope values will differ more than collagen isotope values between slaughter groups, reflecting seasonal changes in fodder composition in the tissue with faster turnover.

2.2 Experimental

2.2.1 Sample origin and selection

To maximise comparability to archaeological samples, the main focus of this study was animals from a ‘medieval model’ of sheep husbandry, the English Heritage Sheep Project flock (Dingwall *et al.* unpublished; EH, n=20). An additional comparator dataset of carcase samples was acquired from an abattoir in South Yorkshire (Escrick, n=5).

EH flock animals were raised at the Scottish Agricultural College (SAC) at Penicuik, UK, on a diet entirely of local grazing. Sheep were derived from a first generation of animals, bred from ewes of the unimproved Shetland type raised in the Voe area of Shetland, and rams of the pure Shetland breed bought at Lerwick Auction Market, also on Shetland. The lambs were born in late April/early May 1996–1999, and raised at SAC, pastured on two different nutritional levels ('Low' diet: unimproved pasture; 'High' diet: improved pasture, with supplementary hay and grass pellets during snow cover), in two adjacent fields at an altitude of 200 m. The high plane pasture consisted of well-drained rotational grassland while the low plane field consisted of poorly drained native grassland (Popkin *et al.* 2012). Males were either entire ('Male') or castrated ('Castrate'), and females were bred 'Early' (first lamb at 2 years old) or 'Late' (first lamb at 3 years old) or not bred ('Unbred') (P. Baker, pers. comm.). The combination of sex, age and breeding time produced a total of 12 treatment cohorts. Annual shearing was in late May/early June. Animals were slaughtered at uneven intervals in either August/September or November/December 1999-2001 ('Slaughter Groups', 4–6 animals per treatment cohort). Sheep within a slaughter group (i.e. of the same age) were not necessarily born and/or slaughtered in the same years.

This study focused on four treatment cohorts: male low diet, male high diet, female low diet/early bred, and female low diet/unbred. Five adult animals in each treatment cohort were chosen at random: two animals from slaughter group 6 (aged 36 months, slaughter in August/September) and three from slaughter group 7 (aged 42 months, slaughter in November/December). Early bred ewes had each lambed twice, the last time in the May before slaughter. Wool samples from slaughter group 6 represented 3–4 months' growth, and those from group 7 represented 6–7 months'. Bone and wool samples from each were prepared for isotope analysis. The bone collagen $\delta^{13}C$ and $\delta^{15}N$ data was taken from a larger study of 20 animals from each of the four treatment cohorts examined here (Hamilton unpublished).

There was no data on breed, age, sex, origin, or husbandry practice for carcase samples from Escrick, which were obtained in February 2009. Previous shearing was assumed to occur in late May/early June, which is typical for the UK (Chapter 3), so wool samples represented 8–9 months' growth.

2.2.2 Sample preparation

Bone collagen. The EH skeletons were prepared by English Heritage at Portsmouth by boiling/simmering, defleshing with enzymes (neutrase, Biotex), and degreasing with acetone. 0.5–1.0 g of bone was taken from a rib. The surfaces of the bone pieces were cleaned by shotblasting and demineralised in 0.5 M HCl at 4°C at the Research Laboratory for Archaeology and the History of Art, Oxford, UK (Hamilton unpublished). Samples were rinsed with distilled water and then gelatinized in pH 3 water at 75°C for 48 h. The

supernatant containing the gelatinized protein (collagen) was filtered (8 μm), frozen, and lyophilised.

The Escrick carcase samples were prepared at BioArCh, York by degreasing in 2:1 methanol/dichloromethane. 0.5–1.0 g of bone was taken from a metatarsal and demineralised in 0.6 M HCl at 4°C. Samples were rinsed with distilled water and then gelatinized in pH 3 water at 75°C for 48 h. The supernatant containing the collagen was filtered (30 kDa, Amicon® Ultra-4 Centrifugal Filter Units, Millipore, Billerica, MA, USA), frozen, and lyophilised.

Wool keratin. Approximately 0.3–0.5 g wool, in the form of 1–2 staples (the locks of hair into which the fleece naturally falls), was selected from each fleece. At York, UK, samples were hand-cleaned to remove particulate matter but without breaking up the staples, and washed according to the procedure in Hedges *et al*. (2005), but with the following changes: using dichloromethane (HPLC grade, Fisher Scientific, Loughborough, UK) instead of chloroform in all solvent mixtures, and employing an additional initial ultra-pure water (ELGA Purelab Ultra, Marlow, UK) wash to ensure thorough cleaning.

2.2.3 Measurement of $\delta^{2}H$ and $\delta^{18}O$ in proteins

Uncertainty associated with measurements of $\delta^{2}H$ in proteinaceous tissues is greater than for $\delta^{13}C$ and $\delta^{15}N$ because of the need to compensate for the sorption of atmospheric water by the tissue, and the exchangeability of H atoms in proteinaceous materials with H from atmospheric water (Bowen *et al.* 2005). Determination of $\delta^{2}H$ is therefore achieved by methods involving comparative equilibration (Wassenaar and Hobson 2003; Sauer *et al.* 2009) with well-characterised standards of similar exchangeability, i.e. similar molecular structure and state of division (cut/ground: Chesson *et al.* 2009).

Many aspects of the experimental conditions for equilibration have recently been shown to affect $\delta^{2}H$ results (Qi and Coplen 2011). Inter-laboratory equilibration standards have therefore been developed for measurement of $\delta^{2}H$ in keratinous materials (Qi and Coplen 2011; Coplen and Qi 2012). No such equivalents have yet been developed for collagen, though collagen $\delta^{2}H$ measurements are becoming more widespread in recent literature (Cormie *et al.* 1994; Leyden *et al.* 2006; Tuross *et al.* 2008). This is potentially problematic because:

- sorption of water into extracted collagen is unlikely to be the same as into keratin,
- collagen and keratin H exchangeabilities are not identical: theoretical whole protein values are 21% for collagen (sequences from The UniProt Consortium 2012; cf Birchall *et al.* 2005, who use a figure of 25%) and 24–25% for the dominant keratin proteins in wool (sequences from Clerens *et al.* 2010), not including racemisation, that is exchange at the α-carbon (Chapter 4). In practice hair keratin exchangeability depends on its state of division, varying between 6 and 17% (Chesson *et al.* 2009).

- collagen may react differently to keratin in the high temperature conditions used in some equibration experimental set-ups (Sauer *et al.* 2009; Qi and Coplen 2011).

Collagen equilibration standards are therefore necessary for $\delta^{2}H$ measurements in collagen. In addition, the measurement of $\delta^{18}O$ in collagen is potentially problematic, as O in protein has been shown to be exchangeable in conditions of low pH (Niles *et al.* 2009), such as those used during demineralisation and/or gelatinisation of collagen (Brown *et al.* 1988; Tuross 2002). Extracted collagen is therefore likely to incorporate an isotopic signal from the water supply of the laboratory where it was prepared. In addition, O exchange between collagen and adsorbed water at high temperature during an equilibration step is possible, as for cellulose (Brand *et al.* 2009).

This study therefore prepared two collagen standards for determination of $\delta^{2}H$ and $\delta^{18}O$ in collagen samples, in addition to keratin standards for the analysis of keratin substrates. Elephant ivory from 1980s Zaire was supplied by H.G.M. Edwards, University of Bradford, and mammoth long bone of indeterminate age from Yukon, Canada by Grant Zazula, Government of Yukon Department of Tourism and Culture. Both were milled (Spexmill 6750 Freezer/Mill, Metuchen, NJ, USA), and collagen was extracted at BioArCh, York, as described above (i.e. using acid demineralisation and gelatinisation).

2.2.4 Sample analysis

EH bone collagen bulk $\delta^{13}C$ and $\delta^{15}N$ analysis (Oxford). Portions of 2.5–3.5 mg prepared collagen were weighed into Sn capsules. Samples were processed in an automated carbon and nitrogen analyser (Carlo Erba carbon and nitrogen elemental analyser) coupled with a continuous-flow isotope ratio-monitoring mass spectrometer (Europa Geo 20/20 mass spectrometer). $\delta^{13}C$ values were measured relative to the VPDB standard, and $\delta^{15}N$ values were measured relative to the AIR standard reference. Each result is the mean of 2–4 measurements. Precision of both $\delta^{13}C$ and $\delta^{15}N$ was better than ±0.2‰.

Escrick bone collagen bulk $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ analysis (Iso-Analytical). $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ data for the Escrick carcase samples were obtained from Iso-Analytical (Crewe, Cheshire). Isotope ratio mass spectrometric (IRMS) analyses were carried out on a 20-20 mass spectrometer with a Roboprep-CN elemental analyser (Europa Scientific, Crewe, UK); Control standards are reported in Table 2.2. Each result is the mean of 2 measurements.

Wool keratin bulk $\delta^{13}C$ and $\delta^{15}N$ analysis (Natural Environment Research Council Life Sciences Mass Spectrometry Facility, East Kilbride). 0.7 mg of washed wool in the form of uncut, whole-length fibres was weighed into 4 x 3.2 mm Sn capsules (Elemental Microanalysis, Okehampton, UK). Whole hairs were analysed to obtain a average value for the whole period of growth. $\delta^{13}C$ and $\delta^{15}N$ analyses were carried out on a ThermoElectron Delta Plus XP with Costech ECS 4010 elemental analyser; internal standards were a gelatine, an alanine enriched with ^{13}C, and a ^{15}N-enriched glycine. C and N content were

calculated using a tryptophan standard. $\delta^{13}C$ and $\delta^{15}N$ results are reported in per mille (‰) relative to PDB and AIR respectively. No duplicate analyses were made. Control standards are reported in Table 2.3.

Bone collagen and wool keratin $\delta^{2}H$ and $\delta^{18}O$ analysis (East Kilbride). 0.1 mg of wool was weighed into 4 x 3.2 mm Ag capsules (Elemental Microanalysis, Okehampton, UK and Pelican Scientific, Stockport, UK). Whole hairs were analysed to obtain a year average value. $\delta^{18}O$ and $\delta^{2}H$ analyses were carried out on a Thermo Fisher Scientific Delta V Plus with TC/EA high temperature furnace.

The contribution of exchangeable hydrogen and oxygen was calculated using: keratin standards BWB-II (whale baleen), CFS (feathers), ISB (feathers) and WG (feathers); collagen standards 3614 (elephant ivory) and 3615 (mammoth long bone) and a comparative equilibration method (Wassenaar and Hobson 2003). Inorganic $\delta^{18}O$ standards were IAEA 601, IAEA CH6 and IAEA 600. The $\delta^{2}H$ and $\delta^{18}O$ of the un-exchangeable H and O in the four keratin and two collagen standards was previously determined using a steam equilibration technique. Calculation of un- exchangeable $\delta^{2}H$ assumed a fractionation factor $\alpha = 1.080$ ($\varepsilon_{x\text{-}w} = 80‰$). $\delta^{18}O$ and $\delta^{2}H$ results are reported in per mille relative to VSMOW. All such results are for the non-exchangeable portion of H and O in these samples. No duplicate analyses were made. Linearity in $\delta^{18}O$ results for Escrick samples was poor, so these data were rejected. Control standards are reported in Table 2.3.

Bone collagen and wool keratin single AA $\delta^{13}C$ analysis (Leipzig). Prepared collagen and washed wool samples from Escrick 3 and Escrick 4 were analysed as in Smith *et al*. (2009). Most sample peaks contained the equivalent of 660–80 ng carbon. Results for Escrick 4 are the mean of 2 measurements. Tryptophan (Trp) is not retrieved using this LC-IRMS technique. Aspartic acid (Asp) and asparagine (Asn) are retrieved together and reported as Asx, and glutamic acid (Glu) and glutamine (Gln) as Glx.

2.2.5 Data analysis

Statistical analysis was carried out using R (R Development Core Team 2008). The dataset was non-parametric (univariate and multivariate Shapiro-Wilk tests, $P<0.05$). No effective data transformations were found.

Table 2.2. Isotopic analytical precision for data from Iso-Analytical: mean ± maximum s.d. in any single run. For abbreviations, see text. Obs. = observed values, Acc. = accepted values.

		$\delta^{13}C$/‰		$\delta^{15}N$/‰		$\delta^{34}S$/‰	
Standard	**n**	**Obs.**	**Acc.**	**Obs.**	**Acc.**	**Obs.**	**Acc.**
IA-R042 (Bovine liver)	3	-21.56 ± 0.09	-21.60	7.60 ± 0.04	7.65	-	-
IA-R045 ($(NH_4)_2SO_4$)	2	-	-	-4.65 ± 0.04	-4.71	-	-
IA-R046 ($(NH_4)_2SO_4$)	2	-	-	22.05 ± 0.06	22.04	-	-
IA-R005 (Beet sugar)	2	-25.97 ± 0.04	-26.03	-	-	-	-
IA-R006 (Cane sugar)	2	-11.76 ± 0.03	-11.64	-	-	-	-
IA-R036 ($BaSO_4$)	4	-	-	-	-	20.55 ± 0.21	20.74
IAEA-SO-5 ($BaSO_4$)	2	-	-	-	-	0.56 ± 0.00	0.50
IA-R027 (whale baleen)	2	-	-	-	-	16.37 ± 0.23	16.30

Table 2.3 Isotopic analytical precision for data from LSMSF: mean ± maximum s.d. in any single run. For abbreviations, see text. Obs. = observed values, Acc. = accepted values.

		$\delta^{13}C$/‰		$\delta^{15}N$/‰		$\delta^{2}H$/‰		$\delta^{18}O$/‰	
Standard	**n**	**Obs.**	**Acc.**	**Obs.**	**Acc.**	**Obs.**	**Acc.**	**Obs.**	**Acc.**
^{13}C-enriched alanine	9	-10.65 ± 0.05	-10.58 ± 0.03	-5.18 ± 0.06	-5.09 ± 0.12	-	-	-	-
^{15}N-enriched alanine	9	-35.5 ± 0.02	-35.46 ± 0.09	19.93 ± 0.25	20.01 ± 0.31	-	-	-	-
^{13}C-enriched tryptophan	4	-10.5 ± 0.09	-10.49 ± 0.11	-2.41 ± 0.41	-2.31 ± 0.14	-	-	-	-
IAEA 601	24	-	-	-	-	-	-	23.23 ± 0.20	23.14 ± 0.19
IAEA CH6	5	-	-	-	-	-	-	36.57 ± 0.27	36.4*
IAEA 600	6	-	-	-	-	-	-	-3.58 ± 0.39	-3.48 ± 0.53
CFS	8	-	-	-	-	-142.56 ± 3.44	-148.61*	5.55 ± 0.05	Unknown
BWB-II	9	-	-	-	-	-100.93 ± 1.74	-109.51*	12.88 ± 0.16	Unknown
ISB	9	-	-	-	-	-59.70 ± 2.26	-68.80*	12.89 ±0.33	Unknown
WG	6	-	-	-	-	-134.64 ± 1.69	-146.57*	6.09 ± 0.16	Unknown
3614 (elephant ivory)	5	-	-	-	-	-36.06 ± 2.65	Unknown	17.44 ± 0.22	Unknown
3615 (mammoth bone)	5	-	-	-	-	-168.76 ± 7.74	Unknown	0.00 ± 0.82	Unknown

*****s.d. undetermined.

2.3 Results

2.3.1 Bulk samples

Full $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$ and $\delta^{34}S$ results for all samples are given in Tables 2.4 (wool keratin) and 2.5 (bone collagen). Results are plotted in Figures 2.1 and 2.2. For $\delta^{13}C$ and $\delta^{15}N$ measurements of bone collagen samples, analytical error (1σ) was better than ±0.2‰ for both isotopes. For wool keratin samples, analytical error was better than ±0.1‰ for $\delta^{13}C$ and ±0.4‰ $\delta^{15}N$. Analytical error in $\delta^{34}S$ was better than 0.3‰ for both collagen and keratin. Analytical error in $\delta^{2}H$ and $\delta^{18}O$ varied by substrate, being ±2.1‰ for $\delta^{2}H$ and ±0.3‰ for $\delta^{18}O$ in keratin, and ±7.7‰ for $\delta^{2}H$ and ±0.8‰ for $\delta^{18}O$ in collagen. Determined non-exchangeable $\delta^{2}H$ values in keratin was 5–13‰ more depleted than accepted values (Table 2.3). The precision of $\delta^{2}H$ results in collagen, and $\delta^{18}O$ for both proteinaceous tissues, could not be established because accepted standard values for these materials have not been determined.

EH flock and Escrick group median collagen and keratin isotope values are reported in Table 2.6. In the EH flock, keratin isotope values were more depleted than collagen isotope values for $\delta^{13}C$ (median -2.0‰ , range -2.4–-1.4‰) and $\delta^{2}H$ (median -29‰, range -44–-21‰), and more enriched than collagen values for $\delta^{15}N$ (median 0.5‰, range -0.6–+1.3‰) and $\delta^{18}O$ (median 1.8‰, range 0.4–2.8‰). In the Escrick group, the depletion in keratin isotope values with respect to collagen values was greater than in the EH flock: median 2.7‰ for $\delta^{13}C$ (range -2.9–-2.2‰) and median 40.5‰ for $\delta^{2}H$ (range -43–-40‰). $\delta^{15}N$ values showed very little difference between tissues (median difference -0.2‰, range -0.5–+0.1‰). Offset in $\delta^{18}O_{keratin\text{-}collagen}$ was not measured. Offset in $\delta^{34}S_{keratin\text{-}collagen}$ was highly variable (median -2.5‰, range -3.3–0.1‰).

The magnitude of these differences was significant for all isotopes in the EH flock (Mann-Whitney U tests, $P<<0.001$ for $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$; $P<0.05$ for $\delta^{15}N$), and for $\delta^{13}C$ and $\delta^{2}H$ but not $\delta^{15}N$ in the Escrick group (Mann-Whitney U tests, $P<0.01$ for $\delta^{13}C$ and $\delta^{2}H$; $P>0.05$ for $\delta^{15}N$; Table 2.7). Differences in $\delta^{34}S$ between tissues in the Escrick group was also not significant ($P>0.05$). Distributions of isotope values were also significantly different between tissues in the EH flock (Kruskal-Wallis tests, $P<<0.001$ for $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$; $P<0.05$ for $\delta^{15}N$), but again only for $\delta^{13}C$ and $\delta^{2}H$ but not $\delta^{15}N$ or $\delta^{34}S$ in the Escrick group (Kruskal-Wallis tests, $P<0.01$ for $\delta^{13}C$ and $\delta^{2}H$; $P>0.05$ for $\delta^{15}N$ and $\delta^{34}S$; Table 2.7).

In the EH flock, $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ were strongly correlated to each other both within and between tissues (Spearman's rank correlation coefficient, all $P<<0.001$). $\delta^{15}N$ was correlated between tissues but not to any other isotope (Spearman's rank correlation coefficient, $P<<0.001$). Offsets between tissues ($\Delta_{keratin\text{-}collagen}$) were not correlated to each other or to any tissue isotope value (Spearman's rank correlation coefficient, all $P>0.05$). In the Escrick group, the same correlations were significant (though they could not be calculated for $\delta^{18}O$),

Table 2.4. Isotopic and elemental composition results, with metabolic and husbandry details, for all wool keratin samples. L= low diet, H = high diet; M = male, F = female; E = early bred, U = unbred; SG = slaughter group; / = not measured; - = not known.

ID	Diet	Sex	Breeding	SG	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$\delta^{34}S$/‰	$C:N_{atom}$
EH33	L	M	/	7	-26.3	7.7	-103.2	12.7	/	3.5
EH8	L	M	/	7	-26.7	7.0	-105.8	12.2	/	3.5
EH34	L	M	/	7	-26.2	6.7	-104.3	11.4	/	3.5
EH30	L	M	/	6	-26.2	6.7	-101.4	12.5	/	3.5
EH31	L	M	/	6	-26.1	6.8	-103.0	11.8	/	3.5
EH2	L	F	E	6	-26.2	6.1	-105.5	13.5	/	3.5
EH37	L	F	E	6	-26.6	6.3	-107.7	12.6	/	3.5
EH3	L	F	E	7	-26.7	6.2	-96.9	14.3	/	3.5
EH40	L	F	E	7	-26.3	6.7	-103.1	12.9	/	3.5
EH41	L	F	E	7	-26.8	6.5	-103.0	12.9	/	3.5
EH52	H	M	/	6	-26.2	7.3	-104.4	11.9	/	3.5
EH57	H	M	/	7	-26.5	7.1	-100.2	12.5	/	3.5
EH60	H	M	/	7	-26.6	6.9	-102.5	12.4	/	3.5
EH50	H	M	/	6	-25.9	7.0	-103.3	12.5	/	/
EH58	H	M	/	7	-26.3	6.8	-97.2	12.3	/	3.5
EH66	L	F	U	7	-26.4	7.0	-101.3	12.9	/	3.5
EH64	L	F	U	7	-26.0	8.0	-98.5	11.7	/	3.5
EH65	L	F	U	6	-25.5	7.6	-99.5	12.2	/	3.5
EH70	L	F	U	6	-25.5	7.6	-103.6	13.2	/	3.5
EH77	L	F	U	7	-26.2	8.6	-99.4	13.4	/	3.5
Escrick 1	-	-	-	-	-27.2	8.3	-117.9	/	4.0	3.6
Escrick 2	-	-	-	-	-26.5	6.9	-109.6	/	2.1	3.6
Escrick 3	-	-	-	-	-27.7	8.3	-114.3	/	4.8	3.6
Escrick 4	-	-	-	-	-26.2	7.9	-105.3	/	6.1	3.6
Escrick 5	-	-	-	-	-27.4	8.0	-103.1	/	5.3	3.6

Table 2.5. Isotopic and elemental composition results, with metabolic and husbandry details, for all bone collagen samples. L= low diet, H = high diet; M = male, F = female; E = early bred, U = unbred; SG = slaughter group; / = not measured; - = not known.

ID	Diet	Sex	Breeding	SG	$\delta^{13}C$/ ‰	$\delta^{15}N$/ ‰	$\delta^{2}H$/ ‰	$\delta^{18}O$/ ‰	$\delta^{34}S$/ ‰	C:N atom	% yield
EH33	L	M	/	7	-24.2	6.7	-69.3	10.0	/	3.2	25
EH8	L	M	/	7	-24.6	6.3	-71.1	10.7	/	3.3	26
EH34	L	M	/	7	-24.3	6.7	-71.7	9.7	/	3.3	23
EH30	L	M	/	6	-24.1	5.8	-67.4	9.8	/	3.2	18
EH31	L	M	/	6	-23.9	5.8	-68.5	9.8	/	3.2	24
EH2	L	F	E	6	-24.5	6.7	-62.5	11.5	/	3.3	28
EH37	L	F	E	6	-24.2	6.3	-63.7	10.7	/	3.1	21
EH3	L	F	E	7	-24.7	6.0	-73.0	11.8	/	3.3	25
EH40	L	F	E	7	-24.3	6.3	-67.2	11.1	/	3.2	23
EH41	L	F	E	7	-24.6	6.1	-80.7	11.4	/	3.3	28
EH52	H	M	/	6	-24.2	5.9	-75.1	10.4	/	3.2	19
EH57	H	M	/	7	-25.0	6.7	/	11.4	/	3.5	22
EH60	H	M	/	7	-24.6	6.9	-76.4	12.0	/	3.3	/
EH50	H	M	/	6	-23.9	5.9	-73.5	10.0	/	3.2	25
EH58	H	M	/	7	-24.2	6.4	-74.7	9.8	/	3.2	24
EH66	L	F	U	7	-24.0	6.3	-77.1	11.4	/	3.2	25
EH64	L	F	U	7	-24.1	7.9	-77.8	10.8	/	3.2	24
EH65	L	F	U	6	-24.0	7.6	-73.5	11.3	/	3.2	19
EH70	L	F	U	6	-24.1	7.0	-77.8	10.7	/	3.2	25
EH77	L	F	U	7	-24.3	7.8	-76.2	12.1	/	3.2	13
Escrick 1	-	-	-	-	-24.4	8.1	-74.5	/	6.6	3.3	21
Escrick 2	-	-	-	-	-24.1	6.5	-68.9	/	4.6	3.4	21
Escrick 3	-	-	-	-	-24.8	8.1	-74.6	/	8.1	3.4	20
Escrick 4	-	-	-	-	-24.0	7.3	-64.8	/	7.2	3.3	21
Escrick 5	-	-	-	-	-24.7	8.1	-63.3	/	5.1	3.3	20

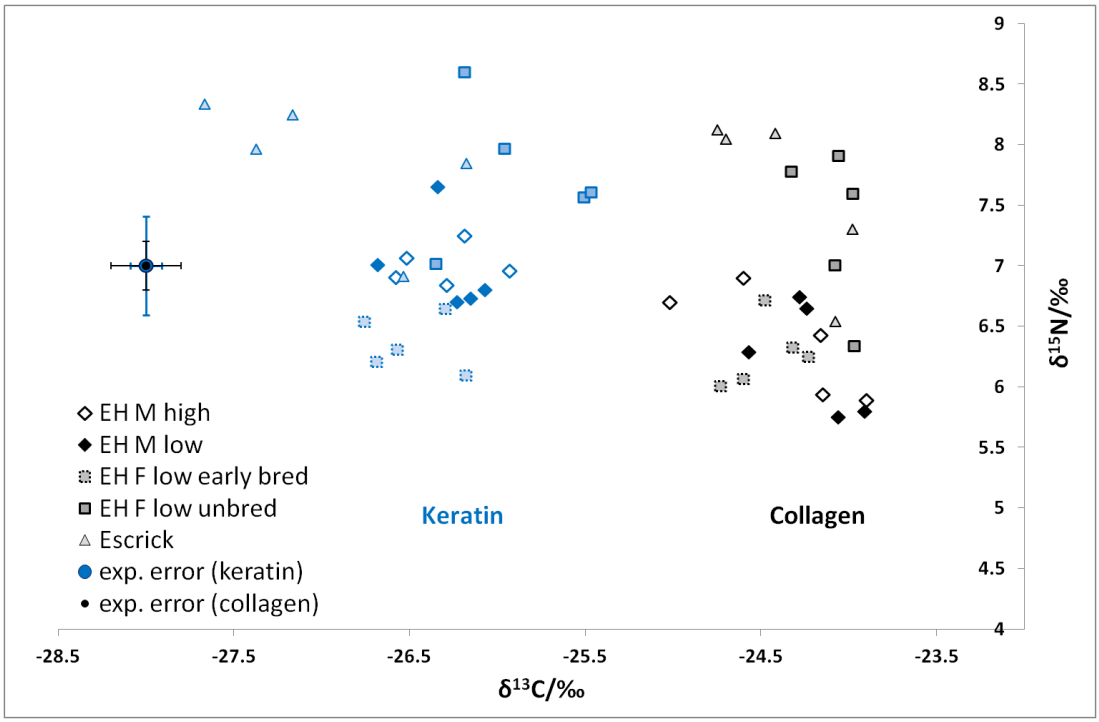

Figure 2.1. Collagen and keratin $\delta^{13}C$ and $\delta^{15}N$ results by flock and treatment cohort.

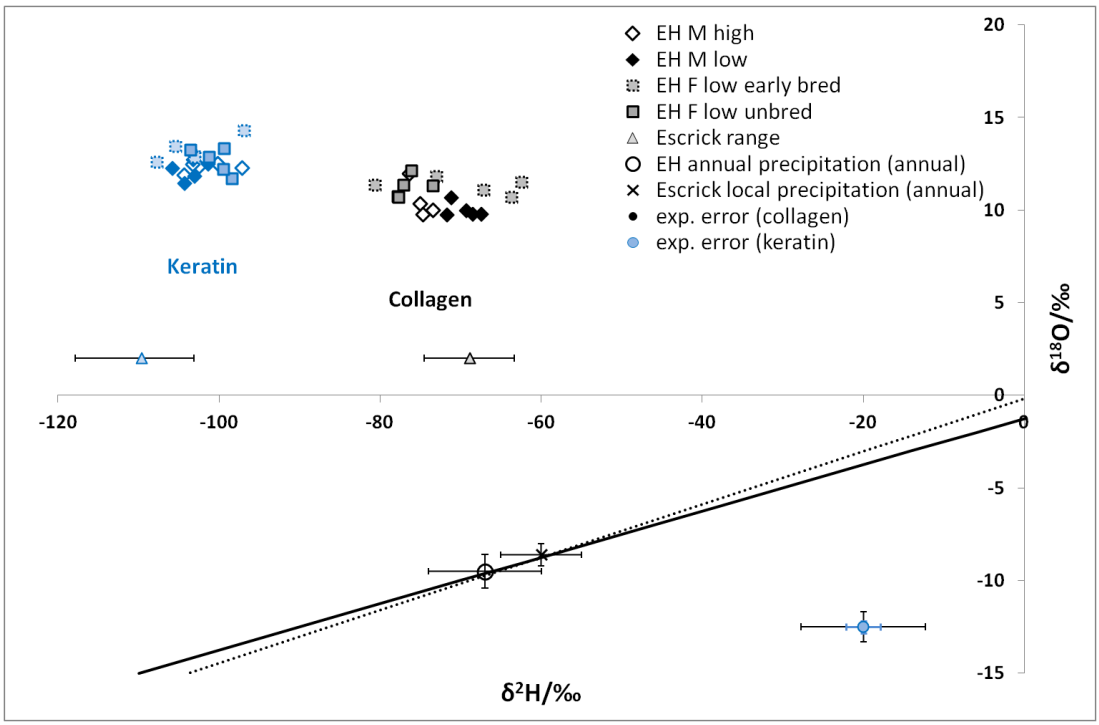

Figure 2.2. Collagen and keratin $\delta^{2}H$ and $\delta^{18}O$ results by treatment cohort. Local precipitation values calculated using the Online Isotopes in Precipitation Calculator (Bowen and Revenaugh 2003; Bowen 2008). Global meteoric water line (solid) according to Craig (1961), UK meteoric water line (dashed) from Darling and Talbot (2003).

Table 2.6. Overall and treatment cohort isotopic medians and ranges. M = male, F = female; L = low diet, H = high diet; E = early bred, U = unbred; SG = slaughter group; NA = not measured.

			Wool keratin isotope values/‰					Bone collagen isotope values/‰					$\Delta_{keratin\text{-}collagen}$/‰				
Flock	**Cohort**	**Statistic**	**$\delta^{13}C$**	**$\delta^{15}N$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{13}C$**	**$\delta^{15}N$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{13}C$**	**$\delta^{15}N$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{34}S$**
EH	Overall	Median	-26.3	6.9	-103.0	12.5	/	-24.2	6.4	-73.5	10.7	/	2.0	-0.5	29.3	-1.8	/
		Minimum	-26.8	6.1	-107.7	11.4	/	-25.0	5.8	-80.7	9.7	/	2.0	-1.3	29.3	-1.8	/
		Maximum	-25.5	6.9	-103.0	12.5	/	-24.2	6.4	-73.5	12.1	/	2.4	0.6	44.0	-0.4	/
EH	M H	Median	-26.3	7.0	-102.5	12.4	/	-24.2	6.4	-74.9	10.4	/	2.0	-0.4	27.7	-1.5	/
		Minimum	-26.6	6.8	-104.4	11.9	/	-25.0	5.9	-76.4	9.8	/	2.0	-1.3	27.7	-1.5	/
		Maximum	-25.9	7.0	-102.5	12.4	/	-24.2	6.4	-74.9	12.0	/	2.1	0.0	29.8	-0.4	/
EH	M L	Median	-26.2	6.8	-103.2	12	/	-24.2	6.3	-69.3	10.0	/	2.1	-1.0	34.0	-2.1	/
		Minimum	-26.7	6.7	-105.8	11.4	/	-24.6	5.8	-71.7	9.7	/	2.1	-1.0	34.0	-2.1	/
		Maximum	-26.1	6.8	-103.2	12.2	/	-24.2	6.3	-69.3	10.7	/	2.2	0.0	34.7	-1.6	/
EH	F L E	Median	-26.6	6.3	-103.1	12.9	/	-24.5	6.3	-67.2	11.4	/	2.0	-0.2	35.9	-1.9	/
		Minimum	-26.8	6.1	-107.7	12.6	/	-24.7	6.0	-80.7	10.7	/	2.0	-0.6	35.9	-1.9	/
		Maximum	-26.2	6.3	-103.1	12.9	/	-24.5	6.3	-67.2	11.8	/	2.3	0.5	44.0	-1.5	/
EH	F L U	Median	-26.0	7.6	-99.5	12.9	/	-24.1	7.6	-77.1	11.3	/	1.9	-0.6	24.1	1.2	/
		Minimum	-26.4	7.0	-103.6	11.7	/	-24.3	6.3	-77.8	10.7	/	1.9	-0.8	24.1	-1.2	/
		Maximum	-25.5	7.6	-99.5	12.9	/	-24.1	7.6	-77.1	12.1	/	2.4	0.0	26.0	-0.9	/

Table 2.6 continued.

			Wool keratin isotope values/‰					Bone collagen isotope values/‰					$\Delta_{keratin\text{-}collagen}$/‰				
Flock	**Cohort**	**Stat.**	**$\delta^{13}C$**	**$\delta^{15}N$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{13}C$**	**$\delta^{15}N$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{13}C$**	**$\delta^{15}N$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{34}S$**
EH	SG 6	Med.	-26.1	6.9	-103.5	12.5	/	-24.1	6.1	-71.0	10.5	/	2.0	-0.8	31.9	2.0	/
		Min.	-26.6	6.1	-107.7	11.8	/	-24.5	5.8	-77.8	9.8	/	2.0	-1.3	31.9	-2.0	/
		Max.	-25.5	6.9	-103.5	12.5	/	-24.1	6.1	-71.0	11.5	/	2.3	0.6	44.0	-0.9	/
EH	SG 7	Med.	-26.4	7.0	-101.9	12.6	/	-24.3	6.5	-74.7	11.2	/	2.0	0.4	24.1	1.5	/
		Min.	-26.8	6.2	-105.8	11.4	/	-25.0	6.0	-80.7	9.7	/	2.0	-1.0	24.1	-1.5	/
		Max.	-26.0	7.0	-101.9	12.6	/	-24.3	6.5	-74.7	12.1	/	2.4	0.0	35.9	-0.4	/
Escrick	Overall	Med.	-27.2	8.0	-119.6	/	4.8	-24.4	8.1	-68.8	/	6.6	2.7	-0.2	-40.5	/	2.5
		Min.	-27.7	6.9	-118.0	/	2.1	-24.7	6.5	-74.6	/	4.6	2.2	-0.5	-43.4	/	-0.1
		Max.	-26.2	8.3	-103.0	/	6.1	-24.0	8.1	-63.3	/	8.1	2.9	-0.1	-39.8	/	3.3

but relationships were not as strong (P=0.02). There were no correlations between $\delta^{34}S$ and any other isotope in either tissue (all P>0.5).

2.3.2 Effect of diet, sex and metabolism on values and offsets (EH flock)

Significant isotopic differences (greater than experimental error) existed between the following treatment cohorts in the EH flock (Table 2.8):

2.3.2.1 Season of sample collection

- $\delta^{13}C$ values for slaughter group 6 were more enriched than those slaughter group 7 by 0.2‰ in keratin and 0.3‰ in collagen (Mann-Whitney U tests, P<0.01 for keratin, P<0.05 for collagen).
- Both keratin and collagen $\delta^{13}C$ values differed in distribution between slaughter groups (Kruskal-Wallis test, P<0.01 for keratin, P<0.05 for collagen).

2.3.2.2 Breeding history (comparing low diet females only)

- $\delta^{13}C_{collagen}$ values in bred females were 0.6‰ more depleted in $\delta^{13}C$ than those from unbred females (Mann-Whitney U test, P=0.03). There was no significant difference between bred and unbred females in $\delta^{13}C_{keratin}$.
- Both collagen and keratin $\delta^{13}C$ values differed in distribution between bred and unbred females (Kruskal-Wallis tests, P<0.05 for both tissues).
- $\delta^{15}N$ values in bred females were 1.4‰ more depleted in collagen and 1.3‰ more depleted in keratin than those from unbred females (Mann-Whitney U tests, P<0.01 for keratin, P<0.05 for collagen).
- Both collagen and keratin $\delta^{15}N$ values differed in distribution between bred and unbred females (Kruskal-Wallis tests, P<0.01 for keratin, P<0.05 for collagen).

2.3.2.3 Sex (comparing low diet animals only, all females unbred)

- $\delta^{15}N_{collagen}$ in males was 1.3‰ more depleted than in females (Mann-Whitney U test, P=0.03).
- Distribution of $\delta^{15}N$ values in collagen and keratin was significantly different between males and females (Kruskal-Wallis test, P<0.05 in both tissues).
- $\delta^{2}H_{collagen}$ in males was 8‰ more enriched than in females (Mann-Whitney U test, P<0.01).
- Distribution of $\delta^{2}H$ values in collagen and keratin was significantly different between males and females (Kruskal-Wallis test, P<0.05 for keratin, P<0.01 for collagen).
- $\delta^{18}O_{collagen}$ from males was 1.6‰ more depleted than in females (Mann-Whitney U test, P=0.03).
- Distribution of $\delta^{18}O$ values in collagen only was significantly different between males and females (Kruskal-Wallis test, P<0.01).
- $\Delta^{2}H_{keratin\text{-}collagen}$ was 10‰ greater in males than females (Mann-Whitney U test, P<0.01).

- Distribution of $\Delta^2H_{keratin\text{-}collagen}$ and $\Delta^{18}O_{keratin\text{-}collagen}$ was significantly different between males and females (Kruskal-Wallis tests, $P<0.01$ for Δ^2H, $P<0.05$ for $\Delta^{18}O$).

2.3.2.4 Diet quality (comparing males only)

- Distribution of $\delta^2H_{collagen}$, and $\Delta^2H_{keratin\text{-}collagen}$ were significantly different between from high and low diet males (Kruskal-Wallis test, $P<0.05$).

2.3.3 Single AA $\delta^{13}C$ values

Single AA $\delta^{13}C$ values for samples Escrick 3 and Escrick 4 are reported in Table 2.9. Keratin and collagen values are plotted against each other in Figure 2.3.

Single AA $\delta^{13}C$ values were used to calculate bulk protein $\delta^{13}C$ values of the corresponding tissues. Collagen AA composition was calculated for whole triple helices, composed of one collagen α-1(I) and two collagen α-2(I) chains, for *Mus musculus*, *Rattus norvegicus*, *Homo sapiens* and *Bos taurus*: protein sequences were obtained from UniProt (The UniProt Consortium 2012). Instead of deriving an overall keratin fibre AA composition, the compositions of the 10 most abundant proteins in wool, which are all Intermediate Filament Proteins (IFPs: protein sequences from Clerens *et al.* 2010) were calculated. These results are compared in Figure 2.4.

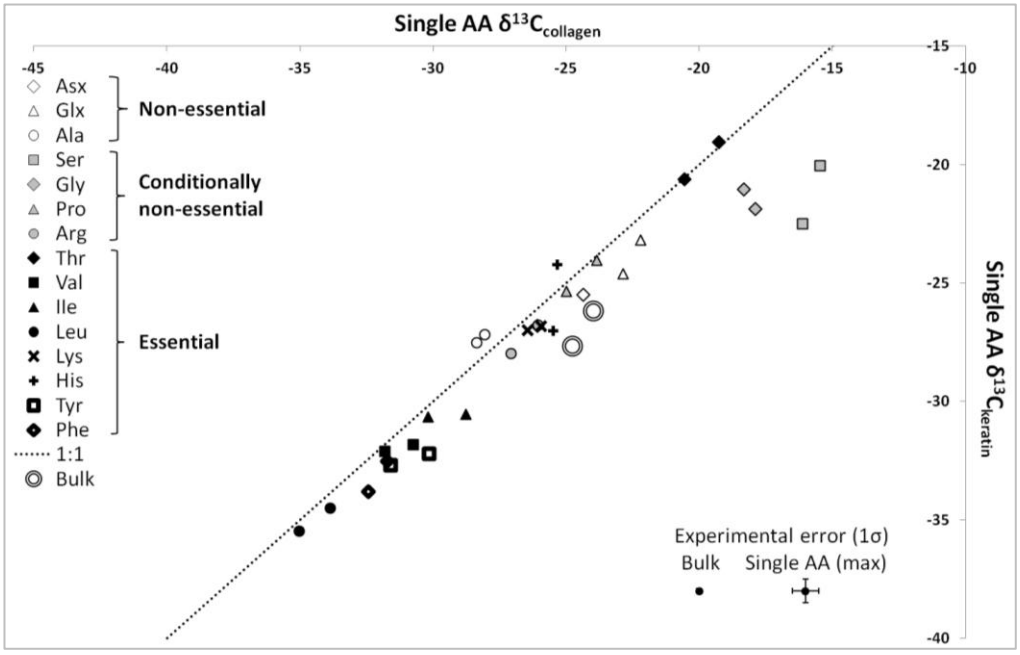

Figure 2.3. Collagen and keratin single AA $\delta^{13}C$ values for samples from Escrick group. Only those AAs present in both collagen and keratin are plotted. Error bars for bulk measurements are no larger than the error marker.

Table 2.7. Significance of differences between tissues of value (Mann-Whitney U test) and distribution (Kruskal-Wallis test) of isotope composition data. /, difference was less than experimental error; ns, not significant; * *P* <0.05; ** *P* <0.01, *** *P*<0.001. NA = not measured.

Flock	Statistic	$\delta^{13}C$	$\delta^{15}N$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{34}S$
EH (n=20[§])	Mann-Whitney	***	/	***	***	NA
	Kruskal-Wallis	***	*	***	***	NA
Escrick (n=5)	Mann-Whitney	**	/	**	NA	ns
	Kruskal-Wallis	**	ns	**	NA	ns

[§]n=19 for $\delta^{2}H_{collagen}$.

Table 2.8. Significance of differences between EH group treatment cohorts in value (Mann-Whitney U test) and distribution (Kruskal-Wallis test) of isotope composition data. M = male, F = female, L = low diet, SG = slaughter group. /, difference < experimental error; ns, not significant; * *P* <0.05; ** *P* <0.01.

			Wool keratin isotope values/‰				Bone collagen isotope values/‰				$\Delta_{keratin-collagen}$/‰			
EH group	N	Statistic	$\delta^{13}C$	$\delta^{15}N$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{15}N$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{15}N$	$\delta^{2}H$	$\delta^{18}O$
Diet	n_{high}=5[§]	Mann-Whitney	/	/	/	/	/	/	/	/	/	/	/	/
(M only)	n_{low}=5	Kruskal-Wallis	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	*	ns
Sex	n_{M}=5	Mann-Whitney	ns	ns	ns	ns	ns	*	**	*	ns	/	**	/
(L only)	n_{F}=5	Kruskal-Wallis	ns	*	*	ns	ns	*	**	**	ns	ns	**	*
Breeding	n_{bred}=5	Mann-Whitney	ns	**	ns	/	*	*	ns	/	/	/	ns	/
(L F only)	n_{unbred}=5	Kruskal-Wallis	*	**	ns	ns	*	*	ns	ns	ns	ns	ns	ns
SG	n_{6}=8	Mann-Whitney	**	/	/	/	*	ns	/	/	/	/	/	/
	n_{7}=12[#]	Kruskal-Wallis	**	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns

[§]n=4 for $\delta^{2}H_{collagen}$, [#]n=11 for $\delta^{2}H_{collagen}$.

Table 2.9. Single AA $\delta^{13}C$ values (in ‰) of wool keratin and bone collagen from Escrick 3 and Escrick 4 individuals. Error estimates are taken from Smith *et al*. (2009) for samples containing *c*. 660 ng C per peak. N = non-essential; N* conditionally non-essential; E = essential.

			Error	Escrick 3		Escrick 4	
AA		**Essential?**	**1σ**	**Collagen**	**Keratin**	**Collagen**	**Keratin**
Aspartic acid/ Asparagine	Asx	N	0.2 (Asp)	-26.1	-26.8	-24.4	-25.5
Hydroxyproline	Hyp	N*	0.2	-24.3	-	-23.4	-
Serine	Ser	N*	0.5	-16.1	-22.5	-15.5	-20.0
Glutamic acid/ Glutamine	Glx	N	0.2 (Glu)	-22.9	-24.6	-22.2	-23.2
Threonine	Thr	E	0.2	-20.6	-20.6	-19.3	-19.1
Glycine	Gly	N*	0.5	-17.9	-21.9	-18.3	-21.1
Alanine	Ala	N	0.1	-28.4	-27.5	-28.1	-27.2
Proline	Pro	N*	0.3	-25.0	-25.3	-23.8	-24.0
Valine	Val	E	0.1	-31.8	-32.1	-30.7	-31.8
Cysteine	Cys	N*	-	-	-28.1	-	-26.2
Methionine	Met	E	0.2	-	-23.0	-	-22.8
Hydroxylysine	Hyl	N	0.3	-25.5	-	-24.6	-
Isoleucine	IIe	E	0.3	-30.2	-30.7	-28.8	-30.6
Leucine	Leu	E	0.4	-35.0	-35.5	-33.9	-34.5
Lysine	Lys	E	0.4	-26.5	-27.0	-26.0	-26.8
Histidine	His	E*	0.3	-25.5	-27.0	-25.3	-24.2
Tyrosine	Tyr	E	0.2	-31.6	-32.7	-30.2	-32.2
Arginine	Arg	N*	0.5	-27.1	-28.0	-26.1	-26.8
Phenylalanine	Phe	E	0.2	-32.4	-33.8	-31.7	-32.5

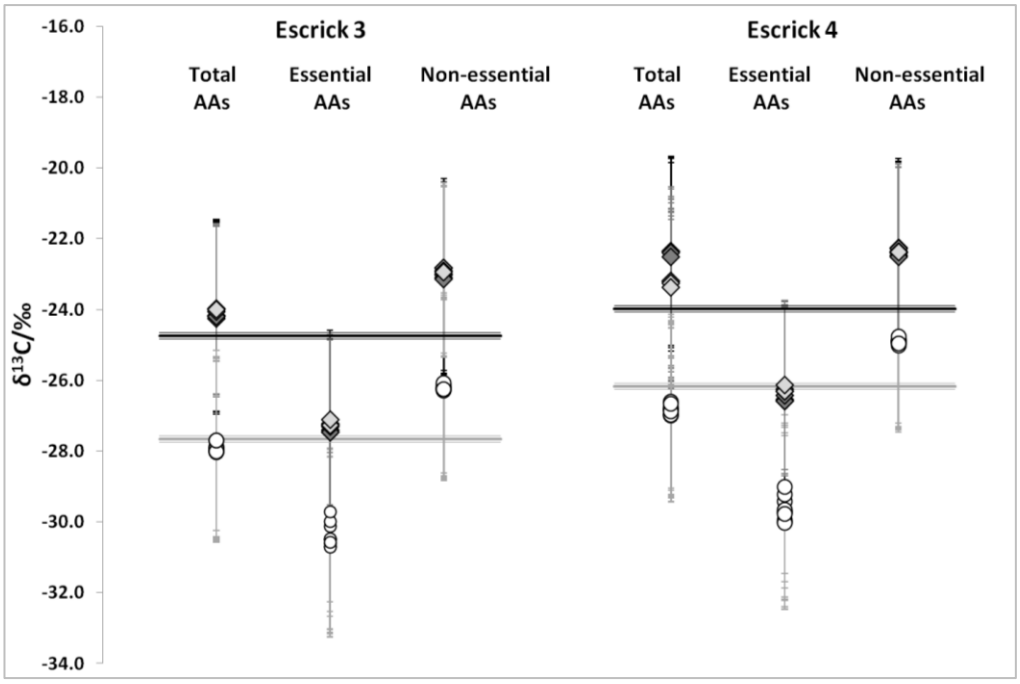

Figure 2.4. Observed (dark bar) *vs*. calculated (filled diamonds) bulk collagen $\delta^{13}C$ values, and observed bulk wool (grey bar) *vs*. IFP (unfilled circles) $\delta^{13}C$ values, for two individual animals. Collagen calculations were made twice: assuming all Pro and Lys were un-hydroxylated (dark filled diamonds) and assuming all were hydroxylated (lighter filled diamonds). Error bars are ±2.5‰ for calculated keratin values, ±2.4‰ for fully hydroxylated collagen; and ±2.7‰ for fully un-hydroxylated collagen.

2.4 Discussion

2.4.1 Uncertainty in δ^2H and $\delta^{18}O$

Experimental uncertainty was greater for collagens than for keratins. Collagen standards' $\delta^{18}O$ values differed substantially (by 107−110‰) after exposure to waters of known isotope composition during the equilibration step at high temperature (data not shown). The experimental set-up used (Sauer *et al.* 2009) has been shown not to remove all adsorbed water after equilibration (Qi and Coplen 2011), so it was not clear whether this effect was due to incomplete desiccation or O-exchange with collagen. The mammoth collagen standard in particular showed greater variation than the elephant standard in both δ^2H (maximum ±7.7‰ *vs*. ±2.7‰) and $\delta^{18}O$ (±0.8‰ *vs*. ±0.2‰). Given the similarity of species and difference in age between these two samples, this was most likely due to differences in the degradation state of the collagen present (Tuross 2002), leading to either more variable collagen composition and/or different molecular responses to the high temperature humid conditions of equilibration (Sauer *et al.* 2009). Characterisation of these samples, to assess the percentage of degraded or non-helical collagen, by microscopic (Koon *et al.* 2003) or x-ray diffractive (Gonzalez *et al.* 2012) methods, would be interesting.

The precision of collagen δ^2H and $\delta^{18}O$ measurements could be improved by: (1) demineralisation of collagen with EDTA to reduce exposure to acidic conditions (Tuross 2002); (2) use of ambient temperature equilibration procedures (Qi and Coplen 2011); and (3) the use of a third collagen standard in all experimental runs. The accuracy of standard measurements used in this study is currently not known, as 'true' isotope values have not been established: in order to do this, measurements from more than one laboratory are necessary. The effect of any contribution to $\delta^{18}O$ from laboratory water could also be assessed by an inter-laboratory comparison.

Uncertainty in keratin δ^2H and $\delta^{18}O$ values (maximum ±3.4‰ and ±0.3‰, respectively) was higher than optimum, which is *c*. ±2.8‰ for δ^2H and ±0.15‰ for $\delta^{18}O$ (Qi and Coplen 2011; Qi *et al.* 2010) but was comparable to values from other studies (Ehleringer *et al.* 2008; Bowen *et al.* 2009; Kirsanow and Tuross 2011). The precision of these measurements was undoubtedly affected by differences in equilibration methods between the LSMSF laboratory and others (Qi and Coplen 2011) as these values are stable at LSMSF. Absolute δ^2H, $\delta^{18}O$, $\Delta^2H_{keratin\text{-}collagen}$ and $\Delta^{18}O_{keratin\text{-}collagen}$ values are therefore difficult to compare between this study and others, but their relative magnitudes within the present study are likely to be robust.

2.4.2 Keratin and collagen isotope values

Sheep $\delta^{13}C_{keratin}$ from both EH and Escrick was typical of mammalian herbivore hair from northern Europe. $\delta^{13}C_{keratin}$ values (-27.7–-25.5‰) resembled those from wool from adult sheep in Ireland (-27.0--26.2‰: Zazzo *et al.* 2008), and were more depleted than sheep wool from the Alps (-27--24‰: Männel *et al.* 2007), Turkey (-26--19‰: Hedges *et al.* 2005), China (C3 feeds only, c. -23--21‰: Sun *et al.* 2010) or lamb wool from Sicily (C3 feeds only, -27--23‰: Moreno-Rojas *et al.* 2008). C_3 herbage only $\delta^{13}C_{keratin}$ values were consistent with wholly C_3 pasture-fed animals: compare wool data from sheep grazing mixed C_3/C_4 pastures in Mongolia (-21.5--16.5‰: Wittmer *et al.* 2010) and China (c. -19‰: Sun *et al.* 2010), or lambs receiving concentrate or mixed feed in Sicily (c. -24‰ and -21--19‰, respectively: Moreno-Rojas *et al.* 2008). Sheep wool from animals grazing wholly C_4 pasture was even more enriched (c. -16‰: Sun *et al.* 2010).

$\delta^{15}N_{keratin}$ values (6.1–8.6‰) were generally at the high end of ranges for cattle tail hair from Germany (Schwertl *et al.* 2003; Schwertl *et al.* 2005; Auerswald *et al.* 2011) and Ireland (Osorio *et al.* 2011), and were higher than values for sheep wool from the Alps (3.5-6.5‰: Männel *et al.* 2007), Mongolia (c. 5.8-6.4‰: Wittmer *et al.* 2011), China (c. 2.9-7.8‰: Sun *et al.* 2010) and lamb wool from Sicily (4.1-6.7‰: Moreno-Rojas *et al.* 2008). They lay within the very wide range for sheep wool from Turkey (2.8-10.1‰: Hedges *et al.* 2005). The consistently elevated values for the UK may be due to fertilizer use (as suggested in Camin *et al.* 2007) but may also be related to typical pasture composition, as low $\delta^{15}N$ values in

Chinese flocks (c. 2.9 vs. 4.5-7.8‰: Sun *et al.* 2010) were linked to grazing on leguminous plants. This may imply smaller use of legumes as graze in the UK than in mainland Europe.

There is little comparative data on modern herbivore bone collagen isotope values from Europe. Wild deer (*Cervus elaphus, Capreolus capreolus*) values from the UK were c. -24.8–-21.2‰ for $\delta^{13}C_{collagen}$ and *c*. 1.5–8.0 for $\delta^{15}N_{collagen}$ (Birchall *et al.* 2005; Stevens *et al.* 2006), while those from Poland were *c*. -23‰ for $\delta^{13}C_{collagen}$ and 2-5‰ for $\delta^{15}N_{collagen}$ (Bocherens and Drucker 2003; Stevens *et al.* 2006) while cattle fed a diet comprising C_4 plants showed $\delta^{13}C_{collagen}$ range of -19.2–-13.5‰ and $\delta^{15}N_{collagen}$ range 4.9–6.9‰ (Balasse *et al.* 1999). Collagen values in the present study are more depleted in $\delta^{13}C$ (-25.0–-23.9‰) and more enriched in $\delta^{15}N$ (5.8–8.1‰) than any of these sets of data. These differences are likely to be in part due to European geographic isotope variation, but features of diet and species metabolism cannot be excluded.

An alternative proxy for modern collagen data is archaeological bone collagen values. Data from the UK lies in the range -22.8–-20.1‰ for $\delta^{13}C_{collagen}$ and 2.6–10‰ for $\delta^{15}N_{collagen}$ (Table 2.10). If $\delta^{13}C_{collagen}$ values are corrected in line with recent anthropogenic ^{13}C change (Friedli *et al.* 1986), this gives a modern equivalent range of approximately -23.9–-21.2‰, which is still more enriched than samples in this study. Total collagen isotope ranges for the EH flock, of 0.79‰ for $\delta^{13}C$, 0.64‰ for $\delta^{15}N$, and 7.20‰ for $\delta^{2}H$, were generally small compared to archaeological site ranges from the UK (Table 2.10). This suggested the presence of sheep from more than one flock in most or all archaeological assemblages, which is not unexpected.

There is much less comparator data available for $\delta^{2}H$ and $\delta^{18}O$ of sheep tissues. Values of $\delta^{2}H_{keratin}$ and $\delta^{18}O_{keratin}$ in this study were consistent with those of cattle tail hair (Auerswald *et al.* 2011), despite any potential differences in experimental precision from different calibrations of exchangeability. $\delta^{2}H_{collagen}$ values for UK herbivores have been determined at *c*. -34–-15‰ (Birchall *et al.* 2005), much more enriched than data in this study, but this study a different (offline) experimental method, so direct comparison is difficult. Archaeological values or $\delta^{2}H_{collagen}$ for herbivores from the UK show a range of 70.1–-9.6‰ (Reynard and Hedges 2008, assuming a fractionation factor of 80‰, as in this study) which is much

wider and also more enriched than with sheep $\delta^{2}H_{collagen}$ data in this study (-80.7–-62.5‰). This may however reflect differences in climate over time, or differences in experimental precision between equilibration methods, plus the likely presence in the archaeological assemblage of sheep from more than one flock. equilibration methods, plus the likely presence in the archaeological assemblage of sheep from more than one flock.

Table 2.10. Caprine collagen isotopic composition variability at archaeological sites in the UK. [§] sheep, [#] sheep/goat

			$\delta^{13}C$/‰		$\delta^{15}N$/‰		$\delta^{2}H$/‰		
Site	**N**	**Period(s)**	**Min–max**	**Range**	**Min–max**	**Range**	**Min–max**	**Range**	**Reference**
Berinsfield, Oxfordshire	2[#]	Early medieval	-21.4–-21.2	0.2	6.4–5.8	0.6	-	-	(Privat *et al.* 2002)
St Giles by Brompton Bridge, North Yorkshire	9[§]	Late medieval	-22.2–-21.3	0.9	4.5–8.8	4.3	-	-	(Müldner and Richards 2005)
Wharram Percy, North Yorkshire	5[#]	High–Late medieval	-22.2–-21.4	0.8	5.0–7.6	2.6	-	-	(Müldner and Richards 2005)
Wetwang Slack, East Yorkshire	16[§]	Iron Age	-22.8–-20.9	1.9	3.5–7.3	3.8	-	-	(Jay and Richards 2006)
York, North Yorkshire	4[§] + 13[#]	Roman–Late medieval	[§]-22.0–-21.0 [#]-22.3–-21.1	[§]1.0 [#]1.2	[§]2.7–6.6 [#]4–8.5	[§]3.9 [#]4.5	-	-	(Müldner and Richards 2007)
Brean Down, Somerset	11[#]	Bronze Age	-22.7–-20.1	2.6	5.9–9.7	3.8	-	-	(Britton *et al.* 2008)
Yarnton, Oxfordshire	10[§]	Iron Age, Romano-British	-21.8–-21.3	0.6	4.5–10.0	5.5	-70.1–-9.6	-60.5	(Reynard and Hedges 2008)
Whithorn, Dumfries and Galloway	6[#]	Late medieval	-22.3–-21.4	0.9	6.2–9.3	3.1	-	-	(Müldner *et al.* 2009)
Danebury Hillfort, Hampshire	57[§]	Iron Age	-22.2–-20.3	1.9	2.6–6.0	3.4	-	-	(Stevens *et al.* 2010)

Table 2.11. Derivation of H and O elements elemental contributions to hair. These relationships have not been derived for bone (Kirsanow and Tuross 2011).

	H		O		
Species	**Drinking water %**	**Food %**	**Drinking water %**	**Food, air %**	**Reference**
Humans	31	69	-	-	(Sharp *et al.* 2003)
Humans	36	64	27	73	(O'Brien and Wooller 2007)
Humans	27	73	35	65	(Ehleringer *et al.* 2008)
Rats	25	75	45	55	(Podlesak *et al.* 2008)
Quails	20-30	60-70	-	-	(Hobson *et al.* 1999)

The depletion of sheep tissue δ^2H values relative to local meteoric water (by 30–60‰ for keratin and 0–5‰ for collagen) and enrichment of $\delta^{18}O$ (by 21–24‰ for keratin and 19–21‰ for collagen; Figure 2.2), is likely to reflect the balance between dietary and drinking water contributions to tissue isotope values. C_3 plants discriminate strongly against ^2H during photosynthesis, leading to depletion of plant tissues relative to plant water (Leaney *et al.* 1985), but incorporation of water O into carbonyl groups leads to an enrichment of $\delta^{18}O$ in plant tissues (Barbour 2007). Given the substantial contributions to keratin H and O from both food and water (Table 2.11), sheep keratin δ^2H and $\delta^{18}O$ values may be expected to be intermediate between food and water δ^2H and $\delta^{18}O$ values. The same is likely to be true of collagen isotopic composition. However as graze and water δ^2H and $\delta^{18}O$ composition were not measured directly in this study, this could not be verified.

Finally, sheep $\delta^{34}S_{keratin}$ from Escrick animals was generally depleted (range 2.1–6.1‰) and less variable than data from Ireland (5.3-17.0‰: Zazzo *et al.* 2011) and Turkey (2.0-9.7‰: Hedges *et al.* 2005). The Escrick data was consistent with an origin in a much less oceanic climate than that of Ireland, and was similar to that from cattle hair from Germany (3.5-6.5‰: Auerswald *et al.* 2011), though the comparability of $\delta^{34}S$ between mammalian species is currently uncertain. Results probably also reflect contributions from greater fossil fuel burning in the UK and possibly also different bedrock and soil $\delta^{34}S$ contributions (Peterson and Fry 1987; Krouse and Herbert 1988; Herut *et al.* 1995). Bone collagen $\delta^{34}S$ values from the same animals (range 4.6–8.1‰) are likely to be dominated by the same factors.

2.4.3 Isotopic differences between keratin and collagen

Highly significant differences were detected between keratin and collagen $\delta^{13}C$, δ^2H and $\delta^{18}O$ compositions, but not for $\delta^{15}N$ (Table 2.7). Keratin was more depleted than collagen in $\delta^{13}C$ (EH median offset -2.0‰, Escrick -2.7‰) and δ^2H (EH median offset -29‰, Escrick -40‰). Collagen was depleted relative to keratin in $\delta^{18}O$ (EH median offset 1.8‰, Escrick not measured). Collagen and keratin were similar in $\delta^{15}N$ value (EH median offset 0.5‰, Escrick -0.21‰). $\delta^{13}C$, δ^2H and $\delta^{18}O$ values were correlated between each other and

between tissues in both groups of animals; $\delta^{15}N$ was correlated between tissues in the EH flock only. The small differences between EH and Escrick groups may have been due to differences in the variability of dietary isotopic inputs under to different flock management (Codron *et al.* 2012).

In $\delta^{15}N$, the differences between collagen and keratin were minimal compared to those previously observed in other mammals (Table 2.1). Routing of N was clearly different to the routing of C, H and O. Firstly, $\Delta_{keratin\text{-}collagen}$ was smaller for $\delta^{15}N$ than for $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$. Secondly, $\delta^{15}N_{collagen}$ was correlated only with $\delta^{15}N_{keratin}$ (cross-tissue correlation) but not with any other isotope. This contrasted with the behaviour of $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$, which were co-correlated in both tissues (within-tissue correlation) and across tissues. This behaviour probably reflected the homogeneity of dietary inputs of $\delta^{15}N$ compared to other elements (Table 2.1), as it was drawn from a restricted number of sources in a monotonous, relatively low-protein herbivorous diet (contrast Codron *et al.* 2012). In addition, it is likely that a significant proportion was routed directly to proteinaceous tissue, further limiting the impact of within-body fractionation for N.

In contrast, C in both collagen and keratin can be derived from all biochemical components of the herbivore diet: protein, carbohydrate and lipid, though cellulose made very little contribution (Tieszen and Fagre 1993). These components vary considerably in isotopic composition, with alkanes and lipids more depleted than monosaccharides, which are similar to bulk measurements (Hobbie and Werner 2004; Dungait *et al.* 2008). The contribution of protein to bulk $\delta^{13}C$ is currently not clear: individual AA $\delta^{13}C$ in C_3 plants ranged from -36‰ (Val) to -17‰ (Gly), around a bulk value of -27‰ (Fogel and Tuross 2003), but these values may have been compromised by experimental procedure (Lynch *et al.* 2011). Inputs to $\delta^{13}C$ are therefore more heterogeneous, and undergo more a wider range of biochemical conversions to AAs in the organism (Bohinski 1979, 366-411, 498-574), leading to a wider offset between proteinaceous tissues. Enrichment in collagen over keratin $\delta^{13}C$ values were consistent with mammalian results so far determined (Table 2.1).

Enrichment of keratin over collagen $\delta^{18}O$ values found in this study was observed in a previous study of pigs (Tuross *et al.* 2008), but not two other studies, one of juvenile pigs (Warinner and Tuross 2010) and the other of rats (Kirsanow and Tuross 2011). In contrast, enrichment in collagen over keratin in $\delta^{2}H$ has been widely reported in other species (Table 2.1). For animals consuming an exclusively local, C_3 plant-based diet, $\delta^{2}H$ and $\delta^{18}O$ in food and local water are expected to be systematically related (Sternberg *et al.* 1984; Sternberg *et al.* 1986). Plant $\delta^{2}H$ was expected to be strongly depleted compared to local water $\delta^{2}H$ (Leaney *et al.* 1985), and plant $\delta^{18}O$ more enriched than local water $\delta^{18}O$. However for O, an additional contribution of atmospheric O_2, where $\delta^{18}O$ = 23.88‰ (Barkan and Luz 2005) must also be considered. The relative contributions of these factors have been estimated for keratin in a number of species (Table 2.10), but not in sheep or other ruminants. These

factors have also not been established in collagen. However without information on dietary isotopic inputs, it is not possible to apply these models to data in this study.

To the authors' knowledge, $\delta^{34}S$ in collagen and keratin have not previously been compared for any species. All S in collagen and keratin is present in the AAs Cys and Met, derived directly from diet, though Cys can also be synthesised from Met in the body (Bohinski 1979, 546-7). The most abundant keratin proteins contain 0.7-1.4% Cys and 0.1-0.4% Met (Clerens *et al.* 2010), whereas collagens have 0.2% of each AA (The UniProt Consortium 2012). Differences in $\delta^{34}S$ value between keratin and collagen are therefore likely to reflect (1) differences in AA composition between tissues; (2) variation in $\delta^{34}S$ of diet over time, incorporated into the tissues at differing timescales; and/or (3) differences in Cys routing (directly from diet or via endogenous synthesis from Met) to tissue.

In this study, $\delta^{34}S$ data was only obtained for animals from the Escrick group. Here, collagen was generally enriched over keratin, but not in all individuals tested: three of five showed enrichment of 2.5–3.3‰; the remaining two showed much smaller differences, which were less than experimental error. It therefore appeared that within a single group of sheep, significant variability exists in diet-tissue fractionation of $\delta^{34}S$. It was unclear whether this was related to environmental, metabolic or anthropogenic factors, for example a period of nutritional stress (Harrison *et al.* 2011), change in pasture type (Schmidt *et al.* 2005) or provision of dietary supplements (Bahar *et al.* 2008) for these two animals. The extension of this methodology to samples from the EH flock, where more details are known, could clarify this.

2.4.3.1 Differences in protein AA composition

Isotope values have been shown to vary substantially between AAs in keratin and collagen (Raghavan *et al.* 2010; Styring *et al.* 2010), so differences in protein composition between these tissues are likely to account for a large proportion of the difference between their bulk values. This was examined by using single AA $\delta^{13}C$ values to calculate bulk collagen and keratin isotope values, and comparing these to observed values.

Calculated bulk $\delta^{13}C_{collagen}$ were within 0.6‰ of observed $\delta^{13}C_{collagen}$, and calculated $\delta^{13}C_{IFPs}$ within 0.4‰ of observed bulk $\delta^{13}C_{keratin}$ (Figure 2.4), well within calculation error (±2.4–2.7‰). The non-essential AA fraction was more enriched than the essential fraction in both tissues, reflecting both enrichment of AA $\delta^{13}C$ during biosynthesis, and the $\delta^{13}C$ values of the various dietary precursors to each AA. Calculated values of bulk $\delta^{13}C_{collagen}$ were more enriched than calculated bulk $\delta^{13}C_{keratin}$, regardless of which set of single AA data was used for the calculation (that is, using single AA $\delta^{13}C$ values from collagen to calculate bulk IFP values in addition to bulk collagen values, and *vice versa*; cross-calculated data not shown). This was true not only of the whole protein, but also of the non-essential AA fraction and the essential AA fraction. Differences in AA composition between collagen and keratin therefore explained only part of the isotopic offset between these tissues, and suggested some

difference in AA origin (either by routing or period of growth) between collagen and keratin. However, these calculations were based on only two sets of AA $\delta^{13}C$ data, which may vary significantly between sheep breeds, locations or husbandry methods. Confirming AA $\delta^{13}C$ patterns in other sheep samples is therefore necessary for increased confidence.

The same calculations were also carried out for $\delta^{15}N$ data from Styring *et al*. (2010). Here sheep collagen single AA $\delta^{15}N$ values were used to calculate bulk collagen and IFP values, though only the former could be compared to observed values. This GC-C-IRMS technique recovered 8 of the 22 AAs present in collagen and keratin, which accounted for 67–68% of N in collagen, and 24–32% of N in keratin IFPs. Calculated IFP bulk $\delta^{15}N$ values were more depleted than collagen bulk values (Figure 2.5). This was however only true of the non-essential contribution to collagen, as the essential component of both proteins showed bulk $\delta^{15}N$ values in the same range. The result of these calculations was very different to observed bulk keratin and collagen results in the present study, where bulk protein $\delta^{15}N$ values were very similar. These differences may have been due to (1) the contributions to bulk $\delta^{15}N$ from the AAs not recovered in Styring *et al*. (2010), and/or (2) differences in $\delta^{15}N$ metabolism between sheep tested in Styring *et al*. (2010) and those in the present study. Error in these calculations was however large.

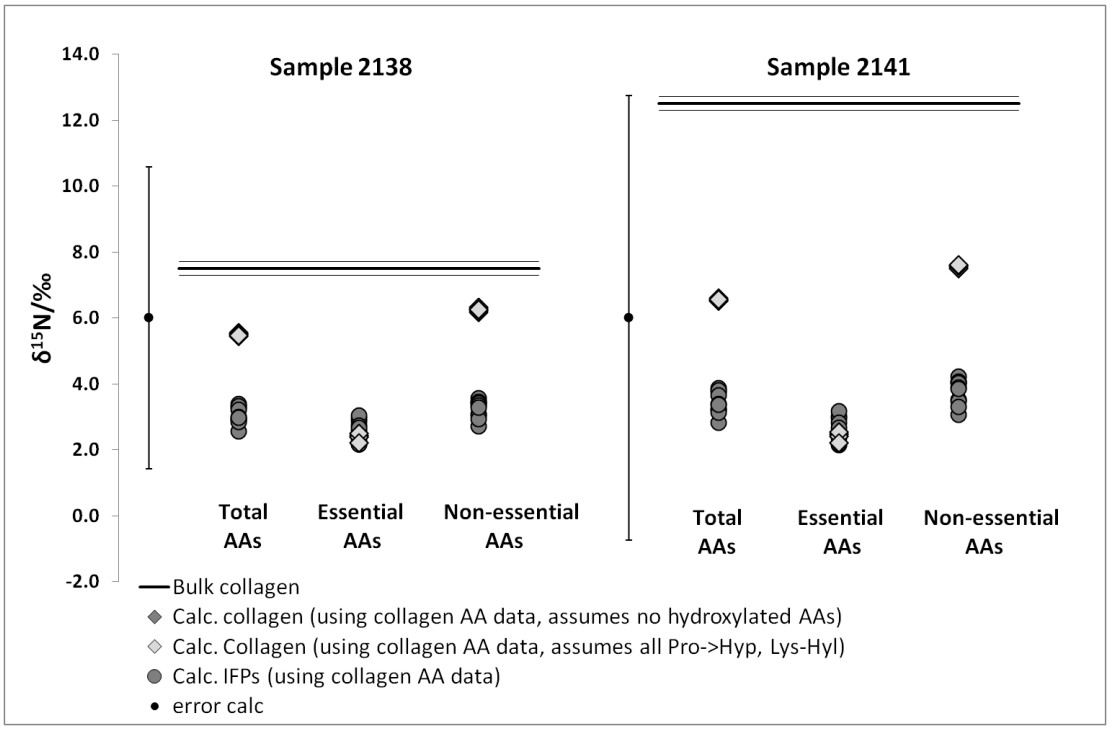

Figure 2.5. Calculated bulk collagen (filled diamonds) and keratin (empty circles) $\delta^{15}N$ values *vs*. observed bulk collagen $\delta^{15}N$ values (dark bar) for Upper Palaeolithic archaeological sheep bone from Kasteelberg, South Africa (data from Styring *et al.* 2010).

2.4.3.2 Differences in protein AA routing

Direct comparison of single AA $\delta^{13}C$ values between tissues (Figure 2.3) indicated that almost all were more enriched in collagen than in keratin, the exceptions being His, Ala and Thr. Ser and Gly showed the greatest deviation from a 1:1 correspondence. They were enriched in collagen over keratin by 4.6–6.4‰ and 2.7–4.0‰ respectively (both ±0.5‰), while other isotopes shown an enrichment range of -1.1–+2.0 ± 0.1–0.4‰. This behaviour of Ser and Gly could not be accounted for by error bar magnitude and was not observed in human bone collagen and hair keratin (Raghavan *et al.* 2010). Ser and Gly are linked by an important biosynthesis pathway in which Gly is produced from Ser, though Gly can also be synthesised via the carnitine pathway, and routed directly from diet (Meléndez-Hevia *et al.* 2009). It was therefore clear that the metabolic routing of Ser and Gly was different between collagen and keratin, but not whether the values were unusually depleted for keratin or unusually enriched for collagen.

Gly and Ser make up 27% and 4–5% of AA residues in collagen, respectively, and 2–9% and 8–12% of AA residues in keratin IFPs. Collagen therefore shows very high demand for Gly in synthesis, which diet is unlikely to supply in total (Meléndez-Hevia *et al.* 2009). If the animal's diet included high-protein supplements, these are more likely to be routed high-demand AAs in both tissues. The samples were from the Escrick flock of unknown husbandry, so the use of high-protein supplements was not excluded. If the supplements were in part C_4-based, which is likely in Europe (Kornexl *et al.* 1997; Schmidt *et al.* 2005) then this could account for the enrichment in Gly values in sheep collagen. However, the high demand of wool for Ser, Leu and Glu (all 8–12% of IFPs) could be expected in the same circumstances to lead to preferential incorporation of enriched versions of these AAs into keratin, which was not observed.

An alternative hypothesis was that the pattern originated in depleted Ser synthesis in keratin, and that Gly values reflected partial routing from this pool of Ser, and partial routing via other, more enriched pathways, e.g. from diet. Ser is an essential reagent in the production of Cys from Met via the transsulfuration pathway (Bohinski 1979, 546-7). Supply of these S-containing AAs, and therefore of Ser, is a major limiting factor for wool growth, though *in vivo* capacity for synthesis of Ser was determined to be high as wool growth rate was little increased by its supplementation (Liu *et al.* 2000). It is possible that high demand for Cys in sheep skin (Liu and Masters 2000) leads to compartmentalised production of highly depleted Ser (and hence Gly) in the skin, which is incorporated into keratin but not collagen. Possible evidence for this in this study was that Cys in sheep wool was highly depleted in $\delta^{13}C$ for a non-essential AA (values -28.1–-26.2‰; Table 2.9; Figure 2.3).

This hypothesis would be very interesting to test in further samples of sheep keratin and collagen, in particular both high and low diet individuals from the EH flock, to explore whether nutrient adequacy is a relevant factor here. (This was not carried out in this study

because Escrick samples were acquired much earlier than EH samples, and were thus the only material available for sampling at the time). Analysis of samples of a variety of sheep breeds might also be illuminating, for example including improved and un-improved wool breeds, as well as hair (non-wool) breeds, in addition to samples from other herbivores (e.g. ruminant/non-ruminant), if this pattern is related to the greater production of hair fibre as a proportion of body mass in sheep compared to other mammals. High mass of clean fleece produced in a year is a trait deliberately selected for in modern sheep (Safari *et al.* 2005). Clean fleece weight in yearling sheep averaged 1.7–2.3 kg per year in animals which weighed 34–41kg (Wuliji *et al.* 1999; Wuliji *et al.* 2011), that is 4–7% of body mass, compared to 2% for rodents (Bedford and Christian 2000), 3% for lemmings (Reid *et al.* 1997) or 1% in seal pups (Brookens *et al.* 2008). Unfortunately, given the availability of human collagen/keratin AA $\delta^{13}C$ data (Raghavan *et al.* 2010), no estimates for human hair production were found (see Park and Ihm 2010).

2.4.4 Metabolic and dietary factors significantly affecting protein isotope values

2.4.4.1 Season of sample collection

Animals slaughtered in November/December (group 7) had more depleted $\delta^{13}C_{collagen}$ values (median -24.33‰) than those slaughtered in August/September (group 6: median -24.07‰). Keratin tissues showed the same relationship (Nov/Dec median -26.4‰, Aug/Sep median -26.1‰). These small differences were nevertheless significant (Table 2.8).

Significant variation in $\delta^{13}C_{collagen}$ by season of sample collection was also present in the larger study of bone isotope values (Hamilton unpublished), where it was ascribed to seasonal variation in diet. Plant tissue $\delta^{13}C$ has a complex seasonal pattern, depending on features of soil type, humidity, temperature, and irradiance, but generally increases in summer (Smedley *et al.* 1991; Garten and Taylor 1992). Lower $\delta^{13}C_{collagen}$ values in November/December-slaughtered samples were therefore generally consistent with this annual variation. The potential effects of natural weathering from environmental humidity and light exposure on keratin isotopic composition can be rejected (Auerswald *et al.* 2011). Analysis of shorter segments of fleece samples, capturing shorter periods of input, could be used to examine seasonal variation in detail.

If seasonality were the causal factor for variation in $\delta^{13}C$ between slaughter groups, it was interesting that no significant variability in $\delta^{15}N$, $\delta^{2}H$ or $\delta^{18}O$ was detected, as these isotopes are also known to cycle seasonally in plant tissues (Handley and Scrimgeour 1997) and rainwater (Darling and Talbot 2003). In these isotopes, other effects were apparently dominant.

2.4.4.2 Breeding history

A history of pregnancy and lactation were significantly associated with depletion in $\delta^{13}C_{collagen}$ (median -24.5‰ *vs.* -24.1‰) and $\delta^{15}N_{collagen}$ (median 6.3‰ *vs*. 7.6‰), and also $\delta^{15}N_{keratin}$ (median 6.3‰ *vs*. 7.6‰; Table 2.8). This depletion in $\delta^{15}N$ is in line with data from human hair (Fuller *et al.* 2004), which also reported no effect on $\delta^{13}C_{keratin}$. No isotopic effect of pregnancy on human bone collagen has been reported (Nitsch *et al.* 2010). However it is possible that such an effect was more readily discernible in sheep because of (1) shorter turnover rates of sheep bone leading to greater isotopic variability in the tissue, and (2) more frequent pregnancies, meaning that a greater proportion of an individual's life was spent pregnant or lactating, thus producing a greater cumulative effect on bone isotopic composition. Depleted $\delta^{13}C_{collagen}$ in bred ewes might however not be a direct effect of pregnancy or lactation. Although all females tested in this study received the 'low' diet with no supplementation, in practice 'low' animals did receive supplementation if they lost too much weight (Hamilton unpublished). Pregnant ewes are likely to lose weight with inadequate diet (Vincent *et al.* 1985), so it is possible that this supplementation could explain $\delta^{13}C_{collagen}$ change. However, consumption of silage and hay has previously been reported to enrich $\delta^{13}C_{keratin}$ over fresh pasture values in cattle (Schnyder *et al.* 2006) rather than producing depletion as observed here. It therefore remained unclear what caused this effect in this study if it was not caused by metabolic changes associated with pregnancy.

2.4.4.3 Sex

Collagen from male sheep was significantly more depleted in $\delta^{15}N$ and $\delta^{18}O$, and more enriched in $\delta^{2}H$, than collagen from females (Table 2.8). Differences between these isotopes were not significant in keratin. $\Delta^{2}H_{keratin\text{-}collagen}$ was greater in males (median -34‰) than females (median -24‰). The distributions of $\delta^{15}N$ and $\delta^{2}H$ were significantly different between males and females in both keratin and collagen. In addition, the distributions of $\delta^{18}O$, $\Delta^{2}H_{keratin\text{-}collagen}$, $\Delta^{18}O_{keratin\text{-}collagen}$ were also significantly different between sexes. All animals in this comparison were on the low diet, and all females were unbred, so these effects were unlikely to be due to differences in nutrition or the effects of pregnancy or lactation.

Previously identified differences in isotope value between sexes (mostly in $\delta^{15}N$) have been attributed to social factors in humans (e.g. Barrett and Richards 2004; Fuller *et al.* 2006; Craig *et al.* 2009; Chenery *et al.* 2011) or to food selection behaviour in birds (e.g. Forero *et al.* 2002; Mariano-Jelicich *et al.* 2008). The differences in $\delta^{2}H$ and $\delta^{18}O$ between male and females sheep in the present inquiry have no parallels in these studies. Potential contributing factors to these differences include: (1) different browse or water intake behaviour, or (2) sex-dependent physiological variations in isotope fractionation during production of collagen or keratin. More specific suggestions regarding their nature could not be made at present.

2.4.4.4 Diet quality

No association with diet quality was present in any isotope or tissue offset. This was in contradiction to the larger bone collagen only study (Hamilton unpublished), in which high diet males had significantly lower $\delta^{13}C$ and higher $\delta^{15}N$ than low diet males. In the males of the same population, low nutrition was been found to delay epiphyseal bone fusion and tooth eruption, but had little effect on bone size (Popkin *et al.* 2012). The isotopic results were unexpected because previous studies showed variable offsets between $\delta^{13}C$ of muscle tissue fractions (protein and lipid) in lambs raised on different diets, being greater with pasture-based diets than on concentrate or milk diets (Piasentier *et al.* 2003; Sun *et al.* 2010). Additional keratin samples from individuals in the EH flock, for which $\delta^{13}C$ and $\delta^{15}N$ collagen values have already been determined, would be useful to confirm this effect.

2.5 Conclusion

Isotope analysis of bone collagen and wool keratin from two sheep flocks in the UK showed that collagen protein was enriched over keratin in $\delta^{13}C$ and $\delta^{2}H$, and depleted in $\delta^{18}O$, while $\delta^{15}N$ values for the two tissues were very similar. Data for $\delta^{34}S$ also suggested an enrichment in collagen over keratin. These patterns were generally in line with other mammalian species for $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ but differed for $\delta^{15}N$, possibly reflecting the low protein diet of these grazers. Both AA composition and AA routing were important factors explaining the offset in bulk isotopic composition between sheep collagen and keratin. In particular, single AA $\delta^{13}C$ analysis identified very different routing of Ser and Gly between keratin and collagen proteins, which was suggested to be related to the high demand for Cys synthesis in sheepskin for wool production. However due to uncertainty in the turnover rate of sheep bone, differences in turnover time, and therefore in dietary and metabolic input, could not be excluded as contributory factors.

A number of specific metabolic and dietary factors were tested for their effect on isotope values and offsets between tissues. Both keratin and collagen $\delta^{13}C$ were found to vary seasonally, suggesting that collagen turnover in sheep ribs is relatively rapid. Pregnancy and lactation depleted $\delta^{15}N$ in both keratin and collagen, in line with expectations, but a depletion in $\delta^{13}C$ in collagen was also observed. Bone collagen $\delta^{15}N$ and $\delta^{18}O$ was found to be significantly depleted, and $\delta^{2}H$ enriched, in males compared to females, which was unexpected. No such effects were found for keratin. Finally, and again unexpectedly, diet quality did not affect significantly isotopic composition in either tissue.

Keratin and collagen isotopic composition has been compared for only a small number of species. This study has added data from a relatively large mammalian herbivore, with results that depend on dietary and metabolic factors differently from species previously tested. It is the first such study to include five independent isotopic measurements. In a

zooarchaeological context, this study provides a baseline for understanding archaeological sheep populations from bone assemblages, and also for relating the isotopic composition of keratin-based artefacts (Hedges *et al.* 2005; Chapter 7) to better-established bone collagen isoscapes. Potential difficulties with this application include differing degrees of dietary heterogeneity between modern and ancient flocks (Codron *et al.* 2012; Chapter 7); potential differences between modern and ancient breeds, for example in rate of maturation; inter-annual isotopic variation; in addition to questions of diagenesis of keratin (Wilson *et al.* 2010; Chapter 4) and collagen (Tuross 2002; Dobberstein *et al.* 2009). In particular, isotopic variability due to differences in sex, if confirmed, will be of great importance in an archaeological context, as sex balance in sheep populations can vary drastically depending on whether farming focuses on meat, milk or wool (Payne 1973; Mainland and Halstead 2005; Warn *et al.* 2006).

Future work suggested by this study includes:

- testing of further individuals from the EH sheep flock to examine effects of castration and frequency of pregnancy.
- direct comparison of single AA $\delta^{15}N$ (Styring *et al.* 2010) and possibly $\delta^{2}H$ (Fogel *et al.* 2010; cited in Boecklen *et al.* 2011) in sheep keratin and collagen, to gain additional perspectives of AA routing.
- further examination of Ser and Gly routing in herbivore keratin, to examine the effects of e.g. species, breed and diet.
- examination of seasonal variability in keratin isotope values, to compare to average (whole-hair) keratin values and also collagen values of uncertain turnover rate.
- inter-laboratory development of collagen standards for $\delta^{2}H$ and $\delta^{18}O$ measurements, and optimisation of collagen equilibration procedures by analogy to Qi and Coplen's work on keratin substrates (Qi and Coplen 2011), including examination of the effect of acid exchange of O during collagen preparation.

Acknowledgements

Funding for this work was provided by the UK Natural Environment Research Council (IvH.: NE/G52421X/1, EK163-08/10). JH made available the $\delta^{13}C$ and $\delta^{15}N$ data from bone samples from the EH flock, as well as prepared collagen samples from 20 of these previous analyses. Thanks to Polydora Baker of English Heritage, Escrick Abattoir, HGM Edwards and G Zazula for samples.

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3. Provenancing modern sheep wool using carbon, nitrogen, hydrogen, oxygen and sulfur isotopes

Abstract

An isotopic method to provenance sheep wool would be useful to examine trade in wool textiles across the North Atlantic in the past, where these objects have long been of great economic and social importance. Previous studies have indicated that metabolic and farming practice variation in sheep wool isotope values may be significant confounding factors of geographic origin, with metabolic effects relatively insignificant. Samples of wool from four sheep flocks in the UK and one in Iceland (total 67 animals) were analysed for carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), un-exchangeable hydrogen ($\delta^{2}H$), oxygen ($\delta^{18}O$) isotopic composition to establish the resolution of the technique in this region. Sulfur ($\delta^{34}S$) composition data was also obtained for one UK flock. $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, and $\delta^{18}O$ isotope values clustered strongly by flock. All were significantly related to flock northing, and $\delta^{15}N$ and $\delta^{2}H$ were additionally related to flock easting. Variation in farming practice (fodder, fertilizer) increased differentiation in $\delta^{13}C$ and between $\delta^{15}N$ between UK flocks, but masked their geographical origin. $\delta^{34}S$ values were more depleted than expected. Differentiation between UK and Icelandic material in $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ was however clear. This is the first study to report geographical variation in un-exchangeable $\delta^{2}H$ and $\delta^{18}O$ values in wool. Combined light stable isotope analysis shows potential as a provenancing tool for sheep wool.

Keywords: Stable isotope analysis; sheep; wool; keratin; provenance

3.1. Introduction

Geographical variation of light stable isotope values of keratinous tissues such as mammalian hair and bird feathers is the basis of isotope studies of migration (Hobson 1999; Ehleringer *et al.* 2008; Bowen 2010; Brattström *et al.* 2010; Valenzuela *et al.* 2011; Wunder 2012). For domesticate species, this methodology offers a way to authenticate animal products, e.g. food. Previous studies of herbivorous mammalian tissues have shown that carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), un-exchangeable hydrogen ($\delta^{2}H$), oxygen ($\delta^{18}O$) and sulfur ($\delta^{34}S$) isotope values reflect geographical origin across Europe (Kornexl *et al.* 1997; Piasentier *et al.* 2003; Schmidt *et al.* 2005; Camin *et al.* 2007). Similar approaches have been tested in China (Guo *et al.* 2010; Sun *et al.* 2010).

Geographical gradients in $\delta^{13}C$ and $\delta^{15}N$ in mammalian tissue largely reflect environmental gradients (e.g. temperature, humidity) affecting local food plant species and growing conditions (Craine *et al.* 2009) and hence indirectly climate. Tissue $\delta^{2}H$ and $\delta^{18}O$ reflect both diet and drinking water isotopic composition, both related to climate, which varies predictably across landscapes (Hobson 1999; Fricke *et al.* 1998; Wassenaar and Hobson 2008). In addition, $\delta^{18}O$ partly reflects air composition, which does not vary geographically (Barkan and Luz 2005). Tissue $\delta^{34}S$ is related to the origin of S in the diet (marine or terrestrial) and can thus distinguish coastal from inland areas (Zazzo *et al.* 2011; Osorio *et al.* 2011). For human tissues, social and cultural practice in food choice may be more dominant than geographical variation in $\delta^{13}C$ and $\delta^{15}N$ (O'Connell and Hedges 1999; Valenzuela *et al.* 2011; Valenzuela *et al.* 2012) though not $\delta^{2}H$ or $\delta^{18}O$, which are more directly derived from local drinking water (Ehleringer *et al.* 2008).

Because they are largely not exposed to the 'continental supermarket' diet (Ehleringer *et al.* 2008), whereby modern food distribution systems ensure isotopic homogeneity over large areas, isotope values in the tissues of domesticated animals should reflect local pasture plants' physiology and growing conditions. However a number of agricultural practices have been shown to affect tissue isotope values (Table 3.1). Further, farmers control metabolic features of livestock such as age, pregnancy and fleece colour, all of which have also been found to affect isotope values, the first in sheep wool $\delta^{13}C$ (Zazzo *et al.* 2008), the second in human hair $\delta^{15}N$ (Fuller *et al.* 2004) and the third in bird feather $\delta^{13}C$ and $\delta^{15}N$ (Michalik *et al.* 2011). These factors are likely differ between sheep flocks and may have to be taken into account when interpreting isotope values for geographical origin.

Keratin proteins, which make up 90% of wool by mass (Popescu and Wortmann 2010) are metabolically inactive and not remodelled once formed (Schwertl *et al.* 2003; Wassenaar and Hobson 2008). Therefore wool records a highly time-resolved isotopic signal, reflecting seasonal change in diet due to both climate and farming practice cycling, as well as short-term metabolic changes, such as pregnancy. Because the absence of subsequent remodelling, wool is likely to show greater isotopic variation than more slowly growing

Table 3.1. Summary of metabolic and farming practice factors found to affect domesticate mammalian herbivore tissue isotope values.

Factor	Isotope	Species	Tissue	Environment	Relationship	Reference
Stocking level	$\delta^{15}N$	Cattle	Hair keratin	Temperate and alpine grassland	Positive correlation	(Schwertl *et al.* 2005)
	$\delta^{15}N$	Sheep	Hair keratin	Semi arid grassland	No relationship	(Wittmer *et al.* 2011)
	$\delta^{15}N$	Cattle	Hair keratin	Temperate grassland	No relationship	(Wrage *et al.* 2011)
Water availability	$\delta^{13}C$	Cattle	Hair keratin	Temperate humid grassland	Positive correlation to plant available soil water; dependent on soil type (peat/mineral)	(Schnyder *et al.* 2006)
Transhumance to altitude	$\delta^{13}C$, $\delta^{15}N$	Sheep, goat, cattle	Hair keratin	Alpine grassland	$\delta^{13}C$: positive correlation, *c*. 1.1‰ km^{-1}; $\delta^{15}N$: negative correlation, *c*. 1.1‰ km^{-1}	(Männel *et al.* 2007)
Salt marsh grazing	$\delta^{15}N$	Cattle	Bone collagen	Coastal salt marsh	*c*. 1.5‰ enrichment	(Britton *et al.* 2008)
Feed type: C_3 *vs.* C_4	$\delta^{13}C$, $\delta^{15}N$	Sheep (juvenile)	Hair keratin, perirenal fat, muscle	Indoor pen	Tissue $\delta^{13}C$ herbage diet $<C_3$ concentrate diet $< C_4$ concentrate diet	(Moreno-Rojas *et al.* 2008)
	$\delta^{13}C$, $\delta^{15}N$	Cattle	Defatted muscle protein, muscle lipid	Pen	C_4 proportion of diet proportional to $\delta^{13}C$ of muscle protein (r^2=0.98) and lipid (r^2=0.93); tissue $\delta^{15}N$ mean grass > mixed > maize silage	(Bahar *et al.* 2005)
	$\delta^{13}C$	Cattle	Hair keratin	Temperate and alpine grassland	C_4 proportion of diet accounted for 96% of $\delta^{13}C$ variation in hair	(Schwertl *et al.* 2005)

Table 3.1 continued.

Factor	Isotope	Species	Tissue	Environment	Relationship	Reference
Feed type: protein content	$\delta^{15}N$	Llama, alpaca, goat, cattle, horse, rabbit	Hair keratin	Indoor pen	Higher range of increase of $\delta^{15}N$ for higher protein diets (19% *vs*. 9%)	(Sponheimer *et al.* 2003)
	$\delta^{34}S$	Horse	Hair keratin	Indoor pen	Greater positive fractionation with low-protein diet	(Richards *et al.* 2003)
Feed type: seaweed	$\delta^{13}C$, $\delta^{18}O$	Sheep	Tooth enamel	Coastal grassland and seaweed from beach	$\delta^{13}C$ reflects enriched marine values; low amplitude $\delta^{18}O$ variation	(Balasse *et al.* 2005)
Feed type: nutritional stress	$\delta^{34}S$	Sheep	Defatted muscle protein	Indoor pen	$\delta^{34}S$ depleted during and following (putative) stress period	(Harrison *et al.* 2011)
Seasonal foddering	$\delta^{13}C$, $\delta^{15}N$	Wild/ domesticate sheep, goat	Dentine collagen	Desert steppe, rocky plateau and mountain, arid valley grassland	Enriched $\delta^{13}C$ in domestic animals *vs.* wild, due to C_4 winter foddering	(Makarewicz and Tuross 2006)
	$\delta^{13}C$, $\delta^{15}N$	Cattle	Hair keratin	Temperate grassland in summer; grass silage and hay in winter	$\delta^{13}C$: summer values depleted compared to winter; $\delta^{15}N$: summer values enriched compared to winter	(Schwertl *et al.* 2003)
	$\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$	Cattle	Defatted muscle protein	Temperate humid grassland	Tissue $\delta^{13}C$: +>2‰ in winter and spring; $\delta^{15}N$ invariant; $\delta^{34}S$ complex (conventional farming)	(Bahar *et al.* 2008)
Weaning age	$\delta^{15}N$	Sheep, goat	Dentine collagen	Desert steppe, rocky plateau and mountain, valley and alpine grassland	Approx 1.5‰ enrichment with prolonged weaning	(Makarewicz and Tuross 2006)
Climatic variation	$\delta^{18}O$	Sheep, cattle, elk, pigs	Tooth enamel	Wide range	Correlated with precipitation values, especially where large annual temperature variation	(Fricke *et al.* 1998)

Table 3.1 continued.

Factor	Isotope	Species	Tissue	Environment	Relationship	Reference
Intensive *vs.* extensive agriculture	$\delta^{13}C$, $\delta^{15}N$	Cattle	Cows' milk: whole, casein, whey	Temperate and alpine grassland	Intensive enriched over extensive in $\delta^{13}C$ due to use of C_4 feeds; in $\delta^{15}N$ due to use of fertilizer	(Kornexl *et al.* 1997)
Organic *vs.* conventional agriculture	$\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$	Cattle	Defatted muscle protein	Temperate humid grassland	Conventional tissues enriched over organic in $\delta^{13}C$ due to use of C_4 feeds, and in $\delta^{15}N$ due to use of fertilizer; depleted relative to organic in $\delta^{34}S$, reasons unclear	(Schmidt *et al.* 2005)
Distance from coast	$\delta^{34}S$	Sheep	Hair keratin	Temperate humid grassland	$\delta^{34}S$ increasingly depleted with increasing distance from coast; effect was greater against prevailing wind direction.	(Zazzo *et al.* 2011)
Bedrock and soil type	$\delta^{34}S$	Sheep	Defatted muscle protein	Wide range	$\delta^{34}S$ higher in rocks and soils derived from evaporates; lower in volcanic and sulfide sediments	(Camin *et al.* 2007)
Weathering (photodegradation and abrasion)	$\delta^{34}S$	Cattle	Hair keratin	Temperate humid grassland	Enrichment in $\delta^{34}S$ with increased weathering	(Auerswald *et al.* 2011)

tissues such as muscle protein (Balasse *et al.* 2005; Bahar *et al.* 2008). This may obscure geographical resolution of isotope values.

This study examined the resolution of a multi-isotope provenancing technique based on wool keratin $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotope values within a small geographical region. It therefore extended the approach of Hedges *et al.* (2005) from a Mediterranean to a temperate Atlantic climate. The study applied $\delta^{34}S$ to one flock only, due to cost and availability. This work is the first stage in establishing a provenancing method for historical and archaeological sheep wool textile artefacts from the North Sea area, objects of central economic and political concern to a number of countries in this region since at least the high Middle Ages (AD 1100-1500: Munro 2003; Spufford 2006, 232-41, 326-9).

3.2. Samples, analytical and statistical methods

The effect of metabolic (breeding history, sex) and dietary (seasonality, diet quality) factors on wool isotope values have already been examined (Chapter 2). This study investigated whether geographic variation in isotope values was obscured by these factors and real variability in flock structure and management, including breed, management, flock size, sex and age balance and wool colour.

The study examined 86 samples of wool from 67 animals from five flocks (Table 3.2, Figure 3.1). Staples represented a year's hair growth (±2 weeks), except for UK Penicuick and UK Escrick where the growth period was shorter. The flocks represented a range of husbandry types:

- grazing on non-fertilised pasture, supplementation with local (unfertilized) hay only, no concentrates (UK Tollesbury and UK Penicuick)
- grazing on pasture receiving fertilizer, with concentrate supplementation during snow cover in winter and during lambing (UK Seaton Ross)
- grazing on fields that may have been treated with a small amount of artificial fertiliser, supplementation with local (possibly fertilized) hay (Iceland Kalmanstunga)
- unknown conditions (UK Escrick).

Animals were mostly of relatively unimproved breeds (Table 3.3). The majority (66%) were female, with 25% male, 7% and 1% castrate (1 animal). Three quarters (74%) were adults (>12 months old), and 18% yearlings (<12 months old). More than half of adult ewes were empty (that is, had not had a lamb; 59%) during the period of wool growth, while 41% had carried a pregnancy (lambed) during this period. Wool colour varied, with most animals having light coloured wool (white 21%, cream 54%) but tan, brown, grey and black fleeces were also sampled.

Table 3.2. Origin of samples of wool: flock location and management details.

Flock	Latitude/ longitude	Altitude /m	Mean temp. range/°C[a]	Mean annual rainfall /mm[a]	Farming type	Wool growth period	Pasture	Feeds
Seaton Ross, North Yorkshire, UK	55.85866 N -0.80955 E	7	Jan: 3.5–4.5; Jul: 15.5–16.5	400–800	Modern (C. Johnstone, pers. comm.)	Jun 2008–Jun 2009	Converted to pasture from fertilized agricultural land, winter 2007–8.	Fresh pasture, local hay, mixed C_3/C_4 concentrate feeds
Tollesbury, Essex, UK	51.75345 N 0.86480 E	2	Jan: 3.5–4.5; Jul 16.5–19.0	400–800	SSSI (Anonymous 1993)	Jun 2008–Jun 2009	Unfertilized embanked salt marsh	Fresh SSSI pasture and SSSI hay
Escrick, North Yorkshire, UK	(53.87573 N -1.04112 E)[b]	Not known	Not known	Not known	Not known (Chapter 2)	Not known (probably May/June 2008)–Feb 2009	Not known	Not known
Penicuick, Midlothian, UK	55.85839 N -3.20955 E	190	Jan: 2–3.5; Jul 13.5–14.5	400–800	Traditional (Dingwall *et al.* unpublished; Chapter 2)	May/Jun 1996–9 to Aug/Sep or Nov/Dec 1999–2001	High: improved pasture Low: unimproved pasture	High: fresh pasture, hay during snow cover. Low: fresh pasture
Kalmanstunga, Borgarfjörður, Iceland	64.73067 N -20.79693 E	253	0–2	1000–1500	Traditional (E. Eyþórsdóttir, pers. comm.)	Apr 2009–Apr 2010	Small quantity artificial fertilizer	Fresh highland pasture, local hay

[a](Jebson 2007; Nawri and Björnsson 2010)

[b]Abattoir location. Flock origin unknown but very likely North Yorkshire, within 30km of abattoir.

Table 3.3. Flock composition.

Flock	Breed	Sex	Age	Lambing[a]
Seaton Ross, North Yorkshire, UK	Shetland n=11 Wensleydale n=1	Male n=2 Female n=10	Adult n=9 Yearling n=3	Lambed n=4 Empty n=3
Tollesbury, Essex, UK	Shetland n=9 North Ronaldsay n=11	Male n=3 Female n=16 Castrate=1	Adult n=14 Yearling n=6	Lambed n=6 Empty n=7
Escrick, North Yorkshire, UK	Not known n=5	Not known	Not known	Not known
Penicuick, Midlothian, UK	Shetland n=20	Male n=10 Female n=10	Adult n=20	Empty n=10
Kalmanstunga, Borgarfjörður, Iceland	Icelandic n=10	Male n=2 Female n=8	Adult n=7 Yearling n=3	Lambed n=5

[a]Adult females only. Wool sampling was after birth for animals from UK, during pregnancy for animals from Iceland.

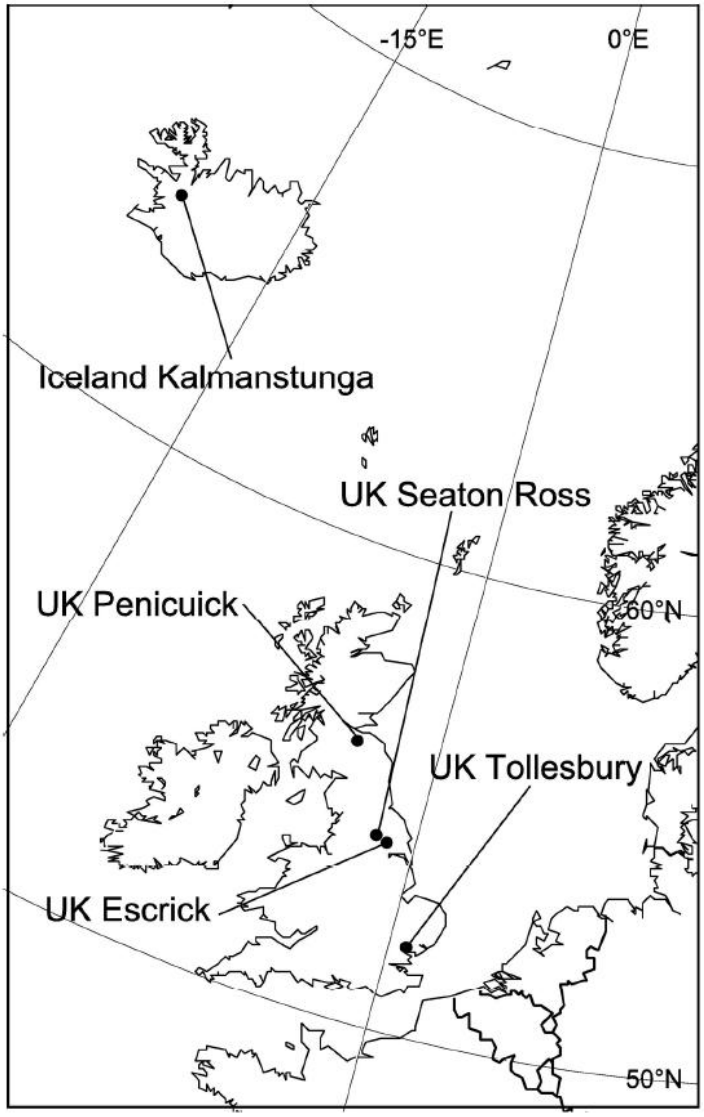


Figure 3.1. Origin of samples of wool: map of flock locations.

3.2.1. Sample cleaning

Approximately 0.3–0.5 g of wool, in the form of 1–2 staples (the locks of hair into which the fleece naturally falls), was selected from each fleece. Samples were hand-cleaned to remove particulate matter but without breaking up the staples, and washed four times with organic solvents and ultra-pure water (ELGA Purelab Ultra, Marlow, UK) according to the protocol in Hedges *et al*. (2005), but using dichloromethane (HPLC grade, Fisher Scientific, Loughborough, UK) instead of chloroform in all solvent mixtures, and employing an additional initial water wash to ensure thorough cleaning. Between 1 and 3 whole fibres were coiled into metal capsules for IRMS analysis without milling. Triplicate samples were selected from eight animals in the UK Tollesbury and Seaton Ross flocks.

3.2.2 Sample analysis

$\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ analysis on samples from UK Escrick was carried out at Iso-Analytical, (Crewe, Cheshire) as reported in Chapter 2. All remaining analyses were carried out at the Natural Environment Research Council Life Sciences Mass Spectrometry Facility (NERC LSMSF) in East Kilbride.

For $\delta^{13}C$ and $\delta^{15}N$ analyses, 0.7 mg of washed wool was weighed into 4 x 3.2 mm Sn capsules (Elemental Microanalysis, Okehampton, UK). For $\delta^{18}O$ and $\delta^{2}H$ analyses, 0.1 mg of wool was weighed into 4 x 3.2 mm Ag capsules (Elemental Microanalysis, Okehampton, UK and Pelican Scientific, Stockport, UK). Whole hairs were analysed to obtain a period average value. $\delta^{13}C$ and $\delta^{15}N$ IRMS analyses were carried out on a ThermoElectron Delta Plus XP with Costech ECS 4010 elemental analyser; internal standards were a gelatine, two alanines enriched with ^{13}C and ^{15}N respectively, and a ^{15}N-enriched glycine (Table 3.4). C and N content and C:N atomic ratios ($C:N_{atom}$) were calculated using a tryptophan standard. $\delta^{18}O$ and $\delta^{2}H$ IRMS analyses were carried out on a Thermo Fisher Scientific Delta V Plus with TC/EA high temperature furnace. The contribution of exchangeable hydrogen was calculated using keratin standards BWB-II (whale baleen), CFS (feathers), ISB (feathers) and WG (feathers) and a comparative equilibration method (Wassenaar and Hobson 2003; Sauer *et al.* 2009). $\delta^{18}O$ standards were IAEA 601, IAEA CH6 and IAEA 600; the $\delta^{2}H$ of the un-exchangeable H in the four keratin standards was previously determined using a steam equilibration technique. Calculation of un-exchangeable $\delta^{2}H$ assumed a fractionation factor $\alpha = 1.080$ ($\varepsilon_{x\text{-}w} = 80‰$). $\delta^{13}C$ and $\delta^{15}N$ results are reported in per mille (‰) relative to PDB and AIR respectively; $\delta^{18}O$ and $\delta^{2}H$ results are reported in per mille relative to VSMOW.

3.2.3 Statistical treatment

Statistical analysis was carried out using R (R Development Core Team 2008). Where multiple samples were tested from a single animal, the arithmetic mean of isotope and elemental composition values was used in statistical calculations at flock level. The dataset was non-parametric (univariate and multivariate Shapiro-Wilk tests, $P<0.05$). No effective data transformations were found. Continuous surface assignment models, based on regression, are therefore no appropriate for this data, despite their wide use elsewhere in isoscape investigations (Wunder *et al.* 2005; Wunder 2012). As an alternative, standard deviations for flocks in this study were estimated using a bootstrapping method. Calculations were made within R using package *boot* (Davison and Hinkley 1997; Canty and Ripley 2011).

Table 3.4. Isotopic analytical precision: mean ± maximum s.d in any single analytical run. For abbreviations, see text. *s.d. undetermined.

		$\delta^{13}C$/‰		$\delta^{15}N$/‰		$\delta^{2}H$/‰		$\delta^{18}O$/‰	
Standards	**n**	**Observed**	**Accepted**	**Observed**	**Accepted**	**Observed**	**Accepted**	**Observed**	**Accepted**
Gelatine	130	-20.34 ± 0.12	-20.35 ± 0.04	5.89 ± 0.14	5.95 ± 0.11				
^{13}C-enriched alanine	45	-10.68 ± 0.14	-10.69 ± 0.09	-4.94 ± 0.19	-4.97 ± 0.12				
^{15}N-enriched alanine	27	-23.52 ± 0.07	-23.51 ± 0.02	17.11 ± 0.11	17.06 ± 0.14				
^{15}N-enriched glycine	18	-35.99 ± 0.22	-36.01 ± 0.06	19.72 ± 0.08	19.71 ± 0.13				
CFS	9					-140.4 ± 1.5	-148.6*	5.80 ± 0.53	
BWB-II	9					-100.3 ± 2.1	-109.5*	13.15 ± 0.23	
ISB	9					-59.9 ± 2.5	-68.8*	13.13 ± 0.56	
WG	9					-136.5 ± 2.1	-146.6*	6.43 ± 0.62	
IAEA-601	41							23.07 ± 0.24	23.14 ± 0.19
IAEA-CH6	16							36.52 ± 0.41	36.40*
IAEA-600	8							-3.29 ± 0.44	-3.48 ± 0.53

3.3. Results

Full $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, and $C:N_{atom}$ results for samples from UK Tollesbury, UK Seaton Ross and Iceland Kalmanstunga flocks are given in Appendices 3.1 (all individuals) and 3.2 (triplicate raw data); data from UK Penicuick and UK Escrick flocks is reported in Chapter 2.

Isotopic effects of breed, sex, age, and lambing status could not be statistically compared within or between flocks in this study because of unequal numbers of samples in each cohort. In the previous study with a balanced block design (Chapter 2), the only metabolic effect to show a significant effect on the isotope composition of keratin was the breeding status of adult ewes: $\delta^{15}N$ in wool from bred ewes was median 1.3‰ more depleted than wool from empty ewes. In this study, lambed and empty ewes' wool isotopic composition could be compared for UK Seaton Ross (n_{lambed}=4, n_{empty}=3) and UK Essex flocks (n_{lambed}=6, n_{empty}=7). Median values were in all cases within experimental error.

Maximum standard deviation (s.d.) in isotope ratio within a single fleece was 0.2‰ for $\delta^{13}C$, 0.3‰ for $\delta^{15}N$, 6.9‰ for un-exchangeable $\delta^{2}H$, 0.7‰ for $\delta^{18}O$, 0.4 for $\delta^{34}S$ and 0.07‰ in $C:N_{atom}$ (n=3 except for $\delta^{34}S$ where n=2). Flock medians, interquartile ranges (IQR) and bootstrapped s.d. 95% confidence intervals (CI) are reported in Table 3.5 and illustrated in Figure 3.2.

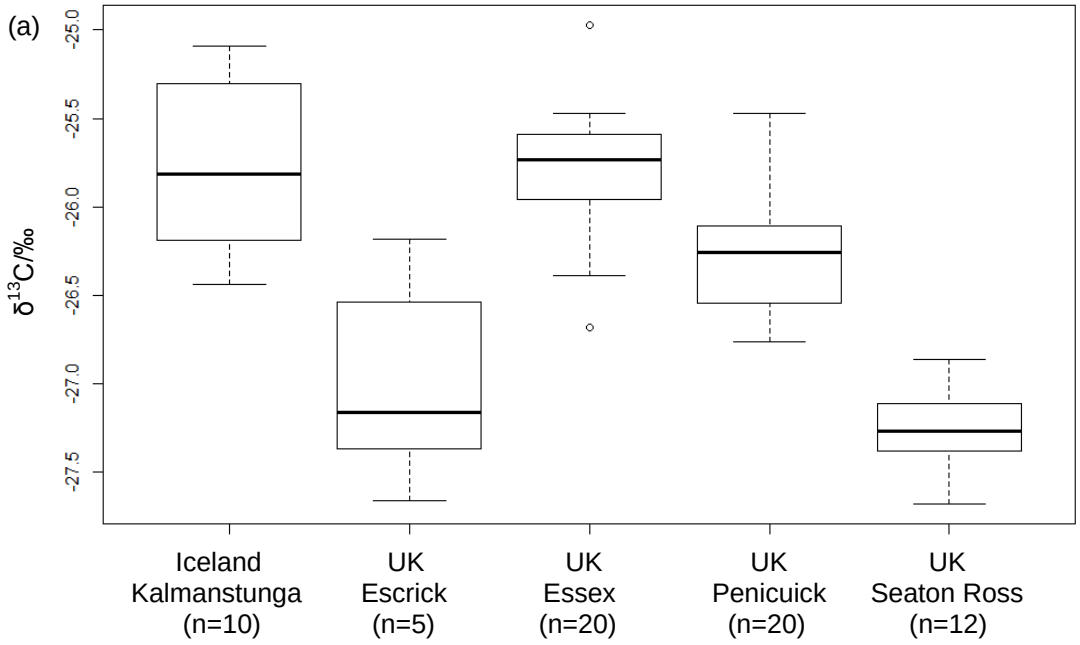
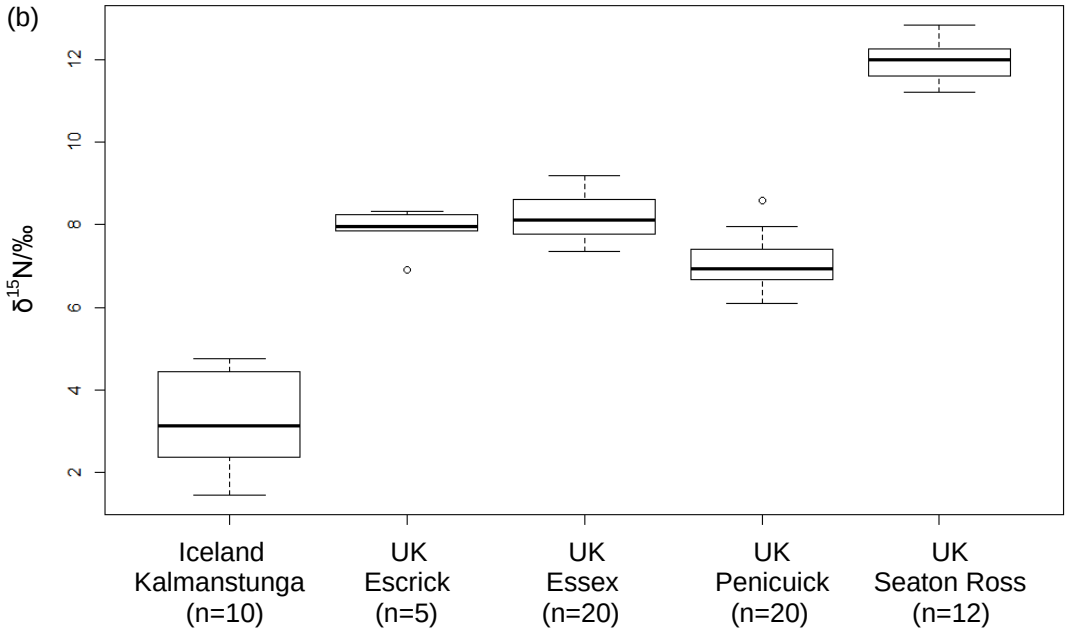


Figure 3.2. Box plots of sheep flock isotope medians and IQRs (circles indicate statistical outliers). (a): $\delta^{13}C$; (b): $\delta^{15}N$; (c): $\delta^{2}H$; and (d): $\delta^{18}O$.



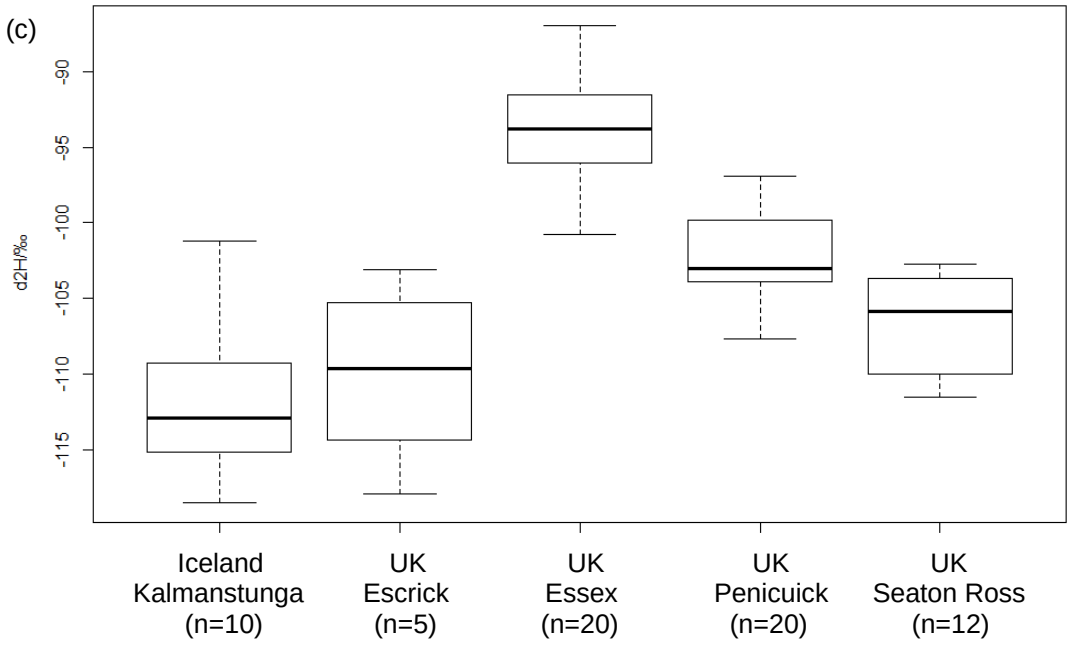


Figure 3.2. continued

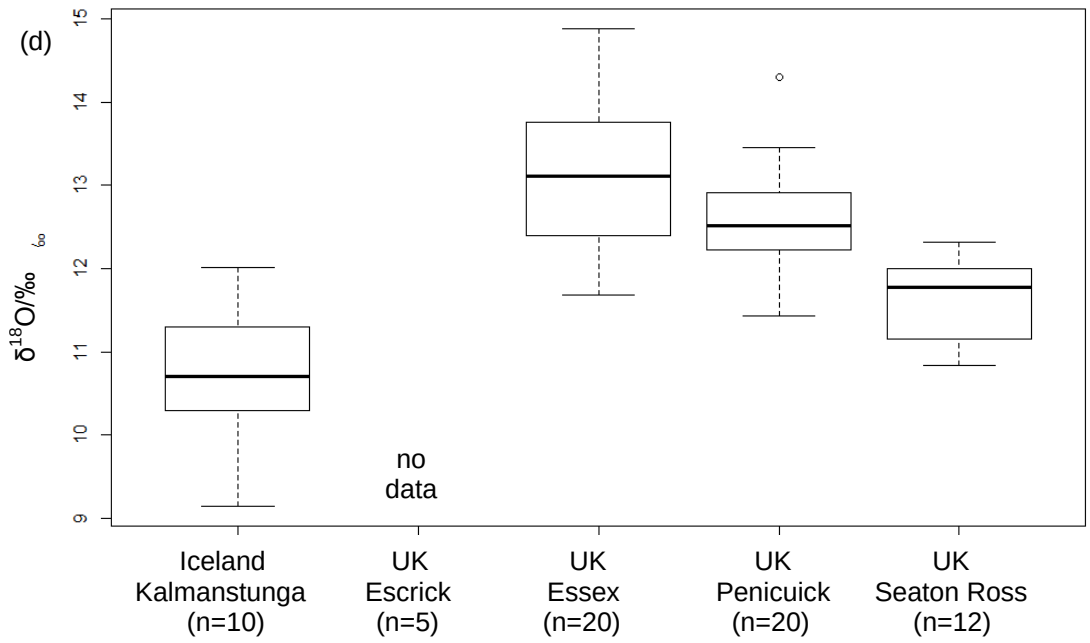


Figure 3.2. continued

Raw isotope values of wool samples clustered strongly by flock (Figure 3.3, Table 3.5). Significant differences in isotope value distribution (Kolmogorov-Smirnov tests, $P<0.05$) and median (Mann-Whitney U test), existed between almost all pairs of flocks (Table 3.6).

Negative correlations existed between all four isotopes and flock northing: these were significant for $\delta^{13}C$ and $\delta^{15}N$ (Spearman's rank correlation coefficient, ρ=-2.8, -2.7; both $P<0.05$) and highly significant for $\delta^{2}H$ and $\delta^{18}O$ (Spearman's, ρ=-0.78, -0.75; both $P<<0.001$). Flock easting was highly significantly positively correlated to $\delta^{15}N$ and $\delta^{2}H$ (Spearman's, ρ=0.71, 0.65; both $P<<0.001$).

$\delta^{13}C$ was negatively correlated with $\delta^{15}N$ (Spearman's, ρ=-0.37; both $P<0.01$) and positively correlated with $\delta^{2}H$ and $\delta^{18}O$ (Spearman's, ρ=0.39, 0.26; both $P<0.05$). $\delta^{2}H$ and $\delta^{18}O$ were also highly positively correlated (Spearman's, ρ=0.67; both $P<<0.001$).

Linear discriminant analysis (LDA) based on the four isotope values for which data from more than one flock was available (omitting UK Escrick data) resulted in 94% correct flock classification. Omission of $\delta^{18}O$ did not affect these results. LDA analysis of all five flocks using only $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ values resulted in 90% correct classification; using only $\delta^{15}N$ and $\delta^{2}H$ 94%; using only $\delta^{13}C$ and $\delta^{2}H$ 90%; and using only $\delta^{13}C$ and $\delta^{15}N$ 85%.

Principal component analysis of $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ measurements of wool samples generated two components (PC1 and PC2) which explained 93% of sample variance (Figure 3.4). $\delta^{18}O$ was omitted from this analysis as this data was not obtained for UK Escrick (Chapter 2).

Table 3.5. Flock medians, IQRs and bootstrapped 95% CIs of s.d. for $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, $\delta^{34}S$ and $C:N_{atom}$ ratio.

		UK Tollesbury	UK Seaton Ross	UK Escrick	UK Penicuick	Iceland Kalmanstunga
$\delta^{13}C$/‰	Median	-27.3	-25.7	-27.2	-26.3	-25.8
	IQR	0.4	0.2	0.8	0.4	0.8
	σ (95% CI)	0.3–0.5	0.2–0.3	0.5–1.0	0.3–0.5	0.4–0.7
$\delta^{15}N$/‰	Median	12.0	8.1	8.0	6.9	3.1
	IQR	0.8	0.6	0.4	0.6	1.8
	σ (95% CI)	0.5–0.7	0.4–0.7	0.4–1.0	0.4–0.9	0.9–1.6
$\delta^{2}H$/‰	Median	-105.9	-93.8	-109.6	-103.0	-112.9
	IQR	4.3	5.9	9.1	3.7	5.7
	σ (95% CI)	2.7–4.7	2.8–4.4	4.7–10	2.3–3.8	3.4–7.6
$\delta^{18}O$/‰	Median	11.8	13.1	-	12.5	10.7
	IQR	1.2	0.8	-	0.7	1.0
	σ (95% CI)	0.7–1.1	0.4–0.7	-	0.5–0.9	0.5–1.2
$\delta^{34}S$/‰	Median	-	-	4.8	-	-
	IQR	-	-	1.3	-	-
	σ (95% CI)	-	-	1.0–2.6	-	-
$C:N_{atom}$	Median	3.52	3.52	3.60	3.47	3.42
	IQR	0.04	0.06	0.01	0.02	0.02
	σ (95% CI)	0.02–0.04	0.04–0.07	0.01–0.03	0.01–0.02	0.02–0.06

Table 3.6. Significant differences in isotope value distribution (Kolmogorov-Smirnov tests, *P*<0.05) and median (Mann-Whitney U test, *P*<0.05) between flocks. Underlined: both median and distribution are significantly different; *italic*: only median is significantly different; plain: only distribution is significantly different. NB: $\delta^{18}O$ differences were not calculable for comparisons to UK Escrick; no comparisons were possible for $\delta^{34}S$.

	UK Seaton Ross	**UK Escrick**	**UK Penicuick**	**Iceland Kalmanstunga**
UK Tollesbury	$\underline{\delta^{15}N}$ $\underline{\delta^{13}C}$ $\underline{\delta^{18}O}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$	$\underline{\delta^{13}C}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$	$\underline{\delta^{15}N}$ $\underline{\delta^{13}C}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$	$\underline{\delta^{15}N}$ $\underline{\delta^{18}O}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$
UK Seaton Ross	/	$\underline{\delta^{15}N}$ $\underline{C:N_{atom}}$	$\underline{\delta^{15}N}$ $\underline{\delta^{13}C}$ $\underline{\delta^{18}O}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$	$\underline{\delta^{15}N}$ $\underline{\delta^{13}C}$ $\underline{\delta^{18}O}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$
UK Escrick		/	$\underline{\delta^{15}N}$ $\underline{\textit{δ}^{13}\textit{C}}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$	$\underline{\delta^{15}N}$ $\underline{\delta^{13}C}$ $\underline{C:N_{atom}}$
UK Penicuick			/	$\underline{\delta^{15}N}$ $\underline{\delta^{13}C}$ $\underline{\delta^{18}O}$ $\underline{\delta^{2}H}$ $\underline{C:N_{atom}}$

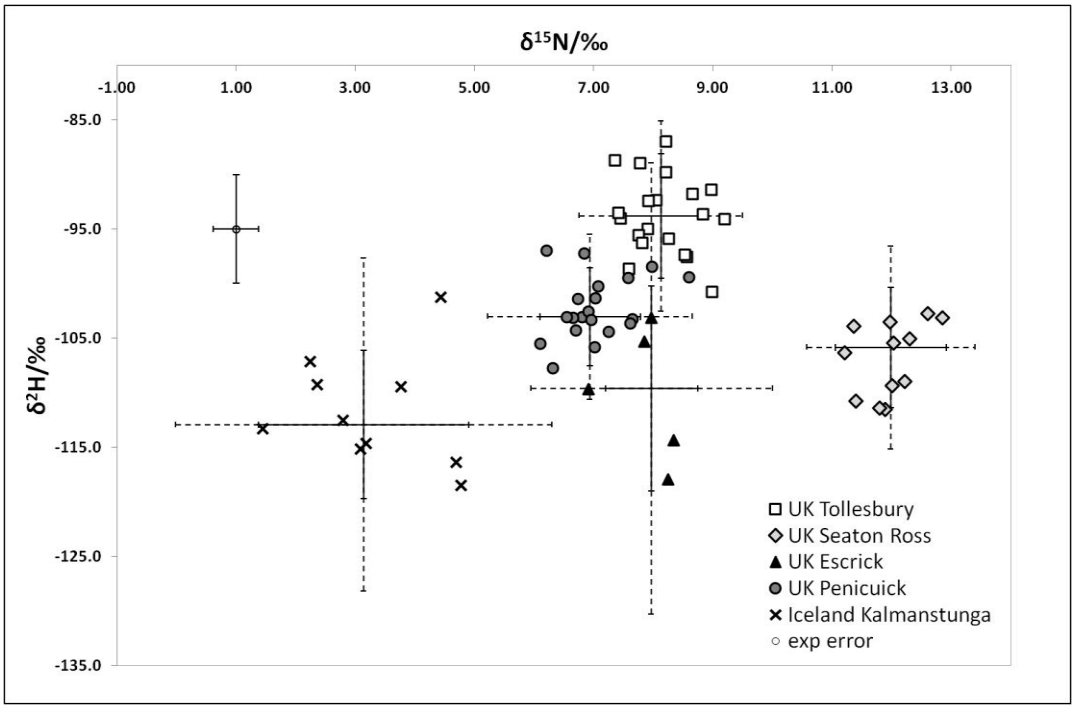


Figure 3.3. Wool keratin $\delta^{15}N$ *vs.* $\delta^{2}H$ for all individual animals, with median ± 2 s.d. bootstrapped 95% CI (minimum: solid line; maximum: dashed line) for each flock.

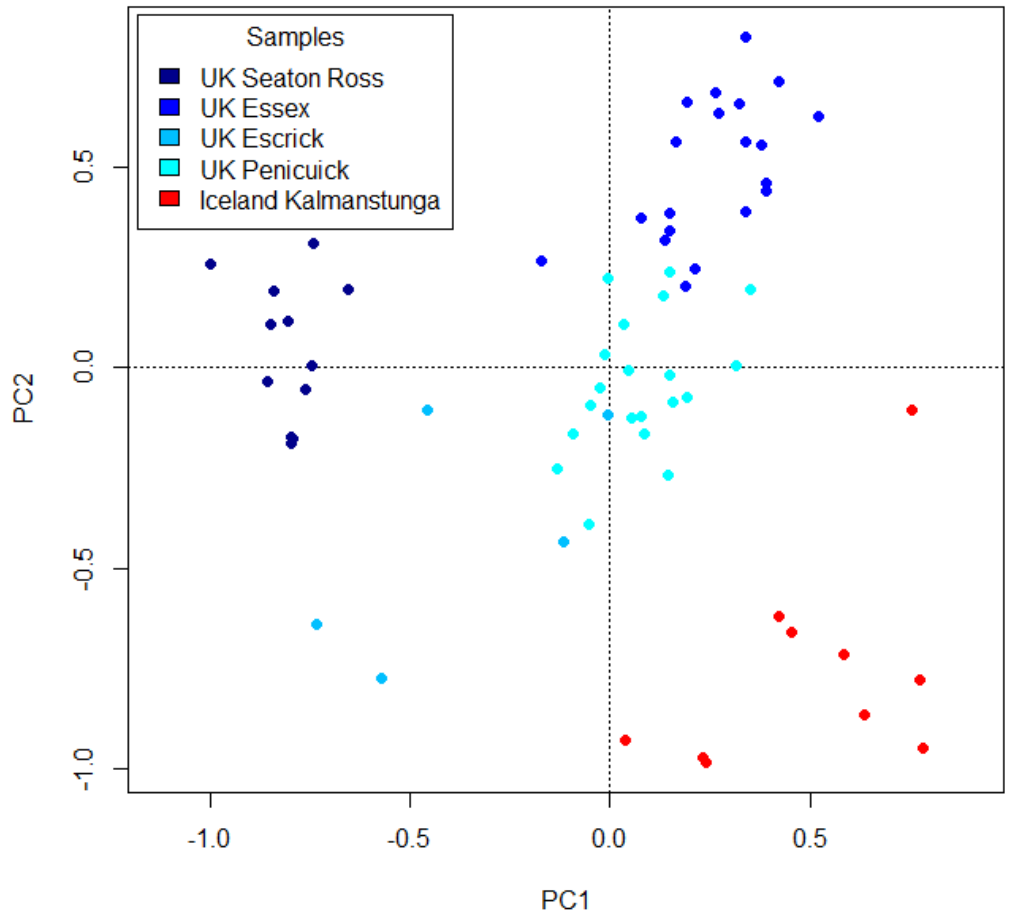


Figure 3.4. Scatter plot of first two principal components of $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ data for wool samples from UK and Iceland.

2.4. Discussion

3.4.1 Flock medians and ranges

The range of sheep wool $\delta^{13}C$ values observed in this study (-27.7–-25.0‰) was consistent with values from wool and other mammalian herbivore hair from northern Europe (see discussion in Chapter 2). $\delta^{13}C$ values were consistent with wholly C_3-fed animals. Values of $\delta^{2}H$ (-119–-87‰) and $\delta^{18}O$ (9.1–14.9‰) in this study were similar to those previously obtained for sheep wool, but $\delta^{15}N$ value range (1.5–12.9‰) was much wider than that previously reported (Chapter 2). Wool $\delta^{15}N$ values within the UK were very similar (c. 7–8‰; Figure 3.2b) except for data from UK Seaton Ross (range 11.2–12.9‰) which were higher than any previously reported for modern mammalian herbivore hair. These were not without parallel among archaeological sheep/goat collagen data (e.g. Britton *et al.* 2008; Reynard and Hedges 2008; Hakenbeck *et al.* 2010; nitrogen isotope values in sheep bone collagen and wool keratin are directly comparable: Chapter 2). In contrast, the generally depleted $\delta^{13}C$ and $\delta^{15}N$ values in wool from Iceland relative to wool from the UK was consistent with the geographical pattern observed in lamb muscle protein (Piasentier *et al.* 2003), which was attributed to variation in fodder $\delta^{15}N$ values, themselves depending on soil type, humidity, plant type and fertilizer use.

There were no consistent patterns in isotopic range between flocks, for example with flock size. Total $\delta^{13}C$ ranges were relatively large (0.8–1.7‰) compared to total observed range (2.7‰), but the inverse was true for $\delta^{15}N$ (flock ranges 1.4–3.3‰, total range 11.4‰). Degrees of variability in $\delta^{2}H$ (flock ranges 9–17‰, total range 32‰) and $\delta^{18}O$ (flock ranges 1.5–3.2‰, total range 5.8‰) were not correlated between flocks. It is interesting that UK Seaton Ross (n=12) showed the smallest $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ ranges, even though animals in this flock were in receipt of more varied feeds than those in other UK groups where husbandry was known (Essex and Penicuick, both n=20). This was against expectations from Codron *et al*. (2012).

3.4.2 Differentiation between flocks

Raw sheep wool $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotope values clustered strongly by flock. All isotope values were significantly negatively related to flock northing, and both $\delta^{15}N$ and $\delta^{2}H$ were correlated with to flock easting. Within-flock variation was not sufficient to confound flock differentiation. Icelandic samples were clearly differentiated from UK samples, particularly by $\delta^{15}N$.

Differences in flock and pasture management therefore clearly affected $\delta^{15}N$ values, in agreement with previous results (Schwertl *et al.* 2005; Hedges *et al.* 2005). Within the UK, these masked geographical differentiation due to climate gradients. UK Tollesbury and Penicuick had the most similar farming types (non-concentrate-fed, non-fertilised pasture and local hay) and had the most similar isotope values, despite their wide geographical

separation. Samples from three of the four UK flocks had $\delta^{15}N$ values within a narrow range (6.1–9.2‰) but samples from the UK Seaton Ross flock were strongly enriched compared to this (range 11.2–12.9‰). This variation was larger than that expected from geographic variation in plant $\delta^{15}N$ between the flock locations, due to either mean annual temperature differences (approximately 1‰; compare to 3‰ across mainland Britain or 4.4‰ between Britain and Iceland) or mean annual precipitation differences (maximum 3‰ within Britain, or 4‰ between Britain and Iceland: Craine *et al.* 2009). Some additional contribution, probably from previous manuring (Bateman and Kelly 2007), the isotope effect of which can be remarkably long lasting (Commisso and Nelson 2008), could be responsible at the UK Seaton Ross pasture (grass $\delta^{15}N$ 11.6–11.8‰ in June 2009, data not shown).

Variation in $\delta^{13}C$ within the UK may also have been related to differences in farming practice. Flocks not receiving concentrate (UK Essex and Penicuick) were similar and relatively enriched, whereas UK Seaton Ross (receiving concentrate) and UK Escrick (unknown farming conditions) were 1–1.5‰ more depleted. This depletion cannot be accounted for by depletion in overall diet isotopic content, as concentrates were likely to be at least part based on C_4, and therefore relatively enriched. A 4‰ depletion in sheep tooth enamel with C_4 concentrate supplementation has however been observed (Zazzo *et al.* 2010). Here it was ascribed to a decrease in digestive methane production (which is highly depleted relative to diet) with decreased diet roughage, and a consequent incorporation of depleted metabolic material into tissue. If this effect was present in this study, then it was much smaller, which was consistent with routing of only part of the C in wool from the general body pool, with the remainder being routed from dietary amino acids.

UK samples in this study were all depleted in ^{13}C and enriched in ^{15}N compared to samples from elsewhere in Europe (Figure 3.5). This mirrored the geographic pattern found in lamb muscle protein, where samples from the UK showed higher $\delta^{13}C$ and $\delta^{15}N$ than samples from mainland Europe (Camin *et al.* 2007; Piasentier *et al.* 2003). For $\delta^{13}C$, this effect was ascribed to the higher humidity of an Atlantic temperate climate affecting pasture isotopic composition; for $\delta^{15}N$ it was it was ascribed to different fertilizer use, though pasture plant composition may plausibly also be a factor (Chapter 2). Icelandic samples in this study were depleted in ^{15}N compared to samples from elsewhere in Europe, and showed $\delta^{13}C$ intermediate between UK and (most) Mediterranean values, as in Piasentier *et al.* (2003). Samples from France and Germany showed a range of compositions intermediate between UK and Mediterranean in both $\delta^{13}C$ and $\delta^{15}N$. It was likely that the spread in $\delta^{13}C$ values visible in Mediterranean samples is at least partly due to C_3/C_4 composition of diet: this was clearly shown by the data from Moreno-Rojas *et al*. (2008) which examined the effect of diet composition in samples from Sicily.

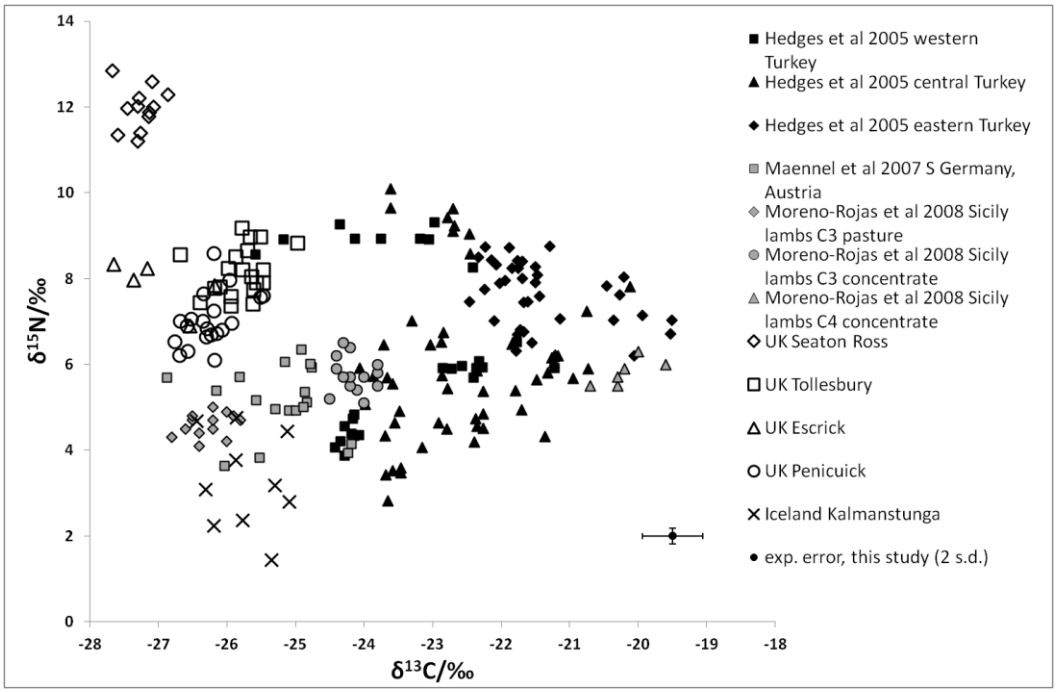


Figure 3.5. Results from this study compared to published sheep wool $\delta^{13}C$ and $\delta^{15}N$ composition data from other regions of Europe.

To the authors' knowledge there is no other published $\delta^{2}H$ and $\delta^{18}O$ data from sheep wool, though Hedges *et al*. (2005) indicated that some $\delta^{2}H$ analyses have been carried out. Given that combined $\delta^{15}N$ and $\delta^{2}H$ was the most useful bivariate visualisation for data from north-western Europe in this study, it would be interesting to obtain additional $\delta^{2}H$ data from sheep wool samples across Europe to examine geographic discrimination with this method. Some systematic variation in $\delta^{2}H$ with geography is evident in defatted lamb muscle (Camin *et al.* 2007) though this did not usefully distinguish Mediterranean from mainland European samples, and did not test samples from Iceland. It is not currently possible to combine the muscle dataset with wool data, however, as offsets in $\delta^{2}H$ between muscle and wool from sheep have not been estimated, though they have for $\delta^{15}N$ (±1‰: Moreno-Rojas *et al.* 2008; Sun *et al.* 2010). The utility of $\delta^{2}H$ and/or $\delta^{18}O$ data, in combination with $\delta^{13}C$ and $\delta^{15}N$ results, to provenance samples of sheep wool was however strongly suggested by this study

The $\delta^{34}S$ composition of UK Escrick wool samples was depleted compared to material from Ireland and Turkey, and similar to values from cattle tail hair from south Germany (Figure 3.6 and Chapter 2). This was unexpected as UK values were anticipated to be intermediate between Irish and continental values, because of its relative exposure to marine sulfate from aerosol deposition (Herut *et al.* 1995; Zazzo *et al.* 2011). For this flock however, other sources of sulfur, such as bedrock, bacteria and fossil fuel burning, must have been significant (Peterson and Fry 1987; Krouse and Herbert 1988; Zhao *et al.* 2003). The potential of $\delta^{34}S$ for provenancing samples of sheep wool remained therefore unclear.

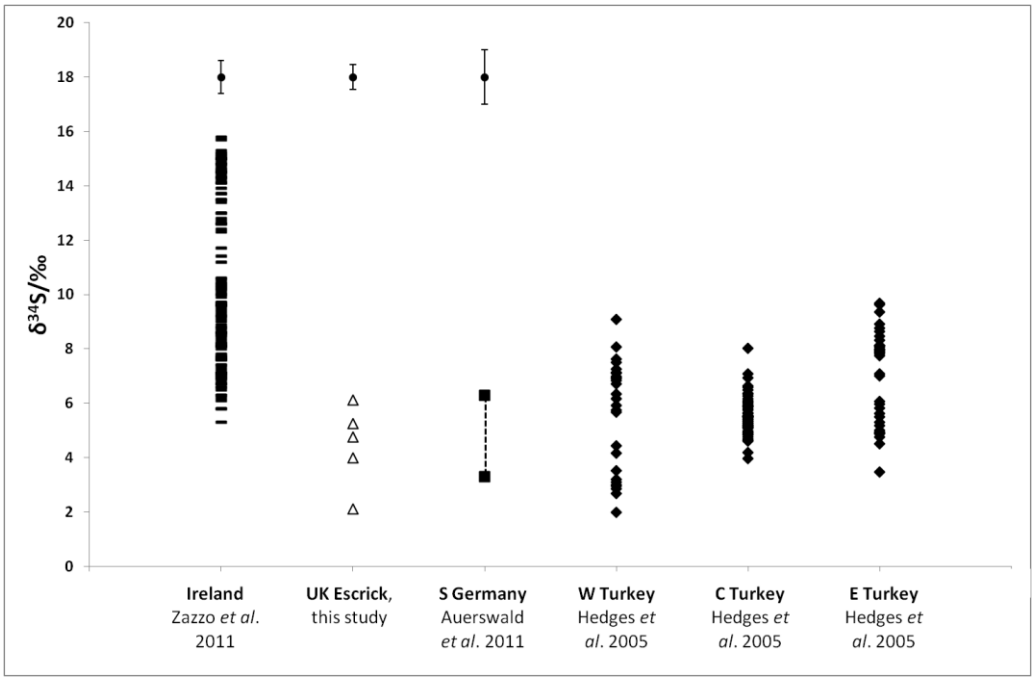


Figure 3.6. Results from this study compared to published sheep wool $\delta^{34}S$ composition data from other regions of Europe. Data from Auerswald *et al.* (2011) indicates maximum and minimum only. Error bars are 2 s.d. (not reported for Hedges *et al*. 2005).

3.5. Conclusion

The gradients in $\delta^{13}C$ and $\delta^{15}N$ composition observed in this study of sheep wool from north-western Europe paralleled those found in other sheep tissues (Piasentier *et al.* 2003; Camin *et al.* 2007), which suggested that common Europe-wide isotopic gradients for sheep tissues exist. Un-exchangeable $\delta^{2}H$ and $\delta^{18}O$ data also usefully distinguished between samples from the UK and those from Iceland. This differentiation was not confounded by within-flock variation but was affected by farming practice, particularly for $\delta^{13}C$ and $\delta^{15}N$. In the UK, this increased resolution of provenancing while obscuring geographic origin. Icelandic material was nevertheless differentiated from UK material in $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotopic composition. The degree of farming variability in a region, determined in part by climate and soil characteristics and in part by social patterns of land use and production, will therefore affect the resolution of this provenancing technique in the present and past. Geographic variability has also been established in $^{87}Sr/^{86}Sr$ measurements of sheep wool from the North Sea region (Frei *et al.* 2009). This technique, which is not affected by farming practice but which depends on geology (principally bedrock age), might therefore usefully be combined with light stable isotope analysis to differentiate between areas with similar environment but different geological substrates, e.g. Iceland *vs*. Norway.

Acknowledgements

Funding for this work was provided by the UK Natural Environment Research Council (IvH: NE/G52421X/1, EK153-15/09, EK163-08/10). Thanks to Cluny Johnstone, Mike Sandison, Escrick Abattoir, Emma Eyþórsdóttir and Polydora Baker of English Heritage for samples.

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4. Microbiological and hydrolytic degradation of wool keratin proteins: amino acid, elemental and isotopic composition

Abstract

Archaeological hair samples have recently become a focus of analytical interest in palaeodietary, provenancing and dating studies. Microbiological and hydrolytic processes in temperate waterlogged conditions cause degradation of proteinaceous hair fibres. The relationship between these processes and the integrity of isotopic properties of the wool fibre are unknown. This study explored the nature of diagenesis in (1) experimental burial for up to 8 years in temperature marine sediment, fenland bog and raised bog environments, and (2) laboratory isothermal hydrous conditions at 80°C, 110°C, and 140°C. The effects of degradation were characterised by amino acid (AA) concentration and racemisation, elemental composition, and isotopic composition in samples of raw wool and wool textiles.

AA, elemental and isotopic composition changes in experimentally buried samples were generally slight, despite extensive macroscopic alteration. AA composition and racemisation change in isothermally heated samples increased with increasing temperature. The more hydrophilic AAs (Asx, Glx, Ser, Gly) were more quickly lost by hydrolysis, leading to an accumulation of hydrophobic AAs (Val, Phe, Leu, Ile) in the residue. The extent of Asx racemisation was significantly higher than all other AAs, rising to a maximum greater than 0.5 at both 110°C and 140°C before decreasing. Change in elemental composition of the fibre with hydrolysis was consistent with loss of AAs, extensive deamidation and oxidation of AAs, elimination of S and retention of melanins. $\delta^{15}N$ showed strong depletion (up to -2.3‰) in densely pigmented samples at low temperatures (80°C). $\delta^{13}C$ was also depleted (up to -0.8‰) in densely pigmented samples, and showed slight enrichment elsewhere. $\delta^{2}H$ and $\delta^{18}O$ both became strongly depleted with increasing temperature of degradation (up to -73‰ for $\delta^{2}H$ and -2.6‰ for $\delta^{18}O$).

Diagenesis in experimentally buried samples was concluded to have been largely microbiological and non-protein-selective. In contrast, high-temperature isothermal hydrous degradation was strongly selective of portions of the protein. Dating methods based on Asx racemisation were undermined by the data. Changes in $\delta^{13}C$ and $\delta^{15}N$ may be significant in archaeological material and not correlated with extent of elemental or AA change.

Keywords: protein, keratin, diagenesis, hydrolysis, racemisation, light stable isotopes

4.1 Introduction

Archaeological mammal hair, including woven textiles, furs and human hair, has recently become the focus of considerable bioanalytical interest (e.g. Araki and Moini 2011; Solazzo *et al.* 2011; Brandt *et al.* 2011). Of these fibres, the most economically important today (and in the past) is sheep wool (Popescu and Wortmann 2010; Ryder 1983). The exploitation of wool occurred early in the development of agriculture (Greenfield 2010), and has continued to be important to sheep breed development (Chessa *et al.* 2009). Wool fibres are found in archaeological deposits across the Old World, often in the form of textiles (Geijer 1938; Bichler *et al.* 2005; Wagner *et al.* 2009). Textile manufacture, which is highly laborious, is important for our understanding of past societies (Barber 1991; Costin 1998; Walton Rogers 2007) and has been highly economically and politically significant (e.g. Murra 1962; Oikonomides 1986; Spufford 2006, 232-41,326-9). Archaeological wool finds therefore represent a potential repository of information on sheep breed development, flock management, and the development of textile trade and technologies.

Previous analytical work on archaeological hair has focused on samples preserved in permafrost or by desiccation (Lubec *et al.* 1987; Macko *et al.* 1999; Iacumin *et al.* 2005; Wilson *et al.* 2007b; Raghavan *et al.* 2010). However in northern Europe, samples preserved by burial under waterlogged conditions are not rare (Karsten *et al.* 2012). Such samples show a range of macroscopic (Wilson *et al.* 2010; Peacock 1996) and chemical (Kempson *et al.* 2010) changes during burial. Microbiological activity is clearly indicated as part of these processes, with some aspects of this activity, such as fungal tunnelling, not apparently selective of particular hair structures (Wilson *et al.* 2007a). However, other degradation processes occur in which different parts of the fibre degradation at different rates (Peacock 1996; Wilson *et al.* 2007a; Chang *et al.* 2005). This degradation may be microbiological or chemical (hydrolytic, oxidative) in origin. Analytical work on ancient proteinaceous fibres, for example for provenancing (Hedges *et al.* 2005; Chapter 3) or dating (Moini *et al.* 2011), must take into account the extent and nature of degradation of the fibre.

The bulk of a hair fibre (c. 90% by weight: Brebu and Spiridon 2011) consists of several hundred keratin proteins, distributed differently across the structures of the fibre (Plowman *et al.* 2007). Hydrolytic protein degradation has been extensively studied in biomineralised proteins, as it forms the basis of amino acid (AA) racemisation dating techniques (e.g. Brooks *et al.* 1990; Sykes *et al.* 1995; Penkman *et al.* 2011). The intra-crystalline fraction of biomineralised proteins forms a closed system which can be isolated by preliminary bleaching (Penkman *et al.* 2008; Demarchi *et al.* unpublished-b). Studying this fraction ensures analysis of indigenous protein only. Wool, in contrast, is an open system which means that: (1) the presence of exogenous peptides introduced by microbiological activity or diffusion cannot be excluded, and (2) the residue represents the insoluble, most diagenetically-resistant parts of the original fibre.

Hydrolytic protein degradation is the sum of at least three sets of reactions: peptide bond hydrolysis, AA racemisation (the interconversion of L- and D- enantiomers of an AA) and AA decomposition to either other AAs or other organic compounds. All three sets of reactions are peptide-selective, depending on AA identity and protein structure (primary or higher, depending on cross-linking); their rates also depend on factors such as temperature, ionic strength and pH (see references in Collins *et al.* 1999; Collins and Riley 2000). In open systems, any metal ions present may additionally catalyse the racemisation, degradation and cross-linking of AAs in residual proteins and in soluble peptides produced by degradation (Pasini and Casella 1974; Beck 2011). This is expected to be particularly important in wool samples which have been dyed using natural dyes, as these processes often require the use of a metal salt as a mordant to fix the dye to the fibre (Ferreira *et al.* 2004).

Bulk measurements of elemental and isotopic composition are also expected to be affected by these reactions. For example, isotopic change may be introduced by:

- alteration of the AA composition of the fibre. Substantial isotopic differences exist between $\delta^{13}C$ and $\delta^{15}N$ of AAs in proteins (Raghavan *et al.* 2010; Hare *et al.* 1991; Styring *et al.* 2010), and the same is likely to be true of $\delta^{2}H$ and $\delta^{18}O$;
- isotopically selective hydrolysis reactions (Bada *et al.* 1989; Silfer *et al.* 1992);
- isotopically selective AA decomposition reactions such as transamination (Macko *et al.* 1986);
- introduction of environmental H via racemisation, thus altering even the 'non-exchangeable' fraction of $\delta^{2}H$ (e.g. Amelung and Brodowski 2002; Chesson *et al.* 2009) though not $\delta^{13}C$ or $\delta^{15}N$ (Engel and Macko 1986).

The behaviour of the non-protein fraction of hair must also be considered. This consists principally of melanin pigments and lipids: the former make up 2–8% of the fibre by mass (Washburn *et al.* 1958) and the latter up to 2% (Popescu and Höcker 2007). Melanins are complex polymers composed of monomer units derived from Tyr and Cys (Borges *et al.* 2001). They are present as granules even in white hair, and overall melanin content depends on season, environment, genotype and area of body (Washburn *et al.* 1958; Brebu and Spiridon 2011). The isotopic composition of melanins is likely to reflect their AA origin (Michalik *et al.* 2011). Fatty acid residues are present on the surface of hair fibres (Popescu and Höcker 2007). Their isotopic ratios probably reflect whole diet values, as do other lipids (Howland *et al.* 2003; Kirsanow and Tuross 2011). The degradation behaviour of these portions of the hair fibre under burial conditions is not known.

The degradation of wool textiles has been examined via experimental burials, although focus on waterlogged preservation remains rare (Peacock 1996). Thermal and hydrolytic protein degradation is typically investigated using high-temperature isothermal heating experiments,

as a convenient method of artificially accelerating protein degradation reactions. High temperature experiments may however be poor mimics of archaeological diagenetic processes as hydrolysis, racemisation and decomposition reaction rates display different temperature sensitivities (Crisp *et al.* unpublished; Demarchi *et al.* unpublished-b; Tomiak *et al.* unpublished). Unfortunately the kinetic parameters for each of these reactions are poorly known.

This study therefore compared and contrasted the diagenesis of wool fibres under high-temperature isothermal hydrolytic conditions and in experimental burials. The study aimed to: (1) identify features of wool degradation at a range of temperatures by measurement of AA concentrations and extent of racemisation; (2) relate elemental and isotopic changes in bulk wool fibres to AA changes in the protein fraction of the fibre; (3) examine how AA and bulk composition variables are affected by the presence of natural pigment and dyeing/mordanting; and (4) provide a model of an open system of protein degradation for comparison to intra-crystalline protein behaviour in closed systems.

4.2 Materials and methods

4.2.1 Sample origins

Four contrasting sample types were used to examine the role of melanin concentration and pre-burial treatments on subsequent degradation: unpigmented raw wool, strongly pigmented raw wool, undyed unpigmented wool textile and madder-dyed/alum-mordanted unpigmented wool textile. Dyeing with madder root and an alum mordant was a widespread pre-industrial wool dyeing method (Chenciner 2000).

4.2.1.1 Experimental burials

Samples of experimentally-buried wool textile were supplied by Elizabeth Peacock (Peacock 2004; Bergstrand and Nyström Godfrey 2007; Turner-Walker and Peacock 2008). Undyed and madder-dyed/alum-mordanted sub-samples of the same fabric (Røros Tweed A/S, Røros, Norway) were buried in three different environments: raised bog (Rørmyra, Norway), fenland bog (Lejre, Denmark), and marine sediment (Marstrand, Sweden) for up to 8 years before retrieval. Raw wool samples were not included in experimental burials.

4.2.1.2 High-temperature isothermal hydrous experiments

Both raw wool and woven textiles were included in the high-temperature degradation experiments. Raw wool samples were from Shetland sheep: samples 2588 (white) and 2589 (dark grey) from the UK Essex flock in Chapter 3. Woven textile samples were the control samples from experimental burial experiments.

4.2.2 Sample cleaning

All samples (buried and unburied) were washed with organic solvents and ultra-pure water (ELGA Purelab Ultra, Marlow, UK) according to the protocol in Hedges *et al*. (2005) but using dichloromethane (HPLC grade, Fisher Scientific, Loughborough, UK) instead of chloroform in all solvent mixtures. A test sieve (Endecotts Ltd, London, UK; aperture 63 μm) was employed to retain fragmentary sections. The most exposed samples from each site from which enough material was available after washing were selected for analysis.

For isothermal heating experiments, 15 mg aliquots of each sample were weighed into sterile glass ampoules. 900 μL ultrapure water was added, and each ampoule was flame-sealed. Samples were placed in an oven maintained at a constant temperature of either 80°C, 110°C or 140°C, for a specified time, ranging from 1 to 1440 h (Table 4.1). Two laboratory replicates were prepared for each time point. At the designated time point, samples were removed from the oven. The supernatant water was removed, the sample rinsed twice with ultrapure water and dried at <40°C for a maximum of 12 hours. The most exposed samples for which enough material was available were selected for analysis.

Table 4.1. Time points per temperature in isothermal heating experiments.

Temperature	Time points (hours)
Controls	0
80°C	120, 720, 1440
110°C	120, 240, 480
140°C	1, 2, 4, 6, 8, 24, 48, 72, 96, 120

4.2.3 Sample analysis

Determination of AA concentration and racemisation ratios was by Reverse-Phase High Performance Liquid Chromatography (RP-HPLC) (Kaufman and Manley 1998) following the methodology for unbleached samples described in Penkman *et al*. (2008) with the following adjustment: hydrolysis was carried out using 50 μL 7 M HCl (HPLC grade, Fisher Scientific) per mg washed wool. Buried samples were analysed in duplicate and isothermally heated samples uniquely (but each time point had a laboratory replicate). The concentration of L- and D-enantiomers of 10 AAs were analysed routinely, and three AAs were recovered as L-enantiomers only. Data are reported as concentration of each AA, percentage of recovered AAs and racemisation ratio (D/L). It is not possible to distinguish between the acidic AAs and their amine derivatives because both asparagine (Asn) and glutamine (Gln) undergo rapid irreversible deamination during preparative hydrolysis to aspartic acid (Asp) and glutamic acid (Glu) respectively (Hill 1965). Asp and Asn are therefore reported together as Asx, and Glu and Gln as Glx. Instrument calibration is currently based on a collagen standard which is known to yield inaccurate absolute AA concentrations. Relative concentrations are however robust, with the exception of glycine (Gly) which is consistently underestimated (B.

Demarchi, pers. comm.). Instrument precision for racemisation values in standard solutions is reported in Table 4.2 (Powell 2012). For comparison to sample data, the value for the standard solution closest in D/L to the group of measurements of interest was selected. Instrument precision for concentration or relative concentration values has not been systematically investigated. None of these measures have been established for keratins substrates in particular.

Carbon, hydrogen, nitrogen, sulfur and oxygen (CHNS-O) elemental analysis (EA) was performed using a Thermo Flash 2000 elemental analyser configured with furnaces, fitted with MAS200R autosamplers. The instrument was calibrated with cystine and sulphanilimide standards (purity >99.97%, Thermo Fisher Scientific, Loughborough, UK). Combustion gases were separated chromatographically and detected using a thermal conductivity detector. For C, H, N and S analysis, samples (*c*. 2 mg) were weighed into 8 x 5 mm Sn foil capsules (Elemental Microanalysis, Okehampton, UK) which were folded to exclude air. The quartz reactor was packed with granules of copper oxide and electrolytic copper wires and held at 900°under a flow of helium carrier gas (140 mL/min) during analysis. Combustion of the sample was achieved in oxygen (250 mL/min for 5 s). For O analysis, samples (*c*. 2 mg) were weighed into 8 x 5 mm Ag capsules (Elemental Microanalysis), which were folded to exclude air. The reactor was packed with nickel plated carbon and quartz turnings and held at 1060°C under a flow of helium (140 mL/min) during analysis. Thermal decomposition of the sample was conducted under helium. An absorption filter, containing granules of soda lime and magnesium perchlorate, was fitted post column. Instrument precision is reported in Table 4.3.

Isotope analysis was carried out at the Natural Environment Research Council Life Sciences Mass Spectrometry Facility (NERC LSMSF) in East Kilbride. 0.7 mg of washed wool was weighed into 4 x 3.2 mm Sn capsules (Elemental Microanalysis, Okehampton, UK). For $\delta^{18}O$ and $\delta^{2}H$ analyses, 0.1 mg of wool was weighed into 4 x 3.2 mm Ag capsules (Elemental Microanalysis, Okehampton, UK and Pelican Scientific, Stockport, UK). Whole hairs were analysed to obtain a year average value. $\delta^{13}C$ and $\delta^{15}N$ IRMS analyses were carried out on a ThermoElectron Delta Plus XP with Costech ECS 4010 elemental analyser; internal standards were a gelatine, two alanines enriched with ^{13}C and ^{15}N respectively, and a ^{15}N-enriched glycine. C and N content and C:N atomic ratios ($C:N_{atom}$) were calculated using a tryptophan standard. $\delta^{18}O$ and $\delta^{2}H$ IRMS analyses were carried out on a Thermo Fisher Scientific Delta V Plus with TC/EA high temperature furnace. The contribution of exchangeable hydrogen was calculated using keratin standards BWB-II (whale baleen), CFS (feathers), ISB (feathers) and WG (feathers) and a comparative equilibration method (Wassenaar and Hobson 2003; Sauer *et al.* 2009). $\delta^{18}O$ standards were IAEA 601, IAEA CH6 and IAEA 600; the $\delta^{2}H$ of the un-exchangeable H in the four keratin standards was

Table 4.2. HPLC instrument precision (three York instruments combined, outliers removed by Cochran's and Grubb's outlier tests) for standard solutions of mixtures of AAs (Powell 2012). Sr: precision of the replicate analyses (analytical precision). sL: between-sample variability, for a given sample material. sR: reproducibility, or overall estimate of the variability expected for a given AA for different sample materials.

AA		Standard solution	mean	final N	Sr	sL	sR
Aspartic acid/ asparagine	Asx	0.167dH20	0.168027034	405	0.001318	0.002219	0.002581
		0.5d	0.506097894	645	0.00453	0.003506	0.005745
		0.91d	0.896268312	571	0.003959	0.017185	0.017635
Glutamic acid/ glutamine	Glx	0.167dH20	0.192719859	425	0.001857	0.003042	0.003564
		0.5d	0.570822934	656	0.004546	0.006657	0.008061
		0.91d	1.006509728	643	0.012148	0.011229	0.016543
Serine	Ser	0.167dH20	0.13176973	423	0.001211	0.001741	0.002121
		0.5d	0.408904167	685	0.003268	0.003832	0.005083
		0.91d	0.70034735	642	0.006299	0.005515	0.008534
Arginine	Arg	0.167dH20	0.167270359	377	0.009045	0.045344	0.046642
		0.5d	0.483270727	636	0.022858	0.090909	0.093732
		0.91d	0.803841066	587	0.040279	0.154176	0.159351
Alanine	Ala	0.167dH20	0.158723208	400	0.00525	0.005208	0.007406
		0.5d	0.55746241	663	0.004492	0.007651	0.0089
		0.91d	0.934813305	583	0.005799	0.008769	0.010513
Valine	Val	0.167dH20	0.1454837	385	0.001274	0.002298	0.002628
		0.5d	0.474500122	627	0.004118	0.005317	0.006725

Table 4.2 continued.

AA		Standard solution	mean	final N	Sr	sL	sR
Valine	Val	0.91d	0.760088117	574	0.006022	0.006979	0.009218
Methionine	Met	0.167dH20	0.19958694	392	0.002668	0.005221	0.005863
		0.5d	0.592124485	617	0.00513	0.008832	0.010214
		0.91d	1.021334034	576	0.009134	0.012175	0.015226
Phenylalanine	Phe	0.167dH20	0.157247747	368	0.000896	0.001798	0.002009
		0.5d	0.486099394	600	0.002818	0.003802	0.004733
		0.91d	0.804942517	566	0.005632	0.007054	0.009027
Isoleucine	Ile	0.167dH20	0.191752549	363	0.002161	0.009694	0.009931
		0.5d	0.580326075	583	0.006911	0.014706	0.016249
		0.91d	0.989155425	553	0.009998	0.018099	0.020677
Leucine	Leu	0.167dH20	0.201701744	387	0.008137	0.016239	0.018155
		0.5d	0.600586407	605	0.011453	0.015071	0.018929
		0.91d	1.061650016	529	0.010795	0.016313	0.019561

Recovered AAs for which racemisation was not calculated: threonine (Thr), histidine (His), tyrosine (Tyr). Glycine (Gly) is also recovered but does not have enantiomers.

Table 4.3. EA instrument precision: (a) difference from theoretical elemental % by mass (b) difference from manufacturer's elemental % by mass; (c) s.d. of measurement.

Standard	**n**		**C**	**N**	**H**	**S**	**n**		**O**
Cysteine	11	(a)	+0.061	-0.108	+0.007	+0.033	7	(a)	-0.136
		(b)	0.000	0.000	0.000	0.000		(b)	-0.114
		(c)	± 0.000	± 0.000	± 0.000	± 0.000		(c)	± 0.212
Sulfanilimide	3	(a)	-0.056	-0.042	-0.064	+0.118	2	(a)	+0.293
		(b)	-0.044	-0.048	-0.061	+0.118		(b)	+0.295
		(c)	± 0.000	± 0.000	± 0.000	± 0.000		(c)	± 0.394

previously determined using a steam equilibration technique (Wassenaar and Hobson 2000; Table 4.4). Calculation of un-exchangeable δ^2H assumed a fractionation factor $\alpha = 1.080$ ($\varepsilon_{x\text{-}w} = 80‰$). $\delta^{13}C$ and $\delta^{15}N$ results are reported in per mille (‰) relative to PDB and AIR respectively; $\delta^{18}O$ and δ^2H results are reported in per mille relative to VSMOW.

4.2.4 Statistical analysis

Statistical analysis was carried out using R (R Development Core Team 2008).

Estimation of effective relative racemisation rates used a 'model-free' approach in which log-transformed time data from each temperature experiment was scaled to overlie as much as possible (Crisp *et al.* unpublished; Demarchi *et al.* unpublished-b; Tomiak *et al.* unpublished). Models were fitted so as to minimise the least squares difference of 17 separate time points derived from third order polynomial functions fitted to the raw (un-averaged) data, using a Generalized Reduced Gradient Algorithm (Microsoft Solver). This allows the user to limit the range of fitting, omitting ranges where the polynomial functions diverge from the overall trend, typically with either very high or very low time points (i.e. very high and very low extents of degradation) in each temperature series. These ranges are reported alongside the relative rates of reaction (normalised to the middle temperature, 110˚C).

4.3 Results

Single AA raw concentrations, percentage contents, racemisation ratios, and isotopic composition variables for all buried samples is reported in Appendix 4.1, and for isothermally heated material in Appendix 4.2. Full raw chromatographic data is reported in Electronic appendix 4.3. The dataset was non-parametric (univariate Shapiro-Wilk test, $P>0.05$). No effective data transformations were found. Grouped data are therefore described throughout by median and inter-quartile range (IQR). Full data from the calculation of effective relative racemisation rates are reported in Electronic appendix 4.4.

4.3.1 Experimental precision of RP-HPLC

Observed AA concentrations, % AA contents derived from these, and D/L values were compared for standard solutions between RP-HPLC runs. No AA concentrations or DL values were significantly different between analytical HPLC runs (Mann-Whitney U tests, all $P>0.05$). However the following % AA contents varied by run: Asx for G483; Glx, Ser, L-His, Arg and Phe for H391 (Mann-Whitney U tests, $n_{G483}=12$, $n_{H391}=9$, $n_{H397}=5$, $n_{H398}=7$, others too small to test for significance; all $P>0.05$). Run G483 was the pilot run, and samples in it were 100 times more concentrated than in following analyses. This indicated that the accuracy of Asx % content measurements were concentration-dependent. For run H391, a laboratory

Table 4.4. Isotopic analytical precision: mean ± maximum s.d. in any single run. For abbreviations, see text.

		$\delta^{13}C$/‰		$\delta^{15}N$/‰		$\delta^{2}H$/‰		$\delta^{18}O$/‰	
Standard	**n**	**Observed**	**Accepted**	**Observed**	**Accepted**	**Observed**	**Accepted**	**Observed**	**Accepted**
Gelatine	52	-20.29 ± 0.21	-20.34 ± 0.03	5.83 ± 0.19	5.67 ± 0.13	-	-	-	-
^{13}C-enriched Ala	18	-10.63 ± 0.14	-10.58 ± 0.03	-4.86 ± 0.12	-5.09 ± 0.12	-	-	-	-
^{15}N-enriched Gly	18	-35.67 ± 0.16	-35.46 ± 0.09	20.21 ± 0.14	20.01 ± 0.31	-	-	-	-
^{13}C-enriched Trp	8	-10.60 ± 0.12	-10.49 ± 0.11	-2.03 ± 0.21	-2.31 ± 0.14	-	-	-	-
IAEA 601	12	-	-	-	-	-	-	23.32 ± 0.28	23.14 ± 0.19
IAEA CH6	3	-	-	-	-	-	-	35.63 ± 0.13	36.4*
IAEA 600	3	-	-	-	-	-	-	-3.70 ± 0.17	-3.48 ± 0.53
CFS	3	-	-	-	-	-143.3 ± 2.3	-148.6*	5.88 ± 0.40	Unknown
BWB-II	3	-	-	-	-	-102.9 ± 2.4	-109.5*	13.37 ± 0.21	Unknown
ISB	3	-	-	-	-	-61.7 ± 2.9	-68.8*	13.58 ± 0.22	Unknown
WG	3	-	-	-	-	-140.0 ± 1.9	-146.6*	6.66 ± 0.16	Unknown

* s.d. undetermined

error in buffer pH adjustment affected some results from almost all unpigmented raw wool samples (n=36). Data from experimental runs G483 and H391 was nevertheless included in all statistical analysis, except the model-free estimation of observed racemisation rates.

4.3.2 Macroscopic features of degradation

Experimentally buried samples showed major macroscopic changes from controls (Table 4.5). Textiles were increasingly heavily stained with time (Figure 4.1). The felted surface of the cloth disappeared from some samples (fenland bog 4 year undyed, raised bog 8 year undyed), leaving the underlying weave visible. In all buried samples, fibres were more brittle to handling, readily losing short sections or dust. During washing some samples crumbled into a mass of short sections (‘sludge’) or into dust which was lost through the sieve. Red-dyed samples were typically less fragile than their undyed counterparts.

Figure 4.1. Undyed samples buried at Lejre, during washing. Left to right: buried 1, 2, 4 and 8 years.

In contrast, isothermally heated material lost mass very quickly at 140°C (Table 4.6), with median 3% left after 120 hr; 57% and 97% remained after the same time at 110°C and 80°C respectively. Samples heated for more than 24 hours at 140°C became brittle and inflexible, with fibres aggregated. Samples heated at 110°C and 80°C were discoloured and more brittle than controls, but still fibrous (Figure 4.2).

Table 4.5. Buried samples: macroscopic description and mass remaining after washing.

		Undyed			Madder-dyed/alum-mordanted		
	Years buried	**As retrieved**	**After wash**	**Mass/%**	**As retrieved**	**After wash**	**Mass/%**
Controls	0	White	Whole	84	Red	Whole	87
Marine sediment	1	Grey	Whole	89	Red	Whole	88
	2	Cream	Whole	90	Red, fragmenting fibres	Sludge	35
	3	Grey	Whole	58	Red	Some structure	Not recorded
Fenland bog	1	Grey	Whole	86	Red	Whole	90
	2	Grey	Sludge	61	Pink	Some structure	22*
	4	Dark grey, weave visible	Some structure	11	Orange	Sludge	40
	8	Dark grey	Dust	4*	Pink, stained	Few fibres	7*
Raised bog	1	Cream	Whole	92	Red	Whole	89
	2	Cream	Whole	90	Red	Whole	92
	4	Cream, soily	Whole	92	Dark red	Whole	90
	8	Grey, weave visible	Whole	73	Dark red	Whole	87

*insufficient material for isotope analysis.

Table 4.6. Description and mass remaining of kinetic samples after isothermal heating. n=2 for each time point.

		Unpigmented raw wool		Pigmented raw wool		Undyed textile		Madder/alum-dyed textile	
Temp./°C	**Time / h**	**Colour**	**Mass/%**	**Colour**	**Mass/%**	**Colour**	**Mass/%**	**Colour**	**Mass/%**
Control	0	White	100	Black	100	White	100	Red	100
80	120	Off-white	100	Black	98	Cream	97	Dark red, fragments	89
	720	Yellow	88	Brown black	87	Grey, fragments	82	Dark red, fragments	97
	1440	Yellow	69	Black	77	Not recorded	67	Red, fragments	66
110	120	Dark tan	51	Black	56	Tan	60	Brown, fragments	59
	240	Dark tan	32	Black	39	Brown	33	Brown	40
	480	Brown	18	Black	22	Brown	20	Brown	23
140	1	Yellow	95	Black	100	Yellow	97	Orange-red	92
	2	Dark yellow	86	Black	91	Yellow	89	Orange-red	92
	4	Dark yellow	74	Black	81	Dark yellow	77	Dark red	71
	6	Dark yellow	64	Black	63	Dark yellow	58	Dark red	64
	8	Yellow-brown	53	Black	53	Tan	54	Brown	58
	24	Tan	16	Black	19	Brown	18	Black	20
	48	Tan	6	Black	12	Brown	8	Black	9
	72	Brown	3	Black	11	Brown	5	Black, fragments	6
	96	Brown	3	Black, fragments	4	Black	3	Black	4
	120	Brown	2	Black, fragments	17*	Brown	3	Black	4

* glass present in sample

Figure 4.2. Isothermally heated undyed textile samples after heating at 110°C and drying. Left to right: controls (2 x), 120 h (2 x), 240 h (2 x) and 480 h (2 x) time points.

4.3.3 AA composition

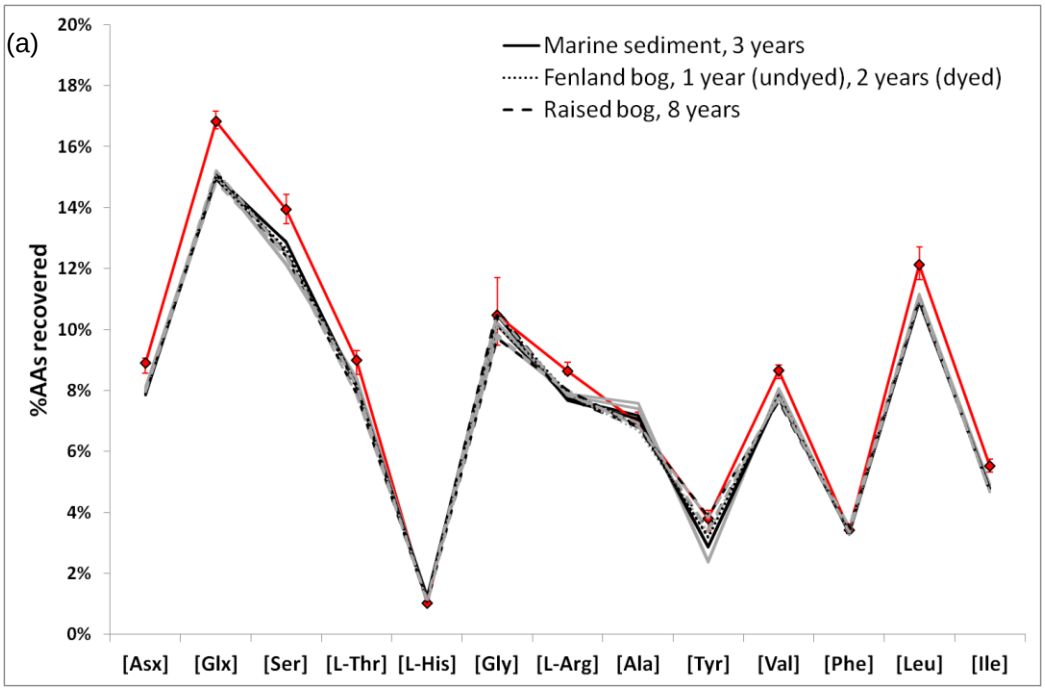
4.3.3.1 Initial control values

The AAs recovered with the RP-HPLC technique employed represented approximately 86% of the residues present in the most abundant protein type in wool, intermediate filament proteins (IFPs; see Appendix 4.5 for derivation from Clerens *et al.* 2010). The most abundant AAs observed were Glx, Ser and Leu, with Phe, Tyr and His the least abundant (Figure 4.3a).

4.3.3.2 Buried samples

Overall AA concentration per unit mass of the samples was on the lower end of the range of modern controls, with marine sediment-buried samples most depleted, and those from the raised bog least depleted. Changes in %AA recovered were minimal: Figure 4.3b shows that greatest variability occurred in the AAs which are least abundant in wool fibres (i.e. L-His, Tyr, Phe). Data are shown normalised to control median to compare variability among buried samples to that among unburied controls. Racemisation was increased in all AAs over control samples, with Ser DL ratios most increased over control median (Figure 4.3c), though Asx DL ratios were highest overall (range 0.085-0.098%; other AAs ranged between 0.013-0.063%). Samples buried in marine sediment showed higher racemisation ratios than samples from other sites.

Samples buried in marine sediment contained significantly less Glx, L-Arg, Phe and Leu per unit mass than samples buried in a raised bog (Mann-Whitney U tests, $n_{marine}=6$, $n_{raised\ bog}=8$, $n_{controls}=15$, all $P<0.05$). Marine sediment-buried samples also contained significantly less L-Thr and Tyr than all samples from both other sites and from modern control material (Mann-Whitney U tests, $n_{marine}=6$, $n_{fenland\ bog}=6$, $n_{raised\ bog}=8$, $n_{controls}=15$, all $P<0.05$).



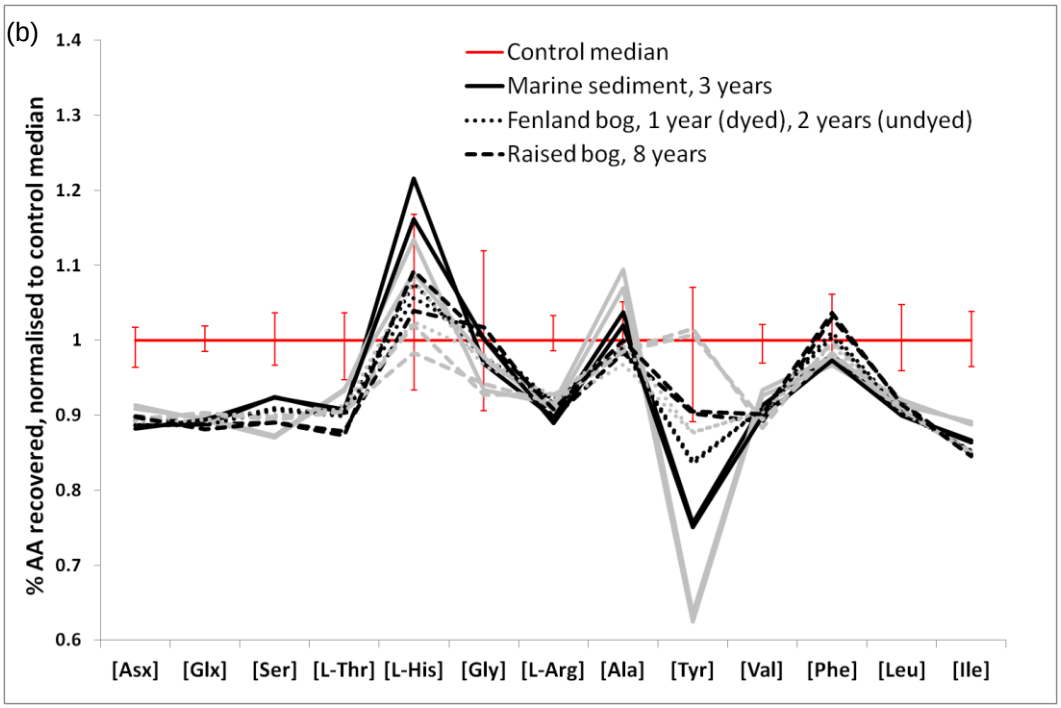


Figure 4.3. AA content and racemisation of buried samples compared to non-buried control median (red). Undyed samples: grey lines; madder/alum-dyed samples: black lines. Red error bars show the IQR of control samples. (a) absolute % recovered AAs. (b) % AA content as a proportion of control median.

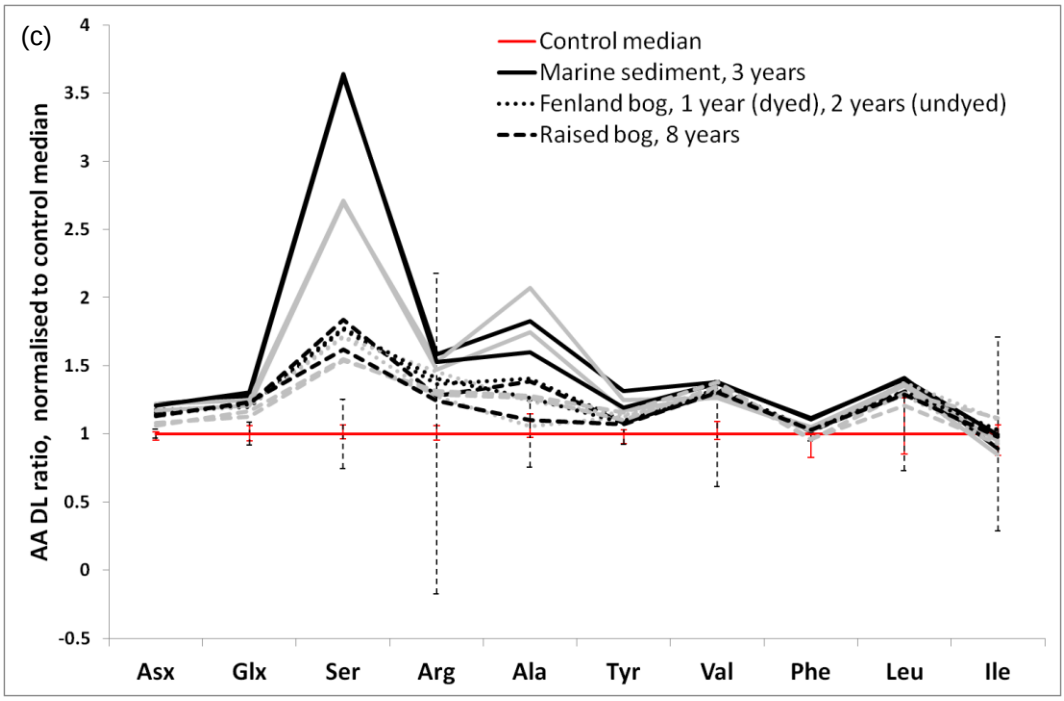


Figure 4.3 continued. (c) extent of racemisation as a proportion of control median. Dashed black error bars indicate reproducibility (sR) of DL measurement of each AA as a proportion of control median (Table 4.2).

Percentage Leu content was significantly less than modern controls at all sites, as was % Tyr in marine sediment and fenland bog environments (Mann-Whitney U tests, n_{marine}=6, $n_{fenland\ bog}$=6, $n_{raised\ bog}$=8, P<0.05). Percentage content of Tyr and Ile were significantly different between all burial sites (Tyr: marine < fenland bog <raised bog; Ile inverse pattern; Mann-Whitney U tests, n_{marine}=6, $n_{fenland\ bog}$=6, $n_{raised\ bog}$=8, all P<0.05). Additionally, % Ala and Phe distinguished marine sediment samples from those at other burial sites (Mann-Whitney U tests, n_{marine}=6, $n_{fenland\ bog}$=6, $n_{raised\ bog}$=8, all P<0.05).

The distribution of racemisation DL values was significantly different between sites for all AAs except Glx, Val and Ile (Kruskal-Wallis tests, all P<0.5). Marine sediment-buried samples was significantly differentiated from all other sites and controls by D/L ratio of Ser, Ala and Tyr (Mann-Whitney U tests, n_{marine}=6, $n_{fenland\ bog}$=6, $n_{raised\ bog}$=8; all P<0.05).

4.3.3.3 Isothermally heated samples

Isothermally heated wool samples showed much greater changes in AA profile than buried material.

AA concentration per unit mass decreased with time in all samples: decreases were greater with longer heating and higher temperatures. All AAs were lost but not equally: the decrease in concentration was greater for the more hydrophilic AAs (Asx, Glx, Ser, L-Thr, L-His and Gly) than for the more hydrophobic AAs (L-Arg, Ala, Val, Phe, Leu and Ile). As expected, AA concentration was significantly different between temperature groups (except between

140°C and 110°C, and between 80°C and controls) but only for hydrophilic AAs (Mann-Whitney U tests; n_{140}=94, n_{110}=26, n_{80}=25, $n_{control}$=15; all P<0.05).

% AA content was also strongly related to temperature, heating time and AA identity. At all three temperatures, proportions of hydrophilic AAs (Asx, Glx, Ser, L-Thr) decreased steadily with increasing time, whereas proportions of hydrophobic AA (Arg, Ala, Tyr, Val, Phe, Leu and Ile) increased steadily with increasing time; extent of change was highest at 140°C and lowest at 80°C (Figure 4.4). The behaviour of % Gly content was complex, rising for an initial period before a decrease. Significant differences were present in % content of all AAs between temperatures (except between 140°C and 110°C, and between 80°C and controls, as for AA concentration), with the exception of Glx, L-His, Gly, L-Ala and Tyr (Mann-Whitney U tests; n_{140}=94, n_{110}=26, n_{80}=25, $n_{control}$=15; all P<0.05).

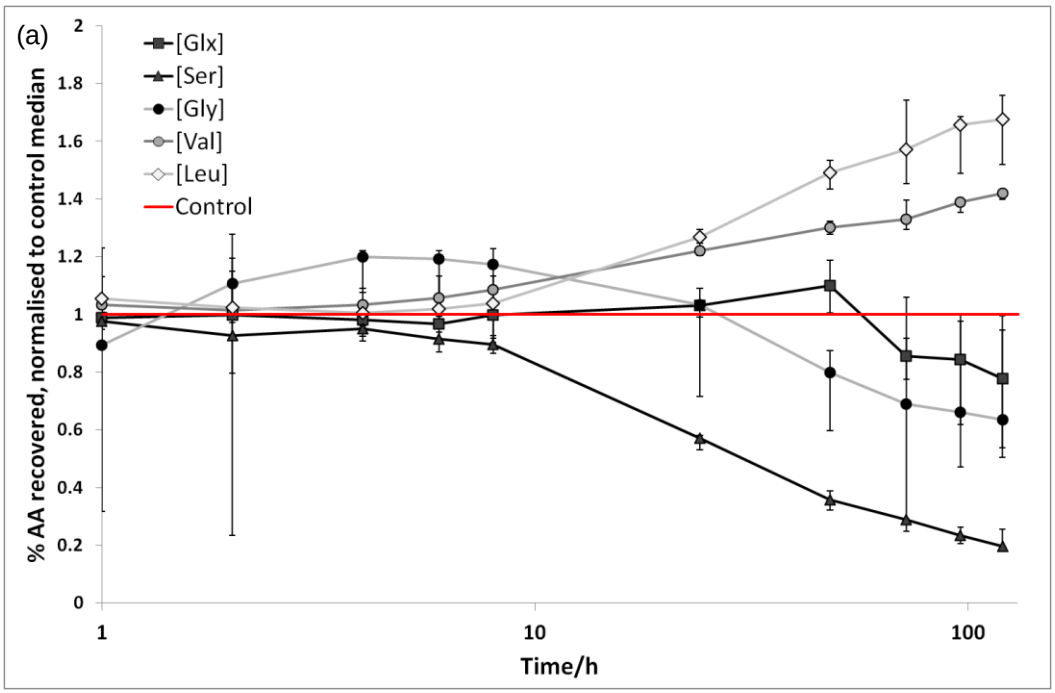
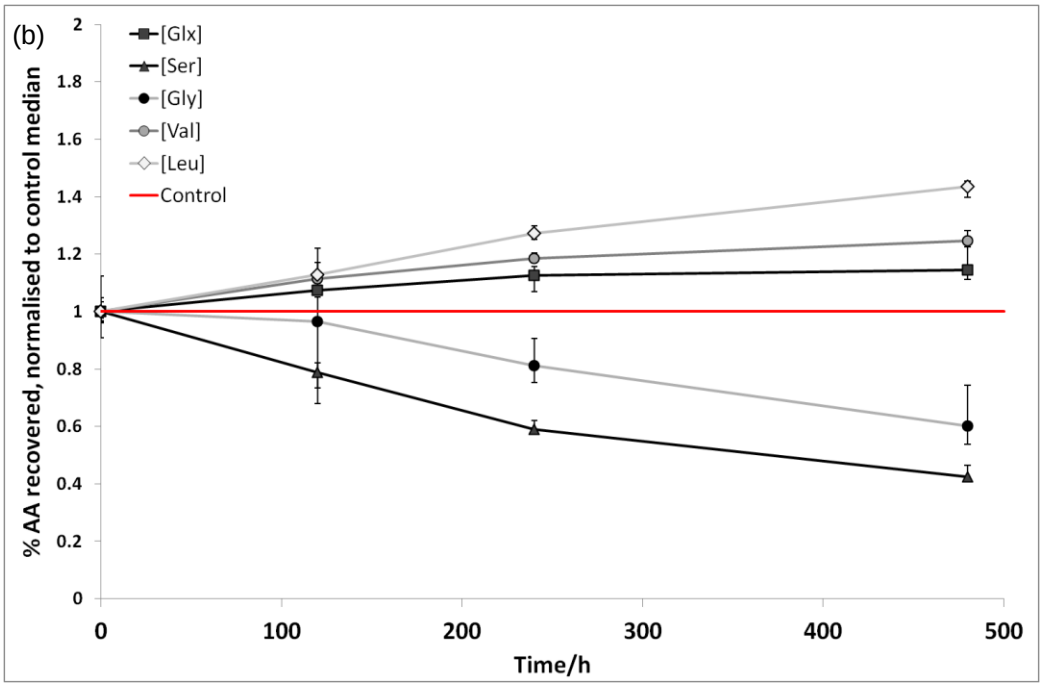


Figure 4.4. % AA content of isothermally heated samples (median for each time point) plotted relative to non-buried modern control median (red). Error bars show IQRs as a proportion of control median. Only the five most abundant AAs in the fibre that are recovered using RP-HPLC are shown. (a) Evolution of **%** AA content at 140°C (time plotted in log_{10} to clarify early time points).



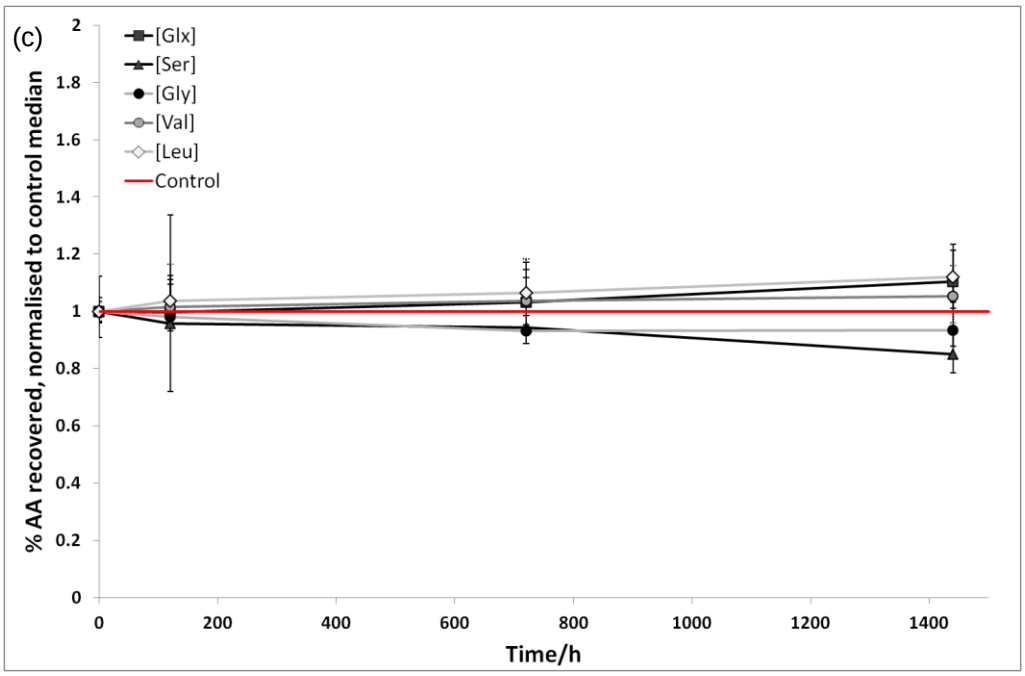
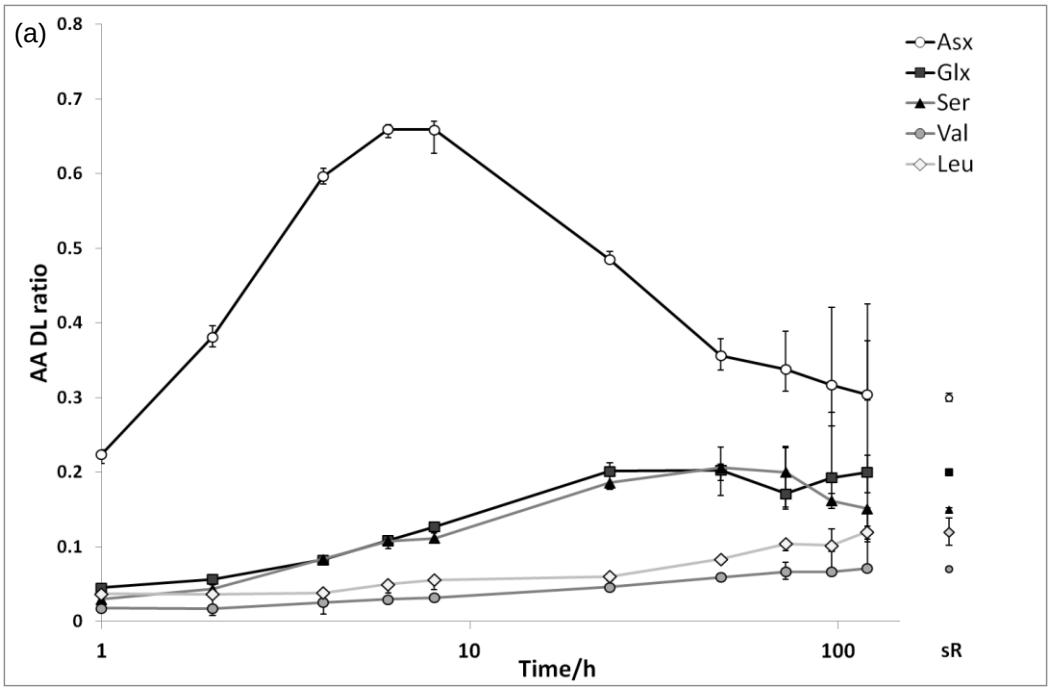


Figure 4.4 continued. (b) evolution of **%** AA content at 110°C. (c) evolution of **%** AA content at 80°C.

Finally, AA racemisation ratios of all isothermally heated samples were higher than controls', and racemisation increased with increasing temperature and time, up to 25 times greater than control for Ser in 140°C-samples. Extent of racemisation for Asx was the highest, rising to >0.6 after 8 hours exposure at 140°C, and decreasing thereafter (Figure 4.5).



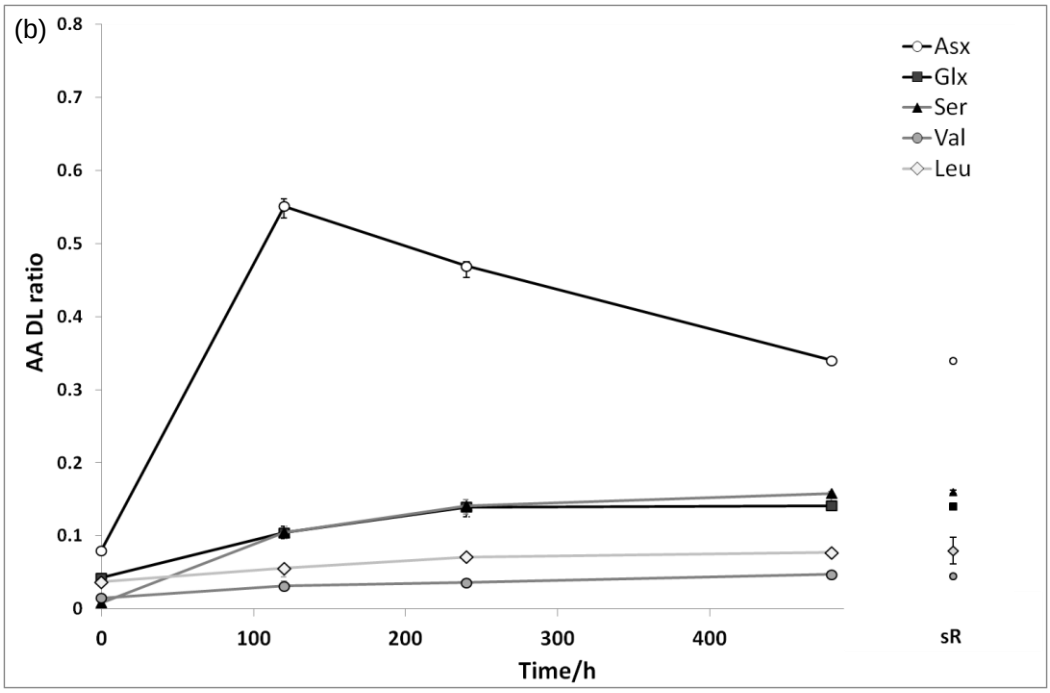


Figure 4.5. Evolution of AA racemisation (median per time point; error bars show IQRs) from 140°C, 110°C and 80°C sequences. Only the four most abundant AAs in the fibre that are recovered using RP-HPLC, and Asx, are shown. sR indicates reproducibility for each individual AA in the standard solution of closest DL equivalence (Table 4.2): in most cases this is smaller than the data point. (a) Evolution of AA racemisation at 140°C (time plotted in $\log_{10}$ for clarity). (b) evolution of AA racemisation at 110°C.

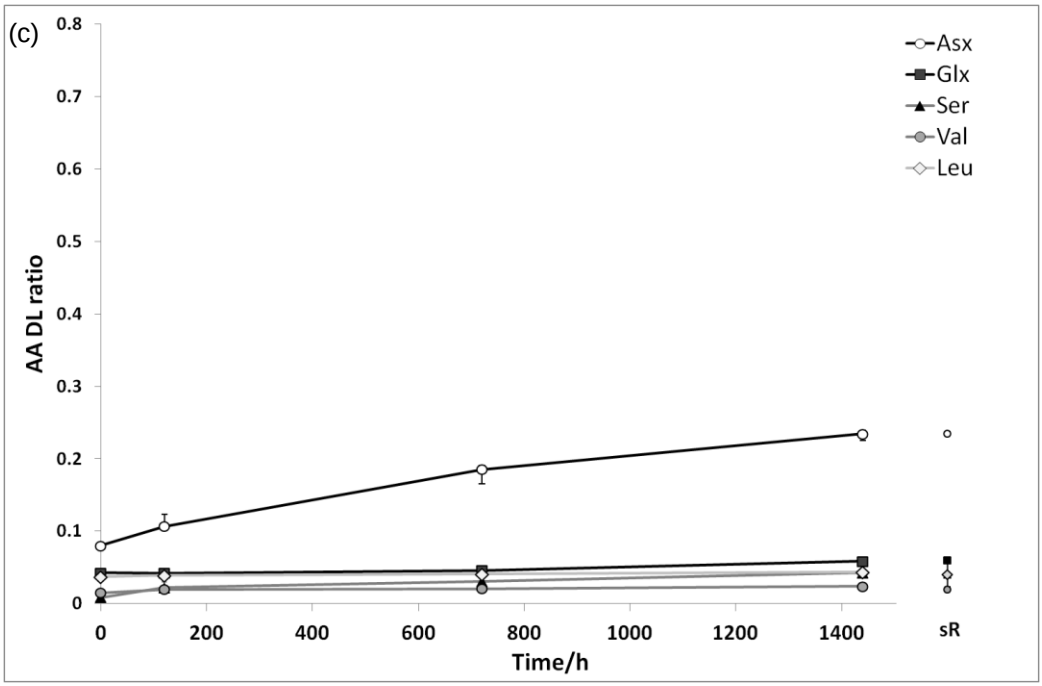


Figure 4.5 continued. (c) evolution of AA racemisation at 80°C.

4.3.3.4 Differences between sample types

Pigmented vs. unpigmented raw wool. No significant differences in AA response to isothermal heating were securely detected between unpigmented and pigmented wool (see *Statistical analysis* above), with the exception of higher D/L values in pigmented wool at high time points at 140°C (Figure 4.6). This pattern was not discernible at 110°C or 80°C. The raw wool samples were not included in the experimental burials.

Dyed vs. undyed samples. In experimentally buried samples, dyed samples showed significantly higher Glx and lower Ser % content than undyed samples (Mann-Whitney U test, n=6 for each group; $P<0.05$). Dyeing had no effect on AA concentration per unit mass or extent of racemisation.

In isothermally heated material, undyed samples contained significantly lower concentrations of all AAs except Gly; and also significantly lower % contents of Glx and L-Arg, and higher of L-His and Gly (Mann-Whitney U, $n_{dyed}=37$, $n_{undyed}=38$; all $P<0.05$). Dyeing had no effect on extent of racemisation in these samples either.

Raw vs. finished wool. The comparison could only be made for isothermally heated samples. Raw wool samples contained significantly lower Glx and Gly concentrations than finished wool textiles; significantly less % content of hydrophilic AAs (Glx, Ser and L-His), significantly more % content of hydrophobic AAs (L-Thr, Gly, L-Arg, Tyr, Val, Leu, Ile); significantly lower Leu DL and significantly higher Ile DL (Mann-Whitney U test, $n_{raw}=76$, $n_{finished}=75$, all $P<0.05$).

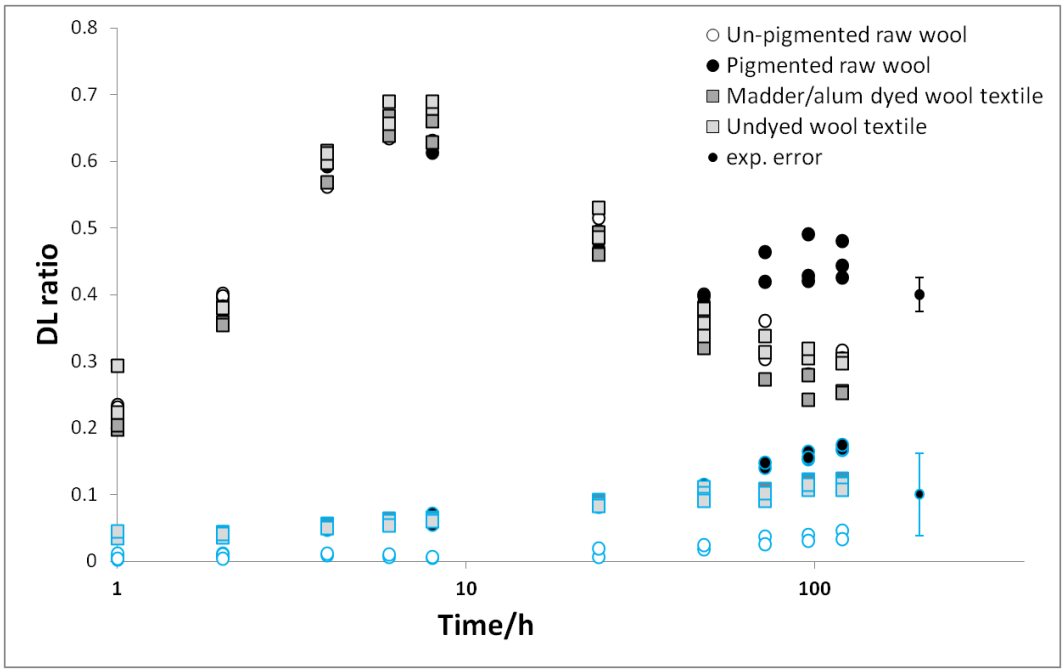


Figure 4.6. Evolution of racemisation ratios of two contrasting, relatively abundant AAs in keratin, Asx (hydrophilic) and Leu (hydrophobic), at 140°C (time plotted in $\log_{10}$ to clarify early time points): comparison between sample types. In both cases, pigmented raw wool samples showed greater extent of racemisation than all other samples at time points over 72 hours. Leu racemisation ratios of unpigmented raw wool samples were depressed by laboratory error in experimental run H391.

4.3.3.5 Modelling of effective relative rates of racemisation

Any accurate calculation of rate constants must *a priori* be carried out in a closed system, so that reagents and products can be accurately quantified. However, unlike degradation due to isothermal heating in biomineralised proteins (Crisp *et al.* unpublished; Demarchi *et al.* unpublished-b; Tomiak *et al.* unpublished), this reaction in wool is not a closed system. As keratin proteins are hydrolysed, peptides are lost from the fibre, and the racemisation of AAs in these peptides will not be reflected by measurements made on the residual wool fraction. The following calculations are therefore interesting as a comparison to biomineralised systems, but are not especially indicative of real racemisation rates in wool.

The 'model-free' method for calculating relative kinetic parameters for the high temperature racemisation data is reported in electronic appendix 4.4, summarised in Table 4.7. Despite the fact that D/L values of standard solutions in run H391 were not significantly different from those of other runs, degree of racemisation for a number of AAs in samples in this run were depressed compared to data from other runs. Affected samples from run H391 (which include most unpigmented raw wool samples) were therefore excluded from modelling calculations except for Asx and Ser where no depression was apparent. Fitting together the scaled data from the three temperature series was complicated by the relative paucity of data points for 110°C and 80°C as opposed to 140°C. Fitting the scaled data by least

Table 4.7. Estimated activation energies for racemisation of AAs. Biomineralised tissue data is from ostrich egg shell (OES: Crisp *et al.* unpublished), mollusc shell *Patella vulgata* (Demarchi *et al.* unpublished-b), and massive coral *Porites* (Tomiak *et al.* unpublished).

		E_A range ($kJmol^{-1}$)								
		Wool (degraded)		Wool (archaeological)		OES	*Patella*		*Porites*	
AA	**Notes**	**Max**	**Min**	**Max**	**Min**	**Mean**	**Max**	**Min**	**Max**	**Min**
Asx		-187	-82	-144	-124	-125	-136	-99	-110	-110
Glx	H391 removed	-147	-127	-151	-127	-143	-143	-104	-128	-124
Ser		-159	-123	-153	-116	-122	-116	-97	/	/
Ala	H391 removed	-147	-137	-154	-129	-133	-128	-106	-100	-87
Val	H391 removed from 110°C and 140°C data	-147	-112	-147	-116	-122	-133	-121	-108	-104
Phe	H391 removed from 110°C and 140°C data	-137	-106	-137	-126	-134	-132	-110	-92	-89
Leu	H391 removed	-127	-121	-143	-122	/	-130	-124	/	/
Ile	H391 removed	-167	-129	-158	-130	-124	-135	-110	/	/

squares generated a plausible solution for only Ser and Val. In all other cases, manual fitting was more credible. Activation energy ranges were estimated by exploring the extremes of fitting data from archaeological samples to the fitted curves based on data from isothermally heated samples.

4.3.4 Elemental analysis

For all samples, elemental content of the bulk fibre was measured directly by mass spectrometric methods (either EA or IRMS, denoted $_{bulk}$). This was compared to the elemental content of the protein fraction of the fibre, calculated from observed % AA content (i.e. relative AA concentration) and the molecular formulas of the AA residues, denoted $_{protein}$, as follows:

$$C\%wt_{protein} = \frac{\sum_{AA} C\%wt}{\sum_{AA} C\%wt + \sum_{AA} N\%wt + \sum_{AA} H\%wt + \sum_{AA} O\%wt}$$

where

$$\sum_{AA} X\%wt = X\%wt_{Asx} + X\%wt_{Glx} + X\%wt_{Ser} + X\%wt_{Thr} + X\%wt_{His} + X\%wt_{Gly} + X\%wt_{Arg} + X\%wt_{Ala} + X\%wt_{Tyr} + X\%wt_{Val} + X\%wt_{Phe} + X\%wt_{Leu} + X\%wt_{Ile}$$

and

$$X\%wt_{AA} = \%\ AA\ recovered \times theoretical\ X\%wt\ of\ the\ AA\ residue$$

This calculation assumes that all AA residues are intact. This is unlikely, so values were also calculated for (1) deamidated proteins ($_{deamid}$, Asn -> Asp and Gln -> Glu), and (2) heavily oxidised proteins ($_{oxid}$, which includes the above deamidations; Table 4.8). Oxidative changes are complex as multiple products are possible for a single AA (Dyer *et al.* 2010; Berlett and Stadtman 1997). In addition, a number of oxidative changes are likely to lead to cross-linking or breaking of peptide bonds. This calculation assumes that neither of these reactions took place.

Changes in elemental % mass content with heating are shown in Figures 4.7 (140°C) and 4.8 (80°C). Elemental % $mass_{protein}$ was significantly higher in controls than in heated samples for O and N, and lower for C and H (Mann-Whitney U tests, n_{140}=89, n_{110}=24, n_{80}=24, $n_{control}$=14, all P<0.001). In contrast, the only significant differences in elemental % $mass_{bulk}$ were in C (lower in controls than heated samples), S (higher in control than heated samples), and O (lower in controls than in 140°C-heated samples), (Mann-Whitney U tests; n_{140}=59, n_{110}=24, n_{80}=24, $n_{control}$=8; all P<0.05).

Table 4.8. Deamidative and oxidative changes to AA residues.

Reaction	Reagent AA residue	Product residue
Deamidation	Asn	Asp
	Gln	Glu
	All other recorded AAs	No change
Oxidation	Asx	Asp
	Glx	Glu
	Thr	2-Amino-3-ketobutyric acid
	His	Asp
	Arg	Glutamic semialdehyde
	Tyr	A dihydroxyphenylalanine
	Phe	A dihydroxyphenylalanine
	All other recorded AAs	No change

Percentage weight $S_{protein}$ could not be calculated as none of the AAs measured by RP-HPLC contain S. Both bulk and protein elemental content were compared to theoretical values (denoted $_{theor}$) for the 10 most abundant proteins in wool fibres, derived from protein sequences in Clerens *et al*. (2010; Appendix 4.5 and Table 4.9). This calculation was made for the proportion of the protein recovered by RP-HPLC (denoted recorded) and again for the total protein (all), and assumed these proteins were intact.

Changes in C % $mass_{bulk}$ with heating largely followed changes in C %$mass_{protein}$ at all three temperatures. The complex evolution of N, H and O % $mass_{bulk}$ at 140°C compared to their respective % $mass_{protein}$ suggested that the non-protein fraction lost N and H and gained O. These changes were not evident at lower temperatures (Figure 4.8), except for H % mass at 110°C (data not shown).

Differences between samples. There were no significant differences in elemental content between dyed and undyed samples (bulk or protein) except in H % $mass_{bulk}$ which was higher in un-dyed samples (Mann-Whitney U test; n_{dyed}=28, $n_{un\text{-}dyed}$=28; P<0.05).

H % $mass_{bulk}$ was significantly higher in un-pigmented samples than in pigmented samples (Mann-Whitney U test; $n_{pigmented}$=27, $n_{un\text{-}pigmented}$=32; all P<0.05). However all elements' % $mass_{protein}$ were significantly different between un-pigmented and pigmented samples, with C, H and O % $mass_{protein}$ being higher in un-pigmented samples, and N % $mass_{protein}$ higher in pigmented samples (Mann-Whitney U test; $n_{pigmented}$=34, $n_{un\text{-}pigmented}$=42; P<0.05).

Raw samples were significantly higher in C, N, H and S % $mass_{bulk}$ than finished samples (Mann-Whitney U tests; n_{raw}=59, $n_{finished}$=56; all P<0.05), and in all elements' % $mass_{protein}$ (raw > finished for C and H; finished > raw for N and O; Mann-Whitney U tests; n_{raw}=76, $n_{finished}$=75; all P<0.05).

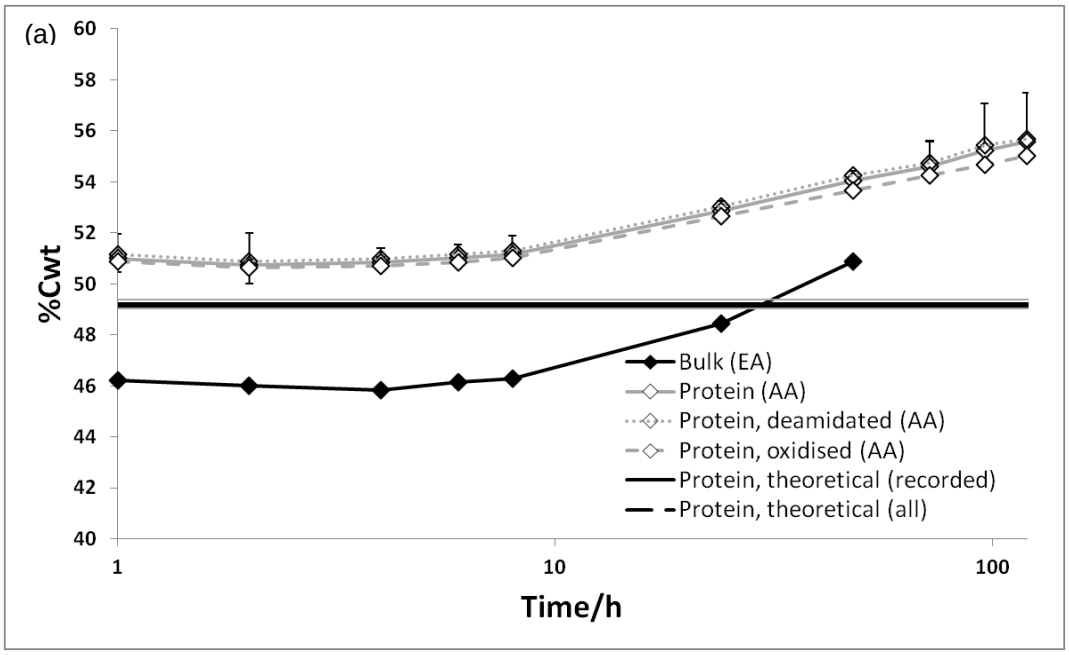
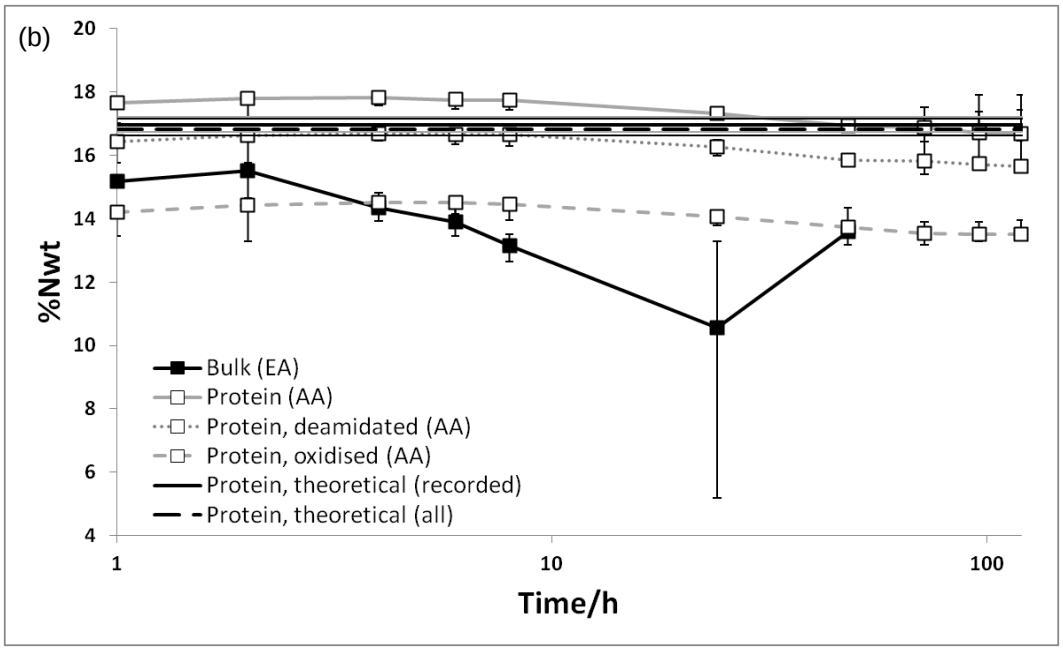


Figure 4.7. Evolution of elemental % content (median ± IQR) of isothermally 140°C-heated samples (time plotted as log_{10} to clarify early time points). Bulk, protein and theoretical contents are shown. Error bars for EA measurements of C, N, H and S are within markers; those for O are shown. Error bars for AA calculations are >50. (a) C; (b) N; (c) H; (d) O; (e) S; (f) C:$Natom_{bulk}$.



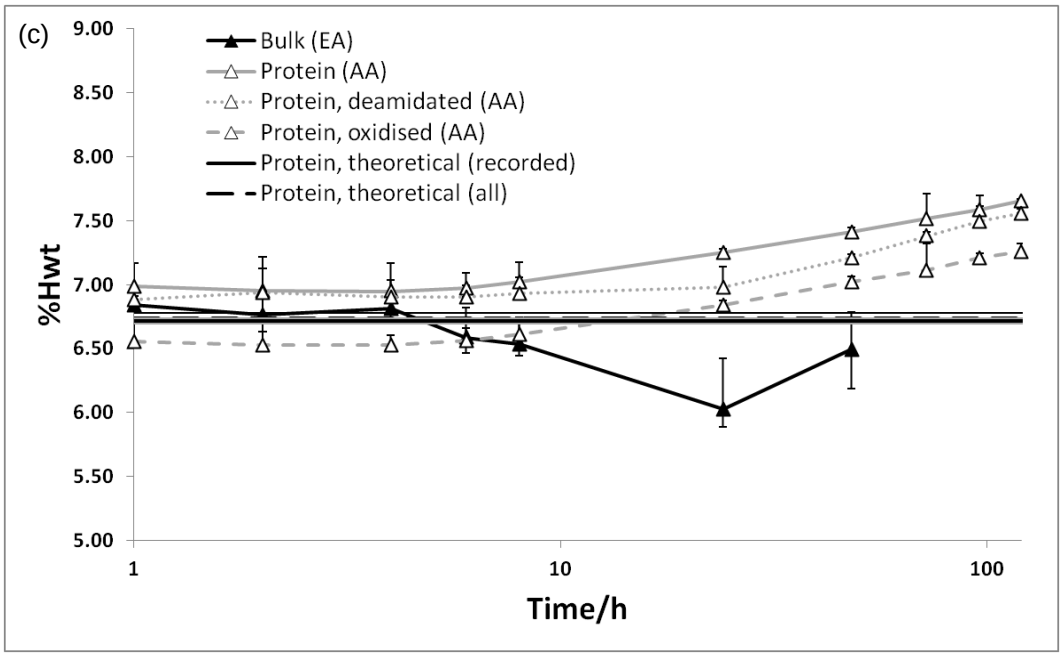
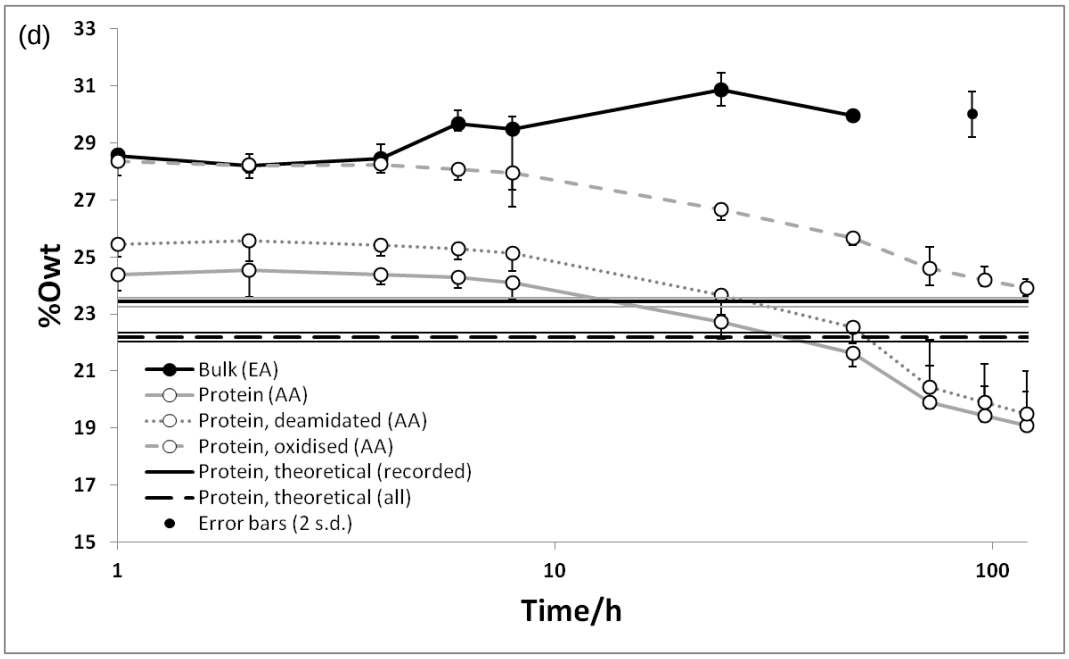
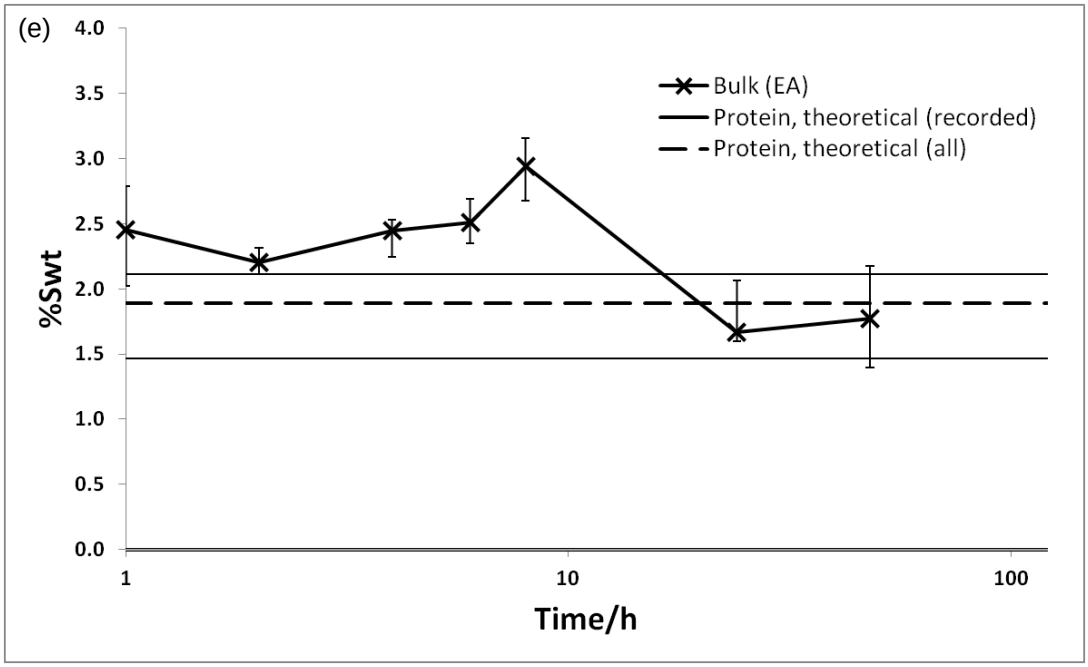


Figure 4.7 continued.





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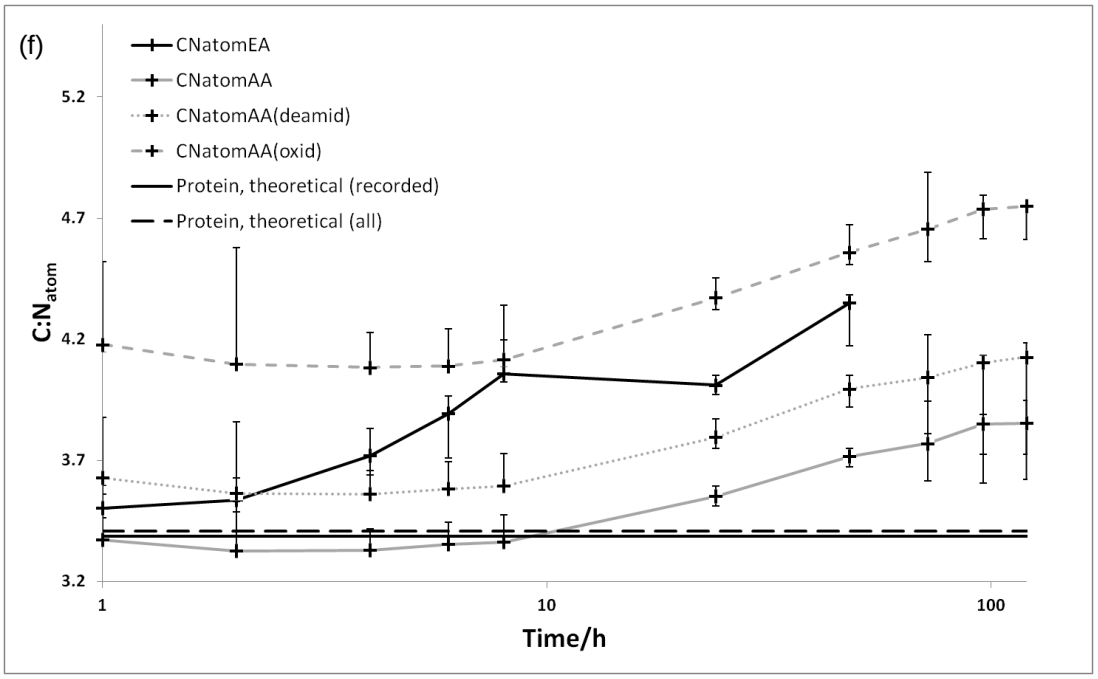


Figure 4.7 continued.

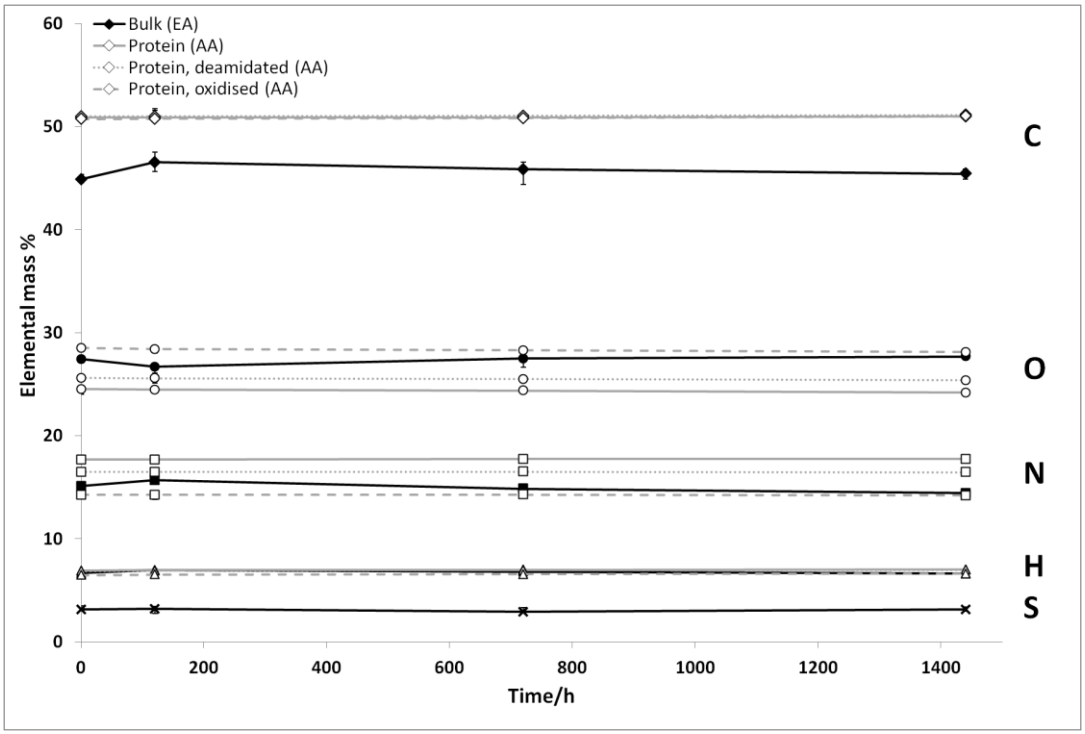


Figure 4.8. Evolution of elemental % content (median ± inter quartile range) of isothermally 80°C-heated samples. Bulk and protein contents are shown.

4.3.5 Isotopic results

Isothermally heated material showed greater changes in isotope values from controls than experimental burials, with the exception of $\delta^{18}O$ (Figure 4.9). The extent of change was dependent on sample type and temperature of exposure, and varied between isotopes.

In isothermally heated samples, change from control values were significant for $\delta^{13}C$ at 80°C only (Mann-Whitney U tests, $n_{140}=10$, $n_{110}=9$, $n_{80}=15$; $P<0.05$) but for $\delta^{2}H$ and $\delta^{18}O$ for 140°C-heated material only (Mann-Whitney U tests, $n_{140}=12$, $n_{110}=8$, $n_{80}=8$; all $P<0.05$). Changes in $\delta^{18}O$ were significantly different between all temperatures (Mann-Whitney U test, $n_{140}=12$, $n_{110}=8$, $n_{80}=8$, $P<0.05$; Figure 4.9d). Changes from controls in $\delta^{13}C$ and $\delta^{15}N$ depended on sample type, specifically the presence of pigmentation, showing greater depletion in pigmented samples (Mann-Whitney U tests, $n_{unpigmented\ raw}=8$, $n_{pigmented\ raw}=11$; $P<0.001$ for $\delta^{13}C$, $P<0.05$ for $\delta^{15}N$). Change in isotope values from control did not differentiate dyed and undyed samples but did finished and un-finished samples in $\delta^{15}N$ and $\delta^{18}O$ (Mann-Whitney U tests, $n_{finished}=15$, $n_{un\text{-}finished,\delta^{15}N=}19$, $n_{un\text{-}finished,\delta^{18}O}13$, $P<0.05$).

Table 4.9. Elemental analysis mass % results for control wool samples. *median calculated for 10 most abundant proteins (see Appendix 4.5).

	C%	N%	H%	O%	S%
Bulk fibre (observed)	44.9	15.1	6.7	27.4	3.2
IQR	44.5–45.3	14.8–15.2	6.7–6.8	27.2–27.7	3.1–3.5
Protein fraction (calculated)	50.9	17.7	7.0	24.5	†
IQR	50.9–51.1	17.5–17.7	6.9–7.0	24.4–24.5	†
Theoretical, recorded AAs*	49	17	6.7	23	0.0
Theoretical, all AAs*	49	17	6.7	22	1.9
Elöd & Zahn (1943)	51	16	6.9	23	3.6
Eumelanin (brown/black)	72-74	9.6-11	5.3-5.5	11-12	0.0
Pheomelanin (red)	62-64	9.3-10	3.7-4.7	0.0	21-24
Fatty acids	50-83	0.0	6-14	43-2	0.0

†not calculable

In experimentally buried samples, there were no significant differences between burial environments in change from control values for any isotope (Mann-Whitney U tests, n_{marine}=6, $n_{fenland\ bog}$=6, $n_{raised\ bog}$=8, all P>0.05). Dyed and undyed samples differed significantly in extent of δ^2H depletion (Mann-Whitney U test; n_{dyed}=10, n_{undyed}=11; P<0.01). There were no significant relationships between isotope change and site of burial or duration of burial.

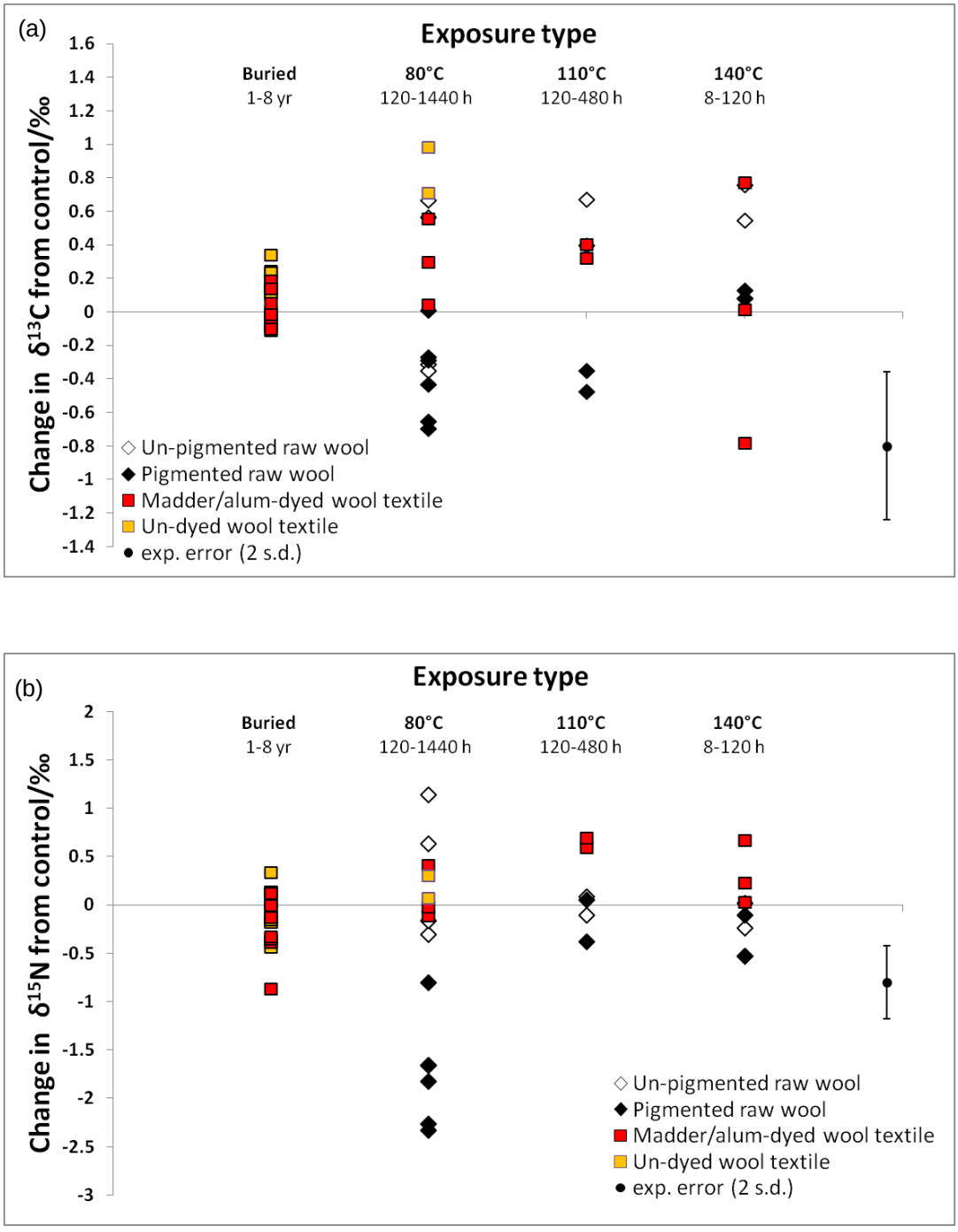
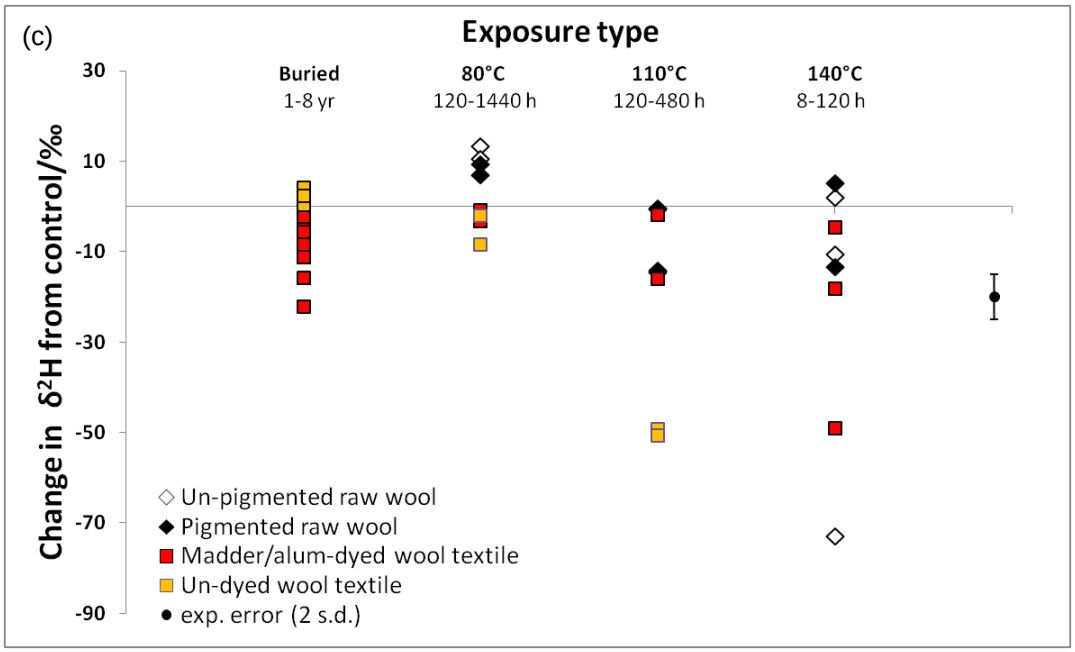


Figure 4.9. Changes in textile (a) $\delta^{13}C$, (b) $\delta^{15}N$, (c) δ^2H (d) $\delta^{18}O$ compositions from control sample median values.



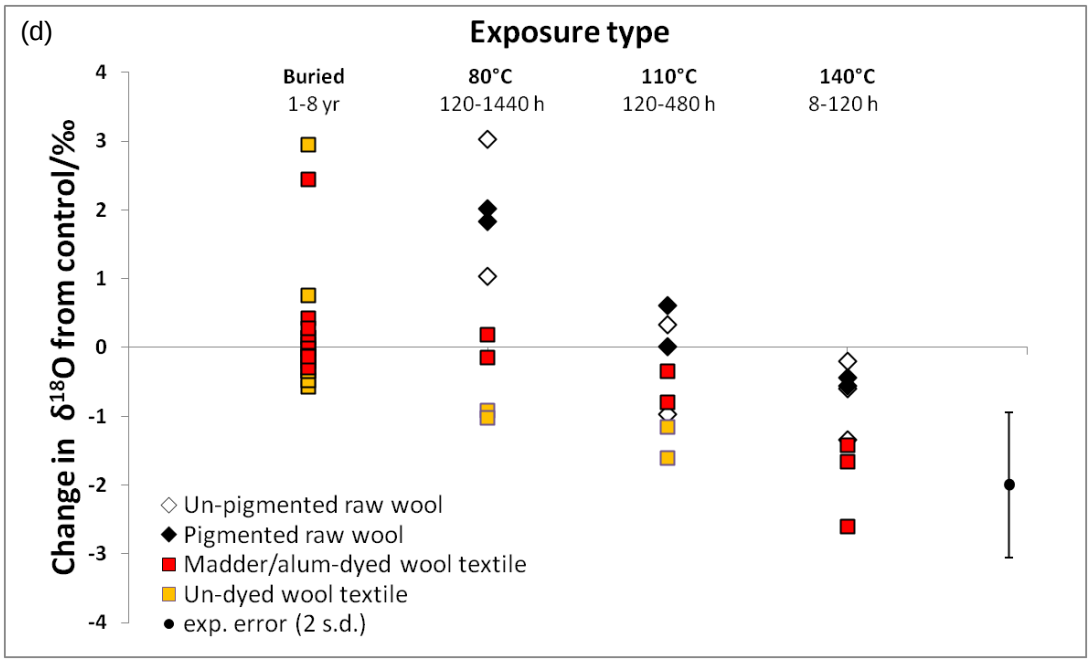


Figure 4.9 continued.

4.4 Discussion

4.4.1 Composition of intact wool

Relative AA concentrations in wool determined by RP-HPLC (Figure 4.3a) closely resembled previous determinations in wool (Bradbury *et al.* 1965; Zahn *et al.* 2005; all differences less than 2%; Table 4.10) and human hair (Macko *et al.* 1999). Median % AA content of un-degraded wool samples was very similar to the theoretical % AA contents of IFP proteins which make up the bulk of the wool fibre (Clerens *et al.* 2010; Plowman 2003) but with a greater proportion of Ser and Thr. Ser contents are higher in the cuticle than in the cortex (Behn (1992) cited in Zahn *et al.* 2005), but other than this, presence of non-IFP proteins in hair appeared to make little contribution to overall AA contribution, as expected.

Elemental composition of the bulk fibre and its protein fraction differed substantially. The protein fraction was calculated to contain more C, more N, and less O than the bulk fibre. Error in error in calculated % $mass_{protein}$ values (>50 for each element) is much larger than that in observed % $mass_{bulk}$ (Table 4.3), which is likely to explain this. Contributing factors include:

- inaccuracies in the calculation of its elemental composition, which was based on AAs recovered from the fibre, that is lacking Cys, Lys, Met, Pro and Trp, and also a proportion of D-racemised AA material. In intact wool, the latter is likely to be small, but the missing residues make up 11-16% of the residues in keratin proteins. These AAs contain generally less %Owt than recovered AAs (range 8–16% as opposed to 10–37%) but are not generally different to recovered AAs in %Cwt or %Nwt.

- the presence of an important non-protein component to wool fibres containing less C, less N, less H and more O than protein. The non-protein fraction of hair was expected to be largely composed of melanin, but the results for C and O are not consistent with this, which may be due to the contribution from fatty acid residues, though these are more likely to have been removed by washing during sample preparation.

4.4.2 Effects of degradation on AA composition

4.4.2.1 Buried samples

Experimentally buried samples, at an effective temperature less than 10°C (Turner-Walker and Peacock 2008), showed small changes in AA % content (i.e. relative AA composition) over up to 8 years' burial, indicating little peptide hydrolysis. Changes were smallest in the most abundant AAs (e.g. Glx, Ser, Gly, Val, Leu; *c*. 10% Figure 4.3b). Larger % changes were observed in L-His, Tyr, and Phe, probably an effect of their scarcity in wool fibre

Table 4.10. Median % AA content (of AAs recovered by HPLC technique).

	Asx	**Glx**	**Ser**	**L-Thr**	**L-His**	**Gly**	**L-Arg**	**Ala**	**Tyr**	**Val**	**Phe**	**Leu**	**Ile**
Control median observed	8.9	17	14	9.0	1.0	10	8.6	6.9	3.8	8.7	3.4	12	5.5
IQR	0.48	0.57	0.98	0.80	0.24	2.24	0.41	0.46	0.68	0.45	0.32	1.07	0.41
Bradbury *et al*. (1965)	8.0	15	13	8.2	1.2	11	8.5	6.7	5.0	6.9	3.7	9.6	3.9
Zahn *et al*. (2005)	7.8	16	14	8.2	0.96	9.8	8.5	6.5	4.8	6.9	3.6	10	3.1

proteins. The increase in % content in Ala may have been due to its formation by the breakdown of Ser (Vallentyne 1964) and probably represents a small amount of AA decomposition. All buried samples were more racemised than controls in all AAs measured (Figure 4.3c). The isotopic compositions of all buried samples were statistically indistinguishable from unburied controls (Figure 4.9).

The consistency of AA composition and racemisation in buried samples was surprising because wool is not a closed system. Buried samples were expected to have acquired some exogenous material from adjacent soil, and washing was expected to remove only the particulate and lipid fractions of this. Its contribution was however apparently negligible, probably because wool is almost wholly proteinaceous, so that the indigenous protein dominated AA results.

The extensive macroscopic degradation of these samples (Figure 4.1) must therefore be reconciled with this lack of change in AA parameters. We hypothesise that degradation in experimentally-buried samples was not primarily protein-specific, but instead degraded all parts of the fibre non-selectively. This is consistent with some aspects of microbiological activity, e.g. fungal tunnelling (Wilson *et al.* 2007a, 2010). However, some AA hydrolysis or decomposition is apparent in: (1) the increase in Ala concentration, and (2) the increased DL values over controls. All AAs are thought to racemise only at the N-terminal position except Asx (Clarke 1994) and possibly Ser (Demarchi *et al.* unpublished-a), so this increase in racemisation rate suggests an increase in N-termini and hence peptide cleavage.

Though changes in AA variables were small, some patterns of change were significant. AA variable values were significantly dependent on site of burial, but not dyeing treatments (with the exception of Glx and Ser %) or duration of burial. Macroscopic features of these samples also supported the idea that the environment of burial was the most important factor controlling the degradation of hair fibres (Wilson *et al.* 2007a). In this study, material buried in a raised bog was the best preserved, despite having been buried the longest (up to 8 years). The material buried in marine sediment was the worst preserved of the samples tested, with fenland bog-buried material in an intermediate position. However, the marine sediment samples had been buried 3 years, and fenland bog samples only 1 or 2, all older samples being too degraded to provide adequate mass for analysis. Relative preservation therefore appears to be raised bog > marine sediment > fenland bog. This variability is unlikely to have a simple relationship to temperature or pH of ambient water (Table 4.11). Good preservation in the raised bog may be related to the presence at this site of sphagnan, a polysaccharide derived from sphagnum moss, which has anti-microbial properties and acts as a sequestering agent for metal cations (Turner-Walker and Peacock 2008). It is not clear why a fenland bog environment should lead to quicker degradation than burial in marine sediment.

Table 4.11. Environmental variables for experimental burial sites (Bergstrand and Nyström Godfrey 2007; Turner-Walker and Peacock 2008).

	Marine sediment	**Raised bog**	**Fenland bog**
Location	Marstrand, SE	Rørmyra, NO	Lejre, DK
Topography	Marine harbour (in use)	Below wooded upland	Low, rolling hills
Geology	Seawater sediment/ clay/silt (some anthropogenic contribution)	Glacial till	Clay
Latitude	57.88678°	63.525°	55.60833°
Longitude	11.58732°	10.29722°	11.93889°
Elevation	-1–+2.5 m	175 m	58 m
Soil water pH	*c*. 7.0	5.0	5.6
Soil water E_h	-	+152 ms	−104 ms
Dissolved O_2	<0.01 mg dm^{-3}	1.6%	0.5%
Average annual air temp.	-	3.30°C	9.25°C
Average annual temp at 1m	-	4.22°C	8.60°C
Water content	33%	100%	100%
Reducing potential	-160–-250 mV (*vs.* standard hydrogen electrode).	-	-

4.4.2.2 Isothermally heated samples

In contrast to buried samples, high-temperature hydrous heating substantially changed the AA composition of wool fibres, indicating significant peptide cleavage. Patterns of protein degradation varied across temperatures. There was a difference in behaviour between the more hydrophilic and the more hydrophobic AAs: hydrophilic AAs were lost from the fibre more quickly than hydrophobic AAs, with the result that the % content of the latter increased over time at all three temperatures (Figure 4.4). Ser was especially susceptible to hydrolysis. Extent of racemisation was substantially increased over control samples at all three temperatures (Figure 4.5), with Asx exhibiting a very different response to experimental conditions to all other AAs. AA change and racemisation was dependent on temperature, being for all AAs highest at 140°C and lowest at 80°C. [Ser]% and Asx D/L usefully characterised the differences between temperatures (Figure 4.10).

No temperature used in the isothermal heating experiments was high enough to cause thermal degradation of keratin, which occurs c. 170°C (Brebu and Spiridon 2011). The highest was close to the temperature of denaturation of keratin in the presence of water, that

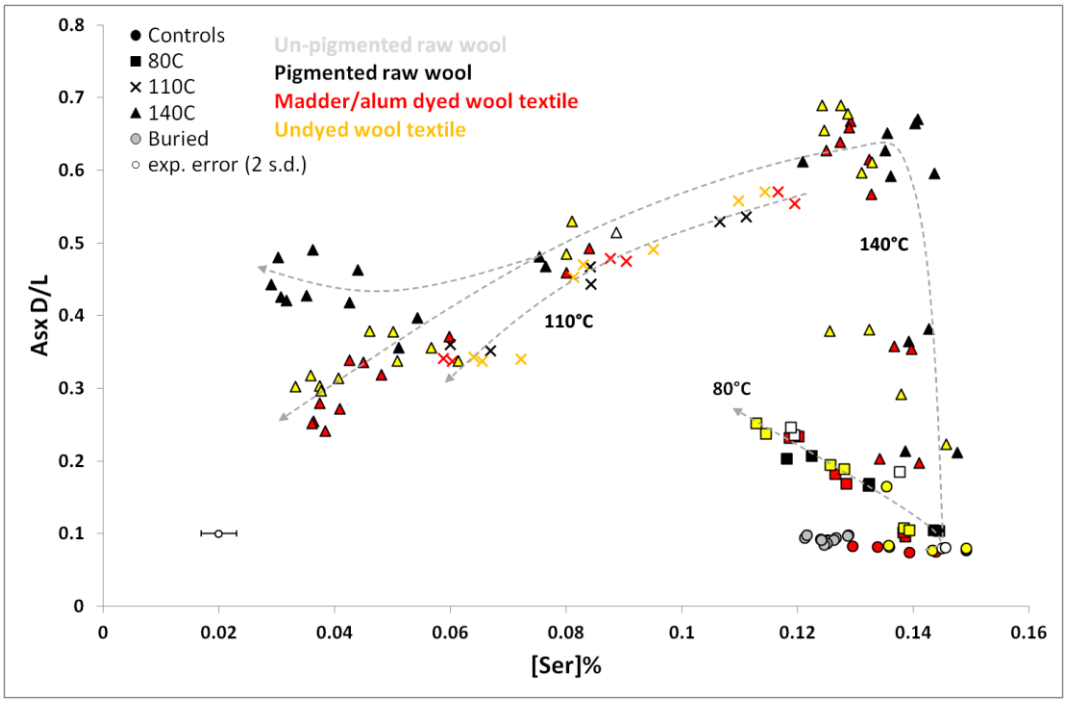


Figure 4.10. Evolution of [Ser]% against Asx D/L with time in isothermally degraded and buried samples. Temperature-dependent decay trajectories are indicated. Only that for 140°C differs by sample type, with pigmented samples showing higher Asx D/L than undyed samples at high timepoints only. Data for run H391 (most unpigmented raw wool) is omitted as [Ser]% values for these samples were depressed by laboratory error. Experimental error in Asx D/L is smaller than the error marker point.

is the disruption of the protein higher-order structures (c. 140°C: Wortmann and Deutz 1998). This was likely to have accelerated degradation observed in 140°C-heated samples, but the similarity between 140°C and 110°C patterns of AA loss (Figure 4.4 a and b) and racemisation (Figure 4.5 a and b) indicated that it did not change the pathways involved. Therefore hydrolysis in wool proteins was not greatly affected by the higher order structure of proteins. The differential loss of hydrophilic AAs over hydrophobic AAs suggests that peptide bonds between hydrophobic AAs were less prone to hydrolysis than those of hydrophilic AAs, as has been previously found (Hill 1965). The availability of water cannot have been a limiting factor in this open system (Walton 1998 and references therein). Therefore peptide hydrolysis in wool was dependent on protein primary structure and temperature, rather than aspects of higher-order structure.

Asx showed the highest extents of racemisation in wool, as in carbonate fossils (e.g. Goodfriend 1991, 1992; Collins *et al.* 1999; Figure 4.5). Additionally, Asx racemisation ratios rose quickly (at all three temperatures) to a peak above 0.5, after which they fell again (at 140°C and 110°C only). The initial rapid racemisation was consistent with the existence of the in-chain cyclic succinimide mechanism for Asx racemisation (Clarke 1994) but only N-terminal racemisation for other AAs. In-chain racemisation of Ser residues (Demarchi *et al.* unpublished-a) did not appear to occur. The evolution of Asx D/L in Figure 4.5 can therefore

be attributed to: (1) an initial phase, where the rate of Asx racemisation was greater than that of Asx loss by chain hydrolysis, leading to build-up of D-Asx in the fibre; followed by (2) a phase where peptide hydrolysis was dominant, leading to the preferential loss of highly degraded peptide sections more likely to contain L-Asx, thus reducing Asx D/L ratio. The peaking behaviour demonstrated at 140°C and 110°C in these experiments may be demonstrated at lower temperatures after sufficient time. Therefore dating methods based on Asx D/L values (Moini *et al.* 2011) could not be applied to waterlogged wool, because a single Asx D/L value could apply to two degradation states. This behaviour of Asx may also occur for other proteins: artificial degradation experiments, such as those examined in this study, are recommended to clarify the situation for silk proteins.

4.4.3 Effects of degradation on elemental composition (isothermally heated samples)

Care must be taken in interpreting composition variables from an open system in water from which mass was being lost. In this situation, any increase in % mass of C, N and S implies either the greater loss of a different element, while decrease in % mass C, N and S does indicate loss of that element. In the case of H and O, increase in % mass could indicate acquisition of these elements from ambient water (by hydrolysis or oxidation), or greater loss of a different element, while decrease in % mass H and O indicates loss of that element, as above.

In this discussion of elemental composition data, % $mass_{bulk}$ and % $mass_{protein}$ values and their change over time were compared. Error in error in observed % $mass_{bulk}$ (Table 4.3) is however very much smaller than calculated % $mass_{protein}$ values (>50 for each element) so these comparisons can be taken as indicative only. However some general trends were evident. Changes in elemental composition were greater at higher temperatures. In all elements, % $mass_{protein}$ elemental values approached melanin values with increasing degradation (Table 4.9).

C % $mass_{bulk}$ and % $mass_{protein}$ both increased over time (Figure 4.7a), indicating loss of other elements from the fibre. This change was consistent with the survival of the melanin fraction of the fibre while proteins are lost, as melanins have a higher % C mass (62–72%) than do keratin proteins (49%; Table 4.9). The changes in C % $mass_{bulk}$ and C % $mass_{protein}$ were largely parallel. This suggests that overall fibre C % mass change can be explained in terms of changes to the AA composition of the protein fraction. Decomposition reactions affecting the carbon backbone of AAs (e.g. decarboxylation) cannot have been significant in keratin degradation, as these would have led to a decrease in C % mass, which was not observed.

At 140°C and 110°C, the offset between bulk and protein C % mass values narrowed after 8 hours and 120 hours respectively, approaching 3–4% from *c*. 6%. This indicated a further contribution to changes in C % mass in addition to AA change. This could have been (1) a change in the composition of the non-protein fraction of the fibre, and/or (2) greater AA degradation than was accounted for in C % $mass_{protein}$ calculations, including deamidated and oxidised versions, leading to the build-up of degraded AAs in the fibre which were not identified and quantified by RP-HPLC. This is probably more likely than the degradation of the non-protein fraction, chiefly melanins, as the degradation of melanins typically requires strong redox conditions not present in this study (Ito *et al.* 2011).

Both N % $mass_{bulk}$ and % $mass_{protein}$ decreased over time. Again, survival of the melanin fraction while AAs are lost was consistent with the observed fall in N % $mass_{bulk}$. This value will however also depend on loss of N from keratin proteins, by (1) deamidation of protein side chains, and/or (2) oxidation of protein side chains. Deamidation of Asn and Gln to Asp and Glu was calculated to decrease N %$mass_{protein}$ by *c*. 1%, but the extent to which this occurred could not be measured as any remaining Asn and Gln were deamidated during preparative hydrolysis. Secondly, the oxidation of protein side chains (Asn, Gln, Thr, His, Arg, Tyr, Phe: that is, including the deamidations discussed previously) was calculated to reduce N % mass by a further 2.5% (Figure 4.7b). These however clearly do not account for all the decrease in N % $mass_{bulk}$ observed. As for C % mass above, further loss of N % mass by additional deamidation or oxidation of AAs (causing increase in O % mass) is the most likely explanation.

For H, % $mass_{bulk}$ decreased while % $mass_{protein}$ increased, and the inverse pattern was shown for O. H % mass was expected to increase over time due to hydrolysis of hydrophilic AAs, which typically contain greater proportions of N, O and S; by the same logic O % mass was expected to decrease. These patterns were observed in H and O % $mass_{protein}$, but the inverse was observed in H and O % $mass_{bulk}$ (Figure 4.7c and d). Much of these changes could be explained by the cumulative effects of deamidation and oxidation of the fibre, but patterns after 8 hours exposure at 140°C (and 240 hours at110°C for H only) implied more extreme protein oxidation than assumed in Table 4.8.

For S, % $mass_{protein}$ could not be calculated, but % $mass_{bulk}$ showed a slight decrease. These values showed a complex pattern, leading overall to a decrease in S content from approximately 2.5 to 1.5%. This is consistent with the elimination of S from Cys under conditions of moist heat (Volkin and Klibanov 1987; Walter *et al.* 2006). The range of % mass of S in Cys in IFPs is 1–2% (with a contribution of *c*. 0.2% from Met). The changes in overall S content were therefore consistent with changes in the protein moiety only.

In summary, changes in elemental composition of the wool fibre suggested: (1) loss of AAs from the wool fibre by protein hydrolysis, (2) deamidation of Asn, Gln, His and Arg, (3)

oxidation of Thr, Tyr, Phe and probably further AAs, (4) elimination of S, and (5) the survival of melanins unchanged.

4.4.4 Effects of degradation on isotopic composition

Change in $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$ values from controls was greater in high-temperature isothermal hydrous experiments than in experimental burials. Change in $\delta^{18}O$ was of approximately equal extent in both models but clearly had different mechanisms (Figure 4.9). This discussion assumed that complete preparative acid hydrolysis of the peptide bond to extract individual AAs did not fractionate any isotopes: however this has so far only been shown for $\delta^{13}C$ (Jim *et al.* 2003).

4.4.4.1 Experimentally buried samples

Though experimentally buried samples differed considerably in macroscopic indicators of degradation, they showed small isotopic changes from control values in $\delta^{13}C$ (range -0.1–+0.3‰) and $\delta^{15}N$ (-0.9–+0.3‰). Ranges of change in $\delta^{2}H$ and $\delta^{18}O$ were larger (-22.1–4.2‰ and -0.6–+3.0‰ respectively). In $\delta^{18}O$, the largest enrichments were in the most degraded samples (<40% remaining after washing: 2879u and 2874m; Table 4.5), with better preserved material showing modest shifts (0.58–0.75‰).

In buried samples, therefore, macroscopic integrity was no indicator of $\delta^{13}C$ or $\delta^{15}N$ isotopic integrity. This was also the case for $\delta^{18}O$ until degradation had gone beyond a certain point, which could be ascertained during washing. The exception was $\delta^{2}H$ which showed significant changes in these degradation states.

4.4.4.2 High-temperature isothermally heated samples

Hydrolysis of the peptide bond was expected *a priori* to favour bonds containing the light isotopes ^{12}C and ^{14}N, leading to enrichment of the residue. As the peptide backbone comprises median 46% of the C in IFPs, but 78% of N (Appendix 4.5), hydrolysis was likely to enrich residual $\delta^{15}N$ more than residual $\delta^{13}C$.

Evidence for the response of $\delta^{13}C$ to peptide hydrolysis is mixed: enrichment was reported for GlyGly, proportional to extent of hydrolysis (Silfer *et al.* 1992), but depletion was found for collagen (Bada *et al.* 1989). In this study, patterns of enrichment or depletion were dependent on sample identity: unpigmented samples showed a small enrichment (median +0.55‰, range -0.78–+0.98‰) while pigmented samples showed a depletion at 80°C and 110°C but an enrichment at 140°C (overall median -0.29‰, range -0.70–+0.13‰). Wool melanin was likely to have $\delta^{13}C$ values more depleted than bulk protein (McCullagh *et al.* 2005; Michalik *et al.* 2011). If wool keratin and melanin $\delta^{13}C$ values were different, then the isotopic effect of relative loss of protein was expected to be greater in highly-pigmented samples. This was consistent with data in this study. However it was also expected to be strongest in samples showing the greatest change in AA content and composition, that is

those heated to 140°C. This was not consistent with the data in this study, which showed much greater depletion in bulk $\delta^{13}C$ at 80°C (Figure 4.9a).

An alternative explanation for the behaviour of $\delta^{13}C$ in pigmented samples was that degradation of melanins themselves caused overall fibre depletion. Given the general resistance of melanins to chemical alteration (cf Liu *et al.* 2003; Ito and Fujita 1985), this appears unlikely. Elemental analysis data from the same wool samples additionally suggested the survival of at least a proportion of the melanin content of the fibres, and again, this effect was expected to be greater in samples exposed to higher temperatures. The behaviour of $\delta^{13}C$ in highly pigmented wool samples under moderate wet heat therefore remained unexplained.

Enrichment in residual $\delta^{15}N$ due to peptide hydrolysis has been reported in collagen (Bada *et al.* 1989) and GlyGly dipeptides (Silfer *et al.* 1992), and was suggested by the behaviour of keratin in unpigmented samples in this study (median change +0.05‰, range -0.23–+0.69‰), but changes were not large. In contrast, strong depletion in $\delta^{15}N$ was observed in pigmented samples (median change -0.53‰, range -2.3–+0.05‰), and the largest depletions were seen at the lowest temperature. This was unlikely to be primarily due to hydrolysis.

An alternative source of isotopic change in $\delta^{15}N$ was deamidation of Asp and Glu. Sacks and Brenna (2005) found that side chain N was typically more enriched than peptide N in AAs from a number of sources. Deamidation of keratin proteins was therefore expected to lead to more depleted bulk $\delta^{15}N$ values. This effect was not generally apparent in samples from this study, as only pigmented samples showed net depletion, but it may be masked by the kinetic enrichment described above.

A third potential source of change in bulk $\delta^{15}N$, as for $\delta^{13}C$, was alteration of the proportions of protein and non-protein moieties of the fibre, if these have significantly different isotope ratios, or (less likely) degradation of the melanin moiety. Tyr, from which melanins are largely derived, was depleted relative to bulk in zooplankton (McClelland *et al.* 2003) but the melanin contribution to $\delta^{15}N$ showed a variable relationship to bulk keratin values in bird feathers (Michalik *et al.* 2011). It was therefore not clear what relationship should be expected in mammalian proteins and melanins. However, as for $\delta^{13}C$, any such effects were expected to be greater in more degraded samples, which was not the case (Figure 4.9b). The behaviour of $\delta^{15}N$ in highly pigmented wool samples under moderate wet heat therefore also remained unexplained.

The relationship between $\delta^{2}H$ and $\delta^{18}O$ ratios and temperature of degradation was clearer. Both isotopes showed similar behaviour, becoming depleted, with stronger depletion at higher temperatures and longer time points, with the exception of raw wool samples at 80°C, which showed enrichment. This pattern was clearer in $\delta^{18}O$ than in $\delta^{2}H$. This is probably due

to the higher proportion of exchangeable O in proteins than H, between 50 and 100% of each AA residue for O (including carboxyl Os: Murphy and Clay 1979; Wedeking and Hayes 1983; in whole proteins: Niles *et al.* 2009) but only 22–63% for H (all N-, O- and S-bound H, plus racemisation, i.e. exchange of the H at the α-carbon). The extent of O exchange was probably increased by deamidation and oxidation of the protein, as this created new side-chain carboxyl groups.

The overall pattern of depletion in both $\delta^{18}O$ and $\delta^{2}H$ was most likely a kinetic isotope effect, with faster exchange of the lighter isotope (Hallaway and Benson 1971; Amelung and Brodowski 2002). This reaction was found to be pH-dependent for H in a study by Leach *et al.* (1964), where alkaline pre-treatment of the wool fibre strongly increased exchangeability of N-, O- and S-bound H atoms. It would be interesting to test whether wool dyed with woad, a process which requires alkaline conditions (Ferreira *et al.* 2004), showed a substantially enhanced extent of racemisation over material in this study. In contrast, the enrichment of $\delta^{2}H$ and $\delta^{18}O$ ratios in raw wool samples at 80°C must have been due to a different mechanism, possibly either the elimination of a depleted fraction from the wool fibre or an equilibrium isotope effect (Wedeking and Hayes 1983).

However this pattern did not hold for all samples, in particular raw wool samples degraded at 80°C (both isotopes). Therefore kinetic enrichment is not the only mechanism acting on $\delta^{18}O$ and $\delta^{2}H$ in degraded wool samples, though it is dominant at high temperature. This suggests that it may not be dominant in archaeological samples either. Changes causing enrichment in isothermally hydrolysed material are probably to be due to equilibrium effects, which are well known for $\delta^{2}H$ in proteins (e.g. Bowers and Klevit 1996) and have been identified for $\delta^{18}O$ in other organic molecules (Rishavy and Cleland 1999). These effects are likely to be present at all temperatures, but dominant only at lower temperatures. It is not clear why they were more evident in raw wool samples than in wool made up into a textile. In contrast, the enrichment in ^{18}O only, seen in experimentally buried material, was probably due to bacterial mechanisms.

4.4.4.3 Indicators of isotopic change in keratin

In previous isotopic work, a bulk fibre $C:N_{atom}$ ratio of 2.9–3.8 has been taken as the accepted range for intact human hair (e.g. Wilson *et al.* 2007b; based on O'Connell and Hedges 1999). Given the similarity of mammalian hairs (Popescu and Höcker 2007), this range can be taken to apply to wool, especially as the theoretical $C:N_{atom}$ for the most abundant proteins in wool is in the range 3.3–3.5 (Table 4.9).

It is therefore important that this study has shown that the change of total fibre $C:N_{atom}$ with high-temperature degradation is not straightforward (Figure 4.7f). Moreover, isotopic change does not necessarily correlate with elemental or AA change. In particular, isotopic change of up to +1.0‰ for $\delta^{13}C$ and -2.3‰ for $\delta^{15}N$ was observed in densely pigmented wool samples heated at 80°C, which had median $C:N_{atom}$ 3.57 (IQR 3.53–3.66), that is, within the

'acceptable' range. AA composition and racemisation for these samples is also relatively unchanged from controls (Figures 4.4c and 4.5c). The situation is more straightforward for δ^2H and $\delta^{18}O$, where greater degradation is seen at 110°C (median $C:N_{atom}$ 3.85, IQR 3.73–3.96) and 140°C (median $C:N_{atom}$ 3.72, IQR 3.55–4.05). Thus currently, AA composition or elemental composition variables cannot be guides to $\delta^{13}C$ or $\delta^{15}N$ integrity in densely pigmented mammalian hair samples, though for unpigmented samples, and for δ^2H and $\delta^{18}O$, these indicators are useful. However, the range of 'acceptable' values should probably be revised for degraded and intact unpigmented sheep wool samples, towards 3.4–3.7, derived from measurements in modern sheep wool (Chapters 2–3) and the limits of elemental change observed without significant isotopic change (this chapter). In general, this data indicates that simple X:Y atomic ratios may not be an appropriate measure of integrity for a tissue like hair, composed of moieties with very different X:Y atomic ratios, unlike bone collagen (Van Klinken 1999; Harbeck and Grupe 2009; Nehlich and Richards 2009).

4.4.5 Comparison to observed racemisation rates in biomineralised tissues

AA concentration data in this study indicated that peptides were lost from wool during high-temperature degradation as a result of hydrolysis. Racemisation ratios for highly degraded residual wool samples were therefore not representative of the fibre as a whole, but were biased towards the most hydrolysis-resistant parts of the fibre, with a higher content of hydrophobic AAs. Comparison of racemisation ratios from early and late in degradation sequences therefore were not strictly comparing like with like. Nevertheless these calculations are reported because they formed an interesting comparator to biomineralised systems, where the residual insoluble fraction of protein could not be analysed separately, being instead subsumed into the Total Hydrolysable AA fraction together with any soluble peptides produced during degradation.

Given that racemisation rates in residual wool samples are biased towards the more degradation-resistant parts of the fibre, it was not surprising that estimates of activation energy were generally higher than for biomineralised systems (Crisp *et al.* unpublished; Demarchi *et al.* unpublished-b; Tomiak *et al.* unpublished; Table 4.7), dipeptides or free AAs (e.g. Collins *et al.* 2000; Smith and Sivakua 1983), and consistently higher than those of hydrolysis. Estimates from wool are likely to have overestimated activation energies and underestimated average reaction rates in wool peptides.

4.4.6 The influence of sample type on decomposition

Pigmented vs. unpigmented raw wool. The effect of the presence of natural pigment in raw wool on AA composition and racemisation was difficult to evaluate because of the unreliability of data from run H391 which contained most unpigmented raw wool samples. Nevertheless, the extent of racemisation in pigmented wool samples was strikingly higher than those of unpigmented raw wool and finished textiles (both of which are also made from unpigmented wool) at time points greater than 48 hours at 140°C (Figure 4.6). This

behaviour may have represented a change in balance between racemisation and hydrolysis reactions, dependent on the presence of natural pigment. This suggested that additional covalent or H-bonding between peptides and melanin granules inhibited the solubilisation of highly degraded protein sections, allowing the accumulation up of highly racemised AAs in highly-degraded wool residues.

Elemental analysis indicated that unheated wool fibres contained a smaller % mass of C, N and H and a greater % mass of O than the protein fraction of the fibre. This suggested the presence of a non-protein moiety with lower C, N and H and higher O % mass than protein. These results for C and O % mass were not consistent with the elemental content of melanin, expected to be the dominant species here, though they were consistent for N and H % mass. This difference have been due to the presence of water in these samples, which were not freeze-dried prior to elemental analysis. However, because all samples were treated equally, this should not have affected the patterns of change of these values with diagenesis. Only H % $mass_{bulk}$ differed significantly between pigmented and unpigmented samples, being higher in the latter. This was consistent with the presence of melanin in the pigmented fibres, though it is unlikely that this effect should only be discernible in H.

Unexpectedly, C, N, O and H % $mass_{protein}$ were significantly different between pigmented and unpigmented raw wool samples. This indicated differences in protein composition between (partially degraded) pigmented and unpigmented samples. This may be related to bonding between melanin granules and protein AAs limiting the solubilisation of hydrolysed peptides. However error bars were very large (*c*. 50 for each element).

Presence of pigmentation was an important factor in understanding change in isotope composition, specifically $\delta^{13}C$ and $\delta^{15}N$. Both became depleted in pigmented samples at 80°C, and $\delta^{13}C$ also was at 110°C, but not at the highest temperature. Unpigmented samples in contrast showed a slight enrichment in both isotopes. Importantly, these strong depletions were not correlated with $C:N_{atom}$. The reasons for this behaviour were obscure. Change in $\delta^{2}H$ and $\delta^{18}O$ values were not significantly different between degraded pigmented and unpigmented samples.

Dyed vs. undyed wool textile. Madder dye and alum mordant were widespread dyeing technologies in antiquity (Chenciner 2000). The mordant, a mixture of aluminium salts (Jecock 2009), was expected slow degradation in experimentally buried samples because of the toxicity of aluminium to many organisms (Wood 1995). This was supported by the observation of the greater fragility of undyed samples than undyed in experimental burials. AA composition indicated that dyeing and/or mordanting also appeared to protect against hydrolysis, as dyed samples contained higher AA concentrations per unit mass than undyed samples.

The active constituents of the dyestuff, alizarin and purpurin (Ferreira *et al.* 2004), were present in quantities too small to affect elemental ratios or isotope values, which were not significantly different between dyed and undyed samples. Madder/alum dyeing, and probably more generally mordant dyeing, was unlikely to be a confounder of origin in isotopic provenancing studies of archaeological textiles, though vat or direct dyes may have other effects.

Raw wool vs. finished textiles. Understanding the differences between these groups of samples was difficult because they had different origins (UK *vs.* Norway), represented different breeds (Shetland vs. unknown, though this may well have been of the Northern Short Tail breed group, which is closely related: Chessa *et al.* 2009) and were of different ages (raw wool samples were shorn in June 2009: Chapter 3; finished wool samples were bought in 1997: E. Peacock, pers. comm.). Differences between the groups could therefore not necessarily be ascribed to the mechanical and chemical processes of modern textile manufacture.

4.5 Conclusions

This study examined wool diagenesis in high temperature isothermal hydrous conditions and experimental burials. High temperature experiments caused extensive wool protein composition change, which was evident in elemental composition, AA composition or racemisation, and $\delta^{2}H$ and $\delta^{18}O$ isotopic composition. Degradation of hair fibres was a complex process, probably composed of multiple reactions: hydrolysis of peptide bonds, in-chain and chain-end racemisation, AA decomposition (deamidation and oxidation), and peptide chain denaturation. These processes were differently temperature-sensitive, so they varied in importance between experimental temperatures. Caution must therefore be used in extrapolating the patterns of degradation of keratin from high temperature experiments to archaeological material, which has survived at a much lower average temperature, at which a number of the reactions seen at high temperatures may not have occurred.

Degradation in buried samples was consistent with domination by microbiological activity causing major macroscopic change but without being protein selective. These samples showed little change in elemental composition, AA composition or racemisation, or isotopic composition, except for enriched $\delta^{18}O$ in the most highly degraded samples. The extent of macroscopic change occurring in less than 10 years of burial presents problems. These processes can destroy the sample rapidly, before hydrolytic changes can develop. Additionally, in ancient samples, the co-facilitation of microbiological and hydrolytic aspects of degradation should also be considered. However, wool samples which appear badly degraded to the curator, but of which more than approximately 40% mass remains after washing, should still be suitable for isotopic analysis.

The presence of natural pigmentation in the wool fibre, in the form of melanins, was important for understanding (1) hydrolysis-associated changes in $\delta^{13}C$ and $\delta^{15}N$ at relatively low temperatures (though still elevated over archaeological degradation conditions) and (2) extent of racemisation in very highly degraded samples. The effect of the presence of pigment (quantified microscopically: e.g. Walton Rogers 2004) will be specifically examined in archaeological textile material. Other future work includes:

- development of a wool standard for RP-HPLC measurements to examine substrate-specific accuracy of the method. Furthermore the re-calibration of the raw concentration data for this method is in hand (B. Demarchi, pers. comm.).
- examination of $\delta^{15}N$ of individual AAs in wool (Styring *et al.* 2010).
- investigation of the $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ values of melanins isolated from wool (Liu *et al.* 2003).
- identifying histological correlates for hydrolytic degradation (Wilson *et al.* 2010) by microscopy of samples examined analytically in this study.
- exploration of the effect of alkaline treatment of the wool fibre, as in woad dyeing (Hurry 1973), on subsequent degradation in experimental burial and high-temperature isothermal hydrous conditions.
- examination of the AA composition and racemisation of the soluble peptides and free AAs released by isothermal hydrous heating of wool samples (the counterpart to the residues examined in this study).

Acknowledgements

The assistance of Richard Allen, Becky Claypole, Beatrice Demarchi, Kirsty Penkman, and John Stewart in the laboratory was invaluable. Thanks to everyone on the AAR team for advice and help. Funding for this work was provided by the UK Natural Environment Research Council (IvH: NE/G52421X/1, EK163-08/10).

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5. An assessment of procedures to remove exogenous Sr before $^{87}Sr/^{86}Sr$ analysis of waterlogged archaeological wool textiles

Abstract

RATIONALE Strontium ($^{87}Sr/^{86}Sr$) isotope analysis has been suggested as a method to provenance archaeological samples of wool textiles, which were extensively traded in medieval Europe. The effect of post-discard (environmental) contamination on keratin samples, which contain only low concentrations of Sr, has not been investigated.

METHODS We compared published methods of removing exogenous Sr from keratinous samples, using compressed N_2 gas, HF(aq) wash and organic solvent wash. $^{87}Sr/^{86}Sr$ isotope ratios and Sr content of undyed and madder-dyed/alum-mordanted moieties of the same wool textile, buried for up to three years in contrasting environments (marine sediment/fenland bog), and two archaeological samples from Iceland (one typical and one atypical of local manufacture), were investigated with ultra-low blank ion-exchange chemistry combined with thermal ionisation mass spectrometry.

RESULTS Experimental burial increased Sr content of wool samples over controls. $^{87}Sr/^{86}Sr$ ratios of all buried samples were enriched over local environmental values. Efficacy of Sr removal was: organic solvents > HF(aq) > compressed N_2. Difference of cleaned samples' $^{87}Sr/^{86}Sr$ ratios to controls was: compressed N_2 < organic solvents < HF(aq). Both archaeological samples showed Sr contents greater than experimental burials (1.19–118 μg g^{-1}), and $^{87}Sr/^{86}Sr$ values consistent with Icelandic origin (0.7036–0.7054).

CONCLUSIONS For undyed samples only, cleaning with compressed N_2 adequately removed exogenous Sr from waterlogged buried wool textiles. No cleaning methods were effective on dyed material. Archaeological samples from Iceland showed $^{87}Sr/^{86}Sr$ ratios suggesting strong contamination from the local environment. We conclude that $^{87}Sr/^{86}Sr$ ratios of archaeological waterlogged wool textiles do not accurately reflect wool provenance.

Keywords: strontium isotope; wool; diagenesis; dye; mordant

5.1 Introduction

Wool textiles are a class of artefact widespread in the historic and prehistoric past in Europe (e.g. Bender Jørgensen 1992; Munro 2003; Walton Rogers 2007). A method to establish the provenance of samples of archaeological textile from waterlogged archaeological deposits would expand our knowledge of the movement of these objects of considerable economic, artistic, technological and social importance (Schneider 1987). Sr isotope provenancing has proved exceptionally useful to discriminate local from non-local enamel in human and animal archaeological remains (Alexander Bentley 2006; Viner *et al.* 2010; Chenery *et al.* 2010), in modern human forensic studies (Aggarwal *et al.* 2008; Font *et al.* 2012) and in ecological studies (Hobson 1999; Ben-David and Flaherty 2012) including in modern bird feather keratins (Font *et al.* 2007; Evans and Bullman 2009; Sellick *et al.* 2009). The approach has been extended to archaeological wool finds (von Carnap-Bornheim *et al.* 2007; Frei *et al.* 2009a; Frei *et al.* 2009b; Frei *et al.* 2010). These studies did not, however, explicitly test the effect of diagenesis under burial conditions on wool textiles' $^{87}Sr/^{86}Sr$ isotope signatures, a process which is known to overprint the Sr isotope signature in bone (e.g. Trickett *et al.* 2003).

Wool has a known affinity for heavy metal cations (Popescu and Wortmann 2010) and is used industrially as a sequestering agent for them (e.g. Homonoff *et al.* 2001). Archaeological and experimentally degraded human hair has been shown to absorb a number of metal ions from the environment (Kempson *et al.* 2003; Kempson *et al.* 2010), including Ca^{2+} which can be interpreted as a proxy for Sr^{2+}, as the ions have similar mass and size. Sr is also present in the lipid fraction of hair (Attar *et al.* 1990). Metal ions in hair are removed with differing efficiency by a variety of washing methods (e.g. studies cited in Morton *et al.* 2002; Chittleborough 1980), with individual element behaviour at least partially dependant on pH (Kar and Misra 2004). It is therefore possible that burial in waterlogged environments, pre-burial washing procedures, including dyeing and mordanting (the application of a complexing agent to bind a dye molecule to the fibre; historically often a mineral ore: Jecock 2009) and post-excavation conservation wet cleaning may all remove endogenous Sr from wool and/or introduce exogenous Sr. If the $^{87}Sr/^{86}Sr$ isotope ratio of the burial environment or of cleaning washes is significantly different from that of the fibre, this may obscure the original provenance signal of the fibre rendering it impossible to retrieve provenance from wool.

The most probable mechanism for long-term entrapment of metals in wool is reaction with the abundant cysteine residues in the keratin associated proteins (KAPs) to form stable metal mercaptides, and ultimately the precipitation of nano-crystalline metal sulphides (a Greco-Roman hair-dyeing method: Walter *et al.* 2006). Metals may also bind to exchangeable (pH reversible) sites, most likely free carboxyl groups of acidic amino acids in KAPs and intermediate filament proteins (IFPs), and in melanins (Morton *et al.* 2002). There may also be some coordination with nitrogen atoms of amine and amide groups at alkaline

pH. The hundreds of proteins present in wool fibres (Clerens *et al.* 2010) decay at different rates under burial conditions (Wilson *et al.* 2007). Thus the decay of the wool fibre itself is therefore likely to change the number and type of binding sites available, which may lead to change of $^{87}Sr/^{86}Sr$ ratios.

This study compared the efficiency of three published methods of cleaning keratin fibres for Sr isotope analysis: method A: high pressure N_2 (Font *et al.* 2007); method B: 20% HF(aq) (Frei *et al.* 2009b); and method C: organic solvents and water (standard light isotope wool preparation procedure: Hedges *et al.* 2005; Chapter 7). We hypothesise that if endogenous Sr in wool binds primarily to:

- exchangeable sites on the protein, HF(aq) cleaning should remove it but not compressed N_2 cleaning, (Font *et al.* 2007) although both should remove exogenous Sr from silicates;
- lipids, organic solvent cleaning (Hedges *et al.* 2005) should remove it but not HF(aq) or compressed N_2 cleaning;
- melanin or cysteine residues, none of these cleaning procedures will show significant differences.

5.2 Experimental

5.2.1 Sample origin

Samples of experimentally-buried wool textile (Bergstrand and Nyström Godfrey 2007; Turner-Walker and Peacock 2008) were supplied by Elizabeth Peacock. Un-dyed and madder root-dyed/alum-mordanted sub-samples of the same wool cloth (Røros Tweed A/S, Røros, Norway) were selected for analysis. Madder root/alum mordant treatment was a widespread pre-industrial wool dyeing method (Walton 1991; Walton Rogers 1997, 1766-71; Chenciner 2000). Un-dyed and dyed aliquots of the same textile were buried in a fenland bog (Lejre, Denmark) and in marine sediment (Marstrand, Sweden) (Table 5.1).

Samples 2000-6-187(b) and 1989-33-380(f) were selected from the 13–14th and 15–16th century phases of the wool textile assemblage at Reykholt, Borgarfjörður, Iceland, respectively (Walton Rogers 2012). The former was identified as of Icelandic origin, and the latter as probably of European manufacture on artefactual/stylistic grounds, and this identification was supported by light stable isotope analysis (Chapter 7; Chapter 8). The young basaltic volcanic rocks of Iceland yield some of the lowest $^{87}Sr/^{86}Sr$ values in Europe ($^{87}Sr/^{86}Sr$ of the rocks, soils and waters lie in the range 0.7030–0.7040 (Evans and Bullman 2009; Voerkelius *et al.* 2010) and it is highly unlikely that the European import had original $^{87}Sr/^{86}Sr$ values as low as this.

Table 5.1. Sample descriptions: origin, burial site and pre-burial treatment.

Sample type	Origin	Geology of origin	Site of burial	Geology of burial site	Approx. soil $^{87}Sr/^{86}Sr$	Burial period / y	Dye/mordant
Control	Rørøs, NO	Caledonian nappe complexes	/	/	0.7050*	0	None
	"	"	"	"	"	"	Madder/alum
Experimentally buried	Rørøs, NO	Caledonian nappe complexes	Lejre, DK	Quaternary drift	0.7076–0.7096*	1**	None
	"	"	"	"	"	"	Madder/alum
	"	"	Marstrand, SE	Marine sediment	0.7092†	3	None
	"	"	"	"	"	"	Madder/alum
Archaeological	Unknown (Icelandic)	Tertiary or Quaternary volcanic rock	Reykholt, Iceland	Tertiary volcanic rock >3.1mya	0.7036–0.7033‡	*c*. 500	Unknown
	Unknown (mainland Europe)	Unknown	"	"	"	"	"

Data from: *Frei *et al*. (2009a), †Veizer (1989), ‡O'Nions and Pankhurst (1973).

**Longer-buried samples were too degraded to provide adequate mass for analysis.

5.2.2 Reagents

35% nitric acid (HNO_3) and 20% hydrofluoric acid (HF(aq)) were purified by sub-boiling distillation in PTFE from initial *pro analisi* > 65% HNO_3 (Sigma-Aldrich, USA) and analysis grade 40% HF (Merck, Germany). 22–26% hydrochloric acid (HCl) was purified by sub-boiling distillation in quartz equipment from initial *pro analisi* > 37% HCl (Sigma-Aldrich, USA). 31% hydrogen peroxide (H_2O_2) of ultra pure quality (Merck, Germany) was used for removal of organic material. Organic solvents dichloromethane (DCM) and methanol (MeOH), both HPLC grade (Fisher Scientific, UK), were used for sample cleaning. Ultra pure water (resistivity >18 MΩ) used throughout the chemistry procedure and for dilution of concentrated acids was obtained from a Milli-Q element system (Millipore, USA).

5.2.3 Sample cleaning

Up to 0.7 g of experimentally-degraded and archaeological wool was taken from each sample/find and subjected to each of the three cleaning methods. Methods A and C were carried out at BioArCh, York, UK under standard laboratory conditions. Method B and all dissolution and spiking procedures were carried out under clean lab conditions (Class 100) at the Petrology Department, Vrije Universiteit (VU) Amsterdam, The Netherlands.

Samples cleaned with N_2 (Series A) were secured in a small plastic container on PTFE mesh, and exposed to several 30 s blasts of high pressure N_2 gas (oxygen-free nitrogen, Linde Group, Munich, Germany). Samples cleaned with HF (Series B and BL) were placed in 7 mL Teflon screw-cap beakers (Savillex™, Minnetonka, USA) and exposed to 20% HF(aq) for 60 minutes in the case of experimentally buried textiles, or 30 minutes in the case of archaeological textiles. The supernatant solution was then removed by pipette and the sample rinsed twice with 1 mL Milli-Q water (Series B). The combined rinsing solution and supernatant was retained for analysis (Series BL). Samples cleaned with organic solvents (Series C) were washed with mixtures of DCM and MeOH, and with Milli-Q water (based on the protocol in Hedges *et al.* 2005), using a test sieve (Endecotts Ltd, London, UK; aperture 63 µm) to retain fragmentary sections.

5.2.4 Sample dissolution

All samples (Series A, B, BL and C) were placed in 7 mL Teflon screw-cap beakers, and a highly enriched ^{84}Sr spike (0.03–0.28 g) was added. To remove organic compounds, 1:1 v/v mixtures of 35% HNO_3 and 31% H_2O_2 were added to each sample for closed-vessel digestion. Samples did not dissolve within 30 min as described previously (Frei *et al.* 2009b), even with heating on a hotplate at 90°C. Larger samples were slower to digest; all samples in series B were quicker to dissolve than their moieties in A and C; red colouration in dyed samples faded within 24 hours. The following additional dissolution steps were carried out with 30 min ultrasonication and digestion on a hotplate at 110–140°C at each step, with partial evaporation between each, as necessary until samples were completely dissolved, over a period of up to 9 days: (1) addition of 50% HNO_3; (2) addition of 4:1 v/v mixture of

50% HNO_3 and 31% H_2O_2; (3) addition of 22–26% HCl; (4) addition of 3:1 v/v mixture of 22–26% HCl and 50% HNO_3 (Font *et al.* 2007).

The residues were taken up with 0.5 mL 50% HNO_3. A number contained a precipitate; all were centrifuged for 5 min at 5000 rpm. The supernatant was removed by pipette and loaded onto cleaned quartz columns containing preconditioned Sr-Spec™ resin (100–125 µm) suspended in Milli-Q water (Horwitz *et al.* 1992). After several washes with 20% HNO_3, Sr was eluted in Milli-Q water and dried before final nitration in 88% HNO_3.

5.2.5 Sample analysis

Sr isotope ratios were measured on a ThermoElectron Triton plus Thermal Ionization Mass Spectrometer (TIMS) at the Petrology department of the VU Amsterdam. The Sr fractions were loaded onto Re filaments using a $TaCl_5$ activator to enhance ionization (Font *et al.* 2012).

$^{87}Sr/^{86}Sr$ ratios were measured using a static multi-collection routine. An analysis consisted of 20 blocks of 10 cycles with an integration time of 8 s per cycle. $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ ratios were corrected for mass fractionation using an exponential law and $^{86}Sr/^{88}S$ ratio of 0.1194.

During the period of this study (2011), 58 analyses of the international Sr standard NBS987 were carried out on load sizes ranging from 10 ng to 100 ng to monitor and document the system's performance. The 10 ng average $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ ratios for the NBS987 measurements were 0.710242 ± 0.000016 (2SD) and 0.056493 ± 0.000008 (2SD), respectively. The 100 ng average $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ ratios for the NBS987 measurements were 0.710242 ± 0.000008 (2SD) and 0.056492 ± 0.000004 (2SD), respectively. The external reproducibility of the standards is below 0.0032 %.

5.3 Results

Results are given in Table 5.2. The total procedure blank contained <50 pg Sr.

5.3.1 Control samples: effect of dyeing

Undyed and dyed control sample residues differed in $^{87}Sr/^{86}Sr$ ratio and Sr content. Undyed samples showed ratios of 0.7117–0.7118 and a narrow range of Sr content between cleaning methods (0.067–0.207 µg g^{-1}), compared with 0.7087–0.7088 and a much wider range of Sr content (0.903–8.92 µg g^{-1}) for dyed samples (Figures 5.1 and 5.2).

Table 5.2. Sample results. Series A: compressed N_2 residue; series B: 20% HF(aq) residue; series BL: 20% HF(aq) combined supernatant; series C: DCM/MeOH/H_2O residue.

Type	Burial site (yrs)	Dye/mordant	Wash	Mass / mg	HF(aq) / mL	$^{87}Sr/^{86}Sr \pm 2SE$ (abs)	Sr content (µg g^{-1})
Control	None (0)	None	A	0.192	/	0.711709 ± 0.000112	0.207
			B	0.201	6	0.711755 ± 0.000074	0.082
			BL	0.201	"	0.711875 ± 0.000188	0.114
			C	0.071	/	0.711766 ± 0.000244	0.067
Experimental burial	Lejre, DK (1)	None	A	0.018	/	0.711615 ± 0.000172	1.02
			B	0.016	2	0.714161 ± 0.000113	0.573
			BL	0.016	"	0.720987 ± 0.000113	1.45
			C	0.098	/	0.713010 ± 0.000134	0.535
Experimental burial	Marstrand, SE (3)	None	A	0.732	/	0.711626 ± 0.000137	0.156
			B	0.032	2	0.716373 ± 0.000179	2.69
			BL	0.032	"	0.721322 ± 0.000138	2.74
			C	0.021	/	0.717900 ± 0.000817	0.111
Control	None (0)	Madder/alum	A	0.134	/	0.708776 ± 0.000129	8.92
			B	0.303	6	0.708815 ± 0.000154	1.45
			BL	0.303	"	0.708905 ± 0.000154	3.12
			C	0.216	/	0.708706 ± 0.000088	0.904

Table 5.2 continued.

Type	Burial site (yrs)	Dye/mordant	Wash	Mass / mg	HF(aq) / mL	$^{87}Sr/^{86}Sr$ ± 2SE (abs)	Sr content (µg g^{-1})
Experimental burial	Lejre, DK (1)	Madder/alum	A	0.022	/	0.711210 ± 0.000199	2.19
			B	0.016	2	0.713407 ± 0.000262	1.29
			BL	0.016	"	0.719100 ± 0.000096	1.78
			C	0.031	/	0.710613 ± 0.000066	0.834
Experimental burial	Marstrand, SE (3)	Madder/alum	A	0.013	/	0.709981 ± 0.000133	14.9
			B	0.012	2	0.711037 ± 0.000081	5.37
			BL	0.012	"	0.711734 ± 0.000112	16.8
			C	0.006	/	0.710103 ± 0.000249	1.88
Archaeological (typical of Icelandic manufacture)	Reykholt, IS (c. 500)	Unknown	A	0.029	/	0.704285 ± 0.000089	36.4
			B	0.088	3	0.703571 ± 0.000012	118
			BL	0.088	"	0.703767 ± 0.000195	2.15
			C	0.016	/	Failed	-
Archaeological (atypical of Icelandic manufacture, probably imported from mainland Europe)	Reykholt, IS (c. 500)	Unknown	A	0.008	/	0.704369 ± 0.000136	5.63
			B	0.004	2	0.704568 ± 0.000158	28.7
			BL	0.004	"	0.704277 ± 0.000126	16.0
			C	0.016	/	0.705398 ± 0.000165	1.19
Blank	2:1 MeOH/DCM	/	C	1.710	/	0.709248 ±0.000506	0.0002
Blank	2:1 MeOH/DCM	/	C	1.171	/	0.709128 ±0.001733	0.0002
Blank	2:1 DCM/MeOH	/	C	1.134	/	0.708407 ±0.000344	0.0002

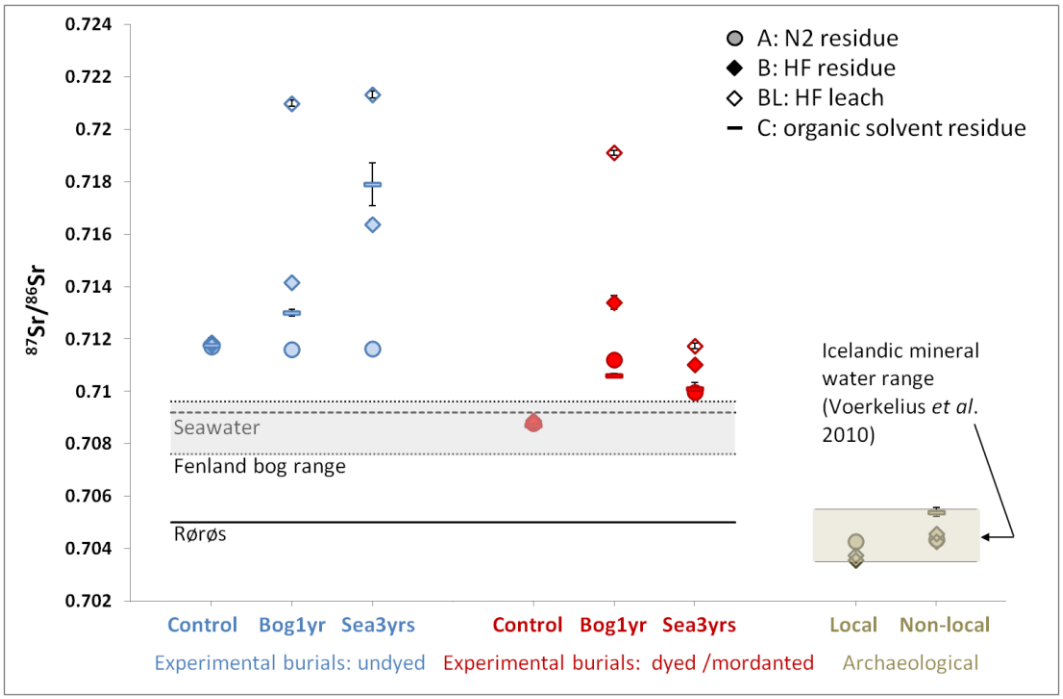

Figure 5.1. $^{87}Sr/^{86}Sr$ values for all samples. Error bars are ± 2 SE (abs). Environmental values for seawater and Rørøs are predicted (Table 5.1) rather than measured directly, as was the fenland bog range.

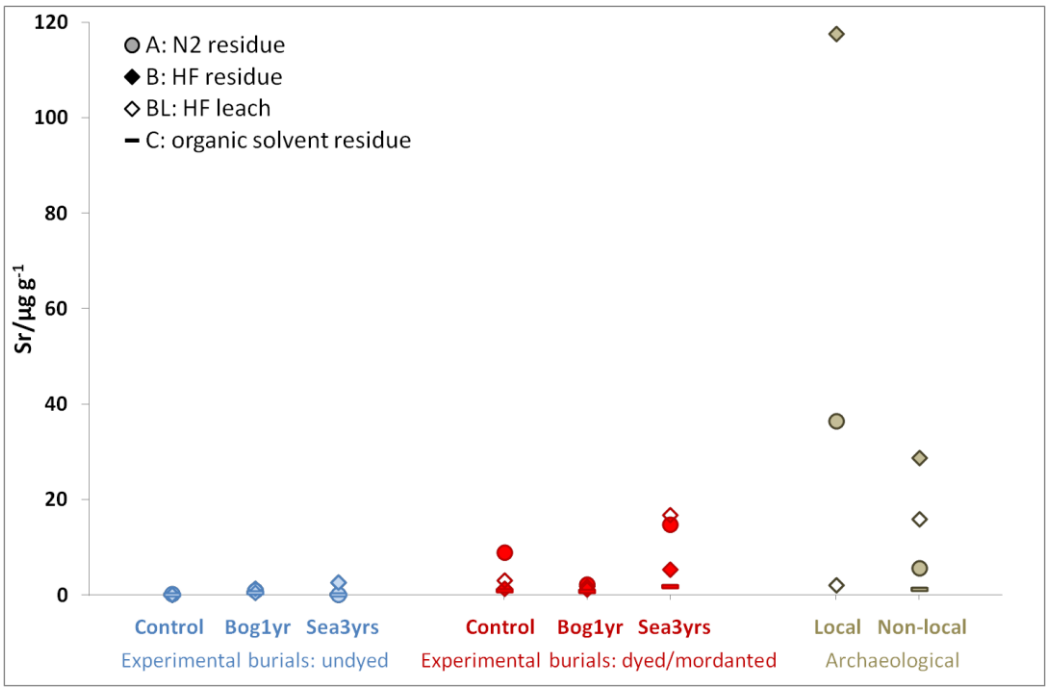

Figure 5.2. Sr content (µg g^{-1}) for all samples.

5.3.2 Experimental burials: effect of burial

All buried samples had equally or more radiogenic $^{87}Sr/^{86}Sr$ ratios than their respective unburied controls, and also varied more between cleaning methods. Buried undyed samples

had $^{87}Sr/^{86}Sr$ ratios of 0.7116–0.7179, compared with 0.7117–0.7118 for controls; dyed samples showed ratios of 0.7100–0.7134 compared with 0.7087–0.7088 for controls (Figure 5.1).

Buried samples also had more radiogenic $^{87}Sr/^{86}Sr$ ratios than expected for their local environments. Burials in the fenland bog showed isotope values of 0.7106–0.7142 compared with expected values of 0.7088 (Frei *et al.* 2009a). Burials in marine harbour sediment showed isotope values of 0.7100–0.7179 compared with expected values of 0.7092 (Veizer 1989; Figure 5.1).

Finally, buried samples also showed greater Sr content, and greater variability in content between cleaning methods, than controls. Dyed samples had greater Sr content than undyed samples (0.834–14.9 µg g^{-1} *vs.* 0.111–2.69 µg g^{-1}) regardless of burial environment. Samples buried in a marine environment showed higher Sr concentrations (0.111–14.9 µg g^{-1}) than samples buried in a fenland bog (0.535–2.19 µg g^{-1}).

5.3.3 Experimental burials: effects of cleaning methods

In control samples, $^{87}Sr/^{86}Sr$ ratios did not differ greatly between cleaning methods. This was not the case in buried material (Figure 5.1). Residues treated with methods A (compressed N_2) and C (organic solvents/water) showed differences in $^{87}Sr/^{86}Sr$ ratios from their respective control samples of approximately the same order of magnitude (method A: range -0.0001–0.0024; method C: range -0.0017–0.0061), though undyed samples treated with method A differed very little from controls (range -0.00010–-0.00008). Residues treated with method B (HF(aq)) showed differences in $^{87}Sr/^{86}Sr$ ratios between buried samples and controls an order of magnitude greater (range 0.0022–0.0046). In all HF-treated samples, buried samples showed more radiogenic $^{87}Sr/^{86}Sr$ ratios than controls.

Sr content also differed between cleaning methods. Residues treated with method A (compressed N_2) had the highest Sr contents (range 0.156–14.9 µg g^{-1}), with method B (HF(aq)-treated material) showing intermediate values (0.573–5.37 µg g^{-1}) and method C (organic solvents/water-treated samples) the lowest values (0.111–1.88 µg g^{-1}). The leaches from the HF procedure (samples BL) showed a range of 1.45–16.8 µg g^{-1}.

5.3.4 Archaeological textiles

The $^{87}Sr/^{86}Sr$ ratios of both typical (local) and atypical (non-local) samples were similar with all cleaning methods (local: 0.7036–0.7043, non-local: 0.7044–0.7054), and both show un-radiogenic isotope values, consistent with Icelandic origin, previously established in avian bone as 0.7056 ± 0.0012 (Evans and Bullman 2009) or in mineral waters as 0.7035–0.7055 (Voerkelius *et al.* 2010). Archaeological textiles showed a wide range of Sr content (1.19–118 µg g^{-1}).

5.4 Discussion

5.4.1 Control samples: effect of dyeing

The quantity of Sr present in dyed/mordanted samples was much higher (and more variable) than that recovered from undyed samples. However $^{87}Sr/^{86}Sr$ ratios from all cleaning residues of each sample type were in close agreement. This indicated that dye/mordant contaminant Sr was present in the dyed/mordanted sample, and that this dominated all binding sites in the fibre, as the $^{87}Sr/^{86}Sr$ ratio was insensitive to washing methods suited to the removal of particulate, lipid-, or protein-bound fractions of Sr.

The dye/mordant contribution to Sr content of red wool samples persisted after burial regardless of cleaning method used: buried dyed samples had higher Sr contents than buried undyed samples (range 0.834–14.9 μg g^{-1} compared with 0.111–2.69 μg g^{-1}). The dye/mordant contribution to $^{87}Sr/^{86}Sr$ ratio also persisted after burial, as dyed/mordanted samples were less radiogenic than their undyed moieties (true for each sample/procedure method pair).

Both dyes and mordants can contain Sr, and their relative contributions a wool sample will vary on the masses of each added to the dye-bath, and the nature of each material. Many historically-used dyestuffs, including madder, are derived from plants (Ferreira *et al.* 2004). The Sr content of plants varies by species, and lies between 0–1500 μg g^{-1}: (Kabata-Pendias and Pendias 2001, 128). Historically-used mordants were one of a small number of mineral ores such as hydrated potassium aluminium sulphate (alum, used in this study) or hydrated ferrous sulphate (copperas) (Jecock 2009). These minerals can have highly variable contents depending on their specific genesis (2–500 μg g^{-1}). Both dyes and mordants have been traded to a significant degree in the past (e.g. McCormick 2001, 651; Spufford 2006, 334) and thus neither may be local to the site of production of a wool fibre. Unless the contribution of Sr from the dye and mordant can be removed from the fibre, it represents a significant confounder of origin.

5.4.2 Experimental burials: effect of burial

The experimentally degraded textiles used in this study have been shown to have undergone relatively little peptide change (Chapter 4). Therefore the number and nature of acidic/basic and reversible binding sites in the protein fraction of the fibre is likely to be little different between controls and seawater- or bog-buried samples. Burial in a marine environment significantly increased Sr content over unburied controls (0.111–14.9 μg g^{-1} *vs.* 0.067–8.92 μg g^{-1}), whilst fenland bog burial had little effect on Sr content (0.535–2.19 μg g^{-1}). We hypothesise that this was related to the higher Sr content and more neutral pH in the marine burial, leading to precipitation of Sr-containing mineral phases. The effect of location of burial was less significant than the effect of dyeing/mordanting.

Buried samples also had more radiogenic $^{87}Sr/^{86}Sr$ ratios than expected for their local environments. For samples buried in a marine environment, this may not be significant as local $^{87}Sr/^{86}Sr$ ratios were not measured directly but were estimated from literature data, and may therefore not reflect local bio-available $^{87}Sr/^{86}Sr$ ratios. However local environmental $^{87}Sr/^{86}Sr$ ratios for the fenland bog were measured directly in soil and snail shell at that site (Frei *et al.* 2009a). In that study, samples of modern sheep wool generally showed more radiogenic $^{87}Sr/^{86}Sr$ ratios than local soil values, so this enrichment may be a general feature of wool samples rather than a feature of burial.

5.4.3 Experimental burials: efficacy of cleaning procedures

Compressed N_2-cleaned samples (series A) contained more Sr than samples in other cleaning series. However the $^{87}Sr/^{86}Sr$ ratios of series A samples resembled control samples' values more closely than those of series B or C. This suggests that most diagenetic Sr, including that from the dye/mordant, is present as particulates, which are removed by high-pressure gas treatment.

Samples treated with procedure B (HF(aq)) contained less Sr than series A and their $^{87}Sr/^{86}Sr$ ratios differed more than those of any other cleaning method from control values. We hypothesise that the HF method removed exogenous (silicate) particulates by dissolution (Frei *et al.* 2009a) and also removed an additional fraction of the Sr in the fibre, probably that bound exchangeably to the protein. This process was not isotopically neutral, as both the residual (B) and leach (BL) fractions showed higher $^{87}Sr/^{86}Sr$ ratios than control samples. It is possible that this was caused by addition of HF contaminated with Sr with a very high $^{87}Sr/^{86}Sr$ ratio, but as there was no correlation between amount of HF added and Sr content (Table 5.2), this effect is unlikely to account for all the elevated $^{87}Sr/^{86}Sr$ ratios of series B and BL. The Sr content and $^{87}Sr/^{86}Sr$ ratio of the HF acid is nevertheless currently under investigation. Alternatively, it may be possible that exogenous Sr from the burial was fractionated by HF treatment, either by mobilisation of the heavier isotope or acid-insoluble precipitation of the lighter.

Frei *et al*. (2010) acknowledged that dye/mordant treatments have the potential to significantly change $^{87}Sr/^{86}Sr$ ratios in wool fibres, and suggest an additional treatment with a strong oxidant (ammonium peroxodisulfate) to remove their contribution. However in the undyed samples in this study, where this procedure should not be necessary, buried samples treated with HF still differed substantially in $^{87}Sr/^{86}Sr$ ratio from controls (fenland bog sample by 0.0024, marine sediment sample by 0.0046). Additional work is underway to directly test the effect of peroxodisulfate treatment to the madder/alum-treated samples tested in this study.

Finally, samples treated with procedure C (DCM/MeOH/H_2O) contained the smallest quantity of Sr of any of the three cleaning methods. We hypothesised that this procedure, which includes 6 separate solvent steps, most efficiently removed Sr from the fibre, including

contaminant particulates by agitation or dissolution, and also some endogenous lipid-bound Sr, resulting in very low Sr contents in the residua. In all buried samples, as for series B, $^{87}Sr/^{86}Sr$ ratios were higher than in controls, which again suggests precipitation/mobilisation of a fraction of the exogenous Sr from the burial environment by this solvent treatment. These differences cannot be explained by the Sr content or $^{87}Sr/^{86}Sr$ ratios of the solvent mixtures used in this procedure, which are reported (Table 5.2).

5.4.4 Archaeological textiles

Both archaeological samples contained higher concentrations of Sr than experimentally buried textiles (Figure 5.2). This is consistent with the results of Kempson *et al*. (2003), and is most likely due to greater exposure time. Both archaeological textile samples show $^{87}Sr/^{86}Sr$ ratios consistent with Icelandic origin, despite the fact that sample 2903 has been independently identified (on art-historical/technical and light stable isotopic grounds) as manufactured in continental Europe (Chapter 7; Chapter 8). The similarity in $^{87}Sr/^{86}Sr$ ratio between cleaning methods in samples 8 (0.7044–0.7054) suggests that soil Sr was present in all fractions of the fibre (cysteine-, lipid- and protein-binding sites).

5.5 Conclusion

We conclude that high pressure N_2 pre-treatment (Font *et al.* 2007) can accurately retrieve original $^{87}Sr/^{86}Sr$ ratios of waterlogged wool textiles, but only in undyed samples. For samples dyed with an mineral mordant, and those given other pre-treatments, measured $^{87}Sr/^{86}Sr$ ratios reflect a combination of pre-burial treatment of the fibre and burial site contamination. $^{87}Sr/^{86}Sr$ ratios may differ significantly between cleaning methods, which also vary in the amount of Sr they remove from the fibre.

The application of $^{87}Sr/^{86}Sr$ ratio provenancing to archaeological samples of wool textile is problematic because:

- the influence of the burial environment on $^{87}Sr/^{86}Sr$ ratio appears to be strong, though this was only tested in one sample in this study. Provenancing of unburied or dry-buried undyed hair samples by this method is in contrast likely to be robust (Benson *et al.* 2006; Coutu 2011; Font *et al.* 2012).
- it is not possible to confidently identify samples which have never been dyed with a mineral mordant. A negative dye test indicates only that a sample at present contains no detectable level of organic dyestuff (e.g. Vanden Berghe *et al.* 2009), not that it has never been dyed. However, the suitability of any of these methods for determining provenance of samples dyed with direct dyes, such as woad (that is, without the use of a mineral mordant), is not established.
- it is likely that post-excavation conservation wet cleaning with organic solvents may change Sr content and $^{87}Sr/^{86}Sr$ ratios.

Acknowledgements

Experimental work in this study was funded by EuroPlanet grant 056-TNA3. IvH is funded by the UK National Environment Research Council (NE/G52421X/1). We are grateful to Jane Evans for comments on the study proposal.

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6. Provenancing archaeological wool textiles from the European Middle Ages: theoretical and methodological background

Abstract

Manufacture of wool textiles, and trade in both the finished artefacts and their raw materials, were of fundamental economic and social importance to countries of northern and western Europe throughout the Middle Ages. The archaeological remains of processes, medieval archaeological textiles, have been used to examine their industrial, social, environmental and cultural contexts. This chapter examines the theoretical basis for the investigation of the provenance of these objects, drawing on examples from the 7th to the 16th centuries from countries around the North and Baltic Seas. It identifies a number of ambiguities and makes a number of suggestions for additional approaches to understanding provenance.

Keywords: textile, wool, provenance, theory, methodology, empirical

6.1 The theoretical basis of archaeological textile analysis

The theoretical basis of archaeological textile analysis and interpretation has so far received little explicit published discussion within any period, not just the Middle Ages, though a number of review articles on the subject are apparently forthcoming (P. Walton Rogers, pers. comm.). Theory and methodology are typically not explicitly addressed in textile publications, in either primary (e.g. Crowfoot *et al.* 2001; Østergård 2004; Gardiner *et al.* 2005, 27-37) or secondary literature (Bichler *et al.* 2005; Gillis and Nosch 2007; Walton Rogers 2007; Gleba and Mannering 2012). There is an exception in Bender Jørgensen's work (1986, 285; 1992, 11-3). Where introductory review matter is present, it most often focuses on explaining the relationships between the many technological processes of textile preparation, their effect on the finished object and the tools used (Crowfoot *et al.* 2001, 15-25; Østergård 2004, 37-61; Walton Rogers 2007, 9-48) or lists and defines the variables measured (Ingstad 2006, 185-6).

Within this unspoken context, archaeological textile analysis includes elements from theoretical traditions which are often considered to be in opposition (Jones 2002, 2004; Pollard and Bray 2007; Hurcombe 2007, 92), though not all researchers agree (Killick 2005). The recording of the textiles themselves is consciously empirical, which is reminiscent of positivist theoretical approaches (Hurcombe 2007, 92). Analysis of European medieval wool textiles is almost entirely technical rather than stylistic, as there are few features to discuss which can be considered purely elements of design (some exceptions are Walton 1983, 222-4; Crowfoot *et al.* 2001, 50-5), unlike excavated figured silks and embroideries (Granger-Taylor 1989; Crowfoot *et al.* 2001, 82-126; Coatsworth 2005). Features typically considered cardinal are weave type and spin direction (e.g. Walton 1981; Bender Jørgensen 1992, 11; Tidow 1995; Crowfoot *et al.* 2001; Østergård 2004), and in some cases additionally judgments of fineness/coarseness (Geijer 1938; Hedges *et al.* 1982; Hägg *et al.* 1984, 100-3; Hägg 1991) or, more technically, measurement of yarncount (Bender Jørgensen 1986). Analysis of later medieval material can also include grouping by yarn preparation technique (woollen *vs*. worsted) and degree of soft-finishing (fulling, napping, shearing), together with yarncount and weave type (Walton 1981; Rammo 2009).

In opposition to this focus on measurable features of object construction, the interpretation of the data is typically very aware of specific context, incorporates evidence from multiple disciplines (section 1.1.1), and focuses on the social contexts of textile production, including ethnic and especially gender approaches (e.g. Walton 1989, 418; Henry 2004; Walton Rogers 2007, 45-7, 234-5; Andersson 2007; Brandenburgh 2010). These foci are more characteristic of interpretative perspectives in archaeological theory (Hurcombe 2007, 92).

Textile specialists have ascribed the absence of published theoretical and methodological discussion in the field to its international and interdisciplinary nature. In a recent discussion in response to a highly critical article written by a non-textile specialist (Sletmo 2009),

Bender Jørgensen (2009) stressed the presence in the field of numerous analysts from countries where processualist approaches continue to dominate, for example in Denmark and Germany as opposed to the UK, Norway and Sweden. Andersson and Mannering (2009) pointed out the importance of contributions from art historians, craftspeople, conservators, people with a background in industrial textile manufacture, and natural scientists, all of whom have relatively little exposure to archaeological artefact theory. A great deal of textile research is published in the form of technical excavation reports, in which a detailed exploration of theoretical context may not be considered appropriate, but where modern archaeological theoretical approaches can underlie interpretation (Blinkhorn 1997, 114; P. Walton Rogers, pers. comm.). Finally, the widespread underrepresentation of textile studies in academic institutions and museums in Europe (Andersson 1996; Bridgeman 2012; Granger-Taylor 2012) is also likely to have contributed to the absence of published theoretical and methodological discussion of textiles (Sommer 2011/12).

The above observations apply to textile research in all archaeological periods. An additional factor is present in the context of textiles from the Middle Ages: the general reluctance of the wider medieval archaeological field to engage in theoretical or methodological discussion (Austin 1990; Gerrard 2003, 217-20; Johnson 2010, x). This may in turn be related to broader perceptions of the relative primacy of historical over archaeological evidence (Moreland 2006; Johnson 2010, 154), which have discouraged the development of independent theoretical frameworks in the cadet discipline.

In summary, medieval textile analysis focuses strongly on a mutually agreed set of core variables, the recording of which is intentionally empirical, though their interpretation is informed by a number of currents of archaeological thought. This can be considered to embody a theoretical contradiction, in which variable selection and measurement is considered a neutral activity, natural to the objects and unaffected by 20th–21st century biases, resulting in a single valid description of a find, which can be more-or-less complete depending on number of variables investigated. However interpretation of finds is highly context-specific, acknowledging differences in past societies over time and place, and also within society, between, for example, ethnic, age or gender groups. The first position, that of neutral recording, has recently been queried, with a growing interest in the difference in points of view between the craftsperson and the academic (Hammarlund 2005; Bender Jørgensen 2007; Ciszuk 2007). However the potential for the recording itself to vary in response to the research question, and conversely the limitations of current descriptive paradigm because of its basis in 20th/21st century research concerns, have not yet been examined. This goes beyond responding to the presence or absence of specific features in assemblages, to a research practice in which the selection of variables to record, their relative importance for understanding textile use and meaning (not just production), and their modes of measurement are acknowledged to be features of their interpretation (cf Rice 1987, 274-88 for pottery).

6.2 Empirical identification of atypical textile features: variable selection

The emphasis in recording archaeological textiles has been described as obtaining the empirical, technical data needed to recreate a specific textile by a skilled craftsperson (Desrosiers 2012). In practice, analysis also includes details of use and wear (Table 1.3; Gleba and Mannering 2012, 4). However, the majority of variables typically recorded focus on the processes of production of a textile. Describing a textile in this way thus emphasises the understanding of these objects by the producers. The view of the textile analyst is thus already close to that of the textile craftsperson, making the recent theoretical explorations of the craftsperson's point of view a short and natural step.

However, later medieval documents generally fail to report the core variables used in archaeological textile analysis, describing their material by perception, such as colour, pattern, weight and feel, as well as by socioeconomic criteria such as origin and price (e.g. van Uytven 1983; Chorley 1988; Walton 1991, 337-42; Munro 2003, 228-31; Spufford 2006, 232-41). Many of these variables are related to technical features of production (Table 1.2), for example cloth weight with total wool content, or fibre type with woollen/worsted production (Munro 2003, 182-4). These relationships were probably evident to contemporaneous observers. However for modern observers, the criteria listed are difficult to relate to features of fragmentary archaeological finds, and only in relatively few cases have specific textile descriptions been matched with objects recovered (see section 1.1.1). This is partly because many of the features recorded in the documents are no longer measureable in samples recovered from archaeological deposits, and partly because it is only rarely clear how to relate the variables measured today to the features described. However, the point remains that even contemporaneous descriptions of textiles do not exclusively focus on the perceptions of producers, and show a range of variables used to characterise these objects which are not directly captured by current standard modes of analysis of archaeological textiles.

Current analysis can therefore be challenged on the basis that it does not fully reflect either the nature or the plurality of contemporaneous textile perception. This is in line with the criticisms made by post-processualist archaeologists in the 1980s (Lucas 2001, 86-8; Hurcombe 2007, 97-9; Johnson 2010, 101-8), who strongly disputed the idea that an archaeological artefact can be completely and objectively described by a modern analyst, and argued that any such measurements and categorisations were not neutral but interpretative. According to them, there is no such thing as a neutral description of an object, which is true and meaningful for all people in contact with that object past and present. Therefore the modern selection of variables to describe a textile is not strictly empirical, but has been guided by the perspective and interests of 20th– 21st century textile archaeologists. Since the frequency of occurrence of these variables is one of the factors used in arguments

for typical- or atypical-ness, it is possible that these discussions omit textiles which are outstanding in variables not currently measured, but which may have been important to contemporary users of these objects.

Processualist *vs*. post-processualist divergences are also evident in the treatment of identified groups of textiles in an assemblage. Explicit construction of typologies is generally avoided in medieval textiles: only the work of Bender Jørgensen (1986; 1992) is of this nature. However other workers have used implicit typologies, discussing an assemblage in terms of groups identified by technical features, rather than only describing it in those terms (Nahlik 1976; Pritchard 1984; Tidow 1995; Crowfoot *et al.* 2001, 26; Ingstad 2006, 390, 392-3; Østergård 2004, 127-35). The choice of variables varies by assemblage. In this work, the selection of these particular categories for discussion (e.g. ZZ tabbies as opposed to all ZZ textiles, all tabbies, or grouping by context or any other variable), however pragmatic, implies that these objects form a coherent group which is more worthy of commentary than the alternatives, that is, that they form a type. Other workers have considered finds using two parallel categorisations, such as both construction features and use group (Hägg *et al.* 1984, 100-49 vs. 19-100; Gardiner *et al.* 2005, 29-30 vs. 31-5, 48-58; Walton Rogers 2007, 67-99 vs. 139-228) or multiple overlapping criteria (Walton 1981). The implications of these differences in approach have not been discussed, but it is clear that processualist approaches have not been entirely rejected in this field of study.

It is therefore significant that there have been two recent developments of alternative sets of variables to understand textiles: surface texture and weave character (Hammarlund 2005) and sensory experience (Harris 2008). Hammarlund's work can be seen as an extension of previous studies examining degree of finish (e.g. Walton 1981; Rammo 2009), but applies this method to a much wider range of textile types. This approach, applied to a medieval archaeological assemblage, grouped textiles very differently to the traditional approach (Hammarlund *et al.* 2008). Assessments of frequency of occurrence of a particular textile type were markedly different between this and traditional methods. Assessments of typical- or atypical-ness could therefore differ between methods, though Hammarlund *et al*. (2008) did not address this specific question.

In contrast, Harris (2008) focused on the approach of a non-specialist observer to a textile. This work explored the point of view of a (modern) consumer and is difficult to apply to archaeological medieval textiles because: (1) their physical nature (e.g. smoothness, flexibility, smell) has been altered by their preservation in the ground; and (2) the perceptions of an observer are rooted in their socialisation and experience (see references in Harris 2008). However, like traditional approaches to archaeological textiles, this work was strongly observational, focusing on empirical responses to a finite series of variables. It differed in that it was interested in the plurality and subjectivity of responses.

These developments are important because they have suggested the possibility of adding variables to the list of those which can be assessed in a textile by observation, not just incidentally as notes or comments in a catalogue, but systematically, as a category of analysis. The authors of these new approaches did not suggest that these variables should replace the traditional set, but instead could be used in parallel, thus adding to potential perspectives. An important novel characteristic of these methods is their relative subjectivity. Assessment of surface type or feel is not as direct as numerically-quantifiable features of yarncount. However this does not make these features incapable of objective measurement by multiple researchers, for example with the aid of image analysis software, or a reference collection. It is worth noting that other fields have developed robust objective measurements of subjective responses, for example quality-of-life data in medical research (Andresen *et al.* 2001; Lohr 2002; Rothman *et al.* 2007). Thus, the development of multiple parallel descriptions of a textile could allow a new focus on the multiplicity and subjectivity of contemporaneous reactions to an artefact, while maintaining the current emphasis on measurement.

Post-processualist challenges to the validity of variable selection are not limited to humanities research: scientific variables can also be considered in this light. In the case of this thesis, the perspectives gained on medieval textiles from isotope analysis (Chapter 7; Chapter 8) are a product of the current popularity of isotopic approaches in archaeological research in the UK (UK Archaeological Sciences Biennial Conference programme, Anon. 2011), due to their relative cost-effectiveness, reliability and accessibility in western industrialised nations in the early 21st century. The data itself must be considered within its temporal and geographical context (Kuhn 1996). Thus scientific methods focus on sets of variables that are not of themselves more neutrally chosen than those examined by any other approach. There is no reason why the same approach could not be extended to other methods of observational measurement, if they can be shown to be valid and reliable.

The textile analysis field has therefore recently started to explore the potential for multiple alternative methods of measuring textile variables. This has included scientific and artefact-based analyses. These methods maintain the existing focus on measurement and observation, but suggest the existence of multiple empirical viewpoints, e.g. those of the non-specialist textile consumer in addition to the producing craftsperson. This plurality is important for studies of provenance, as new identifications of typical or atypical textiles are thus possible. This may allow insight into the relative importance of different aspects of the perception of a textile which contributed to why it was moved.

6.3 Empirical identification of atypical textile features: variable quantification

The lack of explicit discussion of the theoretical or methodological underpinnings of textile studies has an important and unfortunate consequence: it makes it difficult to judge any

variation in robustness. A number of standardised vocabularies and technical guides have been produced (e.g. Centre international d'étude des textiles anciens 1964; Guicherd *et al.* 1987 and other CIETA publications; Walton and Eastwood 1984), and inter-laboratory comparison of features of textile construction have been carried out (P. Walton Rogers, pers. comm.). However these are not typically cited in publications of archaeological textiles, either primary (e.g. Crowfoot *et al.* 2001; Østergård 2004; Ingstad 2006) or secondary (e.g. Bichler *et al.* 2005; Kirjavainen 2007; Walton Rogers 2007; Brandenburgh 2010), which undercuts their utility. It would be interesting to see the rigorous observational focus of textile studies extended to examine explicitly the relative validity, robustness and utility of established and new variables and/or new modes of measurement of existing variables. This work might include:

- examination of researcher definitions of 'fine', 'medium' and 'coarse' categories to describe and understand textile assemblages, to look at how variable these categories are between sites, regions, periods, degradation states, or construction techniques, and how this affects the impact of this variable.

- new measurements of regularity in textiles. At present this is characterised qualitatively, using statements such as 'very even' (see examples in Chapter 8) but it could be approached via more quantitative methods, such as mean and standard deviation of yarncount, yarn diameter, or angle of ply. In this case, the variability of these measurements between samples, assemblages or conditions of degradation would also have to explored to establish their robustness and relevance. The use of image analysis techniques to do this would be very interesting to explore (Cork *et al.* 1996; Cork *et al.* 1997).

In addition, the currently established methodological approaches are not universally equivalently applied, and a number of empirical disagreements exist:

- Where assemblage analysis is based on the established group of variables, selection of technical features to report on can differ (Table 1.3; compare for example Walton 1981; Tidow 1995; Crowfoot *et al.* 2001; Østergård 2004). These differences are in part pragmatic responses to differences in the assemblages themselves. However, a direct examination of how variable selection affects assemblage interpretation would be useful.

- Characterisation of fibre diameter range and distribution in fleeces has included the mean, standard deviation, maximum, range and skew of distribution of fibre diameters, depending on researcher, though all methods have a basis in 20th century wool science (for archaeological material, compare Ryder 1974; Walton Rogers 1995; Rosenqvist 2006, 171; Rast-Eicher 2008; for modern fleeces, see comparison of methods in Qi *et al.* 1994). Technologies of measurement have also varied: for

archaeological material, transmitted light microscopy of longitudinally mounted fibres (Walton Rogers 2004) or scanning electron microscopy of cross-sections of fibres (Rast-Eicher 2008); for modern fleeces, an optical fibre diameter analyser is typically used (e.g. McGregor and Butler 2009). The selection of archaeological samples for analysis also differs: Walton Rogers (Bender Jørgensen and Walton 1986) excludes heavily mineralised samples, but Rast-Eicher (2008) does not. A recent paper (Gleba 2012) has compared fleece type definitions between Ryder and Rast-Eicher's methods. However it remained unclear how comparable results from different archaeological researchers are, as this work did not take into account differences in (1) technology of measurement, or (2) criteria for the selection of samples well preserved enough for analysis. It is therefore not difficult to develop an argument for the correlation of methodological approaches in this area, in order to allow comparisons between archaeologists' work on different assemblages, but also to relate these results to research in modern breeds into environmental and management constraints on fibre diameter types (Geenty *et al.* 2009).

In summary, textile analysis could be strengthened by the expansion of a methodological literature and its wider citation, explicitly establishing relationships between currently used measurements, exploring new methods to measure existing variables, and developing new variables to understand archaeological textiles. The same is true of scientific approaches, discussed in more detail below.

6.4. The development of multiple parallel approaches

The previous two sections have argued that the established empirical focus in archaeological textile analysis could interestingly be extended to include a number of parallel observational approaches to characterising finds. Researchers in other archaeological fields have shown that they can maintain an empirical focus while employing multiple theoretical approaches from related fields, e.g. from economics and the social sciences (Smith 2011). Section 6.2 examined an example (Harris 2008) of the use of concepts of materiality to develop new variables for characterising textiles. A number of such theoretical concepts have been developed by researchers working primarily on prehistoric artefacts. These methods have been little applied to medieval material (section 6.1), possibly because the questions they ask appear to be answered by historical sources for this period. The interest in applying them to medieval material is therefore to see whether the results they generate are consistent with data from historical sources, thus informing on the quality of the method, and/or the relevance of historical data. This section discusses a number of additional ideas which may be of importance to exploring textile provenance.

6.4.1 Concepts of textile value

Isotopic analysis of medieval textiles identified a significant number of textile samples with non-local isotope values which had not previously been identified as atypical (Chapter 7;

Chapter 8), suggesting that current methods of textile analysis may underestimate the movement of textiles, particularly coarse or simple ones. Reasons to value an ordinary or coarse, rough textile are easy to find in a medieval context: consider the strength of sailcloth (Andersson 1999, 13) or sacking (Möller-Wiering 2005), the personal value of an inheritance (Burkholder 2005), or the political value of a gift (Hägg 1994; Curta 2006). Further, by the 13th century, cheap wool cloths were moved via long-distance commercial mechanisms (Chorley 1987), and such movements may have been present earlier. It must also be remembered that some features of quality, such as evenness of finish and desirability of dye colour, may no longer be evident in archaeological material due to decay (Walton and Taylor 1991; Chapter 4). Alternative concepts of value, explored by, among others, Bailey and Mills (1998) and Humphrey and Hugh-Jones (1992), may be of use here.

6.4.2 Concepts of textile markets

Understanding mercantile activity in early medieval towns has advanced greatly in the last thirty years (Hodges 1982; Clarke and Ambrosiani 1991; Graham-Campbell *et al.* 2011) but their role in any contemporaneous textile markets is not yet clear. Here, independently-developed ways of understanding the development of markets (Feinman and Garraty 2010; Garraty and Stark 2010) could be applied to textiles. Alternative ways of exploring the spatial distributions of particular artefact types focus on relationships between sites, through regional market system mapping (Minc 2006), or network analysis (Sindbæk 2007), rather than mapping finds geographically as has been the case with textiles (e.g. Bender Jørgensen 1984; Walton 1989, 415, 417; Bender Jørgensen 1992, 140-6; Walton Rogers 2007, 230-1). In contrast to commercial or down-the-line exchanges, new examinations of the social context(s) of gift-exchange (Muldrew 1998; cited in Tilly 2001; Marcoux 2009) have also been developed, as well as how these might be identified in the archaeological record (Hirth 1998).

6.4.3 Concepts of specialisation in textile production

The organisation of textile production is of interest to provenancing studies because of the association between high volume, standardised production by full-time workers, and production for commercial distribution (Andersson Strand 2011). Additionally, the identification of textiles of 'specialist quality', with evidence for standardisation, has been used as an argument for suggesting types which might have been traded (Bender Jørgensen 1984; Walton 1989, 414; Andersson 2003, 13; Walton Rogers 2007, 68-9). Wider inquiries into the organisation of craft production and its relationships to specialisation (Brumfiel and Earle 1987; Costin 1991), innovation (Doyon-Bernard 1990; Senior 2000) and standardisation (Eerkens and Bettinger 2001) are therefore of interest.

6.4.4 Scientific approaches

Isotopic analysis has already been applied to provenancing textiles, as in the work of Frei *et al*. (2009a; 2009b; 2010) and the present thesis. It is possible that additional approaches

may also be able to identify non-local material, for example by distinguishing between different breeds of sheep by proteomics (Plowman *et al.* 2012) or DNA (Kijas *et al.* 2012; but see Brandt *et al.* 2011).

Bioarchaeological and artefact methods are based in a very different epistemological traditions. Artefact research has a long history of incorporating highly technical research methods (e.g. Geijer 1938, 180-6), but this is not the same as incorporating scientific methodology. This 'aims to be cumulative, evidence-based (empirical), falsifiable, generalizing, nonsubjective, replicable, rigorous, skeptical, systematic, transparent, and grounded in rational argument' (Gerring 2011, 11). The absence of specific hypotheses and explicitly tested methodology in artefact analysis is surprising to researchers trained in the scientific tradition, whereas the scientific preference for generalisable conclusions can appear as a tendency to oversimplify to artefact researchers, even where, as in textile studies, both groups are focused on the generation of empirical data.

In contrast to previous researchers who have been concerned about differences between 'scientific' and 'theoretical' approaches in archaeology (Jones 2004), both biogeochemical and artefact methodologies are capable of multiple parallel understandings of an archaeological object. These can be conceived as dimensions of measurement: thus weave type/spin direction/threadcount (e.g. Maik 1991; Crowfoot *et al.* 2001; Christensen and Nockert 2006), surface texture/weave character (Hammarlund *et al.* 2008), proteomic (Solazzo *et al.* 2011), genetic (Kijas *et al.* 2012; but see Brandt *et al.* 2011) and isotopic (Frei *et al.* 2009a; 2009b; 2010; and this thesis) analysis of a wool textile can all generate different sets of empirically verifiable data which represent aspects of that artefact. Attempting to reconcile any potential contradictions between them opens the way towards exploring the nature and weaknesses of any single approach, which could be methodological (e.g. susceptibility of a variable to diagenesis) or theoretical (e.g. concepts of mass production).

6.5 Conclusion

This chapter has surveyed the theoretical and methodological context of medieval archaeological textile analysis. This has been largely unspoken, and has included strong emphasis on the importance of observation and measurement. Recent development of new textile descriptive variables has suggested the potential of alternative ways to characterise textiles, leading to new groupings of typical or atypical material. These developments have interesting consequences for arguments of provenance based on the frequency of a group of technical features: as choice of variables differs, so can resultant typical/atypical groupings. This chapter argued that this plurality was potentially beneficial, as it reflected the non-uniformity of contemporaneous perceptions of textiles. It also suggested that the application of empirical rigour to developing new textile analysis variables and new methods of measuring existing variables was possible and valuable, which again had consequences

for the identification of textiles as typical or atypical. Finally it suggested a number of alternative theoretical approaches which could provide new perspectives on concepts important to interpreting the features of medieval textiles, such as value, markets and specialisation of production.

The aims of this chapter were not to promote a particular theoretical school of thought, or to suggest that the established empirical methodologies should be replaced. Instead it suggested that multiple parallel empirical ways of understanding textiles were possible. None of these methods are more neutral than others, as all involve some selection of variables in describing an archaeological object. These steps should be consciously described and their implications explored. Comparison between the results and biases of different approaches could help explore the multifaceted meanings and uses of textile artefacts among both producers and consumers in medieval Europe

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7. Provenancing medieval archaeological wool textiles by light stable isotope analysis

Abstract

Light stable isotope analysis is widely applied to keratinous tissues, including mammalian hair and bird feathers, for geographical provenancing in ecological and forensic studies. In this study, analysis of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), non-exchangeable hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) isotopic composition were used to investigate the origin of samples of sheep wool preserved by anoxic waterlogging in medieval archaeological deposits from Northern Europe (*c*. AD 600–1600). These objects represent a wide range of textile types and qualities, from both domestic and specialist production, and are of importance because trans-European movements of raw wool and wool textiles were a cornerstone of economic and political development in the Middle Ages.

$\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotope values in wool textile samples (n=90) clustered by location. Degradation in wool samples, examined by elemental and amino acid composition, was more significant in samples from Iceland (Reykholt) than in samples from Great Britain (York, Newcastle upon Tyne), Germany (Hessens) or Sweden (Birka), but was not significantly associated with outlying isotope values at any site. Local isotope range for an assemblage was defined by assemblage median ± modern sheep flock wool isotopic ranges. Local/non-local isotope results were compared to typical/atypical textile categories identified from the established methods of analysis of these artefacts. In total 70 textiles showed isotope values consistent with find site, and 20 did not. Isotopic and established analysis methods were not always in agreement: 15 textiles with technical features interpreted as typical of local manufacture had non-local isotope values, and 9 atypical textiles had local isotope values. Multiple light stable isotope analysis provided valuable new insights into the origins of wool textiles. Close integration of these results with established methods of artefact analysis are essential in order to distinguish between the movement of raw materials, movement of finished textiles, and movement of manufacturing techniques or stylistic ideas.

Keywords: European Middle Ages, wool textiles, light stable isotopes, provenancing, diagenesis

7.1 Introduction

7.1.1 Archaeological context

Trans-European trade of raw wool and wool textiles was a cornerstone of economic and political development in the later Middle Ages, (c. AD 1100-1500, e.g. Chorley 1987; Munro 1994; Cardon 1999; Spufford 2006, 232-41, 326-9; Bell *et al.* 2007). Documentary sources of this period record professional production and wide distribution of standardised textiles but rarely describe these objects in technical detail, focusing instead on mercantile activity and high-status consumption. These records are thus difficult to relate to archaeological finds of medieval wool textiles, which are regularly found in anoxic waterlogged deposits (Karsten *et al.* 2012) across northern Europe from the 7th century onwards (e.g. Geijer 1938; Walton 1989; Hägg 1991; Maik 1991; Tidow 1995; Crowfoot *et al.* 2001; Østergård 2004). Finds of textile tools in these deposits indicate that many of these finds are the products of small-scale domestic textile manufacture. This was ubiquitous in Europe throughout the medieval period, and coexisted with professional production, the advent of which is unknown. Archaeological wool textiles therefore have a wider chronological and social range than documentary records. Their analysis can: (1) trace the development of the highly-sophisticated later medieval industries and markets from their early medieval village or estate-centre beginnings; and (2) examine production, distribution and consumption of textiles by portions of society or in areas of Europe which are poorly recorded in the documents.

Wool textiles typically require multiple stages of manufacture, to prepare the fibres, produce the yarn and finally cloth, braid or other object (e.g. Walton Rogers 1997; Jenkins 2003). These vary with the environmental, technological and social context of their production (Schneider 1987). In excavated textiles, technical features of textile finds, such as yarn spin direction, yarn diameter, and weave type (Figure 7.1) are identified and quantified, which allows assessment of many of the stages of manufacture. In selected samples, fibre diameter range or dye presence may also be examined. An important aspect of these investigations is the assessment of the typical or atypical nature of each find, within the assemblage, period and region in which they are found. Some atypical textiles may be identified as of non-local origin, in conjunction with other sources of evidence, e.g. textile tools, iconographic evidence, or documentary sources (Chapter 6). Analysts are however aware that atypical nature need not necessarily indicate non-local origin. Alternative hypotheses for differences in frequency of technical textile features include: the advent of new technologies or techniques at a site; differences in volumes of production between textile types; or differential patterns of discard, since wool textiles are relatively highly susceptible to decay (Peacock 1996; Karsten *et al.* 2012; e.g. Crowfoot *et al.* 2001, 2-4). A direct analytical method to establish the origin of the raw material in these finds has therefore been sought.

Figure 7.1. Fragment of sample 2897, an example of *waðmál*, the most abundant textile type at RKH. In this image, the warp runs vertically and weft horizontally. It is clear that warp yarns are more tightly spun than wefts, are spun clockwise (Z) where the wefts are spun anti-clockwise (S), and contain a greater percentage of pigmented fibres. The weave type is 2/2 twill: each yarn runs over-two-under-two of the opposing system. Scale indicates mm.

7.1.2 Isotopic detection of geographical origin

Light stable isotope analysis of modern keratinous tissues, such as mammalian hair and bird feathers, has been shown to reflect geographic origin in humans (Ehleringer *et al.* 2008; Valenzuela *et al.* 2011; Valenzuela *et al.* 2012) and other species (Wassenaar and Hobson 2008). Continental-scale variation in the carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), un-exchangeable hydrogen ($\delta^{2}H$), oxygen ($\delta^{18}O$) and sulfur ($\delta^{34}S$) isotopic composition of animal tissues reflects gradients in the isotope composition of vegetation, precipitation and groundwater with climate, bedrock and vegetation type (West *et al.* 2010 and references in Chapter 3). In tissues derived from domesticated animals, farming practice has been shown to be an important confounding factor, as the isotopic inputs related to provision of fodder during non-growth seasons, or fertilizer use, can obscure geographic variability (see discussion in Chapter 3). Nevertheless, significant variation across the European continent existed in samples of modern sheep muscle tissue (Piasentier *et al.* 2003; Camin *et al.* 2007) and wool (Hedges *et al.* 2005; Chapter 3) in $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{34}S$.

Light stable isotopic approaches to geographic origin in archaeology have typically focused on $\delta^{18}O$ in tooth dentine (e.g. Sykes *et al.* 2006; Viner *et al.* 2010) because of this tissue is mineralised and resistant to diagenesis. Some work in other isotopes ($\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$) has additionally been carried out on bone collagen (e.g. Arnay-de-la-Rosa *et al.* 2010; Barrett *et al.* 2011; Pollard *et al.* 2011), in which diagenetic parameters are also largely understood (Dobberstein *et al.* 2009). Analysis of archaeological keratinous tissues has been carried out only on unusually well-preserved material, such as by permafrost or desiccation (Macko *et al.* 1999; Iacumin *et al.* 2005; Wilson *et al.* 2007b; Raghavan *et al.* 2010), and has included $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$ and $\delta^{34}S$ analysis. Hair from anoxic waterlogged deposits is, in contrast to these samples, clearly altered by diagenesis (Peacock 1996; Wilson *et al.* 2010; Kempson *et al.* 2010). The effects of these changes on isotopic composition must be taken into account when analysing keratin samples preserved in this way. In particular, because of concerns about the possible formation of metal mercaptides in keratin samples during burial (Walter *et al.* 2006), as well as cost and availability, it was decided not to include $\delta^{34}S$ analysis in the present study of archaeological wool samples.

In the present study, isotopic composition of archaeological wool textile samples was compared within and between assemblages. The 'local isotope zone' was defined as the median for an assemblage ± the maximum estimated flock variability for that isotope (Chapter 3). Local range was confirmed by comparison of medians for both finished and un-finished wool objects, that is cloth, yarn and cord *vs*. raw fleece. Sample composition outside this range was taken to indicate a difference in origin, either geographically (non-local origin), or in husbandry type. Sample composition within this range did not necessarily indicate local origin, as it could be consistent with origin in another region of similar environment and husbandry practices. Artefact features of the textile samples and their parent assemblages were used to contextualise these alternatives.

7.1.3 Isotopic integrity of degraded samples

The degradation of wool textiles is largely a question of protein diagenesis, as wool is composed of approximately 90% protein by mass (Brebu and Spiridon 2011). Several hundred different keratin proteins are present in wool (Lee *et al.* 2006), which are distributed heterogeneously throughout the fibre (Plowman *et al.* 2007) and which decay at varying rates under burial conditions (Wilson *et al.* 2007a). Proteins are composed of long chains of amino acids (AAs), which have a wide range of isotope values because some are routed directly from diet while others are synthesised in the body (Raghavan *et al.* 2010; Styring *et al.* 2010; Chapter 2). Isotopic changes due to wool decay can therefore originate from: (1) changes in proportions of AAs present by the degradation of portions of the protein chains; (2) isotopic fractionation (preferential loss of one isotope over the other) during scission of AA chains by hydrolysis, or degradation of individual AAs by oxidation or other reactions; (3) exchange of H and O in proteins with the burial environment; and (4) deposition of

exogenous material in the hair fibre (Chapter 4). The total process of wool decay is therefore extremely complex, and has the potential to alter the original bulk isotopic composition of the fibre substantially.

In previous studies (e.g. Wilson *et al.* 2007b), bulk fibre C:N atomic ratio ($C:N_{atomB}$) was used to identify samples whose isotope values might be compromised by diagenesis. Samples with values outside range 2.9–3.8 were excluded. This range is based on the natural variation of this measure in human and horse hair (O'Connell and Hedges 1999). Experimental bleaching with hydrogen peroxide, which produced definite macroscopic change, was however associated with only small changes in $\delta^{13}C$, $\delta^{15}N$ and $C:N_{atomB}$, which were not significant, and dyeing treatments had even smaller effects. It is therefore clear that keratin protein and/or melanin change may occur without measurable change in $C:N_{atomB}$. The study by O'Connell and Hedges (1999) did not however extend to further characterisation of damage to these samples, such as using AA composition or protein mass spectrometry. Alternative methods of characterising hair fibre damage were therefore sought for the present study.

In modern sheep wool, $C:N_{atomB}$ ranged between 3.4–3.6 (Chapters 2 and 3), in close agreement with theoretical values of 3.3–3.5 for the ten most abundant proteins in wool (calculated from sequences in Clerens *et al.* 2010). However, $C:N_{atomB}$ also reflects the presence of the non-protein fraction of the fibre, largely composed of melanins, which have very different $C:N_{atom}$ ratios of 7.0–9.0 per melanin monomer. The effects of diagenesis on protein and melanin fraction isotope values and overall fibre $C:N_{atomB}$ were investigated in two models: experimental burial for 1–8 years at three different sites in Scandinavia, and high-temperature (80°C, 110°C, 140°C) hydrous laboratory conditions for up to 1440 hours (Chapter 4). Results can be summarised as follows:

- in experimentally buried samples, changes in $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $C:N_{atomB}$ and AA composition were not significant and within experimental error, though all samples changed markedly in visual appearance. Change in $\delta^{2}H$ was larger (range -16–+4. In samples which lost more than 60% mass during preparation, larger changes in $\delta^{18}O$ (up to +3.0‰) were observed, though in these samples $\delta^{13}C$, $\delta^{15}N$ and $C:N_{atomB}$ could not be measured because not enough material remained to carry out the analysis.
- in high-temperature experiments, $\delta^{2}H$ and $\delta^{18}O$ were increasingly depleted with increasing change in AA and elemental composition, which was characterised by loss of hydrophilic AAs, gain in percentage composition of hydrophobic AAs, and increased racemisation. Maximum depletion in $\delta^{2}H$ was -3‰ at 80°C but -73‰ at 140°C; maximum depletion in $\delta^{18}O$ was -0.2‰ at 80°C but -2.6‰ at 140°C. $C:N_{atomB}$ range at 80°C was 3.5–3.7 but range at 140°C was 3.7–5.0. In contrast, at 80°C, both $\delta^{2}H$ and $\delta^{18}O$ were enriched over controls in raw wool samples only (ranges 7.0–13.4‰ and 1.0–3.0‰ respectively).

- again in high-temperature experiments, significant depletion in $\delta^{13}C$ and $\delta^{15}N$ occurred only in densely pigmented samples and at relatively low temperatures, without significant associated AA and elemental composition change. Maximum depletion in $\delta^{13}C$ was -0.7‰ for pigmented samples but -0.4‰ for unpigmented samples at 80°C, and for $\delta^{15}N$ it was -2.3‰ for pigmented samples but -0.3‰ for unpigmented samples, at the same temperature. However $C:N_{atomB}$ for all 80°C-exposed samples was 3.5–3.7, only slightly elevated over control values.

Therefore from human and horse hair we have evidence of keratin protein change without isotope or $C:N_{atomB}$ change; from pigmented sheep wool evidence of $\delta^{13}C$ and $\delta^{15}N$ change without $C:N_{atomB}$ change; and, in sheep wool generally, evidence of $\delta^{2}H$ and $\delta^{18}O$ change with AA and $C:N_{atomB}$ change. In archaeological wool samples preserved by anoxic waterlogging, $C:N_{atomB}$ is therefore unlikely to be an adequate guide to preservation. In this study, $C:N_{atomB}$ data were compared with measures of degradation based on AA composition, specifically the most sensitive AA variables in decay experiments: percentage serine composition ([Ser]%) and aspartic acid/asparagine racemisation rate (rate of conversion of the naturally occurring L isomer to its D mirror image; Asx D/L). Unlike other AAs, Asx D/L values showed a reversal at higher temperatures (140°C and 110°C but not 80°C). This was interpreted as indicating rapid initial racemisation (a process which is highly sensitive to temperature), followed by an apparent decrease as highly degraded sections of the fibre were lost by hydrolysis (which is less sensitive to temperature; Chapter 4).

7.1.4 Special considerations due to the nature of textiles

Unlike hair fibres examined in previous light stable isotope studies, wool fibres in textiles have been processed by a combing/carding step (Chapter 1), which de-aligns the individual fibres from their original relative positions in the fleece. Continuously growing fleeces were shorn once a year across most of Europe (Ryder 1983, 646, 694-708), except in some very hot (Ryder 1983, 646, 373) or very cold/Alpine climates (Ryder 1983, 359-62, 378, 386, 393, 534). Here two shearings were carried out, typically at end of winter (March-May) and end of summer (September-November). Even more frequent shearing was also possible (Ryder 1983, 534). At the combing stage, the wool from several fleeces may be combined. However, given the volume of material that can be processed at a time with hand tools (e.g. Hannaford 2008; Macniven 2008), the combination of fibres from more than one fleece into a single yarn is generally unlikely, unless similar parts of many fleeces have been selected to make a particular type of object, e.g. with either very good or very bad fleece qualities. Additionally, within a single environmental zone, different husbandry practices between flocks may significantly affect wool isotope values (Hedges *et al.* 2005; Chapter 3).

We therefore tested the following hypotheses:

1. a cross-sectional sample of yarn from a medieval textile represented an annual average value from a single flock, with seasonal variation due to annual cycles of

temperature, rainfall and farming practice (e.g. Schwertl *et al.* 2003; Wittmer *et al.* 2010; Zazzo *et al.* 2010; Auerswald *et al.* 2011) largely obscured. Wool grows continuously throughout the year, generally fastest in summer and slowest in autumn, due to responses to photoperiod, temperature and nutrition which are breed-dependent (Winder *et al.* 1995). Average wool isotopic composition is therefore likely to reflect summer inputs more strongly than those from other times of year. In medieval samples, annual wool growth rate is likely to differ between sheep stock from different parts of Europe (Ryder 1984) but to an unknown extent.

2. wool from a single yarn in a textile was drawn from a single flock, and probably from a single fleece.
3. local isotopic range could be defined relative to the size of maximum estimated variation expected within a single modern flock of sheep (Chapter 3). Assuming the existence of only one grazing zone or system is reasonable at rural or low status sites, but less realistic at urban or high status sites, where wool is likely to have been sourced from across a region. At these sites, expected 'local' variation may be greater than that from a single flock, so confirmation of this by analysis of caprine bone collagen from the same or contemporaneous contexts as the textiles will be necessary for confirmation.

In summary, the aims of this study were to: (1) characterise the degree of degradation in archaeological wool textile samples from a variety of locations, with reference to previously established models of diagenesis; (2) evaluate the integrity of light stable isotope data from archaeological wool textiles in the context of degradation results; and (3) compare isotopic and technical indicators of origin in archaeological wool textiles, to inform about medieval movements of these objects and their technology.

7.2 Material and methods

The study examined 90 textiles from eight excavations at five locations, both rural and urban, from Reykholt (RKH), Iceland; York (YCG, YLB and YSG) and Newcastle upon Tyne (NBG and NQS), Great Britain; Hessens (HSS), Germany; and Birka (BKA), Sweden (Table 7.1; Figure 7.2). Samples included both fully processed (combed, spun and woven) and unprocessed (raw staple) textile finds, and were dated by context to the 7th–16th centuries. One phase was tested at HSS and BKA, three at RKH and Newcastle, and five at York.

With the exceptions of BKA and NQS, where sample availability was restricted, sampling focused on the finds identified as atypical, and therefore possibly non-local, by technical criteria (Chapter 6, Chapter 8). Typical material was selected from the same contexts and/or periods as the selected atypical objects, with additional sampling to represent all medieval phases of the site, and including both finished and unfinished objects in each period where

possible (Appendix 7.1). Fleece type definitions follow Ryder's system, as summarised in Walton Rogers (1995), but using the updated term 'Semi-fine' (SF) instead of the earlier 'Shortwool' (S) (as in Walton Rogers 1997, 1714).

7.2.1 Sample preparation

Approximately 0.1 g wool was selected from each sample, and washed according to a procedure amended from Hedges *et al*. (2005). Samples were sonicated in ultra-pure water (ELGA Purelab Ultra, Marlow, UK; 2 x 30 mins), and four times in mixtures of dichloromethane and methanol (both HPLC grade, Fisher Scientific, Loughborough, UK; 2 x 30 mins in 2:1 v/v mixture; 2 x 30 mins in 1:2 v/v mixture). A test sieve (Endecotts Ltd, London, UK; aperture 63µm) was employed to retain fragmentary sections. The exceptions were sample 2950, a raw staple, which was subdivided before washing by cutting across the lock into ten *c*. 1 cm segments representing sequential (but unequal) periods of growth, and sample 4120, for which a range of the standard and published conservation and analytical washing methods employed for keratin samples were compared, to examine their effects on isotope variability. Washes of sample 4120 were with:

1. Triton X100 (Fisher Scientific, Loughborough, UK) (Hedges *et al.* 1982),
2. sodium dodecyl sulfate (Melford Laboratories Ltd, Ipswich, UK) (I. Panter, pers. comm.),
3. 2% solution disodium EDTA (Sigma-Aldrich, St Louis, MO, USA) (Pritchard 1984)
4. pyridine (Fisher Scientific) (Walton and Taylor 1991),
5. dichloromethane/methanol (both HPLC grade, Fisher Scientific) (Hedges *et al.* 2005),
6. deionised water, (ELGA Purelab Ultra, Marlow, UK) (Sharp *et al.* 2003),
7. 2:1 chloroform (VWR International, Fontenay-sous-Bois, France)/methanol (as above) (Bowen *et al.* 2009),
8. 2:1 methanol/chloroform (both as above) (Mekota *et al.* 2006),
9. no treatment (Macko *et al.* 1999; Ehleringer *et al.* 2008).

Table 7.1. Archaeological find sites of samples tested in this study

Excavation	Code	Latitude/ longitude	Altitude/ m	Period selected	Type	N samples (multiples) IRMS	N samples (multiples) HPLC	Reference
Reykholt, Borgarfjörður	RKH	64.66469°/-21.29224°	45	C11–16	Rural, inland	21 (22)	22 (3)	(Walton Rogers 2012)
Hessens	HSS	53.51684°/ 8.07130°	0	C7–8	Rural, coastal (salt marsh)	10	10	(Tidow 1995; Walton Rogers 1995)
16-22 Coppergate, York	YCG	53.95765°/ -1.08083°	20	C9–15	Urban, inland	21 (3)	26	(Walton 1989; Walton Rogers 1997)
6-8 Pavement (Lloyds Bank site), York	YLB	53.95850°/ -1.07990°	21	C11	Urban, inland	11 (2)	15	(Hedges *et al.* 1982; Walton 1989, 396)
Rear of 7-15 Spurriergate, York	YSG	53.95791°/ -1.08244°	18	C11	Urban, inland	4	5	(Walton Rogers unpub)
Black Gate, Newcastle upon Tyne	NBG	54.96929°/ -1.61088°	19	C15–16	Urban, inland	12	14	(Walton 1981)
Queen Street, Quayside, Newcastle upon Tyne	NQS	54.96960°/ -1.60584°	12	C13	Urban, inland	4	4	(Walton Rogers 1988)
Birka cemetery	BKA	59.33720°/ 17.55040°	23	C8–10	Proto-urban, coastal	7	7	(Geijer 1938, 1980)

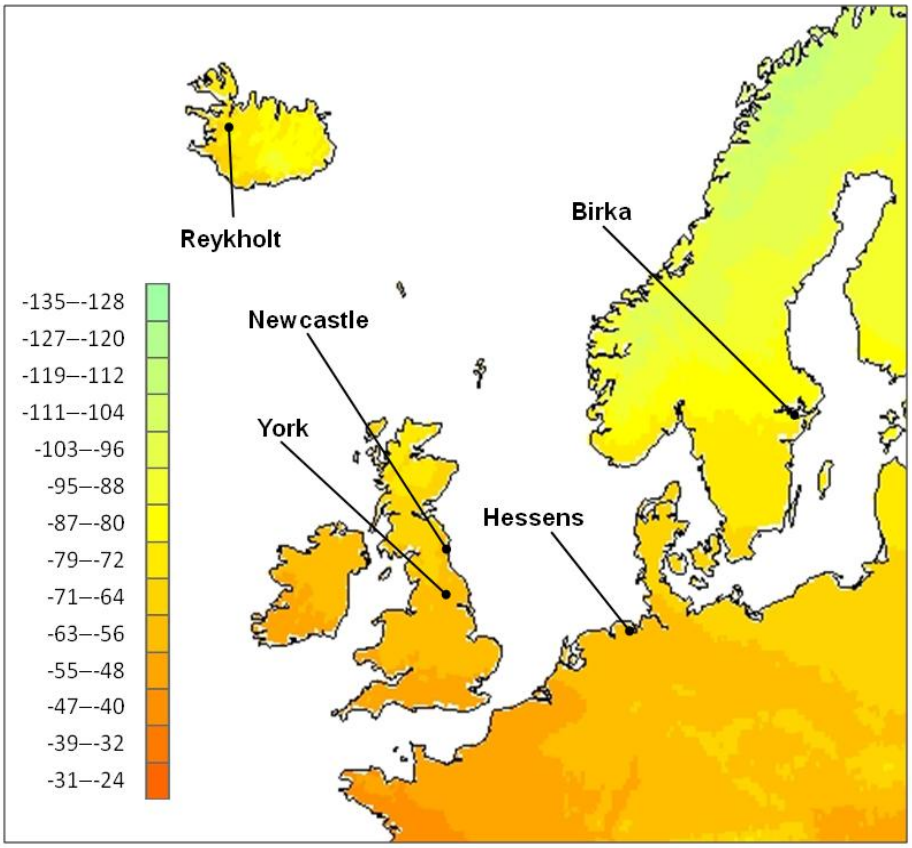

Figure 7.2. Map of annual mean $\delta^{2}H$ (in ‰) in precipitation in north-west Europe, with locations of assemblages tested superimposed (Bowen and Revenaugh 2003; Bowen 2008; adapted from http://wateriso.eas.purdue.edu/waterisotopes/media/IsoMaps/jpegs/h_Euro/hma_Euro.jpg).

7.2.2 Isotopic analyses

For $\delta^{13}C$ and $\delta^{15}N$ analysis, 0.7 mg washed wool was weighed into 4 x 3.2 mm Sn capsules (Elemental Microanalysis, Okehampton, UK). For $\delta^{2}H$ and $\delta^{18}O$ analysis, 0.1 mg washed wool was weighed into 4 x 3.2 mm Ag capsules (Elemental Microanalysis, Okehampton, UK and Pelican Scientific, Stockport, UK). Analysis was carried out at the Natural Environment Research Council Life Sciences Mass Spectrometry Facility in East Kilbride (grants EK153-15/09 and EK163-08/10). When sub-sampling staples, whole fibres were selected; for finished textiles, cross-sectional samples of yarn (typically >50 fibres) from a single yarn were taken.

$\delta^{13}C$ and $\delta^{15}N$ isotope ratio mass spectrometric (IRMS) analyses were carried out on a ThermoElectron Delta Plus XP with Costech ECS 4010 elemental analyser; internal standards were a gelatine standard, two alanine single AA standards enriched with ^{13}C and ^{15}N respectively, and a ^{15}N-enriched glycine single amino acid standard (Table 7.2). C and N content and C:N atomic ratios were calculated using a tryptophan standard.

δ^2H and $\delta^{18}O$ analyses were carried out on a Thermo Fisher Scientific Delta V Plus with TC/EA high temperature furnace. The contribution of exchangeable hydrogen was calculated using keratin standards BWB-II (whale baleen), CFS (feathers), ISB (feathers) and WG (feathers) and a comparative equilibration method (Wassenaar and Hobson 2003). The δ^2H of the un-exchangeable H in the four keratin standards was previously determined using a steam equilibration technique (Sauer *et al.* 2009). Calculation of un-exchangeable δ^2H assumed a fractionation factor $\alpha = 1.080$ ($\varepsilon_{x\text{-}w} = 80‰$). $\delta^{13}C$, $\delta^{15}N$, δ^2H and $\delta^{18}O$ results are reported in Appendices 7.2 (individual textiles) and 7.3 (duplicate analyses) in per mille (‰) relative to PDB, AIR and VSMOW respectively.

7.2.3 AA content analysis

AA content and racemization analysis was carried out using Reverse-Phase High Performance Liquid Chromatography (RP-HPLC: Kaufman and Manley 1998) following the methodology for unbleached samples described in Penkman, *et al.* (2008) with the following adjustment: hydrolysis was carried out using 50 µL 7 M HCl (HPLC-grade, Fisher Scientific) per mg wool, which had previously been prepared as for isotope analysis above. Data are reported in Appendix 7.4 as AA concentration (pmol mg^{-1}), AA % recovered and racemisation ratio (D/L). Full raw chromatographic data is reported in Electronic appendix 7.5. The following AAs were retrieved: aspartic acid/asparagine (Asx), glutamic acid/glutamine (Glx), serine (Ser), threonine (L-isomer only, L-Thr), histidine (L-isomer only, L-His), glycine (Gly), arginine (L-isomer only, L-Arg), alanine (Ala), tyrosine (Tyr), valine (Val), phenylalanine (Phe), leucine (Leu), and isoleucine (Ile).

7.2.4 Statistical analysis

Statistical analysis was carried out using R (R Development Core Team 2008). Where multiple samples were tested from a single textile, the arithmetic mean of isotope and AA composition values was used in statistical calculations at excavation/location level. All isotope and AA data was non-parametric (univariate Shapiro-Wilk test, $P<0.001$). No effective data transformations were found, so parametric statistical tests were not appropriate. Groups were described by median and inter quartile range (IQR), which were calculated using all data points from a excavation, including any potential non-local textiles and any outliers.

Non-local textiles were identified if: (1) the distance of any isotope measurement from excavation/location median was more than twice the standard deviation for that isotope in a modern sheep flock; and (2) the sample's values were identified as outliers using two robust multivariate outlier detection tests, *aq.plot* and *ddplot* in R package *mvoutliers* (Filzmoser *et al.* 2005), applied to all four isotope values. Because flock isotope ranges (Chapter 3), like archaeological sample ranges, were non-parametric, standard deviation was estimated using

Table 7.2. Isotopic analytical precision: mean ± maximum s.d in any single analytical run. For abbreviations, see text.

		$\delta^{13}C$/‰		$\delta^{15}N$/‰		$\delta^{2}H$/‰		$\delta^{18}O$/‰	
Standard	**n**	**Observed**	**Accepted**	**Observed**	**Accepted**	**Observed**	**Accepted**	**Observed**	**Accepted**
Gelatine	156	-20.3 ± 0.21	-20.3 ± 0.04	5.7 ± 0.16	5.8 ± 0.18	-	-	-	-
^{13}C-enriched alanine	54	-10.7 ± 0.14	-10.6 ± 0.09	-5.1 ± 0.13	-5.1 ± 0.12	-	-	-	-
^{15}N-enriched alanine	9	-23.6 ± 0.06	-23.5 ± 0.02	17.1 ± 0.10	17.1 ± 0.14	-	-	-	-
^{15}N-enriched glycine	45	-35.7 ± 0.22	-35.7 ± 0.09	19.9 ± 0.27	19.9 ± 0.31	-	-	-	-
^{13}C-enriched tryptophan	12	-10.6 ± 0.09	-10.5 ± 0.11	-2.3 ± 0.41	-2.3 ± 0.14	-	-	-	-
CFS	18	-	-	-	-	-143 ± 1.9	-149*	6.0 ± 0.22	Unknown
BWB-II	18	-	-	-	-	-102 ± 1.1	-110*	13.4 ± 0.18	Unknown
ISB	18	-	-	-	-	-62 ± 2.3	-69*	13.4 ± 0.30	Unknown
WG	18	-	-	-	-	-138 ± 1.7	-147*	6.6 ± 0.24	Unknown
IAEA-601	78	-	-	-	-	-	-	23.2 ± 0.21	23.1 ± 0.19
IAEA-CH6	24	-	-	-	-	-	-	36.3 ± 0.19	36.4*
IAEA-600	17	-	-	-	-	-	-	-3.5 ± 0.28	-3.5 ± 0.53

* s.d. undetermined.

bootstrap methods (Canty and Ripley 2011; Davison and Hinkley 1997). Values used constitute the maximum bootstrapped 95% confidence interval for the standard deviation.

7.3 Results

A total of 90 textiles were analysed isotopically, and 108 were examined by HPLC.

7.3.1 Keratin degradation: C:N_{atomB}

Archaeological samples showed C:N_{atomB} between 3.3 and 4.6. Maximum variability within a single sample was 0.4 (YCG 4078, n=3). A total of 32% of textiles analysed had C:N_{atomB} outside the limits defined by O'Connell and Hedges (1999), and 79% showed C:N_{atomB} outside the normal range for modern sheep wool (Figure 7.3).

C:N_{atomB} distribution was strongly associated with location (Kruskal-Wallis test, P<<0.001), significantly differentiating YLB and YCG from all other assemblages, and also BKA from all except RKH. However C:N_{atomB} was not significantly associated with any isotope overall (Spearman's rank correlation coefficient, all P>0.1), or at any individual assemblage or location,

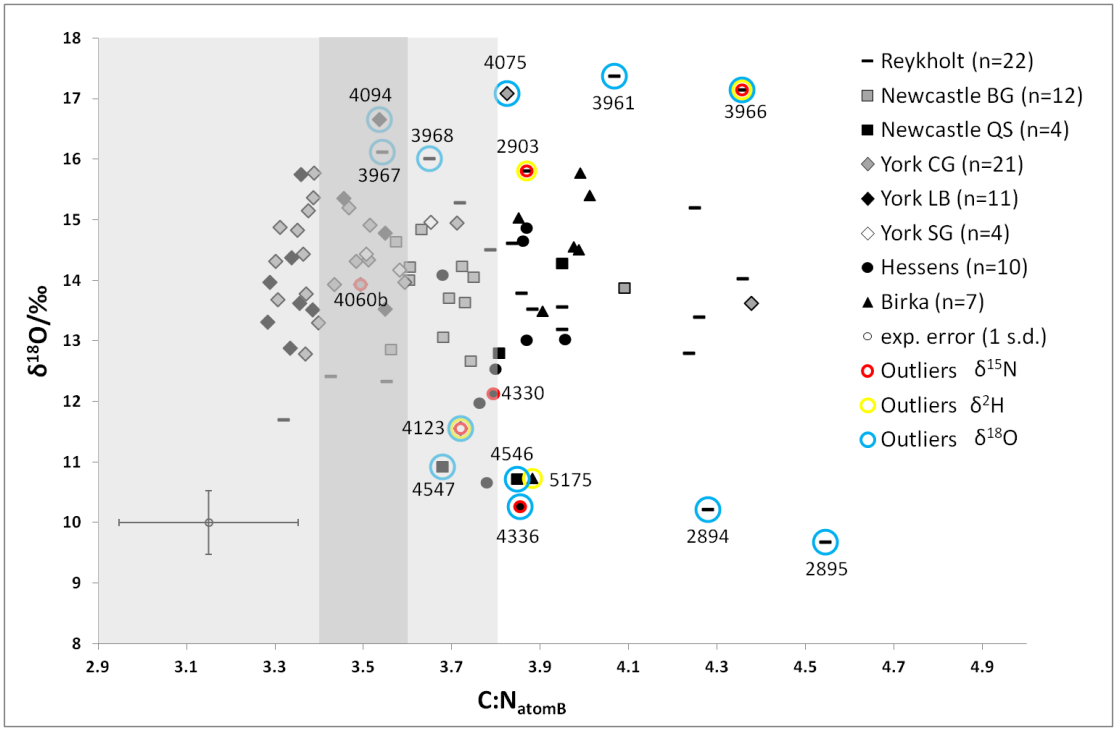

Figure 7.3. C:N_{atomB} for archaeological wool samples, plotted against $\delta^{18}O$ as an example. The dark grey area indicates the modern range for sheep wool C:N_{atomB} (Chapter 3), and the light grey area that for all modern samples, including horse and human hair (O'Connell and Hedges 1999). Also indicated are samples whose isotope values lie outside maximum flock range for their location (see below). Isotopic outliers (see below) are labelled by sample number.

for both raw isotope values and assemblage-normalised isotope values (assemblage median value subtracted from each sample value), except at YLB where a significant positive association with δ^2H was present (Spearman's, ρ= 0.74, P<0.01).

7.3.2 Keratin degradation: AA composition

AA compositions of samples from all archaeological assemblages were significantly different from those of modern control samples (Kolmogorov-Smirnov tests, n_{RKH}=22, $n_{Newcastle}$=18, n_{York}=46, $n_{control}$=9; all P<0.003; HSS and BKA sample sizes too small to test). The extent of racemisation in the archaeological material was lower than in material degraded by high-temperature isothermal hydrolysis, and comparable with that in experimentally buried material (Figure 7.4). In contrast, change in AA % content, which is linked to the extent of hydrolysis, was greater in archaeological material than in experimental burials, tending towards values from the 80°C isothermal heating experiment. The highest degree and the widest range of both racemisation and hydrolysis was present in samples from RKH, Iceland, where the distribution of % AA recovered and D/L values were significantly different from those at other assemblages (Kolmogorov-Smirnov tests, n_{RKH}=22, $n_{Newcastle}$=18,

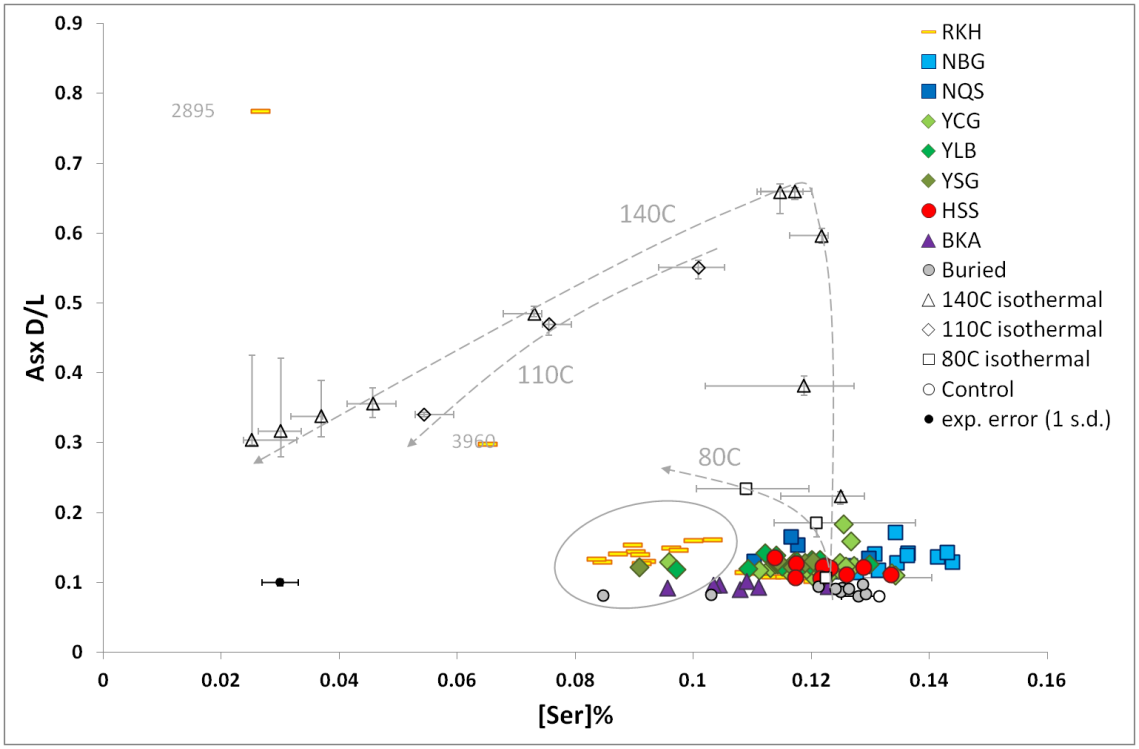

Figure 7.4. AA indicators of diagenesis in archaeological wool samples (grouped by excavation), compared to isothermal hydrolysis (median ± IQR per time point; arrows indicate time sequences at each temperature) and burial experiments (Chapter 4). The initial rapid racemisation of Asx observed in high temperature experiments did not occur in archaeological samples. Experimental error in Asx D/L is smaller than the error marker point. Outliers are marked by sample number. The circled group includes the following samples: RKH 3962, 3963, 3964, 3966, 2896a+b, 2897, 2898, 2899a+b, 2901, 4120ave; YCG 4095; YLB 4093; YSG 4123; BKA 5173; Buried 2873m.

n_{York}=46; all *P*<0.05; Figure 7.4). There were no consistent relationships (i.e. that were present at more than one excavation/location) between any AA variable and the presence of natural melanin pigmentation, evidence of dyeing, degree of wool processing or phase of sample, but these tests were weakened by unequal numbers of samples in comparison groups (Kolmogorov-Smirnov and Mann-Whitney U tests; $n_{unpigmented}$=30, $n_{pigmented}$=12; $n_{dye\ detected}$=19, $n_{no\ dye\ detected}$=50; $n_{processed\ wool}$=108, $n_{raw\ staple}$=18; Newcastle phases n_4=4,n_6=6,n_8=8; RKH phases n_1=3, n_2=12, n_3=7; York phases n_3=4, n_{4B}=12, n_{5B}=3, n_6=4, $n_{Anglo\text{-}Scandinavian}$=23; all *P*>0.05). In addition, Asx D/L values were not related to sample age, either within or between assemblages, as suggested by Moini *et al*. (2011) for museum-kept silks (Figure 7.5).

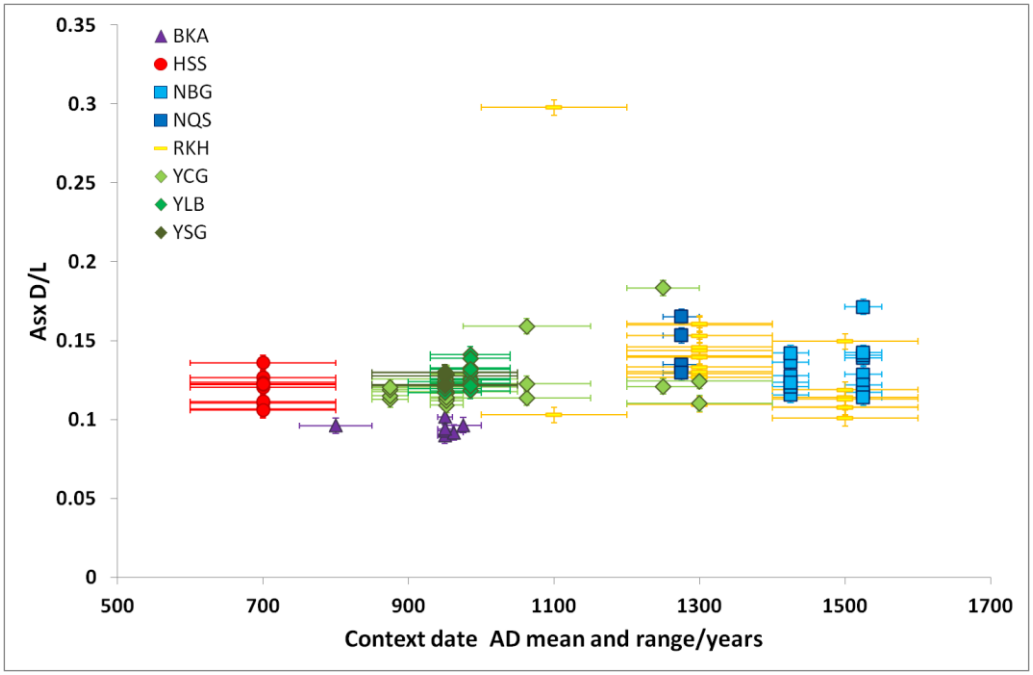

Figure 7.5. Asx D/L against median context date for each sample. Horizontal error bars indicate total range of context date; vertical error bars indicate within-sample Asx D/L s.d. (from duplicate analyses, n=3). Figure omits sample 2895 (RKH) at date AD 1100 ± 100 years, AsxD/L 0.77.

C:N_{atomB} values were very strongly positively correlated with the percentage composition of Glx, Ala, Val, Leu and Ile, and with racemisation ratios of Glx and Arg (Spearman's rank correlation coefficients, ρ=0.36–0.55, *P*<<0.001). C:N_{atomB} values were very strongly negatively correlated with the percentage composition of Gly and Tyr (Spearman's, ρ=-0.42–-0.38, *P*<<0.001).

C:N_{atomB} also showed significant (but weaker) positive correlations with percentage composition of L-His and racemisation ratios of Tyr, Val and Ile (Spearman's, ρ=0.23–0.32, *P*<0.01), and negative correlations with composition of Ser, L-Thr, L-Arg and Phe (Spearman's, ρ=-0.31–-0.23, *P*<0.01; Figure 7.6). AA variables were tested for association

with isotope values. Only the following relationships were present at more than one excavation/location: [Asx]% and [Leu]% with δ^2H at York and Newcastle (Spearman's, ρ=-0.60–-0.30, *P*<0.05).

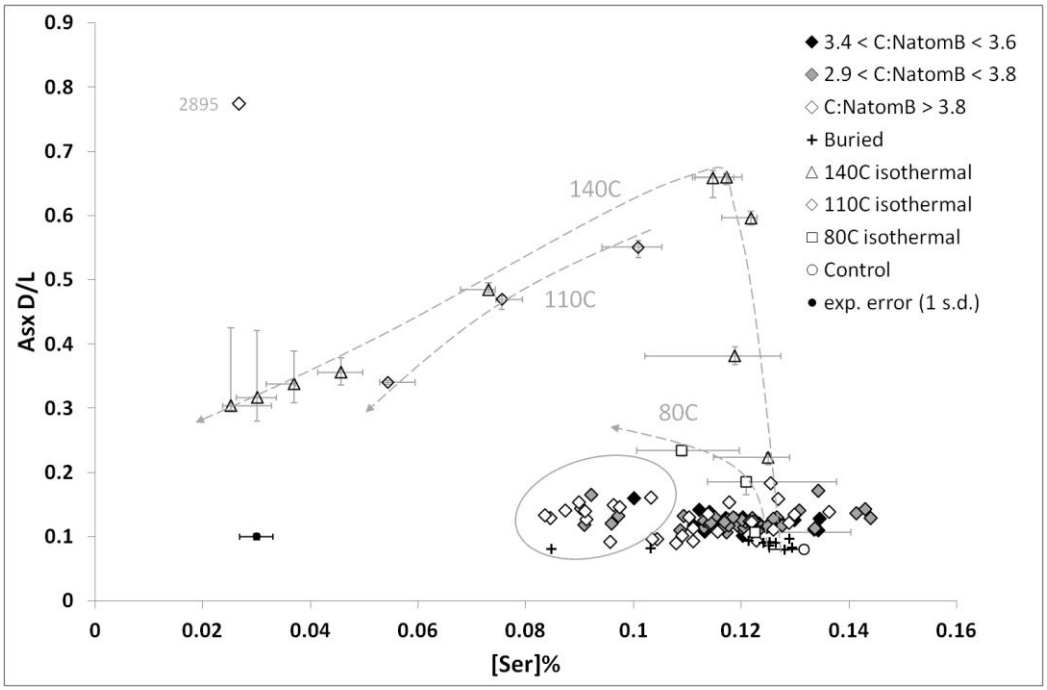

Figure 7.6. AA indicators of diagenesis in archaeological wool samples compared to $C:N_{atomB}$ value. Comparator data, errors and outliers as in Figure 7.4. $C:N_{atomB}$ showed a significant negative correlation with [Ser]% but none with Asx D/L.

7.3.3 Wool fibre integrity

The types of isotopic change observed in degradation experiments (Chapter 4) were specifically tested for in archaeological samples:

7.3.3.1 Enrichment in $\delta^{18}O$ in samples which lost >60% mass during preparation (yield <40%).

Only five samples yielded less than 40% of initial mass after washing, all from RKH. There were no significant differences in isotope value distribution or $C:N_{atomB}$ between yield groups at this assemblage (Kolmogorov-Smirnov test, $n_{>40\%}$=14, $n_{<40\%}$=5, all *P*>0.5). Yield and $C:N_{atomB}$ were however significantly negatively correlated overall (Spearman's rank correlation coefficient, ρ=-0.27, *P*<0.5).

7.3.3.2 Depletion of δ^2H and $\delta^{18}O$ in samples with large losses of hydrophilic AAs.

There was no relationship between the offset between δ^2H or $\delta^{18}O$ and respective assemblage medians and any composition variable, with the single exception of [Asx]% and $\Delta_{median}{}^2H$.

7.3.3.3 Depletion of $\delta^{13}C$ and $\delta^{15}N$ in pigmented samples only, in relatively intact samples.

There was no relationship between $\delta^{13}C$ and $\delta^{15}N$ value or distribution, and presence or density of pigmentation (Kolmogorov-Smirnov and Mann-Whitney U tests, $P>0.05$) in any assemblage.

7.3.4 Sources of isotopic variation other than origin

Sources of isotopic variability in wool textile samples are compared in Table 7.3. Within-sample variability (2σ) was of the same order of magnitude as experimental error (maximum 0.4‰ for $\delta^{13}C$, 0.4‰ for $\delta^{15}N$, 5.0‰ for $\delta^{2}H$ and 1.6‰ for $\delta^{18}O$) . For samples tested from the same rural assemblage (RKH), within-sample variation was larger in raw wool (sample 2950) than in finished textiles (samples 2896 and 4120), even where the latter had been prepared using a variety of washing methods (sample 4120, Appendix 7.3). However, larger within-sample variabilities were found in finished textiles from York (samples 4078 and 4087). Maximum within-sample variability (1σ) was 1.2‰ for $\delta^{13}C$, 1.0‰ for $\delta^{15}N$, 7.0‰ for $\delta^{2}H$ and 1.6‰ for $\delta^{18}O$. Within-sample variabilities were therefore smaller than maximum estimated flock range for $\delta^{15}N$ and $\delta^{2}H$, and of the same order of magnitude for $\delta^{13}C$ and $\delta^{18}O$. There was no relationship between settlement nature (rural/urban) or date range of sample contexts and assemblage isotopic ranges (Table 7.4).

7.3.5 Geographic origin discrimination

$\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotope values in wool textile samples clustered by location (Figure 7.7a-d). Maximum within-site range was 0.5‰ in $\delta^{13}C$, 1.9‰ in $\delta^{15}N$, 13.2‰ in $\delta^{2}H$ and 2.48‰ in $\delta^{18}O$ compared to a total ranges of 3.1‰, 10.7‰, 40.5‰ and 7.7‰ respectively. The relationships between the median compositions of Icelandic and UK samples were very similar to those obtained in Chapter 3. No such comparison could be made for the data from HSS and BKA.

Linear discriminant analysis (LDA) on the basis of all four isotope values permitted discrimination of 73% of samples to location and 85% to region (grouping York and Newcastle together). Among trivariate models, LDA based on $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ allowed discrimination of 73% of samples to location; regional discrimination was better with $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ at 83%. LDA based only on $\delta^{13}C$ and $\delta^{15}N$ allowed discrimination of 62% to location and 84% to region;

Table 7.3. Sources of variation in wool textile bulk isotope composition (1σ). Experimental error and flock range maxima from Chapter 3.

	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomB}$
Experimental error	0.22	0.19	2.48	0.53	-
Processed wool textile RKH 4120 (n=9)	0.09	0.19	2.06	0.75	0.12
Non-processed wool (staple) RKH 2950 (n=10)	0.15	0.26	3.00	0.82	0.04
Maximum wool textile: YCG 4078 (n=3) or YLB 4087* (n=2)	0.58	0.49	3.49*	0.79	0.20
Bulk raw wool flock 95% CI	1.04	1.58	10.34	1.19	0.07

Table 7.4. Location median and IQR (maximum difference) of isotope composition and $C:N_{atomB}$.

		$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomB}$
RKH (n=21)	Median	-23.9	2.8	-101.6	13.8	3.88
	IQR	-24.1–-23.7 (0.31)	2.36–3.87 (1.51)	-104.4–-93.7 (10.7)	12.8–15.3 (2.48)	3.72– 4.25 (0.53)
Newcastle (n=16)	Median	-24.3	6.1	-89.0	13.8	3.71
	IQR	-24.7–-24.0 (0.71)	5.29–7.22 (1.93)	-90.4–-87.5 (3.0)	12.8–14.2 (1.38)	3.63– 3.76 (0.14)
York (n=36)	Median	-24.0	7.0	-92.1	14.3	3.42
	IQR	-24.17–-23.78 (0.39)	6.22–7.57 (1.34)	-97.5–-89.0 (8.5)	13.67–14.95 (1.29)	3.36– 3.54 (0.18)
HSS (n=10)	Median	-23.3	9.7	-88.0	12.8	3.83
	IQR	-23.5–-23. 0 (0.53)	9.05–10.37 (1.32)	-94.7–-81.4 (13.2)	12.0–13.8 (1.81)	3.78– 3.87 (0.08)
BKA (n=7)	Median	-23.0	8.1	-89.2	14.6	3.98
	IQR	-23.2–-22.8 (0.48)	7.17–8.74 (1.57)	-95.4–-85.6 (9.8)	14.0–15.2 (1.22)	3.89– 3.99 (0.10)

all other bivariate LDA models performed more poorly. RKH was significantly distinguished from other assemblages by $\delta^{15}N$ and $\delta^{2}H$ (n=22, Mann-Whitney U tests, $P<0.05$). BKA and HSS were distinguishable from UK and Iceland material by $\delta^{13}C$, but sample sizes were too small for significance testing.

Overall, $\delta^{13}C$ was significantly positively correlated to $\delta^{2}H$ (Spearman's rank correlation coefficient, $\rho=0.28$, $P<0.05$), as was $\delta^{15}N$ (Spearman's, $\rho=0.44$, $P<<0.001$) and $\delta^{18}O$ (Spearman's, $\rho=0.46$, $P<<0.001$).

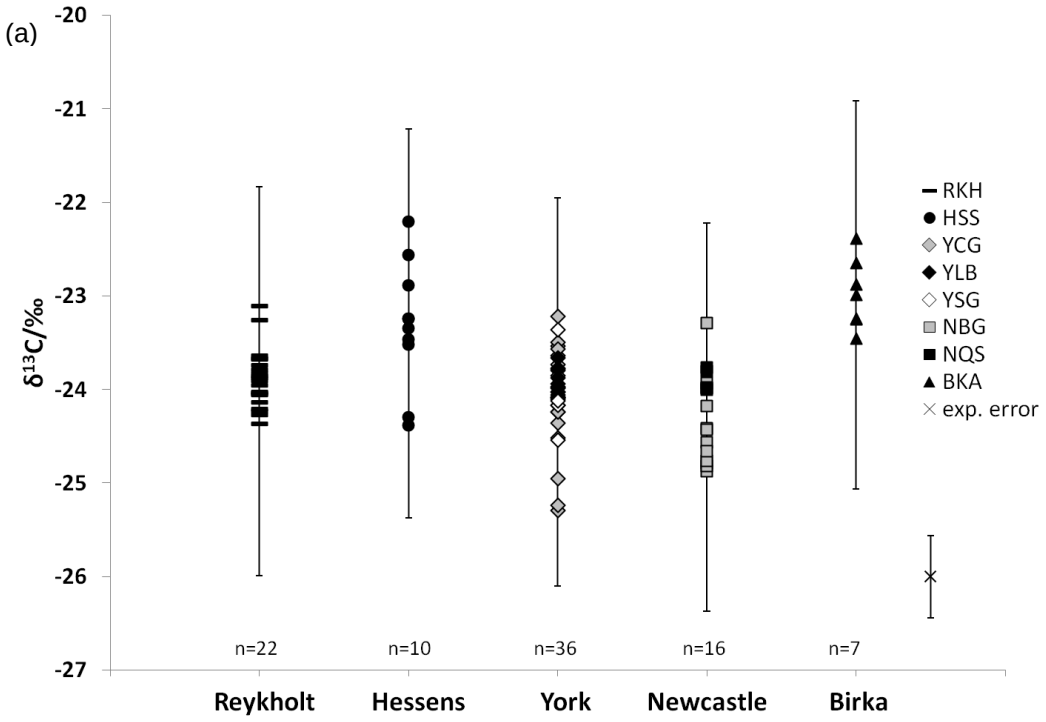

Figure 7.7. Textile isotope values by location. Error bars indicate maximum estimated flock range around location median value. (a) $\delta^{13}C$; (b) $\delta^{15}N$; (c) $\delta^{2}H$; (d) $\delta^{18}O$. Outliers are marked by sample number.

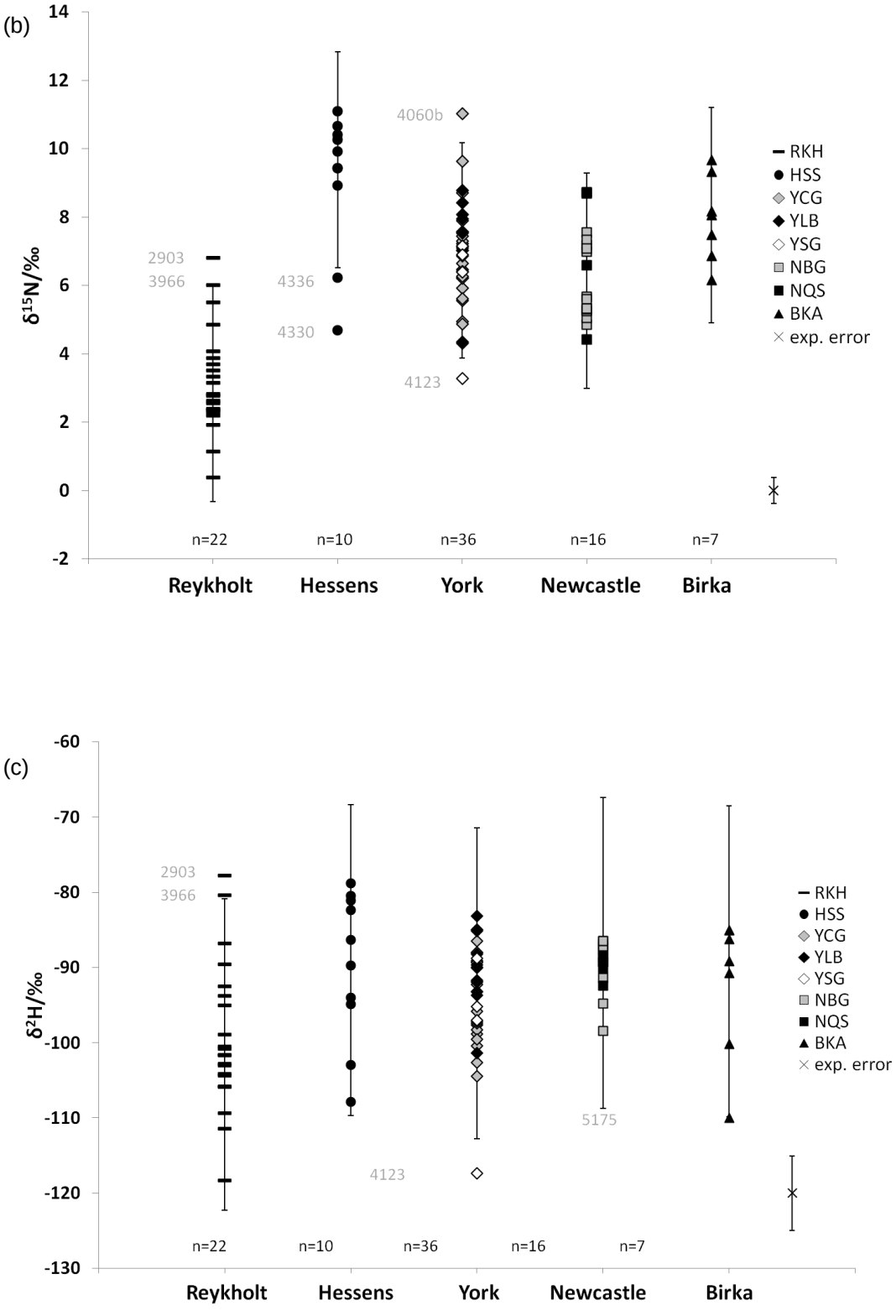

Figure 7.7 continued.

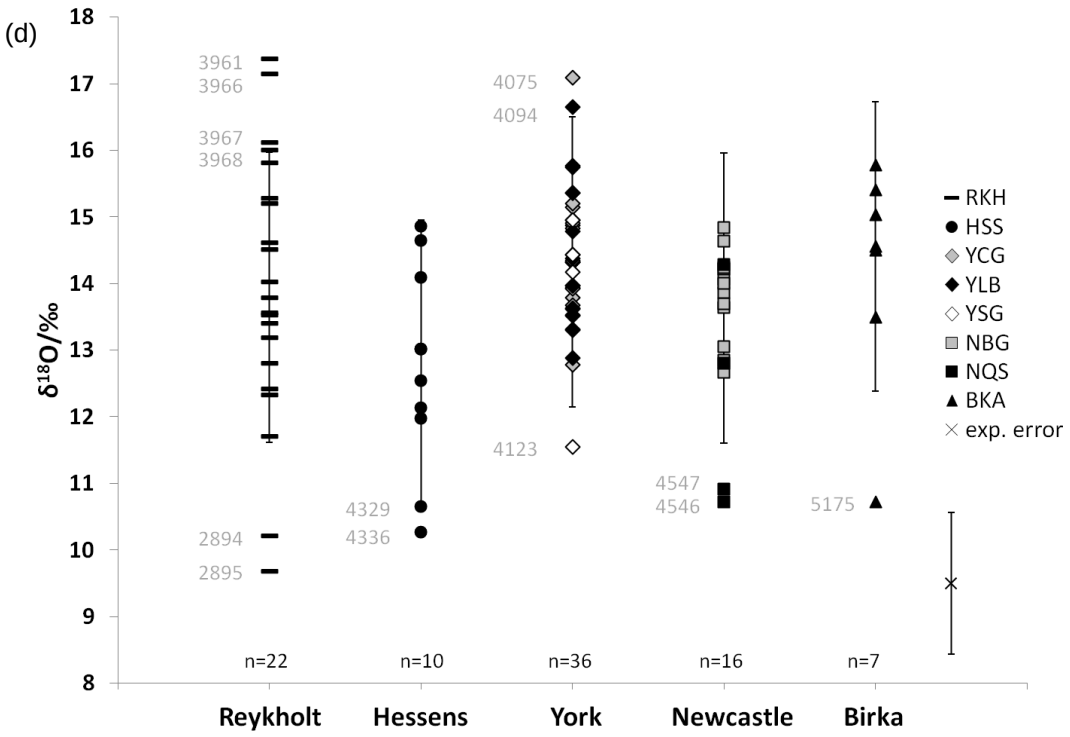

Figure 7.7 continued.

7.3.6 Identification of non-local textiles

Considering each isotope in isolation, 16 of the 90 textile samples showed isotope values lying more than one flock range from location median values: none in $\delta^{13}C$, two in $\delta^{15}N$ only, one in $\delta^{15}N$ and $\delta^{2}H$, one in $\delta^{15}N$ and $\delta^{18}O$, one in $\delta^{2}H$ and $\delta^{18}O$, two in $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$, and nine in $\delta^{18}O$ only (Table 7.5, Figure 7.7a-d). Four samples were outliers from flock range when two isotopes' ranges were considered in combination (4329, 4331, 4095, 4086). All these samples were also identified as outliers by both statistical methods, except for BKA where sample size was not sufficient to apply these tests. An additional seven samples were identified as outliers by statistical methods only (2895ave, 4062, 4073, 4082, 3949, 3957, 4544), including one unprocessed fibre sample (raw staple: 4062). The other 10 raw staples were not isotopically outlying at location level.

Table 7.5. Samples with isotope values outlying from settlement median.

				In one dimension				In two isotope dimensions	In four dimensions	
ID	**Excavation**	**Location**	**Type**	**$\delta^{13}C$/‰**	**$\delta^{15}N$/‰**	**$\delta^{2}H$/‰**	**$\delta^{18}O$/‰**		**By *aq.plot***	**By *dd.plot***
2894	RKH	RKH	typical	-	-	-	YES	YES	YES	-
2895	RKH	RKH	typical	-	-	-	YES	YES	-	-
3961	RKH	RKH	typical	-	-	-	YES	YES	YES	YES
2896ave	RKH	RKH	typical	-	-	-	-	-	YES	YES
2903	RKH	RKH	atypical	-	YES	YES	-	YES	YES	YES
3966	RKH	RKH	atypical	-	YES	YES	YES	YES	YES	YES
3967	RKH	RKH	atypical	-	-	-	YES	YES	YES	YES
3968	RKH	RKH	atypical	-	-	-	YES	YES	YES	-
4329	HSS	HSS	atypical	-	-	-	-	YES, $\delta^{2}H/\delta^{18}O$	-	-
4330	HSS	HSS	typical	-	YES	-	-	YES	YES	YES
4331	HSS	HSS	typical	-	-	-	-	YES, $\delta^{2}H/\delta^{18}O$	-	-
4336	HSS	HSS	typical	-	YES	-	YES	YES	YES	YES
4060b	YCG	York	typical	-	YES	-	-	YES	YES	YES
4073	YCG	York	typical	-	-	-	-	-	YES	YES
4075	YCG	York	typical	-	-	-	YES	YES	YES	YES
4077	YCG	York	typical	-	-	-	-	YES, $\delta^{15}N/\delta^{18}O$	-	-
4095	YCG	York	typical	-	-	-	-	YES, $\delta^{13}C/\delta^{15}N$	YES	YES
4082	YLB	York	unknown	-	-	-	-	-	YES	-
4085	YLB	York	typical	-	-	-	-	YES, $\delta^{15}N/\delta^{18}O$	YES	-
4094	YLB	York	typical	-	-	-	YES	YES	-	-

Table 7.5 continued.

ID	Excavation	Location	Type	In one dimension				In two isotope dimensions	In four dimensions	
				$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$	$\delta^{18}O/‰$		By *aq.plot*	By *dd.plot*
4123	YSG	York	typical	-	YES	YES	YES	YES	YES	YES
3949	NBG	Newcastle	typical	-	-	-	-	-	YES	YES
3957	NBG	Newcastle	typical	-	-	-	-	-	YES	-
4544	NQS	Newcastle	typical	-	-	-	-	-	YES	-
4546	NQS	Newcastle	typical	-	-	-	YES	YES	YES	YES
4547	NQS	Newcastle	typical	-	-	-	YES	YES	YES	YES
5175	BKA	BKA	typical	-	-	YES	YES	YES	*	*

* *aq.plot* and *dd.plot* could not be applied to BKA samples because they were too few.

7.4 Discussion

7.4.1 Wool fibre integrity

AA composition of archaeological samples showed that diagenesis in these objects was consistent with low temperature, hydrolytic and oxidative degradation of wool fibre proteins (Figure 7.4), by analogy with experimental data on wool decay (Chapter 4). Hydrolytic change in archaeological material was greater than that observed in samples from short-term experimental burials, but not as great as that generated by high-temperature hydrous laboratory conditions. Clustering of AA variables by assemblage indicated that the primary determinant of wool fibre integrity was environment, not date of context (Figure 7.5) or pre-burial processing (e.g. weaving, dyeing). Overall, RKH samples showed the highest degree of protein change, and York samples the least. This was consistent with microscopic characterisation of degradation in this material (P. Walton Rogers, pers. comm.).

The higher degree and variability of decay at RKH suggested that the lower average temperatures at this high-latitude location allowed the survival of wool fibres beyond the point at which they would have become invisible to the archaeological record at other sites. Dating methods based on AA variables, for example Asx racemization value (Moini *et al.* 2011), are clearly not appropriate for buried wool samples (Figure 7.5), as these values reflect environment of burial more strongly than age of sample.

According to the previously-employed measure of keratin fibre diagenesis, bulk C:N atomic ratio ($C:N_{atomB}$), the majority of samples in this study were degraded and potentially unsuitable for isotopic analysis. However, AA variables indicated that elevated $C:N_{atomB}$ values could be present even in samples which show good protein preservation (e.g. 3950, NBG), and conversely, acceptable $C:N_{atomB}$ values present in samples which show considerable protein change (e.g. 3962, RKH; Figure 7.6). These measures, however, differ in that $C:N_{atomB}$ reflected the composition of the whole fibre, not just the protein component, in contrast to AA data which reflect protein only. It was therefore possible that the generally high $C:N_{atomB}$ values observed in this study indicated diagenesis principally of the non-protein moiety of the fibre (composed of melanins and fatty acids, up to 10% of fibre dry mass) and/or the presence of exogenous material, despite washing.

Both measures of decay were tested for association with isotope values. No relationships between isotope value (raw or assemblage-normalised) and $C:N_{atomB}$ were present at any excavation/location, with the exception of δ^2H at YLB, which was positively correlated with $C:N_{atomB}$, the inverse pattern to that detected in Chapter 4. Though a number of individual AA variables indicated significant correlations with isotope values in individual assemblages, no patterns of general change in either hydrophilic or hydrophobic AAs were present, of the types observed in Chapter 4. Only two relationships were present at more than one excavation/location: [Asx]% and [Leu]% (which differ strongly in hydrophobicity) with δ^2H at

York and Newcastle. In addition, specific features of isotope change associated with experimental diagenesis (yield, degree of pigmentation) were tested for: again, no relationships were found. It appeared therefore that isotope values of wool samples in this study were not significantly related to elemental or AA composition change, with the possible exception of δ^2H in samples from YLB.

7.4.2 Other sources of isotope variability

Comparison of within-sample isotope variability at RKH suggested that the combing of wool averaged the seasonal variation in isotope values down the length of a year's growth of fibre. Thus the hypothesis that a cross-sectional sample of yarn represented a year-average isotope value from one sheep was not rejected. However, the magnitude of within-sample variation differed between assemblages, being larger in the York material than amongst the RKH samples. It is possible that this indicated the combination of wool from multiple flocks into textiles from York, but may also reflect greater variability in wool isotopic composition (and/or its exaggeration or mitigation by farming practices) in the region supplying York (a major medieval city) with wool, than at RKH (a remote rural farm). Similar complexities may also have lain behind the absence of relationship between total assemblage isotope range and rural or urban settlement type (Table 7.4).

The range of cleaning methods typically used in textile conservation did not significantly change isotope values compared to no treatment (washing with ultra-pure water or no washing at all) or the standard dichloromethane/methanol wash sequence used in this study. Typical conservation cleaning is therefore unlikely to be a barrier to wool keratin light stable isotopic analysis. However the potential effects of consolidants were not tested and these are likely to be prohibitive. These data also suggested that the six-stage cleaning method used in this study, based on that required for modern raw wool samples, was unnecessarily thorough and could be shortened in future.

7.4.3 Assemblage median isotope values

The RKH samples were strongly differentiated from those from all other locations by $\delta^{15}N$ and δ^2H values. Similar depletions in modern Icelandic sheep tissue $\delta^{15}N$ relative to material from mainland Europe was reported by Piasentier *et al*. (2003) and in Chapter 3. Differentiation in δ^2H between samples from Iceland and those from the British Isles was greater in archaeological than in modern material; the reverse was true for $\delta^{18}O$ ranges (Chapter 3). The reasons for these differences were unclear but they could be related to climate differences between AD 1000 and the present day.

Though total $\delta^{13}C$ range in this study was small, the HSS and BKA samples were consistently more enriched than samples from other locations. The HSS $\delta^{15}N$ values were also consistently high on a European scale (compare the following which all report sheep/goat collagen values over 9 per mille: Britton *et al.* 2008; Reynard and Hedges 2008; Müldner *et al.* 2009; Fuller *et al.* 2010; Hakenbeck *et al.* 2010; sheep collagen and keratin

nitrogen isotope values can be directly compared: Chapter 2). One possible explanation for this is salt-marsh grazing (Britton *et al.* 2008) for livestock at HSS and probably at contemporaneous *terp* sites in the region, where very high $\delta^{15}N$ values have also been found (W. Prummel, pers. comm.), but other explanations, such as highly manured pasture or relatively high-protein diets, are possible (Chapter 3).

The isotope values obtained for samples from BKA were intriguing, as $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ values were all more enriched than expected from the sparse extant sheep/goat isotope data from Scandinavia (Eriksson 2004; Craig *et al.* 2006; Kosiba *et al.* 2007; Linderholm *et al.* 2008). Both $\delta^{2}H$ and $\delta^{18}O$ values had been expected to resemble those from Iceland more strongly than those from the UK on the basis of modern precipitation values (Bowen and Revenaugh 2003; Bowen 2008) (Figure 7.2). However the assemblage tested from this location was very small (n=7), and might not include any material of local origin. Additional textile and sheep/goat bone samples from the site are needed to explore this further.

7.4.4 Resolution of geographic provenancing

Isotope values for wool textile samples clustered strongly by location (Figure 7.7a-d). Local isotope ranges were defined by assemblage median ± maximal estimated flock range, and these overlay significantly. Calculation of local median included the values of any outliers, which made it strongly dependent on sampling strategy, and also made the subsequent identification of outliers rather circular. Comparing values from more than one excavation at a location (as in this study for York and Newcastle) increased confidence. Alternatively, examining isotopic composition of contemporaneous sheep/goat bone from the same sites could provide an independent confirmation of local isotope median values, assuming that local wool and mutton were drawn from the same groups of animals. Geostatistical approaches (e.g. Voerkelius *et al.* 2010; Valenzuela *et al.* 2011) may eventually be feasible if a large enough database of period-defined background data can be collected, for example from collagen samples.

In contrast to assemblage medians, assemblage ranges were independently estimated from maximal modern flock ranges (Chapter 3). These were likely to overestimate the degree of isotopic variation due to intra-flock variability in diet and metabolism. They did not, however, take into account two important sources of variability which may be relevant in archaeological assemblages:

- variability in isotope value between flocks due to differences in farming practice, which can be significant even within a single climatic environment (e.g. Bahar *et al.* 2005; Schmidt *et al.* 2005; Britton *et al.* 2008; Chapter 3).
- inter-annual variability in isotope values, which may be negligible over the life of a single animal (compare Auerswald *et al.* 2011) but significant over a 10– to 100–year timescale due to changes in climate (Patterson *et al.* 2010) or developments in farming practice (Müldner and Richards 2007; Hamilton *et al.* 2009).

It was therefore encouraging that no relationship was detected in this study between isotope value range and/or assemblage type (urban/rural), or the date range of sample contexts (e.g. AD 1000–1600 for RKH). Though this is a simplistic approach, isotope variation due to change over time and/or differences in environment or farming in the supply region of a settlement did not appear to dominate the (over-)estimated metabolic variability in flock wool isotope samples. Flock ranges were also an order of magnitude greater than either experimental error or within-sample repeatability. Outlying isotope values were therefore unlikely to be due to experimental error, within- or between-flock variation, intra-sample variability, inter-annual change, or (as demonstrated above) diagenesis, and instead reflect differences in geographical origin between wool samples.

Identification of outlying samples differed between flock-range estimate and statistical methods. The isotope compositions of unprocessed wool material (raw staples) were used as partial confirmation of local range. None of these samples (YCG, RKH, HSS; n=11) were identified as outliers by flock-range estimates, though one was by statistical methods (4062 YSG). Because of this, and the fact that flock range-estimates were generally more conservative than the statistical methods, they were preferred in the following discussion.

7.4.5 Archaeological implications

Isotopic identifications of local/non-local wool fibres and technical features/fleece type/dye type identifications of typical/atypical textile character were not unanimous, and there was considerable variation in their agreement between assemblages. Detailed archaeological and methodological implications of these results are discussed in Chapter 8. All samples, however, fell into one of four categories:

7.4.5.1 Typical textiles with local isotope values (n=53)

The isotope values of the majority of samples from all locations were within flock range of local medians. At none of the locations tested was movement of raw wool (as opposed to movement of finished textiles) detected. All these samples were interpreted as of local manufacture on both technical and isotopic bases, the simplest explanation. However results were also consistent with the following three hypotheses: (1) the samples were manufactured in another site/area/region with similar environment and similar textile production; (2) they were made with non-local wool from another site/area/region with similar environment; (3) they were made with local wool in another site/area/region with similar textile production.

7.4.5.2 Typical or 'unknown'-type textiles with non-local isotope values (n=16)

Among the 70 textiles with wholly typical features tested in this study, 15 showed non-local isotope values (Table 7.5), as did the sample of 'unknown' technical type (typical or atypical nature could not be interpreted) from RKH (3968). Of these, 6 were among the more highly degraded group of samples identified by AA variables (Figure 7.4). Nevertheless, as no relationship was identified between degree of degradation and isotope value in any

assemblage (except δ^2H at YLB, but no samples at this site were outlying in this measure), it is likely these objects' isotope values were due to origin rather than decay. Interesting examples of this group of samples include: three of the four earliest textiles from RKH (2894, 2895 and 3961); 4060b from YCG, a yarn sewn through 4060a, a textile showing features typical of local origin and with local isotope values; 4336, a tabby ?band from HSS; and 4123 from YSG, of construction typical for the British Isles but with relatively unusual use of dye. It is likely that most of these samples were not made at the locations where they were found, despite their technical similarity to local types; alternatively they indicated that local manufacture employed a wider range of techniques than expected. A further hypothesis, that they are the products of unusual farming practices not otherwise represented in the assemblage, may be true for some, e.g. 4060b, outlying in $\delta^{15}N$ only, as this variable is strongly affected by farming practice (Chapter 3). Isotopic identification of non-local origin could be confirmed by better definition of the local isotopic ranges by analysis of contemporaneous sheep/goat bone collagen.

7.4.5.3 Atypical, hybrid or 'unknown'-type textiles with local isotope values (n=17)

Of the 13 textiles which were considered atypical of local manufacture, nine had isotope values which did not fall outside the local isotope range. The three hybrid textiles from York had isotope values consistent with local origin (4064/4065, 4078, 4087), as did the four textiles of 'unknown' technical type (4081-3, YLB; 4121, YSG) from the same location. None of these samples showed AA values consistent with higher protein diagenesis. This combination of results could be due to: (1) similarity of climate and/or husbandry practice in two regions of differing textile production; (2) local production being more varied than previously thought; (3) movement of raw wool (from the local region or another similar in environment/husbandry) to a region of different textile production before movement to the site of recovery.

A number of these results were probably due to the first explanation, the overlap between British flock ranges and those from BKA. Assuming that values from the latter are indicative of southern Scandinavia as a whole, then isotope values from all the Scandinavian-type textiles from York (3959, 4068 YCG; 4125 YSG) were consistent with origins in either location. This combination of light stable isotope analyses may be unable to examine movement of wool between Great Britain and southern Scandinavia.

Any of the three explanations given above could apply to what are probably the most significant results in this group, samples 5169 and 5170, examples of the much-discussed very high-yarncount ZZ diamond twills from BKA (Geijer 1938, 40-7; Hoffmann 1964, 227-57; Ingstad 1979; Hägg 1994). Isotope results in this study suggest that the raw material of these is very unlikely to be consistent with an origin in Syria as suggested by Hoffmann (1964, 227-57):

- Calculated annual average δ^2H and $\delta^{18}O$ in precipitation in eastern Mediterranean climates are 30-60‰ more enriched in δ^2H and 3-7‰ more enriched in $\delta^{18}O$ than values for locations in this study (Bowen and Revenaugh 2003; Bowen 2008). However, the δ^2H and $\delta^{18}O$ values of samples are 5169 and 5170 were not enriched over those from textiles from other locations tested in this study (Figures 7.7c and d), suggesting a northern European origin.

- In modern wool, there was little difference in $\delta^{15}N$ composition between Turkish and northern European (UK) samples, though $\delta^{13}C$ was generally much more enriched in Turkish samples (range -25.6–-19.5‰ *vs*. -27.7–-25.0; Chapter 3). The similarity of $\delta^{13}C$ between archaeological UK range (-25.3–-23.2‰) and samples 5169 and 5170 (-22.4‰ and -22.7‰, respectively) therefore also suggested an origin in northern Europe but could not exclude an origin in the eastern Mediterranean.

These results do not, of course, disprove the suggestion that the finds were made by craftspeople working in a Levantine tradition in northern Europe, as has been suggested elsewhere (Christensen and Nockert 2006, 392)

Alternative hypotheses of origin for these finds were Frisia (Geijer 1938, 40-7) and western Norway (Bender Jørgensen 1992, 138). As to the former, only one BKA sample (5169) had $\delta^{15}N$ values consistent with Frisian origin, assuming that HSS isotope values are indicative of Frisia as a whole. The latter hypothesis could not be tested with the present data set. Furthermore, at present, there is no isotopic evidence to suggest that these samples were not made from wool from Sweden.

In addition, the third explanation suggested above, export of wool from Sweden (or a region of similar climate) to the Levant, Frisia or elsewhere for textile production, before further movement of the finished product to Sweden, cannot be excluded on isotopic grounds. This explanation is likely to apply to very high quality textiles only, like the material from BKA. However because it is more complex, and assumes a higher degree of complexity in contemporaneous economic systems, it can be considered less likely than either of the other explanations.

7.4.5.4 Atypical textiles with non-local isotope values (n=4)

Four textiles with atypical technical features also had non-local isotope values. These included three of the four tabby textiles at RKH (those which were expected to be imports into Iceland), and sample 4329 at HSS. Given the current generous estimate of local flock range, and the minimal isotopic effects of diagenesis observed in this study, these samples seem very unlikely to be mistakenly identified as non-local when they were in fact local.

7.5 Conclusion

This study was the first application of combined $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ stable isotope analysis to geographical provenancing of archaeological artefacts of mammalian tissue from Europe. It is also the first application of light stable isotope analysis to archaeological samples of wool keratin preserved by anoxic waterlogging. Wool fibre integrity results, from $C:N_{atomB}$ values and AA profile, suggested some keratin compositional change, consistent with low-temperature hydrolysis, but without detectable isotopic change. Greatest variability in composition and net change were observed in material from RKH, suggesting that the conditions at more southerly sites promoted the complete degradation of compromised wool samples, while conditions at the Icelandic site did not to the same extent. If this was the case, then the absence of significant effect of diagenesis on isotope values in any of the samples tested in this study appears less surprising.

Confident provenancing of samples was limited by: (1) current generous estimates of flock range based on a single study in modern sheep flocks (Chapter 3); (2) patchy background data for the variation of $\delta^{13}C$ and $\delta^{15}N$ in sheep tissues with geography across Europe; and (3) the almost total lack of $\delta^{2}H$ and $\delta^{18}O$ data from archaeological or modern sheep tissues (exceptions: Balasse *et al.* 2006 and other work by the same author; Camin *et al.* 2007; Reynard and Hedges 2008). In general, identification of non-local raw material was of greater certainty than its assignment to location of origin. An additional weakness in this study was sampling bias, because sample selection was based on technical attributions of origin. In the case of such perishable archaeological artefacts, such bias may be unavoidable, but deliberate sampling across all periods in assemblages, as well as the deliberate inclusion of raw wool samples where available, and contemporaneous sheep bone collagen, should help to reduce it.

Provenancing by $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ values is unlikely to be universally applicable to questions of textile movement. Movement of wool objects between areas of similar climate are unlikely to be discernible by this method. Such movements include: those between the UK and Flanders, which were of fundamental economic and political importance from the early 13^{th} century onwards (Lloyd 1977); and possibly those between the UK and southern Scandinavia, also of great interest to understanding Viking settlement. Movement of textiles to and from regions with highly variable climates and/or farming practices may also be difficult to examine because the extremes of local isotope variability may overlap substantially with non-local values. However the present study showed that discrimination between Iceland and mainland Europe was clear, which indicated that the North Atlantic islands, and probably by extension most of Norway, cannot have been the source of the Scandinavian-style textiles from York. In addition, Syria is unlikely to have been the source of the fine ZZ diamond twills from BKA tested in this study. Established patterns of isotopic geographic discrimination across Europe in modern sheep tissues (Chapter 2) and in precipitation (Figure 7.2), suggest that useful discrimination in wool origin is probable in at

least the following regions: (1) along the length of the Baltic, i.e. Germany–Finland; (2) between the UK/Flanders and Spain/Italy; (3) within Scandinavia, possibly complicated by highland/lowland variation. Textile trades in the former two areas are known to have been significant in the later medieval period (see Jahnke 2009; and Munro 2005, respectively), and movement of wool within the latter is suggested by results in the present study. This methodology could additionally be applied not only to well-preserved keratinous materials (textiles, caulking, fur, hides, pelts) but also to objects of collagenous tissue, including animal bone, antler, parchment and leather, though the potential effects of (non-mineralised) collagen diagenesis on the latter two materials have yet to be examined.

Close integration of analytical results with established artefact-based methods of understanding textiles was an essential component of this study (Chapter 8). Only by combining artefactual and analytical methodologies can distinctions be made between objects made locally of non-local raw materials, those manufactured elsewhere of local raw materials, and those of wholly non-local origin. This integration also allows distinction between objects which were atypical because they are not of local manufacture, and those which were atypical for other reasons, e.g. low frequency of manufacture, or low rates of preservation. In all cases, information derived from artefactual analysis will be an essential part of interpreting isotope results. These insights have the potential to add significantly to understanding of artefacts in both prehistoric and historic periods.

Acknowledgements

Funding for this work was provided by the UK Natural Environment Research Council (IvH: NE/G52421X/1, EK153-15/09, EK163-08/10). Thanks to Guðrún Sveinbjarnardóttir of Þjóðminjasafn Íslands, Reykjavík; Christine McDonnell at York Archaeological Trust; Andrew Parkin at the Great North Museum, Newcastle; Mari-Louise Franzen of Statens Historiska Museum, Stockholm; and Klaus Tidow, former director of Neumünster Textilmuseum, for permission to sample textile assemblages.

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8. Staple diets: provenancing archaeological wool textiles from the European Middle Ages with light stable isotope analysis

Abstract

Manufacture of wool textiles, and trade in both the finished artefacts and their raw materials, were of fundamental economic and social importance to countries of northern and western Europe throughout the Middle Ages. Identifying non-local textiles in archaeological assemblages is therefore essential to understanding the production, distribution and consumption of these goods, and how this changed over time. This article discusses in detail the archaeological implications of results from the first application of a scientific provenancing technique, combined carbon, nitrogen, hydrogen and oxygen stable isotope analysis, to wool samples preserved by anoxic waterlogging. This included 90 medieval textiles from eight archaeological sites in Iceland, Great Britain, Germany and Sweden, from contexts dating from the 7th to the 16th centuries (Chapter 7). This data is integrated into current understanding of these objects, based on established methods of archaeological textile analysis, including technical details of textile type, dye identification and fleece type analysis. In general, isotopic and established methodologies were in agreement on sample origins, but some discrepancies were observed. The implications for understanding textile manufacture and movement of materials at each site are explored in detail, leading to a number of new insights into medieval textile production and distribution.

Keywords: textile, wool, provenance, light stable isotopes, Frisian cloth

8.1 Introduction

Wool textiles are among the most complex artefacts found in medieval archaeological deposits in Europe. Their technology of manufacture and some aspects of their use are largely reconstructable from the artefacts themselves, even where the tools do not survive (Walton Rogers 2012b). These objects are the products of multi-stage and multi-tool manufacturing processes (Jenkins 2003), leading to a very wide range of possible textile types (Figure 8.1), which varied across Europe. Because textiles can be used to encode complex social messages, such as gender, age, origin (however defined), profession, allegiance or occasion (Schneider and Weiner 1986), analyses of these objects have the potential to be highly socially informative.

Wool textiles are bulky, non-fragile, varied and valuable, and constituted the most important class of manufactured object in long-distance trade in the later Middle Ages, and possibly well before this (Munro 2003, 181). Distinguishing local from non-local textiles in an

Figure 8.1. Contrasting textile types from Reykholt, Iceland. Left: a 2/2 twill (1988-214-481); right: a napped tabby (2000-6-063(i)). Scale in cm. © The Anglo-Saxon Laboratory.

archaeological assemblage is an essential step towards (1) establishing the range of textile manufacturing processes occurring locally, and (2) understanding the economic, technological, social and cultural links between that site and others. Established methods of recognising non-local objects rely on:

- identifying technical features of a textile's construction which are atypical for a site, region or period. Such identifications are highly contextualised, depending for example on which technical feature (or more typically, which group of technical features) is under consideration, whether these features are typical at other sites in other regions or periods, the quality of the textile in question, and other historical and archaeological data.

- identifying raw materials which cannot be of local origin on environmental grounds. These include dyes derived from plants or animals whose distributions cannot include the site in question (Ferreira *et al.* 2004), and also fleece types, or wool fibre diameter distributions (e.g. Walton Rogers 2004; Kirjavainen 2005; Rosenqvist 2006; Gleba 2012a). This feature of a sheep's fleece is primarily genetically controlled (Ryder 1968, 1983) and therefore depends on landrace, which varies with geography in the medieval period, though husbandry practices and fibre processing can both alter fleece type also. Both dye and fleece types are however typically measured only on a subset of textiles from an assemblage, if at all,.

Textile archaeologists acknowledge that these methods do not allow absolute confidence in establishing the origin of a textile in deposit (Gleba 2012b). Independent methods of provenancing these objects have therefore been sought. Analysis of the chemical composition of wool fibres to establish origin parallels the well-established use of geochemical provenancing techniques on the inorganic raw materials of other archaeological artefacts (Wilson and Pollard 2005; e.g. Lezzerini *et al.* 2012; Kalkreuth *et al.* 2012), and is also in line with the recent upsurge of interest in applying biochemical techniques to archaeological artefacts made from organic raw materials (Pichler *et al.* 2001; Frei *et al.* 2009b; Araki and Moini 2011; Coutu 2011; Moini *et al.* 2011; Solazzo *et al.* 2011; Brandt *et al.* 2011; von Holstein *et al.* in preparation-a).

The reliability of analytical data from archaeological artefacts must however be clearly established, as the potential effects of diagenesis are significant. For example, $^{87}Sr/^{86}Sr$ results of bone was found to be changed by burial environment, unlike measurements on tooth enamel from the same deposit (Trickett *et al.* 2003). The same factors have now been shown to apply to $^{87}Sr/^{86}Sr$ analysis of wool (Chapter 5), which makes previous data of this type difficult to interpret (von Carnap-Bornheim *et al.* 2007; Frei *et al.* 2009a; Frei *et al.* 2009b; Frei *et al.* 2010). In addition, a dating method based on molecular decay (Moini *et al.* 2011) is not likely to be applicable to buried wool textiles (Chapter 4) despite being

appropriate and widely used for closed-system biomineralised tissues (e.g. Smith *et al.* 1978; Kimber and Griffin 1987; Penkman *et al.* 2011).

8.2 Understanding light stable isotopic composition of sheep wool textiles

The isotopic composition of wool fibres reflects the isotopic composition of the diet the sheep consumed, i.e. largely that of the plants and water in the pastures on which they were grazed. These values depend on vegetation type(s), climate and soil type (Chapter 1). Both non-exchangeable hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) are strongly linked to the isotopic composition of precipitation, which varies geographically with latitude, longitude, altitude and continentality. In contrast, carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) can indicate specific features of farming practice, such as transhumance between pastures (Biddick 1989, 100-15; Stone 2005, 115-8; McGovern *et al.* 2007) or foddering (Amorosi *et al.* 1998; Stone 2003; Stone 2005, 77; Kosiba *et al.* 2007), which also vary in space due to differences in environment and culture. $\delta^{34}S$ values are related to soil type and distance from a coast, reflecting the origin of S from bedrock, soil bacteria or seawater (Zazzo *et al.* 2011). Taken together, $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$ and $\delta^{34}S$ values reflect geographical origin (Piasentier *et al.* 2003; Hedges *et al.* 2005; Camin *et al.* 2007; Chapter 3). Values of the first four isotopes additionally cycle annually in hair fibres, reflecting seasonal variation in temperature, rainfall and farming practice (Auerswald *et al.* 2011). Light stable isotope analysis is therefore more likely to detect long-distance movements of sheep wool than movement within a single climatic or environmental region, as the greater the difference in original environment and climate between two wool samples, the greater the difference between their isotopic composition.

In an archaeological assemblage, the isotope values of textiles made from local wool were therefore expected to cluster, and values from wool from different environments in more distant areas to be outliers (Chapter 7). Local values can be confirmed by testing unprocessed wool finds and sheep bone collagen from the same site and period (corrected to account for the difference in values between bone collagen and wool keratin in a single animal: Chapter 2). When analysing finished textiles, the practical effects of wool fibre preparation must be taken into account: the hypothesis that a single textile contained wool from at least one sheep, and that fibre preparation by combing/carding/bowing (Chapter 1) de-aligned the fibres so that a sample represented a year-average value of wool composition, with seasonal variation obscured, was supported (Chapter 6). The local isotope range for an assemblage was defined with reference to the variability in year-average samples within a whole sheep flock (Chapter 2, Chapter 3). This estimate was conservative and was likely to under-identify non-local material: this increased the likelihood that material with outlying isotope values identified in such a study were non-local.

Chapter 7 described isotope analysis of 90 archaeological textile samples from medieval contexts, including raw wool, spun yarn and finished textiles, from eight archaeological sites at five settlements (Table 8.1; Figure 8.2). This focused on establishing the resolution of the technique and the reliability of the data, in the light of previous studies of experimental wool decay (Chapter 4) and the range of isotopic variability in wool from modern sheep flocks (Chapter 2 and Chapter 3). This showed that, though the wool samples analysed were not intact, isotopic composition could not be shown to be systematically affected by either microbiological or chemical decay. The effect of a variety of solvents and detergents on isotope values was found to be negligible. However the effects of consolidants was not tested.

8.3 Materials and methods

The present chapter examines in detail the implications for understanding textile movements in the Middle Ages by integrating Chapter 7's isotopic and amino acid composition results from with those from established textile analysis methodologies.

This thesis tested samples from textile assemblages (Table 8.1) which were (1) preserved primarily by anoxic waterlogging and (2) included some finds thought to be non-local to the find site, because they showed atypical features of textile construction, dye type and/or fleece type. Assemblages are listed in Table 8.1. Sampling was targeted to the atypical finds, selecting additionally artefacts of typical types from the same contexts and/or periods, with additional material to represent all medieval phases of the site, and including both processed and unprocessed objects in each phase where possible. The exceptions were excavations at BKA and NQS, where sample availability was restricted.

Subsamples of approximately 0.1 g wool were selected from each find, washed, and analysed for $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$isotope composition by standard isotope ratio mass spectrometric (IRMS) methods. Measurement of $\delta^{13}C$ and $\delta^{15}N$ data also generated a measure of sample integrity, carbon to nitrogen bulk atomic ratio ($C:N_{atomB}$). An additional subsample of the washed fibre was hydrolysed with acid, and analysed for amino acid content using Reverse-Phase High Performance Liquid Chromatography (RP-HPLC). This measured the concentration of 13 amino acids (of the 20 present in wool), and also examined the degree of conversion of 10 of them into their mirror images (racemisation). Full details of isotope, elemental and amino acid results were reported in Chapter 7.

Table 8.1. Origin of samples tested in this study.

Site	Code	Location	Region	Period selected	Type	Reference
Reykholt, Borgarfjörður	RKH	Reykholt	Western Iceland	C11–16	Rural, inland	(Walton Rogers 2012a)
Hessens	HSS	Hessens	Northern Germany	C7–8	Rural, coastal (salt marsh)	(Tidow 1995; Walton Rogers 1995)
16-22 Coppergate, York	YCG	York	Northeast England	C9–15	Urban, inland	(Walton 1989; Walton Rogers 1997)
6-8 Pavement (Lloyds Bank site), York	YLB	York	Northeast England	C11	Urban, inland	(Hedges *et al.* 1982)
Rear of 7-15 Spurriergate, York	YSG	York	Northeast England	C11	Urban, inland	(Walton Rogers unpub)
Black Gate, Newcastle upon Tyne	NBG	Newcastle	Northeast England	C15–16	Urban, inland	(Walton 1981)
Queen Street, Quayside, Newcastle upon Tyne	NQS	Newcastle	Northeast England	C13	Urban, inland	(Walton 1988)
Birka graveyard	BKA	Birka	Eastern Sweden	C8–10	Proto-urban, coastal	(Geijer 1938, 1980)

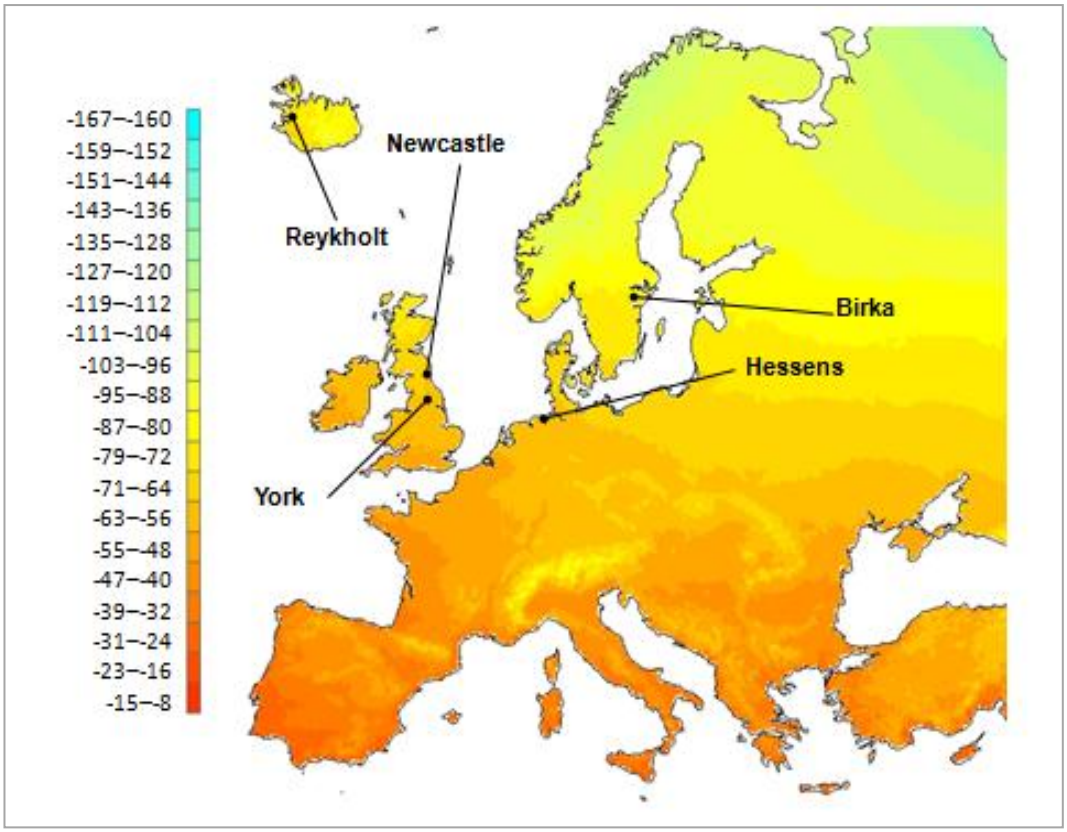

Figure 8.2. Map of annual mean δ^2H (in ‰) in precipitation across Europe, with locations of assemblages tested superimposed (Bowen and Revenaugh 2003; Bowen 2008; adapted from http://wateriso.eas.purdue.edu/waterisotopes/media/IsoMaps/jpegs/h_Euro/hma_Euro.jpg)

For the purpose of examining origin using light stable isotopes, all three York sites (YCG, YLB and YSG) were considered together, as were the two sites from Newcastle upon Tyne (NBG, NQS). A local range of wool isotopic composition was established for each location based on the maximum degree of variability in wool from a single modern sheep flock (Chapter 2, Chapter 3) around the median isotope value for each location. Individual results from each sample were compared to these ranges: where these values lay more than the flock range away from the local median, the sample was considered isotopically outlying. An outlying isotope value was taken to indicate that the sample's isotopic composition was incompatible with an origin in the same composite (i.e. multi-year, whole-site) sheep flock as the site median values. The truth of this statement was clearly dependent on factors such as:

- sampling strategy, which could affect site median;
- diagenesis, which could change individual sample isotope values, and also affect site median;
- changes in farming practice or climate over time, causing alteration of site median;

- variability within a single textile caused by combination of wool from several flocks and/or seasonal variation in wool isotope values.

The potential impacts of all these factors were discussed in detail in Chapter 7 and were established to be negligible in comparison to the large range of isotope variability present within a single sheep flock. Identification of isotopic outliers as flock and/or site outliers, and therefore likely to be non-local, was therefore robust.

8.4 Results and discussion

Core technical descriptions of all samples, with a summary of isotope results, are listed in Appendix 8.1. Isotope distributions are plotted in Figures 8.3, 8.4 and 8.5, in which samples which had isotopic compositions outlying at location level are underlined.

Results are summarised in Table 8.2. Depending on location, 64–94% of samples were expected to have isotope results consistent with local origin. In fact 60-88% of samples had composition typical of local origin. In general therefore, isotopic results were less conservative than established artefact methodologies. However this varied strongly by site: at BKA and York, isotope analysis identified 14–19% fewer outliers than expected, while at HSS, RKH and Newcastle, isotope analysis identified 6–20% more outliers than expected.

8.4.1 Reykholt, 10th–16th centuries

At the high-status lay rural site of RKH (Sveinbjarnardóttir 2012), at least three of the four tabby textiles in the assemblage were expected to be imports to Iceland from continental Europe. These showed multiple features not typical of textiles from Scandinavian sites, such as SS spinning, a dense teaselled and sheared nap, and a soft, lightweight character (samples 2903, 3966, 3967). Sample 3968, the fourth tabby find, was not napped and was of unknown origin. All remaining material, overwhelmingly ZS 2/2 twills of the type called *waðmál*, and *waðmál*-like tabby weaves, but also unspun fibre (3960, 3965, 2950, 2906), a cord (3961), and spinners' waste (2894), were expected to be of Icelandic origin (Walton Rogers 2012a).

All four tabby textiles (2903, 3966, 3967, 3968) were isotopic outliers from RKH median. The four tabbies as a group showed the highest $\delta^{15}N$ and $\delta^{2}H$ values of all samples tested at this site. Their isotope values were consistent with an origin on the European continent, insofar as this can yet be defined isotopically (Figures 8.3, 8.4 and 8.5). Samples 2903 and 3966 showed $\delta^{18}O$ values higher than those from all other settlements except York, and $\delta^{2}H$values higher than those from all other settlements except HSS. These values suggest an origin of their raw material further south on the European continent than any site tested (Figure 8.2). However this suggestion must remain speculative until (1) typical isotope ranges for wool from sheep flocks and/or archaeological sites are more tightly defined, and

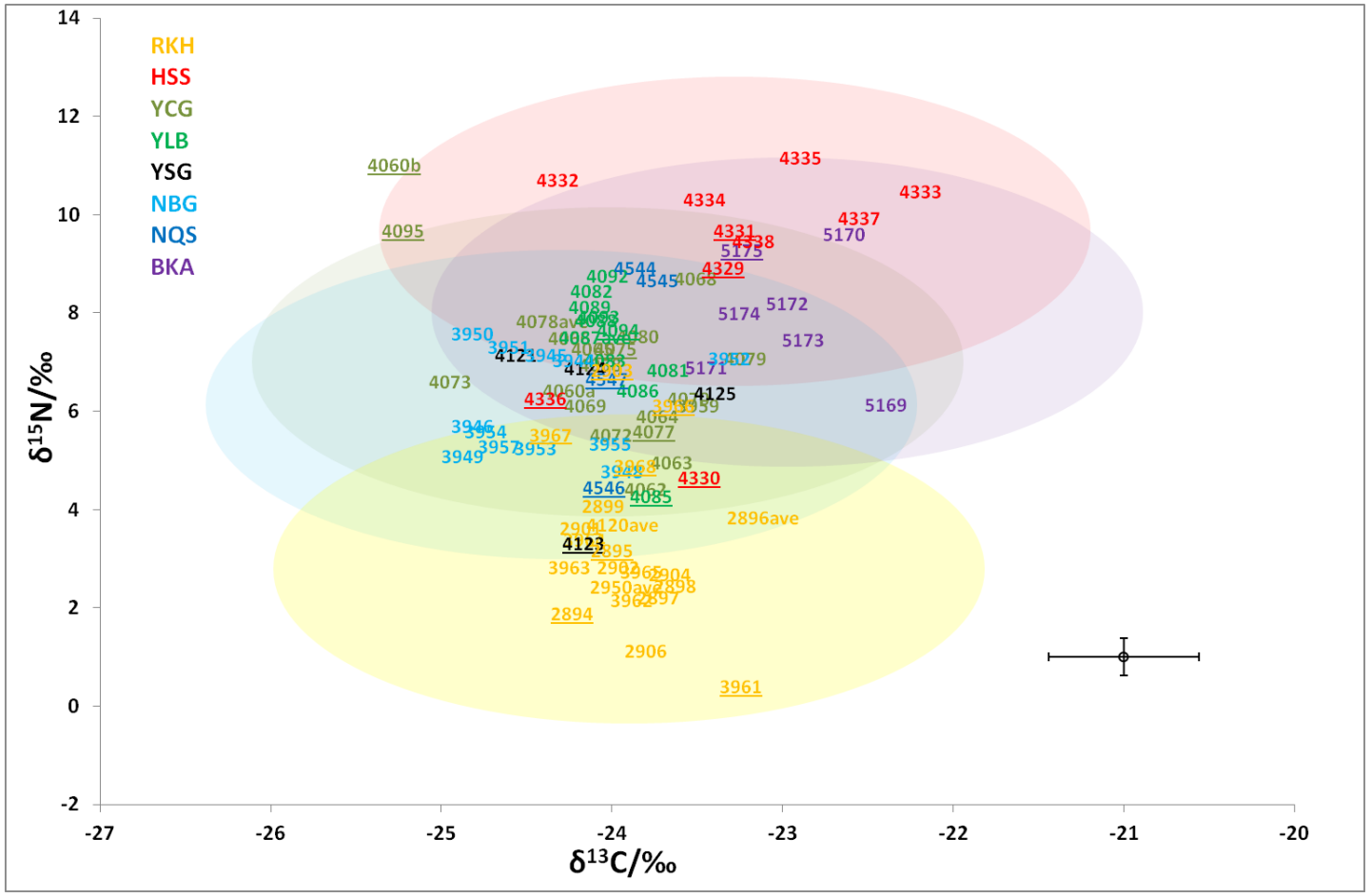

Figure 8.3. Carbon ($\delta^{13}C$) *vs.* nitrogen ($\delta^{15}N$) isotope values for all wool textile samples. The shaded areas represent the local isotope zone (maximum flock variability around site median) for each location. Blue = all Newcastle assemblages; green: all York assemblages.

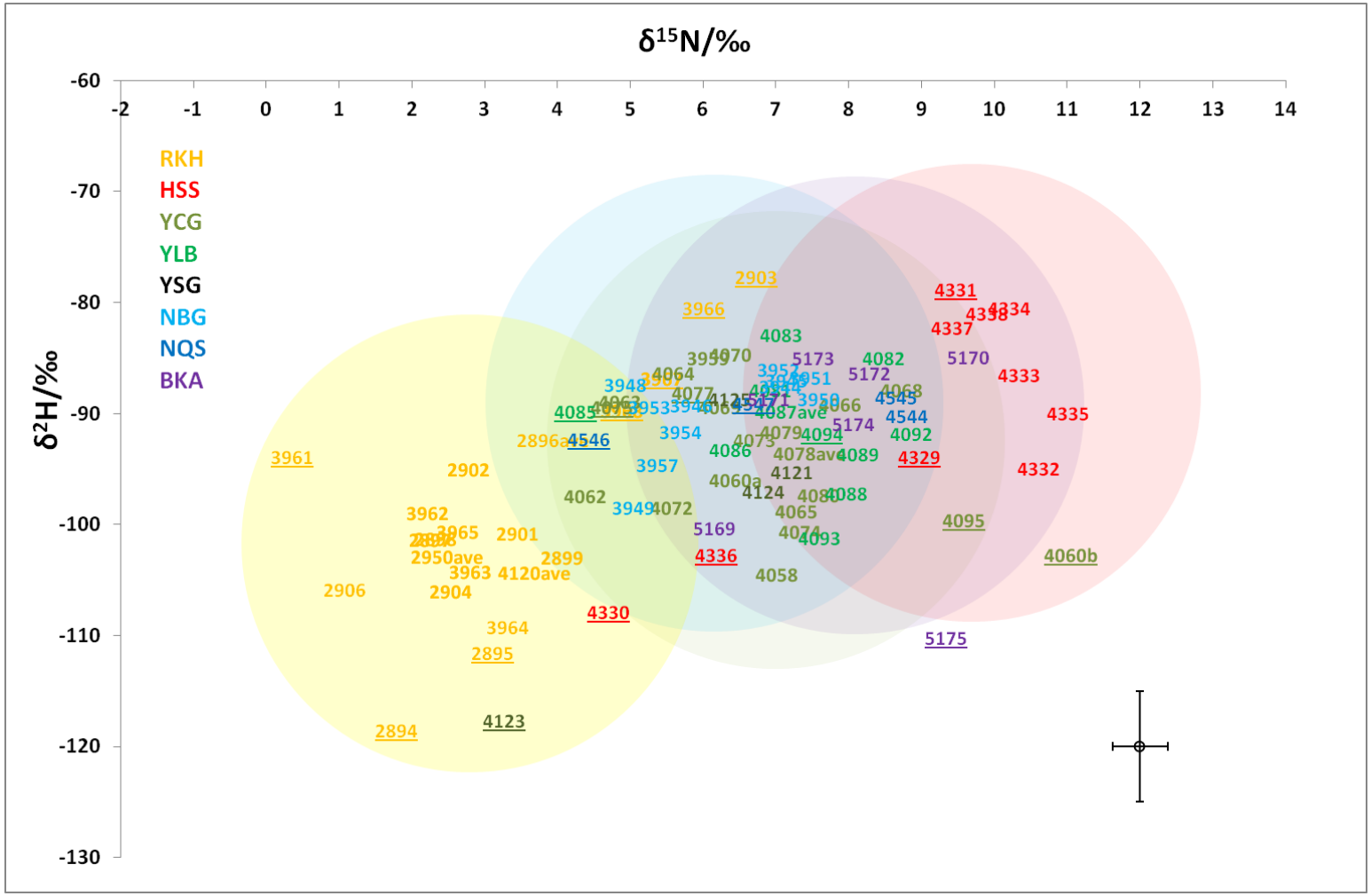

Figure 8.4. Nitrogen ($\delta^{15}N$) *vs.* hydrogen ($\delta^{2}H$) isotope values for all wool textile samples. Shaded areas as for Figure 8.3.

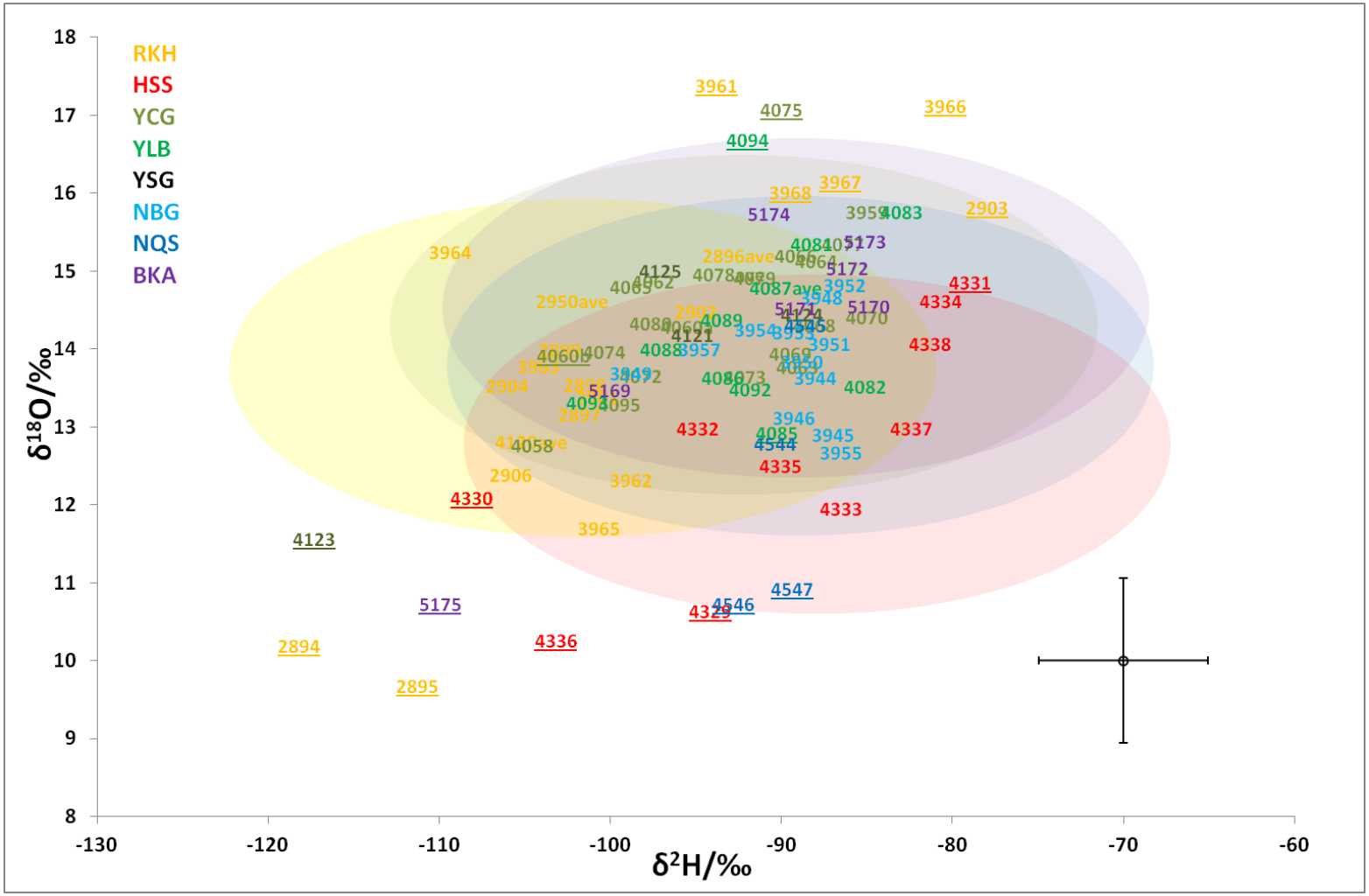

Figure 8.5. Hydrogen ($\delta^{2}H$) *vs.* oxygen ($\delta^{18}O$) isotope values for all wool textile samples. Shaded areas as for Figure 8.3.

Table 8.2. Summary of provenancing results: established methods compared to isotopic methods, by site.

		Stylistic/technical category					Isotopic category		
Site/location	**n**	**Typical**	**Atypical**	**Unknown**	**Hybrid**	**% typical**	**Inlier**	**Outlier**	**% inlier**
RKH	21	17	3	1	0	81%	14	7	67%
York	36	23	5	4	4	64%	30	6	83%
Newcastle	16	15	1	0	0	94%	14	2	88%
HSS	10	8	2	0	0	80%	6	4	60%
BKA	7	5	2	0	0	71%	6	1	86%
NBG	*12*	*11*	*1*	*0*	*0*	*92%*	*12*	*0*	*100%*
NQS	*4*	*4*	*0*	*0*	*0*	*100%*	*2*	*2*	*50%*
YCG	*21*	*14*	*4*	*0*	*3*	*67%*	*18*	*3*	*86%*
YLB	*11*	*7*	*0*	*3*	*1*	*64%*	*9*	*2*	*82%*
YSG	*4*	*2*	*1*	*1*	*0*	*50%*	*3*	*1*	*75%*

(2) $\delta^{2}H$ and $\delta^{18}O$ values from archaeological sheep tissues (wool or bone collagen) are available from a wider area of Europe (Chapter 7).

Of the textiles which showed typical features of Scandinavian manufacture, samples 2894, 2895 and 3961 showed $\delta^{18}O$ values outside local range at RKH. Values for 2894 and 2895 were lower than expected, while the $\delta^{18}O$ value for 3961 was the highest for any sample tested in this study at any site. These samples are all from the earliest phase of the site (AD 1000–1200). Sample 2895 showed the greatest degree of protein degradation of any sample tested in this study: its depleted $\delta^{18}O$ values may therefore be due to exchange of O between protein and ambient water during burial, an effect also observed under strong conditions of experimental degradation (Chapter 5). However no relationship between protein preservation and $\delta^{18}O$ was observed in samples from any archaeological site, possibly because the overall degree of degradation observed in these samples was relatively low. Protein composition variables for 3961 were, in contrast, consistent with good sample preservation, and were not tested for 2894 as insufficient sample remained after preparation to carry out both this and isotopic analysis. This may also indicate a greater degree of degradation. For these three samples, an indication of origin outside Iceland could therefore be made only for 3961, despite its technical features indicating manufacture within a Scandinavian tradition. Its origin remained obscure until further isotope data is available from across Scandinavia.

No further textiles identified as structurally typical lay outside the maximum typical flock isotope range, including the raw staples. This suggests that the RKH range included material from sheep local to RKH itself (supported by the presence of sheep keds in the palaeoecological assemblage there: Buckland 2012, 259) and textiles made from this wool, but cannot exclude the presence of textiles from similar environments, probably within Iceland. At this site, therefore, traditional methods of textile analysis in conjunction with isotopic analysis identified textiles of non-local origin only from contexts dated before approximately AD 1200 and after approximately AD 1400. This was interesting because it excluded the period when RKH first grew into an important central site, including very remarkable built structures, but nevertheless few indications of overseas trade (Sveinbjarnardóttir 2012, 262-70).

8.4.2 Hessens, 7th–8th centuries

At the coastal salt-marsh *terp* site of HSS in east Frisia, unusual 7th–8th century wooden structures were identified as a freshwater sheep dip and a tidal creek-side landing site, suggesting the importance to the inhabitants of both sheep husbandry and exchange links (Siegmüller and Peek 2008). The textiles from contemporaneous contexts were interpreted as mostly typical of the region, with the exception of samples 4329 (2/1 plain twill with madder dye), and 4332 (open weave tabby) because these show technical features which are rare in assemblages of this period (Tidow 1995; Walton Rogers 1995). The open weave

tabbies ('veil weaves') have been identified at a large number of sites, and their distinctive features interpreted as evidence for specialised production (Walton Rogers 2007, 68-9), although no locations for this have yet been indicated. Also of particular interest were results from samples 4330, 4337 and 4338 are 2/2 ZS chevron and diamond twills, identified by Bender Jørgensen as 'Hessens-Elisenhof type' and very widespread in excavations around the English Channel (Bender Jørgensen 1992, 142-3). She suggested that a subset of these textiles, including diamond twills with a pattern repeat (number of warp and weft threads per woven-in diamond) of 20Z (warp) to 18S (weft), could be identified with 'Frisian cloth', a historical term used in the 8th-10th century which clearly referred to cloths that were moved long distances (references in Ingstad 1979; van Uytven 1983; Walton 1989, 416; Hägg 1994). Of the 37 diamond twills recovered from excavations in HSS, 33 showed the 20/18 pattern repeat, though it is not clear whether those selected for this study were of this group (Tidow 1995, 359).

Isotopic analysis showed that the composition of the majority of samples from HSS, including the three raw staples, was similar, and consistent with a single local origin. The typical $\delta^{15}N$ value range (8.9–11.1‰) was high compared to results from medieval sheep tissues from elsewhere in Europe (e.g. Müldner and Richards 2007a; Fuller *et al.* 2010; Hakenbeck *et al.* 2010; nitrogen isotope values for bone collagen and wool keratin in sheep are directly comparable: Chapter 2). Such high values have been linked with salt-marsh grazing at coastal sites (Britton *et al.* 2008), which would be credible for HSS. Importantly, sample 4332, the open weave tabby, had isotopic composition consistent with local origin. This did not imply that all such textiles were made in Frisia, still less at HSS, but there is no reason to suggest that this find was not of local manufacture. However, it remains to be established how region-specific these isotopic compositions were.

Isotopic outliers were the following: 4330 (the chevron twill), in $\delta^{15}N$; 4336 (the tabby ?band) in $\delta^{15}N$ and $\delta^{18}O$; and both 4329 (2/1 twill, madder dye) and 4331 (ZS tabby) in $\delta^{2}H$ and $\delta^{18}O$, but only when both isotopes were considered in combination (Figure 8.5). Samples 4330 and 4336 also had the lowest $\delta^{13}C$ and $\delta^{2}H$ values at the site, though they lay within flock range of the median (Figures 8.3 and 8.4). Commentary on these results is complex:

- low $\delta^{13}C$ and $\delta^{15}N$ values in sample 4330 may be a feature of diagenesis in this sample, which was densely naturally pigmented. Significant depletion in both these isotopes was observed only in experimentally degraded samples which were densely pigmented (Chapter 2). Nevertheless, these changes were associated with amino acid composition changes greater than those observed for this sample, for which preservation was excellent. This suggested that the wool in this textile originated in a similar climatic environment to HSS, but not on coastal salt marsh, which could account for the relatively depleted $\delta^{15}N$ values.

- relatively low values in all four isotopes tested for 4336 were likely to indicate non-local origin. $\delta^{13}C$, $\delta^{15}N$ and $\delta^{2}H$ values were not inconsistent with values from York, Newcastle, or BKA, but $\delta^{18}O$ values were too depleted for any of the sites tested in this study (Figure 8.5). The origin of this sample remained unknown, but might plausibly be north or east of Frisia (Figure 8.2). The same was true for samples 4329 and 4331, both showing low $\delta^{2}H$ and $\delta^{18}O$.

These results, in particular the high $\delta^{15}N$ values for probably local material, have implications for the 'Frisian cloths' debate. If the term did refer to textiles manufactured in Frisia using local wool, then $\delta^{15}N$ values could be a new biomarker for these textiles in other assemblages. The question of the identification of 'Frisian cloths' will be returned to in the discussion of the material from BKA.

8.4.3 York, 9th–15th centuries

$\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotope values from York textiles were very similar to those from Newcastle and London (Watson 2010). $\delta^{13}C$ and $\delta^{15}N$ values were comparable to the (tissue-adjusted) total range of medieval sheep/goat bone collagen values across Great Britain (Figure 8.6). Given the similarity of collagen $\delta^{13}C$ and $\delta^{15}N$ values from across the British Isles, it is unlikely that keratin isotopic data (even with the addition of $\delta^{2}H$ and $\delta^{18}O$ values) will be able to demonstrate movement of wool textiles within Great Britain. This question will be returned to in the discussion of the Newcastle assemblage, below.

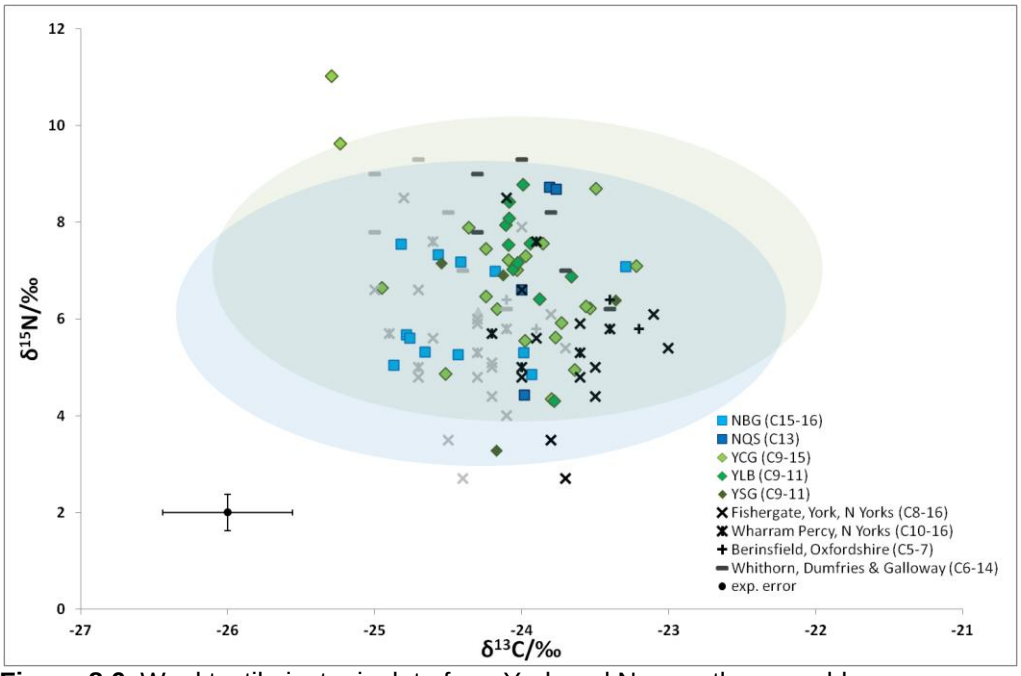

Figure 8.6. Wool textile isotopic data from York and Newcastle assemblages compared to sheep/goat bone collagen data from other medieval sites in the British Isles: Fishergate, York (Müldner and Richards 2007b), Wharram Percy (Müldner and Richards 2005), Berinsfield (Privat *et al.* 2002) and Whithorn (Müldner *et al.* 2009). Two adjustments of literature bone collagen $\delta^{13}C$ data to keratin equivalents are shown: EH flock (black) and Escrick group (grey), based on results in Chapter 2.

Among the textiles from the three assemblages from York, established methods of textile analysis had identified the following samples as atypical, and 'undoubtedly of Scandinavian influence if not necessarily of Scandinavian origin' (Walton 1989, 418, 421; Walton Rogers unpub): sample 3959, a sock in *nålebinding*, a technique of one-needle knitting widespread in medieval Scandinavia (Walton 1990, 66); sample 4068, a fragment of *waðmál*, the textile type common at RKH and other Scandinavian sites; and sample 4125, a tabby with shaggy surface, a surface treatment widely found at Hedeby (Walton Rogers unpub). In addition, there was one textile with a pile made by darning threads into the fabric after weaving (samples 4064/4065), rather than being inserted during the weaving process, as is typical of piled fabrics found elsewhere in northern Europe (Walton 1990). These objects were interpreted as local copies of non-local cloth types (Walton 1989, 336; Walton Rogers 1997, 1826).

Unfortunately, due to the similarity in isotope values between samples from Great Britain and BKA, it was difficult to comment on the origin of most of these samples. Their isotope values were consistent with an origin in the British Isles, but also at BKA, or even HSS (exceptions: 3959 and 4064 by $\delta^{15}N$ and $\delta^{18}O$ values; 4125 by $\delta^{15}N$). While it is possible that these textiles could have been made in York under Scandinavian influence (Richards 2000, 34-8; Hadley 2009b, 205-6), most evidence for Scandinavian craftspeople in the town relates to male-gender crafts such as metal-working (Walton Rogers 1997, 1821-2; Speed and Walton Rogers 2004, 84-7). Alternatively, assuming that the BKA sample values are representative of southern Sweden and Denmark generally (compare Figure 8.2), they may have been made in this region. Further textile and bone samples from sites across this region are needed to assess this possibility. A final alternative is that these textiles were made in one of the Scandinavian colonies, which had trade links to York. A candidate for this is Ireland, in a similar climatic zone to Great Britain, but in an area of stronger Scandinavian cultural influence (Clarke and Ambrosiani 1991, 102-6; Hadley 2009b, 198-203; Hadley 2009a, 222-3) as demonstrated in textiles from Dublin and other sites around the Irish Sea (Pritchard 1992; Heckett 2003; Henry 2004). It is doubtful that they were made in Iceland or northern Scandinavia, as these regions are unlikely to have produced wool with $\delta^{2}H$ and $\delta^{18}O$ values similar to those of York (Figure 8.2).

Also of interest at York were five textiles of excellent quality identified as possibly specialist products: samples 4070 (YCG), a 2/2 chevron twill dyed with lichen purple, which showed affinities with Frisian material (Walton 1989, 414-8); and samples 4081, 4082, 4083 and 4121, all 2/1 diamond twills, which are early examples of a textile type probably to be identified with the term *haberget* which later became widespread (Walton Rogers 2001). Significantly, $\delta^{15}N$ values for 4070 were inconsistent with an origin in Frisia, as defined by the 7^{th}–8^{th} century HSS isotope values. Assuming that these were characteristic of the same region in the 9^{th}–10^{th} centuries, this suggested that the textile was not made of wool from

Frisia, though it may well have been made in a Frisian tradition outside the region, possibly within one of the communities of Frisian merchants present at a number of early urban centres around the North Sea (Walton 1989, 416), its isotope values being consistent with samples from York, Newcastle and BKA. Alternatively, the dye used in this textile, lichen purple, may indicate an origin in Ireland (Walton 1998), also consistent with isotope results. These suggestions were however speculative. Little could be said about the probable origins of samples 4081-3 and 4121, as their isotopic composition was consistent with an origin at any of the sites tested in mainland Europe, except $\delta^{18}O$ values for 4081 and 4083 which excluded HSS.

In addition, seven samples of typical textile types were isotopically outlying. Samples 4060b, a Z2S plied yarn and 4095, a coarse ZS tabby, had the lowest $\delta^{13}C$ and highest $\delta^{15}N$ values of the York assemblages, though their $\delta^{2}H$ and $\delta^{18}O$ values were not significantly different from the median. This may indicate difference in origin (location unknown, as these values are unlike any others tested) or alternatively an origin local to York but with unusual farming practice. Farming practice has been shown to significantly affect both $\delta^{13}C$ and $\delta^{15}N$ in modern samples of sheep tissue (Chapter 3). Sample 4060a, a ZS tabby through which 4060b was sewn, showed isotope values consistent with York, Newcastle and BKA, which may make this latter possibility more likely.

Sample 4123 (2/2 ZS twill in pigmented wool with tannin dye) showed the lowest $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ values of all York samples. This suggested an origin for the wool raw material in a region colder and drier than Iceland (Figure 8.5), for example in northern Scandinavia (Figure 8.2). Tannin dyeing on top of natural pigment has been identified in late Norse Greenlandic textiles (Walton Rogers 2004, 90). It is therefore interesting that the isotope composition of sample 4123 was consistent with a North Atlantic origin. Tannin dying of naturally pigmented wool should perhaps be considered more indicative of origin than hitherto. An alternative explanation for the highly depleted $\delta^{15}N$ values of this sample is the pattern of diagenesis also potentially observed in sample 4330. However this cannot also account for the low values of $\delta^{2}H$ and $\delta^{18}O$, as elemental indicators of diagenesis were not outside the acceptable range.

Samples 4075 (Z/S+Z 2/1 plain twill) and 4094 (ZZ tabby repp) both showed $\delta^{18}O$ values higher than York flock range (Figure 8.5), inconsistent with any other site tested in this study for 4075, and consistent only with BKA for 4094. It was therefore unlikely that these samples originated in the British Isles, although no suggestion as to their origin can be attempted. Finally sample 4085 (ZS 2/1 chevron twill) was an isotopic outlier from York when $\delta^{15}N$ and $\delta^{18}O$ values were considered in combination. These values were consistent with samples from Newcastle, as well as RKH, and may not indicate an exotic origin.

8.4.4 Newcastle upon Tyne, 13th–16th centuries

The assemblages from Newcastle included only two samples identified as atypical on technical grounds. Sample 3944 (knitted cap with kermes dye in Fine-type fleece) was expected to be made of Spanish or French wool (Walton 1981, 200) because the fleece type, dye and knitting itself are all unusual for the British Isles in the mid-15th century. There is documentary evidence for the import of knitted caps from France to Britain at this period (e.g. 'Frenche cappes syngle tarfed [with a turn-up] the dossen xiii.s.iiii.d': Edwards and Nevinson 1970), and the fleece type and dye are both associated with high prices. Sample 3952 (worsted ZZ 2/2 twill), though typical of Great Britain as a whole, is a textile type strongly associated with manufacture in East Anglia, and therefore atypical of Newcastle (Walton 1981, 205).

Neither of these samples were, however, isotopically outlying (Figures 8.3, 8.4 and 8.5). There was therefore no isotopic evidence that sample 3944 originated outside the British Isles, and the origin in Spain previously suggested can be ruled out (Figure 8.2). Either the technique of knitting arrived in Britain earlier than previously thought, or the garment originated in a region which has a similar climate to that of Great Britain, such as northern France (where knitting was established at an earlier stage than in England), northern Germany or southern Scandinavia.

In contrast, two of the very coarsest textiles in this study, identified as sackcloth, samples 4546 and 4547, had very depleted $\delta^{18}O$ values. In neither of these very similar artefacts was there strong amino acid composition evidence for significant decay, so it was unlikely that these values were due to diagenesis. Sample 4547 was made of goat hair, while the identification for 4546 as wool was tentative: it is therefore possible that both these artefacts were made of goat hair, and that it was the difference in species metabolism and/or husbandry that caused these outlying values. The question might be resolved by comparison to sheep and goat bone collagen or tooth enamel $\delta^{18}O$ values on samples from sites in Newcastle, if necessary using ZooMS (Buckley *et al.* 2010) to confirm osteological species identification. Alternatively, if the species difference were not significant, or if it applied only to sample 4547, then it remains possible that one or both of these objects was not made of raw material from the British Isles, but potentially from Scandinavia. Coarse plied tabbies are a widespread textile type in the later medieval period, probably associated with mercantile activity, as packing, wrapping or caulking (Walton 1988). This particular site (Queen Street) included material from a Scandinavian ship: it would not be unlikely, therefore, for these two textiles to have been Scandinavian in origin.

8.4.5 Birka, 8th–10th centuries

The BKA material was the most difficult assemblage to interpret of those tested in this study. Firstly, the seven samples examined constituted a tiny proportion of the total published (Geijer 1938), themselves only 5% of those excavated (E. Andersson Strand, pers. comm.).

Further, these samples did not include any unspun wool or yarn, but only finished cloth, so the local 'isotope zone' could only be tentatively identified. Thirdly, these samples were recovered from graves in a cemetery, rather than deposits from a settlement. They were therefore: (1) probably biased towards the better quality textiles in use in the settlement at the time, and therefore more likely to included non-local objects; and (2) preserved by a process of mineral-preservation (in contact with iron or copper alloy objects in the graves) in addition to anoxic waterlogging. However AA analysis of the protein composition of these samples showed few differences to that of samples from other sites in this study (Chapter 7).

Previous analyses of the BKA assemblage, on the basis of technical features of textile types, concluded that the very high threadcount ZZ diamond twills, here represented by samples 5169 (ZZ 2/2 diamond twill) and 5170 (ZZ 2/1 diamond twill), were unlikely to be of local manufacture. The original analyst suggested that this textile type might be 'Frisian cloth', and suggested that they originated in Frisia (Geijer 1938, 40-7). A number of alternative suggestions for their origin have since been made (Chapter 6), including Syria (Hoffmann 1964, 227-57; Nockert 1988), the British Isles (Ingstad 1979) and western Norway (Bender Jørgensen 1992, 138). All other, coarser, textiles were expected to have been made on site from wool from the area around Lake Mälaren.

All the BKA samples show $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ values broadly intermediate between those for material from the British Isles and Frisia. The possibility that any of them originated in Syria can therefore be excluded, as their values are consistent with temperate environments of north-western Europe, and not with the warmer and drier environment of the eastern Mediterranean (Figure 8.2). The suggestion that they might be Frisian in origin was next considered. Sample 5169 had $\delta^{15}N$ values consistent with a Frisian origin (as so far defined by analysis of samples from HSS), but 5170 did not. The possibility that the high-threadcount, highly elaborate wool twill textiles at this site did not all have the same origin has not been previously discussed. The hypothesis of an origin in western Norway, or indeed elsewhere, either within or outside Scandinavia, could not be tested without comparator samples from these areas.

In contrast, the single isotopic outlier at BKA was sample 5175 (a coarse twill with pile) which had not previously been identified as atypical. Its $\delta^{2}H$ and $\delta^{18}O$ values suggested an origin in a colder/drier/more continental environment than BKA (Figure 8.2). Piled fabrics from Iceland, Ireland and possibly Frisia featured in medieval international trade from the 8th century onwards (Guðjónsson 1962; cited in Walton 1989). However the isotope values from sample 5175 appear to exclude all three of these origins (Figure 8.5). This sample may represent an additional movement of piled textiles inside Scandinavia. However, confirmation of typical isotope values at BKA, by testing of further textile and bone samples, is necessary before this interpretation can be made with confidence.

8.4 Conclusions and implications

This study of 90 samples of medieval wool textiles from five settlements integrated established methods of wool textile analysis with isotopic data from the objects' raw materials. The combination of these approaches led to new insights into the origin of individual textile finds, textile types, and the nature of textile manufacture, distribution and consumption at specific settlements.

In the majority of samples in this study (63%), established and isotopic methodologies were in agreement. Samples with atypical features had non-local isotope values in 4 of 13 cases (e.g. 2903, RKH). These were therefore confirmed as originating in a site/area/region with both different environment (climate/farming practice) and different textile production. Samples with typical technical features showed local isotope values in 53 of 68 cases (e.g. 4089, YCG). However the interpretation here had to be more subtle: though this could mean that the sample was of local manufacture and of local wool, an alternative suggestion, that it originated in another site/area/region with similar environment and similar textile production, could not be excluded. Thus identifications of atypical textiles can be confirmed using isotopic methods, but identifications of typical textiles may always include some material not made locally. This uncertainty is likely to be greater at highly networked settlements, especially urban sites. Interpretation of isotope data must therefore take into account the larger archaeological and historical picture.

Where methods were not in agreement (27% of samples), potential interpretations were more numerous. Samples with atypical technical features showed isotope values within the local zone in 9 of 13 cases (e.g. 3944, NBG). This may mean that: (1) typical manufacture had wider range of techniques than expected; or (2) there was movement of textile techniques and technology; or (3) there was movement of textiles from a site/area/region of similar environment but different textile production. Samples with typical technical features showed non-local isotope values in 15 of 68 cases (e.g. 4123, YSG). For these, possible interpretations included: (1) typical manufacture had narrower range of techniques than expected; or (2) there was movement of raw wool independently of the movement of finished textiles; or (3) there was movement of textiles from a site/area/region with similar textile production but different environment.

In adding the capability to distinguish 'a textile from X' from 'a textile in the style/technology/ technique of X', isotopic analysis has deepened understanding of the origin and movement of textiles. In general, isotopic identification of non-local material was more conservative than artefact methods at two locations tested, and less conservative at three. Data supported the majority of previous suggestions of textile origin made on the basis of technical features of textiles, dye analysis and fleece type identifications. The only one definitely refuted was the suggestion that the high quality ZZ diamond twills at BKA might originate in the Levant. In the majority of cases, isotope data modified previous proposals:

- Tannin-dyeing on top of pigmented wool may be more closely associated with North Atlantic origin than previously thought for 9th–10th century samples from the British Isles (sample 4123, YSG). If 'Frisian cloths' were made in Frisia, they probably do not include 2/1 twills (sample 5170, BKA) but could include 2/2 twills (diamond and chevron), both ZS (samples 4337 and 4338, HSS) and ZZ (sample 5169, BKA).

- Either high-quality knitted garments were being made in Britain by the mid 15th century, earlier than previously thought, or they were imported from an area with a similar climate, such as northern France. Southern France and Spain, the areas of origin previously identified, can be discounted (samples 3944 NBG).

- The Scandinavian type textiles in York (samples 3959 and 4068, YCG and 4125, YSG) are very unlikely to have originated in a North Atlantic colony or in northern Scandinavia, given the similarity of their isotope composition to material from the British Isles, and dissimilarity to material from RKH.

These results have implications for methods of textile analysis. This was clearest in the RKH assemblage, where understanding of origin was not complicated by significant overlap with other sites (as for material from the British Isles), or uncertainty regarding the local median (as for BKA). At RKH, all material identified as atypical or unknown type was shown to be isotopically non-local (n=4). However, three typical textiles were also shown to have isotopic composition consistent with non-local origin. It would now be interesting to re-examine these objects to see whether they show technical features, perhaps not among those typically recorded, which might be proxies for non-Icelandic origin, and then extrapolate these to other sites. The same approach might be also be extended to other find types at other sites.

It is important to state that the light stable isotopic approach used in this study has a number of drawbacks. First, since the method relies on differences of environment between origin of wool and find site, trade between areas of similar climate (such as that between Britain and Flanders: Lloyd 1977) will not be isotopically visible, unless systematic differences in farming practice somehow exaggerate the distinction. This method will therefore not be universally applicable to all questions of European wool textile trade.

Second, the sampling strategy of this study was based on technical criteria, such that isotopic results are not wholly independent of technical features. The discrepancies between technical and isotopic identifications of typical/atypical origin indicated, however, that this is likely to overlook samples of typical technical types but non-local origin. Random sampling across all periods and areas of a site is therefore recommended, in addition to analysis of objects of interest.

Third, the geographical resolution of the technique is likely to improve as the isotopic effects of sheep metabolism and farming become better understood, and as more data on geographical variation in isotope values of archaeological material are generated. This

should lead to a reduction of the estimated flock range for a site, defined conservatively in this study, and consequently to an increase in the potential for identifying non-local material, and for estimating its origin.

Finally, understanding the effects of fibre decay on wool isotope values was very important. Significant changes in fibre structure are visible microscopically in archaeological samples (e.g. Wilson *et al.* 2007; Rast-Eicher 2008; Wilson *et al.* 2010; Kempson *et al.* 2010). The relationship between these changes and diagenesis in isotope values was fundamental to confidence in isotope data: wool fibre integrity was therefore a central focus in the development of this technique (Chapter 7).

Future applications of isotopic analysis to provenancing medieval textiles could include:

- analysis of the other types of 8th–10th century textiles identified as 'Frisian cloth', to compare their isotopic composition to those of samples from HSS and other sites in the coastal marshes of northern Germany and the Netherlands (Tidow 1995);
- sampling a greater proportion of the 9th–10th century assemblage from BKA, to explore the relationship between production and import of a complex manufactured product in an early urban setting;
- identifying Hanseatic trade in 13th–16th century assemblages from Baltic towns (e.g. Turku, Tartu, Gdansk: Jahnke 2009), to link documentary and archaeological indices of trade more closely, and compare biases in each;
- identifying wool from Spain in northern European or Italian assemblages of the 13th–16th centuries: here isotope analysis might be used to identify samples for aDNA testing to examine the development of the Merino breed (Sabatino Lopez 1953; Lawson Handley *et al.* 2007; Chessa *et al.* 2009; Brandt *et al.* 2011; Kijas *et al.* 2012).

In addition, correlation of microscopic and analytical observations for fibre integrity would be useful to improve selection of appropriate samples for analysis. In addition, the potential for links between isotope values, pasture type, pasture adequacy and wool fibre diameter warrant further investigation.

Isotopic analysis of wool textiles from medieval deposits has been shown to add considerably to current understanding of trade and exchange in this important commodity. It must be stressed that the new methodologies currently being piloted (Barrett *et al.* 2000; Orton *et al.* 2011; Lezzerini *et al.* 2012; von Holstein *et al.* in preparation-b) will be of most use when combined with existing methods of knowledge. The isotope methodology used in this study to examine provenance of textiles could also be developed to apply to other proteinaceous raw materials present in the archaeological or historical record, such as leather, parchment, silk and animal bone, and thus examine movements of objects made

from these materials. Analysis of technical and/or stylistic features of these objects, as for textiles, will provide important information on the technological and cultural context in which to interpret isotope data. Textile studies are in a position to establish new interdisciplinary ways of understanding among the most complex and informative of archaeological artefacts.

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9. Conclusions

9.1 Answers to research questions

This thesis described the development and application of a biochemical provenancing method, light stable isotopic analysis of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), non-exchangeable hydrogen ($\delta^{2}H$), oxygen ($\delta^{18}O$) and sulfur ($\delta^{34}S$), to wool textiles from the European Middle Ages preserved by anoxic waterlogging. Chapters 2–4 focused on studies of modern wool samples to examine the resolution of the technique in northern Europe, and identify and quantify possible confounding factors. Chapter 5 explored the possible confounding effects of diagenesis on another isotopic technique based on a radiogenic isotope system ($^{87}Sr/^{86}Sr$). Chapters 6–8 focused on archaeological samples, summarising the theoretical background to artefactual methods of provenancing in Chapter 6 before combining these with light stable isotopic results in Chapters 7 and 8.

The research questions asked in this thesis were:

3. *Can light stable isotopic analysis identify the origin of samples of archaeological wool?*
4. *How can isotopic data can be understood in textile artefactual context?*

The answer to the first was emphatically that it can. However confidence of provenancing was affected by: (1) the existence (or otherwise) of comparator data from modern sheep tissue samples from the region(s) of interest; (2) the existence (or otherwise) of useful isotopic variation between regions of interest; and (3) the expected degree of isotopic variation between samples of wool from a single flock, which was probably overestimated in this work. In contrast, the effects of degradation during burial (chemical and microbiological) proved to be relatively minor for most light stable isotopic data ($\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$) but significant for $^{87}Sr/^{86}Sr$.

To answer the second question, isotopic data indicating local/non-local raw material origin were considered alongside artefactual data indicating typical/atypical manufacture. Different combinations of these results could be read in different ways for individual textiles (Table 9.1). However, at this stage, it was often impossible to distinguish between alternative interpretations of these results for each specific sample. This may be achievable via further development of either isotopic or artefactual methods, that is: (1) improvement of resolution of isotopic provenancing to better distinguish between sites/areas/regions of relatively similar environment and/or husbandry practice(s); and/or (2) reassessment of textile technical variables, either by developing new ones or re-interpreting existing ones, to modify judgments of the typical/atypical nature of a given textile. It was argued that the latter step would be aided by greater theoretical discussion and exploration in the field of textile studies, to increase awareness of the potential implications of variable selection on interpretative scope.

Table 9.1. Possible interpretations of isotopic and artefact provenancing results.

Isotopic composition	Artefactual category	Interpretation(s)
Local	Typical	(1) local manufacture from local wool. (2) manufacture of textiles in another site/area/region with similar environment and similar textile production. (3) local manufacture from wool from another site/area/region with similar environment. (4) movement of local wool to another site/area/region with similar textile production.
Local	Atypical	(1) local manufacture had wider range of techniques than expected, i.e. previous identification of a particular technique as 'atypical' was incorrect. (2) movement of finished textiles manufactured in a site/area/region of similar environment but different textile production. (3) movement of local wool to site/area/region of different textile production for manufacture, before another movement of finished textiles to site/area/region of recovery.
Non-local	Typical	(1) local manufacture had narrower range of techniques than expected, i.e. previous identification of a particular technique as 'typical' was incorrect (2) wool was product of unusual farming practices not otherwise represented in the assemblage. (3) movement of raw wool produced in a site/area/region of different environment towards site/area/region of recovery for manufacture.
Non-local	Atypical	(4) from a site/area/region with both different environment (climate/farming practice) and different textile production.

9.2 Commentary on research design

9.2.1 Strengths

Interpretation of isotope results from medieval wool textiles was strengthened by the inclusion of studies of modern wool in three ways: (1) ascertaining the nature of geographical variation in isotope values in the region(s) of interest; (2) establishing the degree of isotopic variance due to metabolic, environmental and farming factors within a single population of sheep; and (3) finding out the nature and degree of isotopic changes expected in degraded wool, and linking these to other measures of fibre integrity.

Establishing the existence of geographical variation in modern material strengthened confidence when the same patterns were found in archaeological material. In addition to the $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ data reported in this thesis, and the modern sheep wool comparator data examined, a meta-analysis of published $\delta^{13}C$ and $\delta^{15}N$ data from medieval

archaeological collagen samples from across Europe was carried out (non-systematic data collection; data not shown). This work established that even in archaeological material, some of the same geographical patterns are evident (e.g. samples from mainland northern Europe are slightly more enriched in ^{13}C than those from the British Isles; samples from the Mediterranean show greater enrichment and greater range than either), which do not appear to be affected by chronological changes.

The examination of isotopic variance in both sheep wool and bone within a given environment has implications for the interpretation of work in this thesis and elsewhere. Natural isotopic variation within a single group of mammals, constrained by climatic, vegetation and animal husbandry factors, has not previously been characterised. However it is fundamental to interpretation of mammalian archaeozoological isotope data (Hamilton and Thomas 2012; Fisher and Thomas 2012). as for fish data (Barrett *et al.* 2008; Barrett *et al.* 2011; Orton *et al.* 2011). The difference between these two contexts is that in domesticated animals, the isotopic unit is the flock/herd, whereas in (unfarmed) fish, it is a regional population. The estimates for intra-flock variability made in this thesis are however preliminary and likely to be overestimates, even though they do not take into account inter-annual variation.

A second strong point of this thesis was the molecular perspective on diagenesis employed in Chapters 4 and 5. This comprised the use of: (1) two different models of keratin diagenesis, by experimental burial and high-temperature isothermal hydrous laboratory conditions; and (2) elemental and amino acid (AA) measures of composition, in addition to $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ isotope data, to characterise the results of these experiments. Chapter 4 in particular was parallels studies in other materials (Dobberstein *et al.* 2009; Demarchi *et al.* unpublished; Tomiak *et al.* unpublished; Crisp *et al.* unpublished). The inclusion of multiple measures of composition allowed exploration of the possible mechanisms behind isotopic change, and the conditions under which these are likely to occur. The work on $^{87}Sr/^{86}Sr$ indicated the cardinal role of such direct studies of diagenesis when applying biomolecular methods for archaeological material.

Finally, the discussion of the theoretical background of textile provenancing by artefactual (technical/technological/stylistic) methods has contributed to the sparse theoretical literature in the field of textile studies. This work was prompted by the need to be able to understand the relative epistemological bases of isotopic and artefactual modes of analysis and interpretation of origin. However this work showed that the identification of provenance in archaeological textiles is currently unexamined and unsystematic. The identification of a textile as atypical at a site depends on the choice of technical or stylistic variables used to characterise the assemblage and develop counts of relative frequency: what has not been examined is how the choice of variables (including that of features which are currently not systematically recorded) can affect results. In particular, the acquisition of isotopic data focused understanding on the difference between the origin of a textile's raw material and

cultural context of its production. In cases where results were unexpected, it is hoped that the isotopic data will prompt identification and possibly re-examination of the hypotheses underlying artefactual interpretation of provenance.

9.2.2 Weaknesses

The interpretation of archaeological isotope data from Iceland and the British Isles was aided by the collection of data from modern sheep wool from the same regions. However the data from archaeological finds from sites in Sweden and Germany, and that from textile samples with outlying isotope values, could not be interpreted with the same confidence. This part of the work would have been improved by the inclusion of samples from flocks in Scandinavia and mainland Europe, as a minimum, and ideally from all areas of interest in this study (Syria, Spain, France, Norway, the Baltic area). This was however beyond the scope of the present thesis. Appropriate flocks for sampling, that is those kept without modern feeds, may be difficult to identify in some regions, especially in Mediterranean environments (C. Spiteri, pers. comm.). A future study of this type should ideally include more than one flock in each region, including a second from Iceland.

Though $\delta^{34}S$ data has been employed in other studies provenancing sheep tissues (Camin *et al.* 2007; Perini *et al.* 2009; Zazzo *et al.* 2011), this experimental approach was not widely used in this thesis due to the cost and availability of these analyses. What little $\delta^{34}S$ data was obtained (Escrick group: Chapter 2) suggested that the metabolism of S in sheep wool and bone is complex, and dependent on factors which are less well understood than those controlling other isotopes. A further study in samples from the EH sheep flock, about which considerable details of animal management are known, could be a way of pursuing this. This work could provide useful preliminary information on the likely resolution of $\delta^{34}S$ data between sheep flocks, before direct testing of its geographical variation across the study area.

While the single AA $\delta^{13}C$ data described in Chapter 2 had very interesting implications for the relative metabolic origins of Ser and Gly in keratin and collagen, interpretation of this data would have been stronger if the samples tested had come from a well-characterised flock, rather than a blind control group. This data was obtained at pilot stage, and further analyses were not available. However, given the difference between results here for sheep and those obtained for humans (Raghavan *et al.* 2010), analysis of additional material, for example from the EH flock, is warranted.

As discussed above, the inclusion of multiple measures of fibre integrity (elemental, molecular and isotopic: Chapters 4 –5) was a strength of this thesis. However this data was not related to existing methods of characterising fibre integrity, using microscopy (Wilson *et al.* 2010; see also Walton Rogers 2004; Rast-Eicher 2008). Microscopic methods are generally more available to textile researchers than are analytical methods. The identification of histological correlates of the analytical measures of decay employed in this

thesis would be useful to: (1) allow textile specialists to identify samples appropriate for isotopic analysis with confidence; and (2) explore the relationships between fibre structural change and elemental, molecular and isotopic change.

The limited number of isotopic analyses available for this thesis meant that few samples were tested more than once. At least duplicate analysis is standard in zooarchaeological studies even in well-characterised tissues (e.g. Fisher and Thomas 2012; Hamilton and Thomas 2012). This meant that the inherent variation isotope value in degraded keratin, and within a single textile, was only briefly examined (Chapter 7), so that uncertainty of isotopic composition within a single archaeological textile is currently tentatively identified. Though this analysis must currently be regarded as preliminary, the data suggested that the contribution to error from within-sample variation was relatively minor. More accurate characterisation of this factor would however be useful.

This work did not attempt to pursue an isoscape approach, generating a map of isotope data across the study area (West *et al.* 2010). This approach has been used elsewhere in keratin provenancing studies (Ehleringer *et al.* 2008; Valenzuela *et al.* 2011) and in archaeological material (Coutu 2011). Such model-based approaches used so far have relied on the assumption of normality in the data (Wunder 2012), and typically require very widespread sampling patterns. Data in the present study could clearly not be described using Gaussian statistics, and sampling was highly targeted. For these reasons, a nominal assignment approach (*Is composition of sample X consistent with location A? Yes/No*) was used. However the usefulness of this paradigm depends on the selection of target locations. Confidence is higher where locations are well defined and highly contrasted (e.g. UK and Iceland data) and lower where locations are less defined (e.g. samples not consistent with any of the locations sampled) or less clearly differentiated (e.g. Sweden and the British Isles).

The development of a model-based method may not be feasible in archaeological sheep tissue in Europe because of:

- the relative complexity of isotopic patterning across the region (e.g. Figure 8.2) compared to the continental USA, due to climatic, geological and vegetation factors (Ehleringer *et al.* 2008; Valenzuela *et al.* 2011) and also cultural factors (Valenzuela *et al.* 2012),
- potentially larger error estimates associated with non-Gaussian probability models to predict variation in non-normal datasets,
- the greater time-range of archaeological inquiry, taking into account both inter-annual variation and also long-term environmental and/cultural trends (e.g. Fisher and Thomas 2012; Hamilton and Thomas 2012).

An area of considerable difficulty in developing the nominal approach, however, was how to define the local isotope range for a location, given that textile sample groups included material expected to be non-local. This was achieved by, firstly, using two different methods to define outliers and inliers: (1) median ± range, but here the value of the median was calculated including outlying values, and therefore depended strongly on sampling strategy; and (2) statistical methods of robust outlier detection. These were less dependent on sampling strategy. These two methods were generally in agreement (Chapter 7).

A second strategy for confirming the local isotopic range at any site is to use independent sample sets from a site/area/region to confirm its isotopic range (e.g. Barrett *et al.* 2008). In the present study, these included raw staples and sheep/goat bone collagen samples. However neither of these were ideal, because both groups of samples could also include non-local material. No raw staples included in this study (n=11) had isotopic composition identified as non-local. Collagen from bone samples from the same contexts as the textiles at RKH, York, Newcastle and HSS were also analysed for $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ (n=59, data not included), and at three sites outliers were identified (RKH: 1 of 7; NBG: 1 of 14; NQS: 1 of 15). This data was therefore difficult to use to confirm local isotope zones, especially as this process also requires a conversion calculation which is dependent on the universality (and relevance to medieval husbandry) of offset data obtained in Chapter 2.

Published collagen composition data from other research groups can also be used in this way (Figure 8.6), but this is currently almost universally restricted to $\delta^{13}C$ and $\delta^{15}N$. However, given the usefulness of $\delta^{2}H$ data in distinguishing between samples from Iceland and the British Isles (Chapters 2 and 7), the wider availability of such data from archaeological samples would be very interesting for provenancing studies. Gathering this dataset would however probably require a separate dedicated study, not least to improve the accuracy of $\delta^{2}H$ and $\delta^{18}O$ determination in collagen samples, where uncertainty is currently much greater than in keratin samples (Chapter 2).

Finally, the sampling strategy for archaeological textiles used in this study was shown to be weak by scientific standards. It was clear that artefactual identifications of local and non-local material were not always correct. Targeting sampling towards atypical objects therefore risks failing to identify non-local samples which are not technically, technologically, or stylistically different from the bulk of the material. Alternative strategies include:

- universal sampling, which is inefficient and destructive, but might be acceptable for a pilot study in an assemblage of low profile, at least to explore the risk of Type 2 errors (failure to reject a false null hypothesis, in this case that typical textiles are local).
- random sampling across assemblages, which risks omitting atypical material, and a different Type 2 error (in this case that atypical textiles are non-local).
- a balanced block design, controlling for example for pigmentation, fleece type, age of sample, effects of pre-burial processing, or AA composition. This method would

increase confidence in the robustness of isotopic data to these potential confounding factors, and would probably be worth pursuing in a low profile assemblage as a preliminary part of further studies.

Many of these weaknesses (definition of local isotope zone, archaeological sampling strategy, requirements for duplicates, insufficient background data to understand regional variation) could be addressed by careful design of future studies applying isotope analysis to modern sheep wool and archaeological textiles. This data will allow interpretation of the data in this thesis with greater confidence.

9.3 Contributions

9.3.1 To scientific methods in archaeology

This study applied a biomolecular provenancing method to objects from a relatively recent period of human development, from which both historical and archaeological evidence is available. These other sources of information provided a framework in which the scientific data could be understood, for example regarding the size and nature of the settlements where samples were found, and the probable origin of certain samples. Had $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ results in archaeological samples been widely affected by diagenesis, for example, this would have been evident. Thus, developing and testing a new method in a historical period (e.g. Orton *et al.* 2011; Lamb *et al.* 2012) is an advantage over doing so initially in a prehistoric period, where potentially misleading results may be less readily identifiable.

This thesis established that light stable isotopic analysis can be used to provenance archaeological artefacts composed of proteinaceous animal tissues. Though data has so far only been obtained for sheep wool and bone, important potential applications include studies of the origins of leather, silk, antler, feather, fur and parchment. This work established that these studies will need to include observation of: (1) modern baseline isotopic trends in the region(s) in question; (2) modern inherent variation in isotopic composition within the basic unit of animal population, however defined; (3) data from archaeological samples of a comparator tissue, element or species to confirm the existence of isotope trends and variance in archaeological material independently; and (4) direct testing of the effects of diagenesis on the material of interest. The epistemological gap between scientific and artefactual approaches to empirical data will also be relevant to such studies.

9.3.2 To textile studies

This study has provided the first opportunity for testing hypotheses of origin based on technical, technological and stylistic analysis of medieval wool textiles. This has been useful for, firstly, understanding of origin of particular textile samples, and secondly, exploring how these hypotheses have been constructed.

In the first case, results in this study have made a real contribution to the debate over the nature and origin of 'Frisian cloth' (Chapter 8). Though no definite conclusions can be reached, a number of previously-suggested hypotheses (made in Syria, made in Frisia, made in Norway) have been evaluated and some have been rejected (composition was not consistent with origin in a Mediterranean climate; only one sample had composition consistent with Frisian origin, at least as so far defined). Testing of additional material from BKA and other highly-networked proto-urban sites, as well as from sites in putative regions of origin, should help further address this question. The same isotopic methodology should be able to make a useful contribution to questions regarding long distance movements of raw wool and/or textiles between western and eastern Europe (Russia: Nahlik 1976; or the Baltic region: Jahnke 2009), or northern and southern Europe (England and Flanders to/from Spain and Italy, looking for archaeological correlates of the movements described in Chorley 1988; Munro 2005).

In the second case, isotopic analysis clearly focused attention on the difference between the location of production of the raw material and that of the finished textile, and provided a clear framework for interpretation (Table 9.1). The methods used to identify the location of production of a textile are currently based on a frequency analysis of a number of standard variables, which are then interpreted in context. This process depends on the selection of variables, which can differ between analysts and sites, at least partly in response to the nature of the assemblage (Chapter 6). Results from this study suggested that the most appropriate variables to differentiate local from non-local material may not always have been selected (Chapter 8). It was also suggested that additional features of textiles not currently measured (or only measured qualitatively) could be investigated if they show a correlation with isotopic indicators of origin.

9.3.3 To other research fields

Results from Chapters 2–4 are readily applicable to non-archaeological fields. Analyses reported in Chapters 2 and 3 made a useful contribution to the literature on bulk isotopic composition of domesticate tissues and the relative importance of metabolic, farming practice, dietary and climatic inputs. The archaeological results from RKH and BKA reported in Chapter 7, in addition to the Icelandic samples in Chapter 3, add significantly to the body of isotopic data from Scandinavia, which is as yet relatively sparse (see Piasentier *et al.* 2003 and references in Chapter 8). The isotopic patterns associated with sex (Chapter 2: $\delta^{15}N$ and $\delta^{18}O$ depleted and $\delta^{2}H$ enriched in males compared to females) were without reported precedent. The very striking differences in the $\delta^{13}C$ values of Ser/Gly compared to other AAs in sheep collagen and keratin suggested that further single AA $\delta^{13}C$ studies of routing to these tissues in other species of herbivorous mammal and/or sheep breeds would be informative.

Keratin $\delta^{2}H$ and $\delta^{18}O$ isotopic methodologies are currently well developed compared to such measurements in collagen. However the latter tissue is more important in archaeological studies because of its more frequent preservation. Results in Chapters 2 and 3 indicate that $\delta^{2}H$ and $\delta^{18}O$ measurements would be useful indicators of the geographic origin of sheep bone. Further research to strengthen the precision and comparability of these measurements, such as the development of inter-laboratory collagen standards, and optimisation of collagen preparation protocols, is therefore important.

The investigations of diagenesis reported in Chapters 4, 5 and 7 have implications for establishing the reliability of isotopic analysis of industrial, forensic and archaeological hair samples. The AA composition data used in these investigations (Chapters 4 and 7) were an improvement on previous methods of assessing sample integrity based only on C:N atomic ratio. Comparison of preparative washing methods for $^{87}Sr/^{86}Sr$ analysis provided information on the binding sites of Sr in the wool fibre (Chapter 5). The molecular perspective of these chapters provided a useful link to proteomic investigations of keratinous tissues (Clerens *et al.* 2010; Dyer *et al.* 2010; Solazzo *et al.* 2011; Thomas *et al.* 2012; Plowman *et al.* 2012). Useful future work includes the identification of histological correlates for hydrolytic degradation by microscopy (Wilson et al. 2010).

Though not closely linked, this set of ideas indicates that the research foci of archaeology can be a useful adjunct to more conventional approaches in mammalian ecology and protein science. Though sheep wool, as an important industrial product, has been widely studied from some perspectives (e.g. AA demand: Liu *et al.* 2000; genetic constraints of yield: Safari *et al.* 2005; proteome: Plowman *et al.* 2012), it has been relatively little used in ecological studies of bulk isotopes (compared to cattle hair; see Chapter 3), or in single amino acid isotope work (Chapter 2). Analysis of keratin has been generally overlooked in bioarchaeology in favour of analysis of collagen and tooth dentine, entirely understandably. This situation contrasts strongly with modern ecological research which has generated little data on these tissues, as they cannot be sampled non-invasively. Relating keratin and collagen metabolic behaviour (Chapter 2) is therefore an important step towards linking these bodies of research. This thesis has shown that combining ecological, diagenetic and archaeological research foci can lead to new and useful perspectives on organic raw materials of considerable industrial importance today and in the past.

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Appendix 3.1. Metabolic parameters, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$ results and $C:N_{atom}$ ratios for animals from UK Seaton Ross, UK Tollesbury and Iceland Kalmanstunga flocks. For animals measured in triplicate (indicated by -ave affixed to sample ID), arithmetic mean is given. See Appendix 3.2 for full triplicate data. M = male, F= female, C = castrate.

ID	Flock	Breed	Sex	Age	Lambed?	Main fleece colour	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atom}$
2368-70	UK Seaton Ross	Shetland	F	Adult	Empty	white	-27.46	11.97	-103	11.07	3.49
2349	UK Seaton Ross	Shetland	F	Adult	Empty	brown	-27.30	12.03	-105	11.09	3.55
2353	UK Seaton Ross	Shetland	F	Adult	Empty	cream	-27.26	11.40	-111	11.79	3.48
2354	UK Seaton Ross	Shetland	F	Adult	Lambed	white	-27.07	12.01	-109	11.62	3.47
2359ave	UK Seaton Ross	Shetland	F	Adult	Lambed	white	-27.13	11.88	-111	11.90	3.49
2363	UK Seaton Ross	Shetland	F	Adult	Lambed	black	-27.68	12.85	-103	10.83	3.59
2350	UK Seaton Ross	Shetland	F	Yearling	Empty	cream	-27.14	11.79	-111	12.06	3.53
2351	UK Seaton Ross	Shetland	F	Yearling	Empty	black	-27.60	11.36	-104	11.23	3.62
2355	UK Seaton Ross	Shetland	F	Yearling	Empty	brown	-27.28	12.22	-109	11.76	3.52
2365	UK Seaton Ross	Shetland	M	Adult	-	tan	-26.86	12.30	-105	12.27	3.55
2367	UK Seaton Ross	Shetland	M	Adult	-	white	-27.09	12.60	-103	12.32	3.51
2390ave	UK Seaton Ross	Wensleydale	F	Adult	Empty	white	-27.30	11.21	-106	11.93	3.46
2586	UK Tollesbury	Shetland	F	Adult	Empty	grey	-26.39	7.45	-94	11.99	3.51
2593	UK Tollesbury	Shetland	F	Adult	Empty	tan	-25.94	7.36	-89	12.24	3.53
2591ave	UK Tollesbury	Shetland	F	Adult	Empty	grey	-25.47	7.90	-95	13.48	3.50
2585ave	UK Tollesbury	Shetland	F	Adult	Empty	black	-26.68	8.56	-98	12.56	3.57
2592	UK Tollesbury	Shetland	F	Yearling	Empty	cream	-25.98	8.25	-96	12.62	3.49
2595	UK Tollesbury	Shetland	C	Yearling	-	brown	-25.77	8.21	-87	13.47	3.53
2601	UK Tollesbury	Shetland	F	Adult	Lambed	grey	-25.62	7.41	-93	11.68	3.56

Appendix 3.1 continued.

ID	Flock	Breed	Sex	Age	Lambed?	Main fleece colour	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atom}$
2602	UK Tollesbury	Shetland	F	Adult	Lambed	black	-25.94	7.59	-99	12.17	3.57
2603ave	UK Tollesbury	Shetland	F	Adult	Lambed	cream	-25.61	7.75	-96	13.33	3.50
2588ave	UK Tollesbury	North Ronaldsay	F	Adult	Empty	white	-25.47	8.21	-90	12.90	3.53
2589	UK Tollesbury	North Ronaldsay	F	Adult	Empty	grey	-25.64	8.05	-92	12.20	3.49
2590	UK Tollesbury	North Ronaldsay	F	Adult	Empty	white	-26.18	7.78	-89	12.89	3.48
2587	UK Tollesbury	North Ronaldsay	F	Yearling	Empty	white	-25.66	8.97	-91	14.15	3.51
2594	UK Tollesbury	North Ronaldsay	F	Yearling	Empty	white	-25.70	8.65	-92	14.15	3.52
2596	UK Tollesbury	North Ronaldsay	M	Yearling	-	white	-25.51	8.98	-101	13.85	3.52
2597	UK Tollesbury	North Ronaldsay	M	Yearling	-	white	-25.87	8.52	-97	13.94	3.55
2599ave	UK Tollesbury	North Ronaldsay	M	Adult	-	white	-25.78	9.19	-94	13.66	3.57
2600	UK Tollesbury	North Ronaldsay	F	Adult	Lambed	cream	-26.10	7.81	-96	12.56	3.52
2604	UK Tollesbury	North Ronaldsay	F	Adult	Lambed	tan	-24.97	8.83	-94	14.89	3.50
2605	UK Tollesbury	North Ronaldsay	F	Adult	Lambed	white	-25.57	7.91	-92	13.58	3.50
3650	Iceland Kalmanstunga	Icelandic	F	Adult	Pregnant	cream	-25.09	2.80	-113	11.31	3.41
3651	Iceland Kalmanstunga	Icelandic	F	Adult	Pregnant	cream	-25.35	1.45	-113	10.27	3.41
3652	Iceland Kalmanstunga	Icelandic	F	Adult	Pregnant	cream	-25.87	3.77	-109	10.87	3.40
3653	Iceland Kalmanstunga	Icelandic	F	Adult	Pregnant	cream	-25.30	3.18	-115	10.33	3.43

Appendix 3.1 continued.

ID	Flock	Breed	Sex	Age	Lambed?	Main fleece colour	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atom}$
3654	Iceland Kalmanstunga	Icelandic	F	Adult	Pregnant	black	-26.31	3.09	-115	10.54	3.51
3655	Iceland Kalmanstunga	Icelandic	M	Adult	-	brown	-25.86	4.77	-119	9.14	3.45
3656	Iceland Kalmanstunga	Icelandic	F	Yearling	Empty	cream	-25.77	2.37	-109	12.01	3.42
3657	Iceland Kalmanstunga	Icelandic	M	Adult	-	cream	-26.44	4.69	-116	10.30	3.42
3658	Iceland Kalmanstunga	Icelandic	F	Yearling	Empty	cream	-25.12	4.44	-101	11.30	3.41
3659	Iceland Kalmanstunga	Icelandic	F	Yearling	Empty	cream	-26.19	2.25	-107	11.18	3.43

Appendix 3.2. Metabolic parameters, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$ results and $C:N_{atom}$ ratios for all animals measured in triplicate. M = male, F= female. See Appendix 3.1 for mean data.

ID	Flock	Breed	Sex	Age	Lambed?	Main fleece colour	Section	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atom}$
2591-1	UK Tollesbury	Shetland	F	Adult	Empty	grey	Shoulder	-25.46	7.74	-93	12.98	3.52
2591-2	UK Tollesbury	Shetland	F	Adult	Empty	grey	Shoulder	-25.65	7.95	-95	13.76	3.51
2591-3	UK Tollesbury	Shetland	F	Adult	Empty	grey	Shoulder	-25.30	8.02	-97	13.71	3.48
2603-1	UK Tollesbury	Shetland	F	Adult	Lambed	cream	Shoulder	-25.51	7.67	-100	13.15	3.49
2603-2	UK Tollesbury	Shetland	F	Adult	Lambed	cream	Shoulder	-25.71	7.82	-88	12.75	3.51
2603-3	UK Tollesbury	Shetland	F	Adult	Lambed	cream	Shoulder	-25.62	7.75	-99	14.08	3.49
2588-1	UK Tollesbury	North Ronaldsay	F	Adult	Empty	white	Shoulder	-25.51	8.14	-89	12.37	3.53
2588-2	UK Tollesbury	North Ronaldsay	F	Adult	Empty	white	Shoulder	-25.27	8.11	-92	12.98	3.52
2588-3	UK Tollesbury	North Ronaldsay	F	Adult	Empty	white	Shoulder	-25.64	8.38	-89	13.33	3.56
2599-1	UK Tollesbury	North Ronaldsay	M	Adult	N/A	white	Shoulder	-25.65	9.23	-89	13.63	3.66
2599-2	UK Tollesbury	North Ronaldsay	M	Adult	N/A	white	Shoulder	-25.85	9.08	-101	13.19	3.53
2599-3	UK Tollesbury	North Ronaldsay	M	Adult	N/A	white	Shoulder	-25.84	9.27	-93	14.15	3.52
2585-1	UK Tollesbury	Shetland	F	Adult	Empty	black	Shoulder	-26.66	8.50	-100	12.85	3.56
2585-2	UK Tollesbury	Shetland	F	Adult	Empty	black	Shoulder	-26.72	8.60	-89	12.23	3.58
2585-3	UK Tollesbury	Shetland	F	Adult	Empty	black	Shoulder	-26.67	8.58	-99	12.58	3.59

Appendix 3.2 continued.

ID	Flock	Breed	Sex	Age	Lambed?	Main fleece colour	Section	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$	$\delta^{18}O/‰$	$C:N_{atom}$
2359-1	UK Seaton Ross	Shetland	F	Adult	Lambed	white	Shoulder	-27.16	11.53	-112	11.92	3.49
2359-2	UK Seaton Ross	Shetland	F	Adult	Lambed	white	Shoulder	-27.17	11.97	-109	11.79	3.49
2359-3	UK Seaton Ross	Shetland	F	Adult	Lambed	white	Shoulder	-27.06	12.15	-113	11.99	3.47
2390-1	UK Seaton Ross	Wensleydale	F	Adult	Empty	white	Shoulder	-27.51	11.38	-105	11.98	3.47
2390-2	UK Seaton Ross	Wensleydale	F	Adult	Empty	white	Shoulder	-27.23	11.05	-105	12.33	3.43
2390-3	UK Seaton Ross	Wensleydale	F	Adult	Empty	white	Shoulder	-27.17	11.20	-109	11.49	3.48
2368	UK Seaton Ross	Shetland	F	Adult	Empty	white	Shoulder	-27.52	12.08	-104	11.08	3.48
2369	UK Seaton Ross	Shetland	F	Adult	Empty	white	Flank	-27.41	11.92	-103	11.07	3.50
2370	UK Seaton Ross	Shetland	F	Adult	Empty	white	Britch	-27.44	11.90	-103	11.05	3.50

Appendix 4.1. Experimentally buried samples: AA concentrations (pmol mg^{-1}), % AA content, AA racemisation and isotopic composition.

ID	Environment	Years buried	Dyed	Pigmented	RP-HPLC run	[Asx]	[Glx]	[Ser]	[L-Thr]
2876u.1	Marine sediment	3	N	N	H316	385568	713718	575294	397808
2876u.2	Marine sediment	3	N	N	H316	401882	749394	604620	417711
2876m.1	Marine sediment	3	Y	N	H316	382949	725066	625213	393860
2876m.2	Marine sediment	3	Y	N	H316	386484	740837	633553	401609
2878u.1	Fenland bog	2	N	N	H316	378171	719975	598715	390406
2878u.2	Fenland bog	2	N	N	H316	443258	849285	701750	458697
2877m.1	Fenland bog	1	Y	N	H316	411494	774771	656271	419220
2877m.2	Fenland bog	1	Y	N	H316	405005	766027	648712	414646
2884u.1	Raised bog	8	N	N	H316	400628	761445	628647	410319
2884u.2	Raised bog	8	N	N	H316	423835	809526	663016	432844
2884m.1	Raised bog	8	Y	N	H316	416209	772963	646406	408787
2884m.2	Raised bog	8	Y	N	H316	507231	947956	787266	501039

Appendix 4.1 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx]%	[Glx]%	[Ser]%	[L-Thr]%
2876u.1	463416	375000	359556	114733	383566	158297	530168	232810	8.12%	15.04%	12.12%	8.38%
2876u.2	507813	389313	368098	118118	398983	163909	550622	245005	8.08%	15.07%	12.16%	8.40%
2876m.1	491702	376088	348835	139665	384132	162278	530069	232336	7.89%	14.94%	12.88%	8.12%
2876m.2	515874	378209	347711	140531	383077	163522	537262	235145	7.85%	15.05%	12.87%	8.16%
2878u.1	482948	383083	328821	159682	374536	162070	524373	225667	7.91%	15.06%	12.52%	8.16%
2878u.2	573483	441014	374614	186404	438951	187278	614401	263715	7.93%	15.19%	12.55%	8.20%
2877m.1	529217	411849	355472	165324	407656	178571	568683	243958	7.94%	14.96%	12.67%	8.09%
2877m.2	538334	405941	351464	163161	404153	175993	563228	242026	7.89%	14.92%	12.63%	8.08%
2884u.1	487624	403015	343569	194182	384375	171368	553371	236284	7.97%	15.14%	12.50%	8.16%
2884u.2	524275	421034	363114	203841	412395	178519	586212	250135	7.96%	15.21%	12.46%	8.13%
2884m.1	546878	408995	360947	179478	407116	184357	578197	243588	7.98%	14.83%	12.40%	7.84%
2884m.2	675349	491599	431916	217855	489548	222891	706048	297336	8.00%	14.94%	12.41%	7.90%

Appendix 4.1 continued.

ID	[Gly]%	[L-Arg]%	[Ala]%	[Tyr]%	[Val]%	[Phe]%	[Leu]%	[Ile]%	Asx DL	Glx DL	Ser DL
2876u.1	9.77%	7.90%	7.58%	2.42%	8.08%	3.34%	11.17%	4.91%	0.094	0.051	0.023
2876u.2	10.21%	7.83%	7.40%	2.38%	8.03%	3.30%	11.08%	4.93%	0.097	0.053	0.023
2876m.1	10.13%	7.75%	7.19%	2.88%	7.92%	3.34%	10.92%	4.79%	0.098	0.054	0.030
2876m.2	10.48%	7.68%	7.06%	2.85%	7.78%	3.32%	10.91%	4.78%	0.097	0.055	0.030
2878u.1	10.10%	8.01%	6.88%	3.34%	7.83%	3.39%	10.97%	4.72%	0.091	0.051	0.014
2878u.2	10.26%	7.89%	6.70%	3.33%	7.85%	3.35%	10.99%	4.72%	0.090	0.052	0.014
2877m.1	10.22%	7.95%	6.86%	3.19%	7.87%	3.45%	10.98%	4.71%	0.094	0.051	0.015
2877m.2	10.48%	7.91%	6.84%	3.18%	7.87%	3.43%	10.97%	4.71%	0.091	0.051	0.015
2884u.1	9.70%	8.02%	6.83%	3.86%	7.64%	3.41%	11.01%	4.70%	0.086	0.048	0.013
2884u.2	9.85%	7.91%	6.82%	3.83%	7.75%	3.35%	11.01%	4.70%	0.085	0.049	0.013
2884m.1	10.49%	7.85%	6.92%	3.44%	7.81%	3.54%	11.09%	4.67%	0.092	0.052	0.015
2884m.2	10.65%	7.75%	6.81%	3.43%	7.72%	3.51%	11.13%	4.69%	0.091	0.052	0.014

Appendix 4.1 continued.

ID	Ala DL	Tyr DL	Val DL	Phe DL	Leu DL	Ile DL	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomISOT}$
2876u.1	0.063	0.042	0.019	0.039	0.050	0.022	-26.00	4.25	-113.3	11.06	3.54
2876u.2	0.053	0.040	0.019	0.040	0.050	0.024	-	-	-	-	-
2876m.1	0.056	0.045	0.021	0.043	0.052	0.023	-26.07	3.58	-115.3	11.58	3.59
2876m.2	0.049	0.041	0.021	0.043	0.051	0.025	-	-	-	-	-
2878u.1	0.038	0.039	0.020	0.039	0.047	0.024	-26.30	3.94	-108.1	10.83	3.51
2878u.2	0.032	0.038	0.020	0.040	0.050	0.028	-	-	-	-	-
2877m.1	0.043	0.037	0.020	0.040	0.048	0.025	-26.11	4.56	-109.0	11.72	3.50
2877m.2	0.039	0.037	0.020	0.040	0.048	0.026	-	-	-	-	-
2884u.1	0.039	0.039	0.021	0.037	0.044	0.024	-25.85	4.22	-107.9	11.27	3.53
2884u.2	0.039	0.038	0.020	0.037	0.048	0.028	-	-	-	-	-
2884m.1	0.042	0.037	0.020	0.039	0.048	0.024	-25.96	4.44	-112.5	11.31	3.54
2884m.2	0.034	0.036	0.020	0.040	0.047	0.025	-	-	-	-	-

Appendix 4.2. Isothermally heated samples: AA concentrations (pmol mg^{-1}), % AA content, AA racemisation, elemental composition and isotopic composition.

ID	RP-HPLC run	Sample	Temperature/°C	Time/h	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]
1402588030h	G483	2588	0	0	962454	1905599	1681200	1072781	137529
1402588040h	G483	2588	0	0	875082	1713415	1501549	942516	117600
Control2588-01	H391	2588	0	0	453803	786518	583010	494189	0
Control2588-02	H391	2588	0	0	354308	595635	480579	399748	0
802588120-01	H391	2588	80	120	416534	729419	494781	441504	0
802588120-02	H391	2588	80	120	381062	670216	463177	414972	0
802588720-01	H391	2588	80	720	422838	780830	450450	438723	0
802588720-02	H391	2588	80	720	323840	645817	629534	514751	0
802588720-02	H420	2588	80	720	543871	1184485	885192	599358	57623
8025881440-01	H420	2588	80	1440	538783	1212203	761539	555279	56180
8025881440-02	H420	2588	80	1440	517928	1125411	749513	554506	56721
1102588120-01	H391	2588	110	120	267038	632223	275592	305366	0
1102588120-02	H391	2588	110	120	352669	832031	427374	465538	0
1102588240-01	H391	2588	110	240	117633	352623	144193	183041	0
1102588240-02	H391	2588	110	240	237087	664748	218151	286078	0
1102588480-01	H391	2588	110	480	187422	641824	151663	243857	0
1102588480-02	H391	2588	110	480	124964	426192	96250	155351	0
140258801-01	H391	2588	140	1	249126	436560	340665	267860	0
140258801-01	H391	2588	140	1	347235	586454	448979	375227	0
140258801-02	H391	2588	140	1	357872	688902	464688	369808	0
140258801-02	H391	2588	140	1	454894	845812	557332	472185	0
140258802-01	H391	2588	140	2	271423	559684	323276	248609	0
140258802-01	H391	2588	140	2	473666	947828	529943	436465	0
140258802-02	H391	2588	140	2	240148	517605	252772	231505	0
140258802-02	H391	2588	140	2	528770	1172337	625512	520270	0
140258804-01	H391	2588	140	4	211965	414097	250352	237445	0
140258804-02	H391	2588	140	4	460442	849616	602240	550309	0
140258806-01	H391	2588	140	6	438560	822145	572178	556380	0
140258806-02	H391	2588	140	6	501097	981865	684475	660395	0
140258808-01	H391	2588	140	8	153570	325408	195517	202345	0
140258808-02	H391	2588	140	8	95968	207600	122179	132025	0

Appendix 4.2 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx] %	[Glx] %	[Ser] %
1402588030h	1398897	989013	790847	421248	969891	359138	1303579	597489	8.30%	16.43%	14.49%
1402588040h	1235970	878299	703632	327330	867404	322032	1164254	541094	8.49%	16.62%	14.56%
Control2588-01	46717	467671	303806	298738	465668	173293	724719	366731	9.66%	16.74%	12.41%
Control2588-02	82872	365239	276948	295283	371771	144662	573105	252048	9.26%	15.56%	12.56%
802588120-01	55345	439748	305282	221870	437879	147768	813380	336670	9.47%	16.58%	11.24%
802588120-02	54238	415131	278019	231578	407493	144395	818559	328611	9.09%	15.99%	11.05%
802588720-01	53683	431646	333179	101853	446371	143829	784074	329830	9.87%	18.22%	10.51%
802588720-02	408701	514264	393670	158265	471841	205543	816945	296630	6.66%	13.27%	12.94%
802588720-02	627205	578864	490362	68068	584164	189816	817206	383654	8.46%	18.42%	13.76%
8025881440-01	623299	557913	504941	91688	582989	200866	863834	381942	8.45%	19.02%	11.95%
8025881440-02	707382	535564	498488	105071	569966	213961	841014	364260	8.22%	17.85%	11.89%
1102588120-01	50359	326296	294271	79063	411203	164117	699601	307912	7.66%	18.13%	7.90%
1102588120-02	66887	463963	378849	130350	513010	166202	828692	368060	7.79%	18.37%	9.44%
1102588240-01	23313	212818	182564	98179	260982	119847	589978	248405	5.07%	15.19%	6.21%
1102588240-02	46628	377060	333580	117195	436904	151091	765417	335006	6.60%	18.51%	6.07%
1102588480-01	8392	355911	295895	126732	405338	134597	727363	330122	5.76%	19.73%	4.66%
1102588480-02	23951	247534	225718	119005	323389	142131	643204	278431	4.88%	16.66%	3.76%
140258801-01	102523	264077	208153	126200	266978	120680	417927	168912	9.21%	16.14%	12.59%
140258801-01	79856	353118	270567	172146	364061	139132	626306	249316	9.49%	16.03%	12.27%
140258801-02	115210	362447	281049	91992	363767	124797	507905	223880	9.97%	19.19%	12.94%
140258801-02	88182	457996	363503	145975	465886	156641	711790	322390	9.92%	18.45%	12.16%
140258802-01	82300	274224	217265	66914	272783	95365	400766	169403	10.02%	20.67%	11.94%
140258802-01	87295	469735	354246	134936	477711	161688	854593	336804	9.88%	19.77%	11.05%
140258802-02	57416	272978	206253	82771	247950	79654	401781	164882	9.67%	20.85%	10.18%
140258802-02	108089	561465	402092	174821	556907	185341	1000072	395750	9.33%	20.68%	11.03%
140258804-01	49361	265185	213753	90107	260061	84338	427801	178905	8.77%	17.12%	10.35%
140258804-02	116202	560991	444353	264273	554244	194487	854361	358330	8.77%	16.19%	11.47%
140258806-01	104415	566012	392309	191594	633461	269664	1145267	474416	7.83%	14.68%	10.22%
140258806-02	125200	611893	466961	249684	676176	228959	1101055	450926	8.18%	16.03%	11.17%
140258808-01	31089	225123	178278	98657	222860	73802	451721	172081	7.29%	15.46%	9.29%
140258808-02	21458	158376	125903	52777	136910	50623	286447	109515	7.15%	15.48%	9.11%

Appendix 4.2 continued.

ID	[L-Thr] %	[L-His] %	[Gly] %	[L-Arg] %	[Ala] %	[Tyr] %	[Val] %	[Phe] %	[Leu] %	[Ile] %
1402588030h	9.25%	1.19%	12.06%	8.53%	6.82%	3.63%	8.36%	3.10%	11.24%	5.15%
1402588040h	9.14%	1.14%	11.99%	8.52%	6.82%	3.17%	8.41%	3.12%	11.29%	5.25%
Control2588-01	10.52%	0.00%	0.99%	9.96%	6.47%	6.36%	9.91%	3.69%	15.43%	7.81%
Control2588-02	10.45%	0.00%	2.17%	9.54%	7.24%	7.72%	9.71%	3.78%	14.98%	6.59%
802588120-01	10.03%	0.00%	1.26%	9.99%	6.94%	5.04%	9.95%	3.36%	18.48%	7.65%
802588120-02	9.90%	0.00%	1.29%	9.90%	6.63%	5.52%	9.72%	3.44%	19.53%	7.84%
802588720-01	10.24%	0.00%	1.25%	10.07%	7.77%	2.38%	10.42%	3.36%	18.30%	7.70%
802588720-02	10.58%	0.00%	8.40%	10.57%	8.09%	3.25%	9.70%	4.22%	16.79%	6.10%
802588720-02	9.32%	0.90%	9.75%	9.00%	7.62%	1.06%	9.08%	2.95%	12.71%	5.97%
8025881440-01	8.71%	0.88%	9.78%	8.75%	7.92%	1.44%	9.15%	3.15%	13.55%	5.99%
8025881440-02	8.80%	0.90%	11.22%	8.50%	7.91%	1.67%	9.04%	3.39%	13.34%	5.78%
1102588120-01	8.76%	0.00%	1.44%	9.36%	8.44%	2.27%	11.79%	4.71%	20.06%	8.83%
1102588120-02	10.28%	0.00%	1.48%	10.24%	8.36%	2.88%	11.33%	3.67%	18.29%	8.13%
1102588240-01	7.89%	0.00%	1.00%	9.17%	7.87%	4.23%	11.25%	5.16%	25.42%	10.70%
1102588240-02	7.96%	0.00%	1.30%	10.50%	9.29%	3.26%	12.16%	4.21%	21.31%	9.33%
1102588480-01	7.50%	0.00%	0.26%	10.94%	9.10%	3.90%	12.46%	4.14%	22.36%	10.15%
1102588480-02	6.07%	0.00%	0.94%	9.67%	8.82%	4.65%	12.64%	5.56%	25.14%	10.88%
140258801-01	9.90%	0.00%	3.79%	9.76%	7.69%	4.66%	9.87%	4.46%	15.45%	6.24%
140258801-01	10.25%	0.00%	2.18%	9.65%	7.39%	4.70%	9.95%	3.80%	17.12%	6.81%
140258801-02	10.30%	0.00%	3.21%	10.10%	7.83%	2.56%	10.13%	3.48%	14.15%	6.24%
140258801-02	10.30%	0.00%	1.92%	9.99%	7.93%	3.18%	10.16%	3.42%	15.53%	7.03%
140258802-01	9.18%	0.00%	3.04%	10.13%	8.02%	2.47%	10.07%	3.52%	14.80%	6.26%
140258802-01	9.10%	0.00%	1.82%	9.80%	7.39%	2.81%	9.96%	3.37%	17.82%	7.02%
140258802-02	9.32%	0.00%	2.31%	11.00%	8.31%	3.33%	9.99%	3.21%	16.18%	6.64%
140258802-02	9.18%	0.00%	1.91%	9.90%	7.09%	3.08%	9.82%	3.27%	17.64%	6.98%
140258804-01	9.82%	0.00%	2.04%	10.97%	8.84%	3.73%	10.75%	3.49%	17.69%	7.40%
140258804-02	10.48%	0.00%	2.21%	10.69%	8.47%	5.03%	10.56%	3.71%	16.28%	6.83%
140258806-01	9.93%	0.00%	1.86%	10.11%	7.01%	3.42%	11.31%	4.82%	20.45%	8.47%
140258806-02	10.78%	0.00%	2.04%	9.99%	7.62%	4.08%	11.04%	3.74%	17.97%	7.36%
140258808-01	9.61%	0.00%	1.48%	10.69%	8.47%	4.69%	10.59%	3.51%	21.46%	8.17%
140258808-02	9.84%	0.00%	1.60%	11.81%	9.39%	3.93%	10.21%	3.77%	21.35%	8.16%

Appendix 4.2 continued.

ID	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
1402588030h	0.080	0.045	0.007	0.041	0.035	0.039	0.015	0.039	0.047	0.027
1402588040h	0.080	0.045	0.008	0.040	0.030	0.034	0.016	0.041	0.046	0.027
Control2588-01	0.076	0.029	0.008	0.074	0.029	0.022	0.012	0.027	0.003	0.346
Control2588-02	0.076	0.030	0.009	0.058	0.085	0.034	0.012	0.029	0.008	0.199
802588120-01	0.107	0.028	0.024	0.075	0.046	0.032	0.012	0.042	0.006	0.321
802588120-02	0.108	0.028	0.025	0.085	0.034	0.030	0.014	0.040	0.002	0.377
802588720-01	0.192	0.033	0.030	0.074	0.071	0.055	0.018	0.057	0.003	0.243
802588720-02	0.191	0.040	0.048	0.051	0.033	0.064	0.027	0.153	0.012	0.055
802588720-02	0.185	0.050	0.039	0.039	0.041	0.041	0.022	0.051	0.043	0.022
8025881440-01	0.235	0.061	0.049	0.044	0.045	0.059	0.024	0.063	0.046	0.024
8025881440-02	0.246	0.059	0.048	0.047	0.049	0.069	0.024	0.068	0.048	0.025
1102588120-01	0.506	0.073	0.108	0.098	0.122	0.091	0.074	0.240	0.014	0.124
1102588120-02	0.547	0.071	0.110	0.095	0.133	0.086	0.027	0.097	0.010	0.194
1102588240-01	0.469	0.102	0.177	0.148	0.245	0.091	0.092	0.446	0.005	0.318
1102588240-02	0.439	0.092	0.157	0.131	0.176	0.101	0.034	0.133	0.017	0.191
1102588480-01	0.321	0.096	0.170	0.142	0.175	0.099	0.049	0.149	0.023	0.174
1102588480-02	0.316	0.093	0.159	0.169	0.266	0.169	0.165	0.435	0.014	0.167
140258801-01	0.226	0.036	0.036	0.064	0.103	0.075	0.037	0.149	0.007	0.018
140258801-01	0.224	0.032	0.037	0.059	0.072	0.025	0.013	0.038	0.002	0.186
140258801-02	0.234	0.038	0.030	0.047	0.060	0.037	0.015	0.037	0.010	0.016
140258801-02	0.230	0.034	0.030	0.058	0.079	0.008	0.014	0.032	0.003	0.133
140258802-01	0.401	0.047	0.044	0.052	0.069	0.042	0.016	0.042	0.012	0.014
140258802-01	0.396	0.042	0.042	0.061	0.035	0.030	0.012	0.044	0.006	0.153
140258802-02	0.395	0.035	0.063	0.064	0.101	0.051	0.015	0.039	0.009	0.087
140258802-02	0.397	0.039	0.062	0.062	0.033	0.026	0.013	0.043	0.003	0.163
140258804-01	0.561	0.058	0.067	0.092	0.170	0.067	0.021	0.062	0.008	0.174
140258804-02	0.605	0.054	0.103	0.083	0.131	0.062	0.023	0.063	0.010	0.091
140258806-01	0.664	0.072	0.113	0.086	0.064	0.063	0.068	0.279	0.006	0.166
140258806-02	0.633	0.073	0.110	0.090	0.068	0.075	0.023	0.087	0.009	0.169
140258808-01	0.630	0.084	0.098	0.107	0.217	0.069	0.031	0.101	0.005	0.342
140258808-02	0.661	0.077	0.133	0.090	0.192	0.058	0.030	0.085	0.006	0.373

Appendix 4.2 continued.

ID	C%wtEA	N%wtEA	H%wtEA	O%wtEA	S%wtEA	C%wtAA	N%wtAA	H%wtAA	O%wtAA
1402588030h	-	-	-	-	-	50.50	17.84	6.87	24.79
1402588040h	-	-	-	-	-	50.45	17.86	6.88	24.82
Control2588-01	46.43	15.53	7.06	27.30	3.79	52.77	16.57	7.23	23.43
Control2588-02	45.90	15.45	6.81	27.19	3.68	52.76	16.57	7.17	23.50
802588120-01	47.72	15.76	7.17	27.45	3.44	52.97	16.63	7.34	23.06
802588120-02	47.52	15.99	7.45	25.72	3.50	53.26	16.53	7.37	22.84
802588720-01	47.03	15.22	7.14	26.85	2.91	52.58	16.86	7.37	23.20
802588720-02	46.57	15.46	6.98	26.36	2.81	52.09	17.43	7.23	23.25
802588720-02	46.57	15.46	6.98	26.36	2.81	50.58	17.83	7.01	24.59
8025881440-01	45.78	14.58	6.76	27.91	3.45	50.94	17.74	7.04	24.28
8025881440-02	46.60	14.70	6.80	26.65	3.45	50.93	17.79	7.01	24.27
1102588120-01	46.13	14.59	6.64	29.42	3.28	53.79	16.56	7.53	22.13
1102588120-02	46.11	14.73	6.74	29.42	2.91	53.07	16.80	7.43	22.70
1102588240-01	49.06	14.45	6.76	25.67	3.17	55.50	16.03	7.78	20.68
1102588240-02	49.10	14.40	7.14	26.50	3.08	54.24	16.67	7.61	21.48
1102588480-01	51.41	15.02	7.23	24.06	2.32	54.76	16.55	7.69	21.00
1102588480-02	50.60	15.03	6.91	24.67	2.09	55.94	16.11	7.81	20.13
140258801-01	46.45	15.65	6.92	28.56	2.84	52.35	16.92	7.18	23.55
140258801-01	46.45	15.65	6.92	28.56	2.84	52.63	16.73	7.26	23.38
140258801-02	46.87	15.10	6.84	28.84	2.62	51.54	17.19	7.15	24.12
140258801-02	46.87	15.10	6.84	28.84	2.62	52.08	16.97	7.23	23.73
140258802-01	47.17	15.51	6.92	29.17	2.21	51.68	17.20	7.16	23.96
140258802-01	47.17	15.51	6.92	29.17	2.21	52.37	16.89	7.29	23.46
140258802-02	47.05	15.74	7.02	28.19	2.11	52.11	17.19	7.23	23.46
140258802-02	47.05	15.74	7.02	28.19	2.11	52.34	16.89	7.28	23.49
140258804-01	47.02	14.73	6.94	28.53	2.50	52.76	17.02	7.36	22.87
140258804-02	46.97	15.23	6.95	28.32	2.62	52.66	16.92	7.28	23.14
140258806-01	46.83	13.97	6.52	29.61	2.68	53.73	16.57	7.50	22.20
140258806-02	46.34	15.31	6.79	29.72	2.61	52.96	16.72	7.37	22.94
140258808-01	47.20	13.50	6.76	26.87	3.07	53.75	16.67	7.52	22.06
140258808-02	46.26	13.12	6.69	29.98	3.05	53.58	16.94	7.52	21.95

Appendix 4.2 continued.

ID	C%wtAA (deamid)	N%wtAA (deamid)	H%wtAA (deamid)	O%wtAA (deamid)
1402588030h	50.63	16.69	6.83	25.85
1402588040h	50.58	16.69	6.83	25.90
Control2588-01	52.98	15.32	7.19	24.51
Control2588-02	52.96	15.39	7.13	24.53
802588120-01	53.18	15.40	7.31	24.11
802588120-02	53.47	15.34	7.34	23.85
802588720-01	52.79	15.54	7.33	24.34
802588720-02	52.22	16.52	7.20	24.06
802588720-02	50.71	16.59	6.96	25.74
8025881440-01	51.09	16.47	6.99	25.45
8025881440-02	51.07	16.58	6.97	25.38
1102588120-01	54.01	15.34	7.50	23.15
1102588120-02	53.27	15.58	7.40	23.74
1102588240-01	55.72	15.07	7.76	21.45
1102588240-02	54.47	15.50	7.58	22.45
1102588480-01	55.00	15.37	7.67	21.96
1102588480-02	56.17	15.10	7.79	20.93
140258801-01	52.54	15.73	7.14	24.59
140258801-01	52.83	15.51	7.23	24.43
140258801-02	51.72	15.83	7.10	25.35
140258801-02	52.28	15.63	7.19	24.91
140258802-01	51.88	15.77	7.11	25.24
140258802-01	52.59	15.49	7.25	24.68
140258802-02	52.32	15.78	7.19	24.71
140258802-02	52.56	15.48	7.24	24.73
140258804-01	52.96	15.82	7.32	23.90
140258804-02	52.85	15.76	7.24	24.15
140258806-01	53.93	15.51	7.48	23.08
140258806-02	53.16	15.59	7.34	23.92
140258808-01	53.95	15.61	7.50	22.95
140258808-02	53.78	15.90	7.50	22.82

Appendix 4.2 continued.

ID	C%wtAA (oxid)	N%wtAA (oxid)	H%wtAA (oxid)	O%wtAA (oxid)	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$
1402588030h	50.40	14.44	6.44	28.72	-25.47	8.21	-99.17
1402588040h	50.37	14.45	6.45	28.74	-	-	-
Control2588-01	52.66	13.00	6.75	27.59	-	-	-
Control2588-02	52.55	13.14	6.68	27.63	-	-	-
802588120-01	52.98	13.08	6.87	27.07	-	-	-
802588120-02	53.22	13.04	6.91	26.83	-25.78	8.84	-
802588720-01	52.73	13.21	6.90	27.16	-25.82	9.35	-
802588720-02	52.14	14.09	6.77	27.00	-	-	-
802588720-02	50.69	14.30	6.58	28.43	-	-	-
8025881440-01	50.99	14.22	6.61	28.17	-24.91	7.90	-85.78
8025881440-02	50.92	14.38	6.59	28.11	-24.81	8.05	-88.66
1102588120-01	53.73	13.14	7.09	26.04	-	-	-
1102588120-02	53.17	13.22	6.97	26.64	-	-	-
1102588240-01	55.28	12.92	7.36	24.44	-25.08	8.11	-113.28
1102588240-02	54.26	13.08	7.18	25.48	-24.80	8.29	-99.55
1102588480-01	54.78	12.87	7.26	25.10	-	-	-
1102588480-02	55.66	12.83	7.41	24.09	-	-	-
140258801-01	52.23	13.43	6.71	27.63	-	-	-
140258801-01	52.58	13.26	6.79	27.37	-	-	-
140258801-02	51.67	13.48	6.67	28.18	-	-	-
140258801-02	52.17	13.31	6.76	27.76	-	-	-
140258802-01	51.80	13.40	6.70	28.10	-	-	-
140258802-01	52.47	13.20	6.84	27.50	-	-	-
140258802-02	52.28	13.25	6.76	27.71	-	-	-
140258802-02	52.45	13.17	6.82	27.56	-	-	-
140258804-01	52.88	13.31	6.89	26.92	-	-	-
140258804-02	52.67	13.30	6.80	27.23	-	-	-
140258806-01	53.66	13.17	7.04	26.13	-	-	-
140258806-02	52.98	13.27	6.90	26.84	-	-	-
140258808-01	53.80	13.17	7.07	25.97	-24.93	7.98	-97.27
140258808-02	53.72	13.25	7.06	25.98	-24.72	8.23	-

Appendix 4.2 continued.

ID	$\delta^{18}O$/‰	$C:N_{atomISOT}$
1402588030h	12.90	3.53
1402588040h	-	-
Control2588-01	-	-
Control2588-02	-	-
802588120-01	-	-
802588120-02	-	3.51
802588720-01	-	3.57
802588720-02	-	-
802588720-02	-	-
8025881440-01	15.91	3.66
8025881440-02	13.93	3.67
1102588120-01	-	-
1102588120-02	-	-
1102588240-01	13.22	3.93
1102588240-02	11.91	3.94
1102588480-01	-	-
1102588480-02	-	-
140258801-01	-	-
140258801-01	-	-
140258801-02	-	-
140258801-02	-	-
140258802-01	-	-
140258802-01	-	-
140258802-02	-	-
140258802-02	-	-
140258804-01	-	-
140258804-02	-	-
140258806-01	-	-
140258806-02	-	-
140258808-01	12.69	3.71
140258808-02	-	3.77

Appendix 4.2 continued.

ID	RP-HPLC run	Sample	Temperature/°C	Time/h	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]
140258824-01a	H391	2588	140	24	91260	286301	110117	154237	0
140258824-01b	H420	2588	140	24	65536	296605	151105	127581	21147
140258824-02	H391	2588	140	24	103836	330215	108732	151054	0
14025880148h	G483	2588	140	48	256290	1239853	372428	385810	68142
14025880248h	G483	2588	140	48	229058	1149478	353390	360970	66495
140258848-01	H391	2588	140	48	115152	418945	99695	167650	0
140258848-02	H391	2588	140	48	138692	511996	119070	197983	0
140258872-01	H391	2588	140	72	97170	388477	80761	147776	0
140258872-02	H391	2588	140	72	100328	396959	73163	134884	0
140258896-01	H391	2588	140	96	102157	429328	77844	148351	0
140258896-02	H391	2588	140	96	99170	410826	80289	148281	0
1402588120-01	H391	2588	140	120	110602	463169	86664	168550	0
1402588120-02	H391	2588	140	120	67516	287587	55676	105194	0
Cont2589-01	H402	2589	0	0	525634	1028781	942795	577143	92750
Cont2589-02	H402	2589	0	0	578732	1184940	1067875	685888	120176
802589120-01	H397	2589	80	120	584770	1146848	1061364	645333	73679
802589120-02	H397	2589	80	120	625333	1257728	1042370	644335	84284
802589720-02	H397	2589	80	720	400946	804318	611430	404924	38629
802589720-02	H402	2589	80	720	324874	646270	490610	327968	35735
8025891440-02	H402	2589	80	1440	458463	998875	671893	470335	62212
8025891440-01	H402	2589	80	1440	563656	1208624	762031	538253	77670
1102589120-01	H397	2589	110	120	238133	639925	387152	289817	40326
1102589120-02	H397	2589	110	120	154570	408681	253362	184456	27371
1102589240-01	H397	2589	110	240	230275	756804	347093	298769	50609
1102589240-02	H402	2589	110	240	153117	508118	224222	192246	35478
1102589480-01	H397	2589	110	480	241751	974436	340157	348380	66668
1102589480-02	H402	2589	110	480	133792	532214	164198	169032	39689
140258901-01	H397	2589	140	1	513907	973002	832835	499628	67384
140258901-02	H397	2589	140	1	416457	831884	777807	483722	61487
140258902-01	H397	2589	140	2	552763	1134578	951462	606408	64143
140258902-02	H397	2589	140	2	501472	1021711	894281	563623	71662

Appendix 4.2 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx] %	[Glx] %	[Ser] %
140258824-01a	31807	225138	155812	99487	237387	76952	575948	232148	4.45%	13.96%	5.37%
140258824-01b	202278	139784	146669	68670	178294	73683	248342	123519	3.85%	17.41%	8.87%
140258824-02	5961	195502	208107	93863	252405	91527	454335	197685	5.20%	16.53%	5.44%
14025880148h	689712	501161	647984	243876	783364	341598	1176249	597284	3.77%	18.23%	5.47%
14025880248h	658212	475036	595763	257961	715572	319464	1065591	544872	3.63%	18.20%	5.59%
140258848-01	6359	265809	276465	145549	329420	118982	649964	297010	4.39%	15.96%	3.80%
140258848-02	8811	311839	320557	147186	411063	148634	675578	348931	4.58%	16.91%	3.93%
140258872-01	8775	259597	288196	131043	372912	159003	618510	325658	3.71%	14.84%	3.08%
140258872-02	6527	269923	283701	133425	352990	157307	726714	335664	3.71%	14.69%	2.71%
140258896-01	8399	283036	304257	130464	415563	186211	754918	368942	3.49%	14.67%	2.66%
140258896-02	10370	274990	312166	159509	454423	240278	843511	412280	3.13%	12.96%	2.53%
1402588120-01	8258	310454	360294	126361	508434	241353	918721	455452	3.21%	13.43%	2.51%
1402588120-02	5214	199540	245447	105652	362512	199810	676191	327830	2.77%	11.79%	2.28%
Cont2589-01	770135	567656	449974	304792	550413	219231	754886	354879	8.00%	15.66%	14.35%
Cont2589-02	721001	641559	504726	244472	623581	224505	803023	401369	8.08%	16.55%	14.91%
802589120-01	948359	620405	517331	262257	620842	251363	854065	376435	7.96%	15.62%	14.45%
802589120-02	751496	636206	548905	126105	648782	235970	887002	407130	8.61%	17.33%	14.36%
802589720-02	502012	399651	355062	88306	415866	150229	592494	260039	8.67%	17.39%	13.22%
802589720-02	373744	336807	290149	44090	349108	122273	480434	221732	8.76%	17.43%	13.23%
8025891440-02	538277	523081	446595	74206	523765	179405	734932	329260	8.35%	18.20%	12.24%
8025891440-01	633260	596697	506564	104848	592934	206881	870677	384749	8.74%	18.74%	11.81%
1102589120-01	426095	324084	295777	100386	348238	145597	492686	229426	6.55%	17.61%	10.65%
1102589120-02	259936	211888	185154	49223	218776	85153	312595	142004	6.78%	17.91%	11.11%
1102589240-01	436569	435893	358005	86678	434990	185866	640734	296874	5.58%	18.35%	8.42%
1102589240-02	255675	256320	227046	66821	276916	112924	410319	200129	5.75%	19.08%	8.42%
1102589480-01	432589	547829	443474	198952	556847	231126	840761	412536	4.75%	19.15%	6.69%
1102589480-02	220108	311447	245640	97835	306999	130457	470272	229572	4.88%	19.43%	5.99%
140258901-01	667541	512925	427015	199062	505904	240685	754991	324441	8.56%	16.20%	13.87%
140258901-02	653206	449877	365242	136833	452950	190611	619572	279688	7.90%	15.79%	14.76%
140258902-01	792871	580853	491541	199409	598072	238328	832543	374717	8.09%	16.60%	13.92%
140258902-02	737081	543890	446164	157453	545335	224223	752866	349780	8.00%	16.31%	14.27%

Appendix 4.2 continued.

ID	[L-Thr] %	[L-His] %	[Gly] %	[L-Arg] %	[Ala] %	[Tyr] %	[Val] %	[Phe] %	[Leu] %	[Ile] %
140258824-01a	7.52%	0.00%	1.55%	10.97%	7.60%	4.85%	11.57%	3.75%	28.08%	11.32%
140258824-01b	7.49%	1.24%	11.87%	8.21%	8.61%	4.03%	10.47%	4.33%	14.58%	7.25%
140258824-02	7.56%	0.00%	0.30%	9.79%	10.42%	4.70%	12.63%	4.58%	22.74%	9.90%
14025880148h	5.67%	1.00%	10.14%	7.37%	9.53%	3.59%	11.52%	5.02%	17.29%	8.78%
14025880248h	5.71%	1.05%	10.42%	7.52%	9.43%	4.08%	11.33%	5.06%	16.87%	8.63%
140258848-01	6.39%	0.00%	0.24%	10.13%	10.53%	5.54%	12.55%	4.53%	24.76%	11.31%
140258848-02	6.54%	0.00%	0.29%	10.30%	10.58%	4.86%	13.57%	4.91%	22.31%	11.52%
140258872-01	5.64%	0.00%	0.34%	9.91%	11.01%	5.00%	14.24%	6.07%	23.62%	12.44%
140258872-02	4.99%	0.00%	0.24%	9.99%	10.50%	4.94%	13.07%	5.82%	26.90%	12.42%
140258896-01	5.07%	0.00%	0.29%	9.67%	10.40%	4.46%	14.20%	6.36%	25.80%	12.61%
140258896-02	4.68%	0.00%	0.33%	8.67%	9.84%	5.03%	14.33%	7.58%	26.60%	13.00%
1402588120-01	4.89%	0.00%	0.24%	9.00%	10.45%	3.66%	14.75%	7.00%	26.65%	13.21%
1402588120-02	4.31%	0.00%	0.21%	8.18%	10.06%	4.33%	14.87%	8.19%	27.73%	13.44%
Cont2589-01	8.78%	1.41%	11.72%	8.64%	6.85%	4.64%	8.38%	3.34%	11.49%	5.40%
Cont2589-02	9.58%	1.68%	10.07%	8.96%	7.05%	3.41%	8.71%	3.14%	11.21%	5.61%
802589120-01	8.79%	1.00%	12.92%	8.45%	7.05%	3.57%	8.46%	3.42%	11.63%	5.13%
802589120-02	8.88%	1.16%	10.35%	8.76%	7.56%	1.74%	8.94%	3.25%	12.22%	5.61%
802589720-02	8.76%	0.84%	10.86%	8.64%	7.68%	1.91%	8.99%	3.25%	12.81%	5.62%
802589720-02	8.85%	0.96%	10.08%	9.09%	7.83%	1.19%	9.42%	3.30%	12.96%	5.98%
8025891440-02	8.57%	1.13%	9.81%	9.53%	8.14%	1.35%	9.54%	3.27%	13.39%	6.00%
8025891440-01	8.34%	1.20%	9.82%	9.25%	7.85%	1.63%	9.19%	3.21%	13.50%	5.96%
1102589120-01	7.98%	1.11%	11.73%	8.92%	8.14%	2.76%	9.58%	4.01%	13.56%	6.31%
1102589120-02	8.09%	1.20%	11.39%	9.29%	8.12%	2.16%	9.59%	3.73%	13.70%	6.22%
1102589240-01	7.25%	1.23%	10.59%	10.57%	8.68%	2.10%	10.55%	4.51%	15.54%	7.20%
1102589240-02	7.22%	1.33%	9.60%	9.63%	8.53%	2.51%	10.40%	4.24%	15.41%	7.52%
1102589480-01	6.85%	1.31%	8.50%	10.77%	8.72%	3.91%	10.95%	4.54%	16.53%	8.11%
1102589480-02	6.17%	1.45%	8.03%	11.37%	8.97%	3.57%	11.21%	4.76%	17.16%	8.38%
140258901-01	8.32%	1.12%	11.11%	8.54%	7.11%	3.31%	8.42%	4.01%	12.57%	5.40%
140258901-02	9.18%	1.17%	12.40%	8.54%	6.93%	2.60%	8.60%	3.62%	11.76%	5.31%
140258902-01	8.87%	0.94%	11.60%	8.50%	7.19%	2.92%	8.75%	3.49%	12.18%	5.48%
140258902-02	9.00%	1.14%	11.76%	8.68%	7.12%	2.51%	8.70%	3.58%	12.02%	5.58%

Appendix 4.2 continued.

ID	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
140258824-01a	0.495	0.145	0.198	0.167	0.131	0.096	0.047	0.165	0.006	0.601
140258824-01b	0.514	0.233	0.206	0.126	0.149	0.138	0.045	0.134	0.085	0.051
140258824-02	0.480	0.140	0.205	0.173	0.268	0.126	0.047	0.158	0.019	0.242
14025880148h	0.400	0.249	0.237	0.156	0.170	0.159	0.061	0.161	0.105	0.066
14025880248h	0.386	0.252	0.254	0.159	0.174	0.165	0.063	0.166	0.107	0.068
140258848-01	0.332	0.133	0.208	0.190	0.267	0.129	0.053	0.181	0.018	0.251
140258848-02	0.333	0.130	0.205	0.175	0.265	0.126	0.062	0.149	0.024	0.195
140258872-01	0.303	0.131	0.200	0.224	0.235	0.149	0.066	0.166	0.037	0.129
140258872-02	0.360	0.131	0.208	0.258	0.323	0.150	0.076	0.214	0.025	0.236
140258896-01	0.317	0.129	0.158	0.273	0.244	0.163	0.062	0.211	0.039	0.136
140258896-02	0.280	0.124	0.176	0.266	0.281	0.202	0.149	0.446	0.030	0.123
1402588120-01	0.315	0.133	0.151	0.313	0.211	0.167	0.070	0.212	0.045	0.131
1402588120-02	0.304	0.134	0.161	0.320	0.296	0.225	0.156	0.433	0.033	0.113
Cont2589-01	0.077	0.040	0.006	0.037	0.035	0.027	0.017	0.032	0.035	0.025
Cont2589-02	0.077	0.042	0.006	0.036	0.028	0.039	0.019	0.035	0.032	0.008
802589120-01	0.104	0.040	0.020	0.037	0.027	0.027	0.018	0.032	0.039	0.022
802589120-02	0.105	0.042	0.015	0.038	0.028	0.014	0.019	0.035	0.039	0.031
802589720-02	0.165	0.046	0.035	0.040	0.034	0.038	0.019	0.045	0.041	0.039
802589720-02	0.168	0.049	0.029	0.042	0.034	0.036	0.020	0.048	0.040	0.028
8025891440-02	0.207	0.056	0.038	0.047	0.044	0.044	0.024	0.060	0.041	0.032
8025891440-01	0.203	0.054	0.040	0.042	0.035	0.057	0.022	0.059	0.039	0.031
1102589120-01	0.530	0.104	0.097	0.079	0.074	0.088	0.043	0.105	0.053	0.044
1102589120-02	0.537	0.103	0.097	0.070	0.065	0.087	0.027	0.073	0.056	0.046
1102589240-01	0.467	0.135	0.137	0.102	0.089	0.110	0.036	0.106	0.071	0.055
1102589240-02	0.444	0.135	0.130	0.095	0.090	0.105	0.033	0.103	0.065	0.059
1102589480-01	0.352	0.152	0.188	0.123	0.107	0.118	0.048	0.129	0.078	0.059
1102589480-02	0.361	0.141	0.158	0.129	0.103	0.109	0.044	0.131	0.073	0.037
140258901-01	0.213	0.045	0.023	0.041	0.027	0.033	0.019	0.035	0.039	0.032
140258901-02	0.211	0.047	0.024	0.041	0.030	0.038	0.020	0.034	0.041	0.028
140258902-01	0.364	0.058	0.034	0.045	0.033	0.042	0.020	0.039	0.042	0.029
140258902-02	0.381	0.057	0.050	0.046	0.035	0.049	0.021	0.040	0.043	0.037

Appendix 4.2 continued.

ID	C%wtEA	N%wtEA	H%wtEA	O%wtEA	S%wtEA	C%wtAA	N%wtAA	H%wtAA	O%wtAA
140258824-01a	48.45	5.20	6.42	30.31	1.42	55.69	16.31	7.89	20.10
140258824-01b	48.45	5.20	6.42	30.31	1.42	52.55	17.46	7.18	22.81
140258824-02	48.66	9.02	6.56	29.04	2.45	55.18	16.28	7.72	20.82
14025880148h	-	-	-	-	-	53.76	17.04	7.37	21.83
14025880248h	-	-	-	-	-	53.72	17.07	7.35	21.87
140258848-01	50.63	13.58	6.44	-	2.18	55.92	16.18	7.84	20.06
140258848-02	51.70	14.02	6.81	-	2.16	55.65	16.30	7.79	20.26
140258872-01	-	-	-	-	-	56.50	16.08	7.90	19.52
140258872-02	-	-	-	-	-	56.78	16.01	7.97	19.24
140258896-01	-	-	-	-	-	56.86	15.96	7.97	19.20
140258896-02	-	-	-	-	-	57.57	15.60	8.02	18.82
1402588120-01	-	-	-	-	-	57.26	15.79	8.05	18.90
1402588120-02	-	-	-	-	-	58.00	15.45	8.10	18.45
Cont2589-01	45.02	14.78	6.65	27.70	3.50	50.86	17.76	6.89	24.49
Cont2589-02	45.33	15.04	6.49	27.66	3.47	50.68	17.81	6.92	24.59
802589120-01	47.21	15.48	6.96	27.31	3.49	50.62	17.85	6.89	24.65
802589120-02	47.53	15.71	6.94	26.56	3.38	50.58	17.84	6.96	24.62
802589720-02	45.85	15.04	6.72	27.54	2.76	50.73	17.79	6.98	24.49
802589720-02	46.06	14.78	6.72	27.97	3.28	50.77	17.85	7.02	24.35
8025891440-02	46.20	14.61	6.68	27.75	3.29	50.96	17.91	7.05	24.08
8025891440-01	45.66	14.38	6.46	27.94	3.34	50.96	17.86	7.03	24.14
1102589120-01	46.22	14.38	6.54	31.30	2.63	51.57	17.77	7.07	23.60
1102589120-02	45.89	14.33	6.59	29.40	2.59	51.37	17.87	7.07	23.68
1102589240-01	48.70	14.12	6.58	27.51	2.55	52.27	17.88	7.22	22.62
1102589240-02	49.38	14.20	6.97	26.66	3.05	52.37	17.65	7.22	22.75
1102589480-01	54.40	16.55	6.52	#REF!	2.51	53.13	17.57	7.32	21.98
1102589480-02	49.55	15.12	5.73	23.85	1.87	53.32	17.65	7.36	21.68
140258901-01	46.00	15.43	6.70	27.96	2.29	50.99	17.70	6.93	24.38
140258901-02	46.29	15.20	6.85	28.92	3.15	50.57	17.87	6.91	24.64
140258902-01	46.03	14.23	6.64	28.64	2.19	50.78	17.75	6.94	24.53
140258902-02	45.97	14.67	6.53	28.57	2.04	50.69	17.84	6.94	24.53

Appendix 4.2 continued.

ID	C%wtAA (deamid)	N%wtAA (deamid)	H%wtAA (deamid)	O%wtAA (deamid)
140258824-01a	55.89	15.46	7.88	20.77
140258824-01b	52.69	16.49	7.15	23.67
140258824-02	55.40	15.27	7.70	21.64
14025880148h	53.93	16.01	7.34	22.71
14025880248h	53.89	16.06	7.31	22.74
140258848-01	56.14	15.23	7.82	20.81
140258848-02	55.87	15.31	7.77	21.06
140258872-01	56.71	15.22	7.88	20.19
140258872-02	56.99	15.16	7.95	19.90
140258896-01	57.07	15.11	7.96	19.86
140258896-02	57.77	14.84	8.00	19.39
1402588120-01	57.46	15.00	8.04	19.50
1402588120-02	58.19	14.76	8.09	18.97
Cont2589-01	51.00	16.66	6.84	25.50
Cont2589-02	50.81	16.67	6.87	25.65
802589120-01	50.75	16.75	6.84	25.66
802589120-02	50.71	16.64	6.91	25.73
802589720-02	50.88	16.58	6.94	25.61
802589720-02	50.91	16.64	6.98	25.47
8025891440-02	51.10	16.69	7.01	25.20
8025891440-01	51.12	16.60	6.98	25.30
1102589120-01	51.71	16.66	7.02	24.60
1102589120-02	51.51	16.75	7.03	24.71
1102589240-01	52.42	16.81	7.19	23.57
1102589240-02	52.54	16.52	7.18	23.76
1102589480-01	53.31	16.50	7.28	22.92
1102589480-02	53.50	16.57	7.32	22.61
140258901-01	51.13	16.55	6.89	25.43
140258901-02	50.70	16.78	6.87	25.66
140258902-01	50.91	16.61	6.89	25.59
140258902-02	50.82	16.72	6.89	25.57

Appendix 4.2 continued.

ID	C%wtAA (oxid)	N%wtAA (oxid)	H%wtAA (oxid)	O%wtAA (oxid)	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$
140258824-01a	55.72	12.98	7.49	23.82	-	-	-
140258824-01b	52.24	14.28	6.78	26.69	-	-	-109.68
140258824-02	55.03	12.99	7.30	24.68	-	-	-
14025880148h	53.34	14.01	7.01	25.64	-	-	-
14025880248h	53.27	14.02	6.98	25.74	-	-	-
140258848-01	55.75	12.89	7.44	23.93	-	-	-
140258848-02	55.47	12.92	7.38	24.22	-	-	-
140258872-01	56.16	12.90	7.51	23.44	-	-	-
140258872-02	56.46	12.83	7.59	23.12	-	-	-
140258896-01	56.49	12.84	7.60	23.07	-	-	-
140258896-02	56.95	12.75	7.65	22.65	-	-	-
1402588120-01	56.81	12.87	7.69	22.63	-	-	-172.10
1402588120-02	57.31	12.77	7.75	22.17	-	-	-
Cont2589-01	50.66	14.35	6.46	28.54	-25.64	8.05	-101.84
Cont2589-02	50.57	14.25	6.47	28.71	-	-	-
802589120-01	50.49	14.55	6.46	28.49	-25.92	7.24	-
802589120-02	50.57	14.35	6.53	28.54	-26.29	6.39	-
802589720-02	50.74	14.37	6.56	28.33	-26.07	6.39	-
802589720-02	50.83	14.32	6.60	28.25	-26.33	5.72	-
8025891440-02	51.02	14.25	6.62	28.11	-25.91	6.22	-92.43
8025891440-01	50.99	14.20	6.60	28.21	-25.63	5.78	-94.85
1102589120-01	51.43	14.34	6.65	27.59	-	-	-
1102589120-02	51.31	14.34	6.65	27.70	-	-	-
1102589240-01	52.19	14.14	6.80	26.86	-26.11	7.67	-
1102589240-02	52.23	14.02	6.81	26.94	-25.99	8.10	-102.44
1102589480-01	52.96	13.77	6.89	26.38	-	-	-116.47
1102589480-02	53.15	13.70	6.93	26.22	-	-	-
140258901-01	50.79	14.29	6.51	28.41	-	-	-
140258901-02	50.47	14.53	6.48	28.52	-	-	-
140258902-01	50.68	14.41	6.51	28.40	-	-	-
140258902-02	50.60	14.45	6.51	28.44	-	-	-

Appendix 4.2 continued.

ID	$\delta^{18}O$/‰	$C:N_{atomISOT}$
140258824-01a	-	-
140258824-01b	11.55	-
140258824-02	-	-
14025880148h	-	-
14025880248h	-	-
140258848-01	-	-
140258848-02	-	-
140258872-01	-	-
140258872-02	-	-
140258896-01	-	-
140258896-02	-	-
1402588120-01	12.30	-
1402588120-02	-	-
Cont2589-01	12.20	3.49
Cont2589-02	-	-
802589120-01	-	3.55
802589120-02	-	3.57
802589720-02	-	3.62
802589720-02	-	3.62
8025891440-02	14.03	3.73
8025891440-01	14.22	3.73
1102589120-01	-	-
1102589120-02	-	-
1102589240-01	-	4.06
1102589240-02	12.21	4.02
1102589480-01	12.81	-
1102589480-02	-	-
140258901-01	-	-
140258901-02	-	-
140258902-01	-	-
140258902-02	-	-

Appendix 4.2 continued.

ID	RP-HPLC run	Sample	Temperature/°C	Time/h	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]
140258904-01	H397	2589	140	4	597447	1290987	1064153	670562	95804
140258904-02	H397	2589	140	4	213981	478615	437823	278233	38127
140258906-01	H397	2589	140	6	38512	91699	79057	51676	6497
140258906-02	H397	2589	140	6	147649	347027	291258	189443	23804
140258908-01	H397	2589	140	8	168875	507903	409879	283313	33071
140258908-02a	H397	2589	140	8	35775	93068	84918	52621	7829
140258908-02b	H402	2589	140	8	206128	568671	384725	269184	31903
140258924-01	H397	2589	140	24	203157	811034	359658	316101	54281
140258924-02	H402	2589	140	24	58849	236093	104412	92662	17625
140258948-01	H397	2589	140	48	100845	483647	144328	155325	34364
140258948-02	H397	2589	140	48	44215	220643	77872	80289	18883
140258972-01	H397	2589	140	72	25965	147462	48601	54852	15780
140258972-02	H397	2589	140	72	19313	112129	40548	43708	12901
140258996-01a	H397	2589	140	96	11870	72567	24230	27789	9984
140258996-01b	H402	2589	140	96	11654	68618	19795	24798	8908
140258996-02	H397	2589	140	96	44928	282385	86538	107750	34536
1402589120-02a	H397	2589	140	120	7008	44771	14627	19255	7867
1402589120-02b	H402	2589	140	120	7476	42069	13604	16371	5472
1402589120-02c	H420	2589	140	120	5927	41349	12679	17456	5974
1404126030h	G483	4126	0	0	1206964	2317868	1725591	1129001	137703
1404126040h	G483	4126	0	0	938264	1782969	1400741	890910	105248
Cont4126-01	H398	4126	0	0	424406	827877	689913	431181	48750
Cont4126-02	H398	4126	0	0	440010	831393	695483	430543	52038
804126120-01	H398	4126	80	120	573487	1142016	791948	528531	43988
804126120-02	H420	4126	80	120	611905	1218690	883106	591511	67999
804126720-01	H398	4126	80	720	544249	1063144	851608	543774	59632
804126720-02	H420	4126	80	720	600541	1160119	979840	616168	81013
8041261440-01	H420	4126	80	1440	419300	889001	567513	412748	35263
8041261440-02	H420	4126	80	1440	212075	451289	291149	214662	18523
1104126120-01	H398	4126	110	120	416877	1088100	677217	503893	47113
1104126120-02	H398	4126	110	120	589919	1496163	928252	693151	66235

Appendix 4.2 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx] %	[Glx] %	[Ser] %
140258904-01	952254	685198	561425	216541	682808	283030	953142	450258	7.64%	16.51%	13.61%
140258904-02	414969	255694	209817	86295	264323	108014	348644	168218	7.02%	15.71%	14.37%
140258906-01	71512	48678	40880	13935	50641	20551	66083	32679	6.83%	16.27%	14.02%
140258906-02	270170	176396	156615	64479	192577	82230	259492	125052	6.87%	16.14%	13.55%
140258908-01	389332	257271	223674	80372	285887	112143	356268	182236	5.57%	16.75%	13.51%
140258908-02a	83928	48127	43120	24233	52099	22073	69713	34055	5.93%	15.42%	14.07%
140258908-02b	375127	267644	251166	47056	304312	126618	414427	203792	6.48%	17.87%	12.09%
140258924-01	522068	443129	411676	246241	477252	234253	722140	344760	4.32%	17.25%	7.65%
140258924-02	152224	134807	128187	48285	149693	70870	217037	109547	4.25%	17.04%	7.54%
140258948-01	267780	302804	265578	116148	325101	170051	511483	254226	3.56%	17.10%	5.10%
140258948-02	158969	174585	135329	66484	164411	88290	252422	127253	3.08%	15.38%	5.43%
140258972-01	133018	156242	111350	46268	142670	84931	217795	113213	2.27%	12.91%	4.26%
140258972-02	113873	132161	89005	41074	112715	69423	175344	90228	2.10%	12.18%	4.41%
140258996-01a	82526	95920	65408	34894	83537	53569	133068	70161	1.77%	10.84%	3.62%
140258996-01b	70437	92129	61402	33254	83398	49878	124860	67645	1.87%	10.99%	3.17%
140258996-02	294188	350826	247478	118798	315173	194082	486752	252455	1.82%	11.46%	3.51%
1402589120-02a	67288	72168	51213	21945	64622	40676	93421	50147	1.45%	9.27%	3.03%
1402589120-02b	51393	66404	44659	20756	61472	38323	91222	50043	1.69%	9.50%	3.07%
1402589120-02c	54321	66332	45626	21095	60867	37204	86864	47863	1.36%	9.46%	2.90%
1404126030h	1393436	1183109	863264	546661	1132113	473479	1658974	736373	9.06%	17.40%	12.95%
1404126040h	1164386	902842	700801	407829	881104	356985	1269194	564631	8.97%	17.04%	13.39%
Cont4126-01	414546	420551	353451	153023	422331	164976	594747	269672	8.85%	17.27%	14.39%
Cont4126-02	467725	422022	362231	189908	432398	186033	628969	275429	8.81%	16.65%	13.93%
804126120-01	549149	543850	486700	110326	572200	232131	856107	373449	9.16%	18.24%	12.65%
804126120-02	694966	588141	533291	166863	597554	229582	888758	393456	8.90%	17.72%	12.84%
804126720-01	551952	537208	453382	192763	539795	219706	779514	345889	8.86%	17.30%	13.86%
804126720-02	790920	600644	513849	228353	606991	250617	863474	392042	8.48%	16.38%	13.83%
8041261440-01	405941	419507	394832	126528	434796	155589	657896	285956	8.76%	18.58%	11.86%
8041261440-02	212891	213365	203062	31746	226643	77859	332386	149397	8.76%	18.64%	12.02%
1104126120-01	511380	511215	464143	23253	561714	214045	785721	375043	7.35%	19.20%	11.95%
1104126120-02	744205	718862	646317	95534	783925	305197	1095549	517526	7.41%	18.79%	11.66%

Appendix 4.2 continued.

ID	[L-Thr] %	[L-His] %	[Gly] %	[L-Arg] %	[Ala] %	[Tyr] %	[Val] %	[Phe] %	[Leu] %	[Ile] %
140258904-01	8.58%	1.23%	12.18%	8.76%	7.18%	2.77%	8.73%	3.62%	12.19%	5.76%
140258904-02	9.13%	1.25%	13.62%	8.39%	6.89%	2.83%	8.67%	3.54%	11.44%	5.52%
140258906-01	9.17%	1.15%	12.69%	8.64%	7.25%	2.47%	8.98%	3.65%	11.72%	5.80%
140258906-02	8.81%	1.11%	12.57%	8.21%	7.29%	3.00%	8.96%	3.83%	12.07%	5.82%
140258908-01	9.34%	1.09%	12.84%	8.48%	7.37%	2.65%	9.43%	3.70%	11.75%	6.01%
140258908-02a	8.72%	1.30%	13.91%	7.98%	7.15%	4.02%	8.63%	3.66%	11.55%	5.64%
140258908-02b	8.46%	1.00%	11.78%	8.41%	7.89%	1.48%	9.56%	3.98%	13.02%	6.40%
140258924-01	6.72%	1.15%	11.10%	9.42%	8.75%	5.24%	10.15%	4.98%	15.36%	7.33%
140258924-02	6.69%	1.27%	10.99%	9.73%	9.25%	3.49%	10.80%	5.12%	15.67%	7.91%
140258948-01	5.49%	1.21%	9.47%	10.70%	9.39%	4.11%	11.49%	6.01%	18.08%	8.99%
140258948-02	5.59%	1.32%	11.08%	12.17%	9.43%	4.63%	11.46%	6.15%	17.59%	8.87%
140258972-01	4.80%	1.38%	11.65%	13.68%	9.75%	4.05%	12.49%	7.44%	19.07%	9.91%
140258972-02	4.75%	1.40%	12.37%	14.36%	9.67%	4.46%	12.25%	7.54%	19.05%	9.80%
140258996-01a	4.15%	1.49%	12.32%	14.32%	9.77%	5.21%	12.48%	8.00%	19.87%	10.48%
140258996-01b	3.97%	1.43%	11.28%	14.75%	9.83%	5.32%	13.35%	7.98%	19.99%	10.83%
140258996-02	4.37%	1.40%	11.93%	14.23%	10.04%	4.82%	12.79%	7.87%	19.75%	10.24%
1402589120-02a	3.99%	1.63%	13.94%	14.95%	10.61%	4.54%	13.38%	8.42%	19.35%	10.39%
1402589120-02b	3.70%	1.24%	11.60%	14.99%	10.08%	4.69%	13.88%	8.65%	20.60%	11.30%
1402589120-02c	3.99%	1.37%	12.42%	15.17%	10.44%	4.82%	13.92%	8.51%	19.87%	10.95%
1404126030h	8.48%	1.03%	10.46%	8.88%	6.48%	4.10%	8.50%	3.55%	12.45%	5.53%
1404126040h	8.51%	1.01%	11.13%	8.63%	6.70%	3.90%	8.42%	3.41%	12.13%	5.40%
Cont4126-01	8.99%	1.02%	8.65%	8.77%	7.37%	3.19%	8.81%	3.44%	12.40%	5.62%
Cont4126-02	8.62%	1.04%	9.37%	8.45%	7.26%	3.80%	8.66%	3.73%	12.60%	5.52%
804126120-01	8.44%	0.70%	8.77%	8.69%	7.77%	1.76%	9.14%	3.71%	13.68%	5.97%
804126120-02	8.60%	0.99%	10.10%	8.55%	7.75%	2.43%	8.69%	3.34%	12.92%	5.72%
804126720-01	8.85%	0.97%	8.98%	8.74%	7.38%	3.14%	8.78%	3.58%	12.68%	5.63%
804126720-02	8.70%	1.14%	11.16%	8.48%	7.25%	3.22%	8.57%	3.54%	12.19%	5.53%
8041261440-01	8.63%	0.74%	8.48%	8.77%	8.25%	2.64%	9.09%	3.25%	13.75%	5.98%
8041261440-02	8.86%	0.76%	8.79%	8.81%	8.39%	1.31%	9.36%	3.22%	13.73%	6.17%
1104126120-01	8.89%	0.83%	9.02%	9.02%	8.19%	0.41%	9.91%	3.78%	13.86%	6.62%
1104126120-02	8.71%	0.83%	9.35%	9.03%	8.12%	1.20%	9.85%	3.83%	13.76%	6.50%

Appendix 4.2 continued.

ID	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
140258904-01	0.592	0.081	0.082	0.053	0.046	0.058	0.023	0.049	0.047	0.041
140258904-02	0.596	0.081	0.085	0.058	0.051	0.057	0.027	0.051	0.052	0.057
140258906-01	0.664	0.105	0.109	0.062	0.061	0.071	0.026	0.061	0.055	0.050
140258906-02	0.651	0.108	0.095	0.071	0.067	0.073	0.027	0.060	0.056	0.052
140258908-01	0.628	0.132	0.111	0.075	0.077	0.079	0.029	0.072	0.057	0.048
140258908-02a	0.670	0.130	0.111	0.099	0.087	0.097	0.033	0.077	0.071	0.082
140258908-02b	0.612	0.126	0.085	0.072	0.070	0.083	0.030	0.080	0.054	0.054
140258924-01	0.468	0.199	0.186	0.124	0.118	0.126	0.043	0.128	0.083	0.073
140258924-02	0.481	0.210	0.175	0.136	0.148	0.128	0.044	0.129	0.081	0.062
140258948-01	0.356	0.214	0.211	0.202	0.165	0.165	0.060	0.181	0.110	0.093
140258948-02	0.397	0.236	0.257	0.220	0.167	0.173	0.059	0.180	0.115	0.108
140258972-01	0.418	0.278	0.264	0.319	0.210	0.243	0.083	0.220	0.139	0.129
140258972-02	0.463	0.302	0.258	0.339	0.212	0.246	0.085	0.224	0.148	0.144
140258996-01a	0.490	0.337	0.262	0.411	0.241	0.295	0.092	0.258	0.164	0.185
140258996-01b	0.420	0.332	0.263	0.397	0.239	0.291	0.093	0.255	0.152	0.146
140258996-02	0.427	0.321	0.297	0.379	0.231	0.282	0.094	0.249	0.155	0.133
1402589120-02a	0.480	0.381	0.250	0.485	0.289	0.325	0.110	0.266	0.167	0.139
1402589120-02b	0.425	0.392	0.223	0.459	0.267	0.331	0.109	0.277	0.168	0.156
1402589120-02c	0.443	0.376	0.284	0.456	0.267	0.344	0.112	0.285	0.174	0.129
1404126030h	0.082	0.046	0.008	0.040	0.035	0.039	0.016	0.041	0.045	0.025
1404126040h	0.081	0.045	0.009	0.039	0.030	0.035	0.015	0.040	0.046	0.025
Cont4126-01	0.074	0.040	0.009	0.036	0.031	0.031	0.014	0.031	0.037	0.021
Cont4126-02	0.074	0.040	0.011	0.035	0.029	0.035	0.015	0.032	0.036	0.022
804126120-01	0.182	0.049	0.024	0.041	0.032	0.072	0.023	0.052	0.041	0.033
804126120-02	0.169	0.045	0.026	0.037	0.034	0.037	0.021	0.049	0.039	0.021
804126720-01	0.095	0.039	0.011	0.034	0.027	0.041	0.018	0.034	0.036	0.024
804126720-02	0.102	0.042	0.012	0.035	0.034	0.038	0.021	0.035	0.041	0.019
8041261440-01	0.231	0.055	0.041	0.044	0.047	0.073	0.021	0.062	0.043	0.024
8041261440-02	0.233	0.061	0.042	0.053	0.057	0.059	0.024	0.074	0.047	0.027
1104126120-01	0.555	0.105	0.101	0.068	0.076	0.097	0.029	0.086	0.061	0.047
1104126120-02	0.571	0.105	0.105	0.069	0.073	0.107	0.036	0.090	0.062	0.042

Appendix 4.2 continued.

ID	C%wtEA	N%wtEA	H%wtEA	O%wtEA	S%wtEA	C%wtAA	N%wtAA	H%wtAA	O%wtAA
140258904-01	46.61	15.02	6.83	28.38	2.65	50.84	17.87	6.95	24.34
140258904-02	45.67	14.61	6.69	26.88	2.46	50.61	17.93	6.91	24.56
140258906-01	46.80	14.75	6.66	29.50	3.00	50.76	17.88	6.95	24.41
140258906-02	45.57	13.50	6.46	29.22	2.72	50.99	17.75	6.96	24.30
140258908-01	46.11	13.09	6.39	29.48	4.24	50.98	17.80	6.99	24.23
140258908-02a	46.42	12.17	6.51	29.90	3.42	50.96	17.78	6.92	24.34
140258908-02b	46.42	12.17	6.51	29.90	3.42	51.20	17.76	7.05	23.99
140258924-01	0.68	3.79	5.75	31.10	1.86	53.02	17.47	7.20	22.31
140258924-02	48.76	0.00	5.95	-	1.67	52.98	17.62	7.27	22.14
140258948-01	215.91	72.44	32.52	-	12.41	54.07	17.45	7.42	21.07
140258948-02	-	-	-	-	-	53.94	17.78	7.40	20.88
140258972-01	-	-	-	-	-	54.62	17.94	7.53	19.91
140258972-02	-	-	-	-	-	54.58	18.07	7.51	19.83
140258996-01a	-	-	-	-	-	55.12	17.95	7.57	19.35
140258996-01b	-	-	-	-	-	55.34	17.91	7.61	19.14
140258996-02	-	-	-	-	-	55.04	17.95	7.57	19.44
1402589120-02a	-	-	-	-	-	55.09	18.23	7.58	19.10
1402589120-02b	-	-	-	-	-	55.59	17.91	7.67	18.83
1402589120-02c	-	-	-	-	-	55.42	18.05	7.64	18.90
1404126030h	-	-	-	-	-	51.04	17.66	6.93	24.38
1404126040h	-	-	-	-	-	50.86	17.71	6.91	24.53
Cont4126-01	44.57	14.73	6.65	27.95	3.10	50.95	17.57	6.97	24.51
Cont4126-02	43.73	14.61	6.43	27.98	3.07	51.13	17.52	6.95	24.40
804126120-01	45.90	14.73	6.64	26.99	2.81	51.11	17.58	7.04	24.27
804126120-02	45.47	14.93	6.90	26.71	2.58	50.90	17.71	6.98	24.42
804126720-01	10.11	2.80	1.15	28.33	0.32	51.02	17.58	6.97	24.43
804126720-02	44.40	14.51	6.92	27.52	3.36	50.85	17.74	6.93	24.48
8041261440-01	45.21	14.31	6.61	27.65	3.01	51.25	17.55	7.05	24.15
8041261440-02	44.34	14.03	6.55	27.73	2.51	51.05	17.66	7.07	24.22
1104126120-01	45.15	14.15	6.84	28.00	2.60	51.23	17.69	7.12	23.96
1104126120-02	45.35	14.14	6.57	31.06	2.48	51.34	17.67	7.11	23.89

Appendix 4.2 continued.

ID	C%wtAA (deamid)	N%wtAA (deamid)	H%wtAA (deamid)	O%wtAA (deamid)
140258904-01	50.97	16.76	6.90	25.37
140258904-02	50.72	16.88	6.87	25.53
140258906-01	50.88	16.82	6.91	25.39
140258906-02	51.12	16.68	6.92	25.28
140258908-01	51.09	16.79	6.95	25.17
140258908-02a	51.07	16.80	6.88	25.25
140258908-02b	51.34	16.64	7.01	25.02
140258924-01	53.17	16.50	7.17	23.16
140258924-02	53.13	16.66	7.23	22.98
140258948-01	54.23	16.53	7.39	21.85
140258948-02	54.08	16.98	7.37	21.56
140258972-01	54.74	17.30	7.51	20.45
140258972-02	54.70	17.48	7.49	20.33
140258996-01a	55.23	17.43	7.55	19.79
140258996-01b	55.45	17.37	7.60	19.58
140258996-02	55.16	17.39	7.56	19.90
1402589120-02a	55.18	17.79	7.57	19.46
1402589120-02b	55.69	17.44	7.66	19.21
1402589120-02c	55.51	17.60	7.63	19.26
1404126030h	51.19	16.42	6.88	25.50
1404126040h	51.00	16.49	6.86	25.64
Cont4126-01	51.10	16.35	6.92	25.63
Cont4126-02	51.28	16.33	6.91	25.49
804126120-01	51.28	16.30	6.99	25.43
804126120-02	51.05	16.47	6.93	25.55
804126720-01	51.17	16.36	6.93	25.54
804126720-02	50.99	16.58	6.89	25.55
8041261440-01	51.41	16.27	7.00	25.31
8041261440-02	51.21	16.39	7.02	25.38
1104126120-01	51.38	16.47	7.08	25.07
1104126120-02	51.49	16.46	7.06	24.99

Appendix 4.2 continued.

ID	C%wtAA (oxid)	N%wtAA (oxid)	H%wtAA (oxid)	O%wtAA (oxid)	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$
140258904-01	50.72	14.45	6.53	28.30	-	-	-
140258904-02	50.48	14.65	6.48	28.39	-	-	-
140258906-01	50.66	14.56	6.53	28.25	-	-	-
140258906-02	50.82	14.51	6.54	28.13	-	-	-
140258908-01	50.87	14.57	6.56	28.00	-25.51	7.94	-96.58
140258908-02a	50.72	14.64	6.50	28.14	-25.56	7.51	-
140258908-02b	51.11	14.44	6.64	27.81	-	-	-
140258924-01	52.65	14.05	6.79	26.51	-	-	-115.28
140258924-02	52.69	14.14	6.86	26.30	-	-	-
140258948-01	53.70	13.82	7.02	25.46	-	-	-
140258948-02	53.62	13.99	6.98	25.41	-	-	-
140258972-01	54.27	14.02	7.11	24.60	-	-	-
140258972-02	54.24	14.07	7.09	24.59	-	-	-
140258996-01a	54.68	14.01	7.15	24.15	-	-	-
140258996-01b	54.92	13.89	7.20	23.99	-	-	-
140258996-02	54.64	14.01	7.16	24.20	-	-	-
1402589120-02a	54.66	14.25	7.17	23.92	-	-	-
1402589120-02b	55.16	13.96	7.26	23.62	-	-	-
1402589120-02c	55.00	14.06	7.22	23.71	-	-	-
1404126030h	50.88	14.11	6.49	28.51	-26.01	4.45	-113.16
1404126040h	50.72	14.24	6.48	28.56	-	-	-
Cont4126-01	50.86	14.08	6.53	28.54	-	-	-
Cont4126-02	50.94	14.11	6.52	28.43	-	-	-
804126120-01	51.09	14.10	6.61	28.21	-	-	-
804126120-02	50.84	14.24	6.55	28.36	-	-	-
804126720-01	50.92	14.09	6.54	28.45	-25.97	4.85	-
804126720-02	50.71	14.34	6.51	28.44	-	-	-
8041261440-01	51.23	14.05	6.62	28.10	-25.71	4.33	-113.89
8041261440-02	51.11	14.16	6.64	28.09	-25.45	4.43	-116.29
1104126120-01	51.28	14.18	6.69	27.84	-	-	-114.96
1104126120-02	51.34	14.17	6.68	27.81	-	-	-

Appendix 4.2 continued.

ID	$\delta^{18}O$/‰	$C:N_{atomISOT}$
140258904-01	-	-
140258904-02	-	-
140258906-01	-	-
140258906-02	-	-
140258908-01	11.64	3.87
140258908-02a	-	3.81
140258908-02b	-	-
140258924-01	11.76	-
140258924-02	-	-
140258948-01	-	-
140258948-02	-	-
140258972-01	-	-
140258972-02	-	-
140258996-01a	-	-
140258996-01b	-	-
140258996-02	-	-
1402589120-02a	-	-
1402589120-02b	-	-
1402589120-02c	-	-
1404126030h	11.45	3.53
1404126040h	-	-
Cont4126-01	-	-
Cont4126-02	-	-
804126120-01	-	-
804126120-02	-	-
804126720-01	-	3.53
804126720-02	-	-
8041261440-01	11.30	3.70
8041261440-02	11.63	3.69
1104126120-01	10.65	-
1104126120-02	-	-

Appendix 4.2 continued.

ID	RP-HPLC run	Sample	Temperature/°C	Time/h	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]
1104126240-01	H398	4126	110	240	127033	416535	186461	160011	20504
1104126240-02	H398	4126	110	240	260252	837518	359316	317011	35606
1104126480-01	H398	4126	110	480	269357	1066373	293238	309597	47747
1104126480-02	H398	4126	110	480	174931	691393	188863	201076	31800
140412601-01	H397	4126	140	1	416075	830334	700997	444216	52092
140412601-02	H420	4126	140	1	431629	836955	678983	426239	57255
140412602-01	H397	4126	140	2	521865	1047490	863051	554209	69128
140412602-02	H397	4126	140	2	517189	1051998	863977	550389	58776
140412604-01	H397	4126	140	4	387564	856483	703868	470582	59498
140412604-02	H397	4126	140	4	589158	1279229	1017967	672670	84141
140412606-01	H397	4126	140	6	460325	1127744	873610	610170	66227
140412606-02	H398	4126	140	6	381829	897121	663259	458021	59728
140412608-01	H398	4126	140	8	387935	984315	701480	496242	61373
140412608-02	H398	4126	140	8	420083	1036901	754260	522596	51276
140412624-01	H398	4126	140	24	228397	885531	349664	312885	29458
140412624-02	H398	4126	140	24	236511	865521	371859	317148	34549
14041260148h	G483	4126	140	48	516098	2396720	497934	575280	86215
14041260248h	G483	4126	140	48	438451	2020695	396245	473118	95532
140412648-01	H398	4126	140	48	185076	735077	215610	208537	34814
140412648-02	H398	4126	140	48	177842	795598	186182	206544	40643
140412672-01	H420	4126	140	72	156006	737096	147131	169045	36085
140412696-01	H398	4126	140	96	81993	417428	82420	94510	21927
140412696-02	H398	4126	140	96	91901	445200	85300	99338	25352
1404126120-01	H420	4126	140	120	166813	872506	167018	192824	55909
1404126120-02	H420	4126	140	120	113896	597625	113137	133204	41363
1404129030h	G483	4129	0	0	1171091	2195579	1771849	1110645	125762
1404129040h	G483	4129	0	0	897653	1688520	1347494	843249	95885
Cont4129-01b	H429	4129	0	0	362383	687927	588858	370574	49884
Cont4129-01	H420	4129	0	0	39418	78120	59995	36183	3932
Cont4129-02	H402	4129	0	0	239365	469255	395812	248310	33939
804129120-01	H398	4129	80	120	239271	465198	382207	244813	33778

Appendix 4.2 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx] %	[Glx] %	[Ser] %
1104126240-01	167976	188996	180622	35826	216780	83148	316533	153022	6.15%	20.18%	9.03%
1104126240-02	326195	382678	361425	56216	434056	170929	640759	304542	6.34%	20.41%	8.76%
1104126480-01	277425	472190	448299	114197	550307	210300	865478	409804	5.54%	21.93%	6.03%
1104126480-02	185769	314125	293143	86987	363381	142906	578245	278602	5.44%	21.49%	5.87%
140412601-01	565706	422776	362615	117484	421709	176937	613052	271438	8.37%	16.70%	14.10%
140412601-02	541154	419516	382407	181879	434598	176308	629643	282630	8.53%	16.54%	13.42%
140412602-01	761621	530824	465651	127055	553640	224647	781262	345012	8.26%	16.59%	13.67%
140412602-02	709857	528140	456713	101020	545677	218896	768704	343561	8.36%	17.00%	13.96%
140412604-01	664534	440539	387637	174061	478975	196746	634876	300841	7.29%	16.11%	13.24%
140412604-02	957721	650830	573174	150641	687316	282053	937797	434270	7.69%	16.69%	13.28%
140412606-01	832061	557467	515708	144255	641317	256787	833435	405002	6.80%	16.67%	12.91%
140412606-02	622519	428328	387915	110399	480494	188986	645231	310795	7.33%	17.23%	12.74%
140412608-01	686766	467032	424296	126390	523767	203939	685419	333413	6.91%	17.53%	12.49%
140412608-02	554301	511875	459003	119309	577539	233102	757190	367325	7.18%	17.72%	12.89%
140412624-01	327743	373651	403684	136663	480619	190526	689476	333370	5.23%	20.27%	8.01%
140412624-02	352927	372325	395447	156020	479870	196454	684737	332525	5.35%	19.57%	8.41%
14041260148h	690808	913639	967889	562657	1233032	514073	2039192	990303	4.66%	21.65%	4.50%
14041260248h	610764	768930	820458	381999	1050888	423776	1740459	851759	4.71%	21.72%	4.26%
140412648-01	227154	304680	334183	137777	407035	167389	640093	312374	5.13%	20.39%	5.98%
140412648-02	226362	330546	365694	157738	445625	187442	725658	353851	4.60%	20.56%	4.81%
140412672-01	207507	296914	356154	152149	419493	167225	698601	352960	4.33%	20.48%	4.09%
140412696-01	107285	190181	205858	94334	262491	118442	437729	221312	3.82%	19.45%	3.84%
140412696-02	118490	208562	219715	98002	274053	127812	463449	233416	4.03%	19.51%	3.74%
1404126120-01	261447	389162	442630	196622	562288	247294	944635	490149	3.63%	18.97%	3.63%
1404126120-02	181651	262266	302214	121966	384083	168248	643819	333154	3.63%	19.07%	3.61%
1404129030h	1526495	1104273	892166	515013	1075550	436220	1538439	684438	8.98%	16.83%	13.58%
1404129040h	1146933	844536	687158	346925	825505	337831	1182623	522872	9.05%	17.02%	13.58%
Cont4129-01b	462962	361702	318257	159666	364032	148934	517482	235566	9.18%	17.42%	14.91%
Cont4129-01	43949	37581	35251	9123	39112	15242	56771	25951	8.90%	17.63%	13.54%
Cont4129-02	264680	245483	201955	92960	244592	90331	327545	154059	8.66%	16.98%	14.33%
804129120-01	292963	236143	201846	79533	240549	97956	333335	149356	8.67%	16.85%	13.84%

Appendix 4.2 continued.

ID	[L-Thr] %	[L-His] %	[Gly] %	[L-Arg] %	[Ala] %	[Tyr] %	[Val] %	[Phe] %	[Leu] %	[Ile] %
1104126240-01	7.75%	0.99%	8.14%	9.15%	8.75%	1.74%	10.50%	4.03%	15.33%	7.41%
1104126240-02	7.72%	0.87%	7.95%	9.32%	8.81%	1.37%	10.58%	4.17%	15.61%	7.42%
1104126480-01	6.37%	0.98%	5.71%	9.71%	9.22%	2.35%	11.32%	4.33%	17.80%	8.43%
1104126480-02	6.25%	0.99%	5.77%	9.76%	9.11%	2.70%	11.30%	4.44%	17.97%	8.66%
140412601-01	8.93%	1.05%	11.38%	8.50%	7.29%	2.36%	8.48%	3.56%	12.33%	5.46%
140412601-02	8.42%	1.13%	10.70%	8.29%	7.56%	3.59%	8.59%	3.48%	12.44%	5.59%
140412602-01	8.78%	1.09%	12.06%	8.41%	7.37%	2.01%	8.77%	3.56%	12.37%	5.46%
140412602-02	8.90%	0.95%	11.47%	8.54%	7.38%	1.63%	8.82%	3.54%	12.42%	5.55%
140412604-01	8.85%	1.12%	12.50%	8.29%	7.29%	3.27%	9.01%	3.70%	11.94%	5.66%
140412604-02	8.77%	1.10%	12.49%	8.49%	7.48%	1.97%	8.97%	3.68%	12.23%	5.66%
140412606-01	9.02%	0.98%	12.30%	8.24%	7.62%	2.13%	9.48%	3.79%	12.32%	5.99%
140412606-02	8.80%	1.15%	11.96%	8.23%	7.45%	2.12%	9.23%	3.63%	12.39%	5.97%
140412608-01	8.84%	1.09%	12.23%	8.32%	7.56%	2.25%	9.33%	3.63%	12.21%	5.94%
140412608-02	8.93%	0.88%	9.47%	8.75%	7.84%	2.04%	9.87%	3.98%	12.94%	6.28%
140412624-01	7.16%	0.67%	7.50%	8.55%	9.24%	3.13%	11.00%	4.36%	15.78%	7.63%
140412624-02	7.17%	0.78%	7.98%	8.42%	8.94%	3.53%	10.85%	4.44%	15.48%	7.52%
14041260148h	5.20%	0.78%	6.24%	8.25%	8.74%	5.08%	11.14%	4.64%	18.42%	8.95%
14041260248h	5.09%	1.03%	6.56%	8.26%	8.82%	4.11%	11.29%	4.55%	18.71%	9.15%
140412648-01	5.78%	0.97%	6.30%	8.45%	9.27%	3.82%	11.29%	4.64%	17.76%	8.66%
140412648-02	5.34%	1.05%	5.85%	8.54%	9.45%	4.08%	11.52%	4.84%	18.75%	9.15%
140412672-01	4.70%	1.00%	5.76%	8.25%	9.89%	4.23%	11.65%	4.65%	19.41%	9.81%
140412696-01	4.40%	1.02%	5.00%	8.86%	9.59%	4.40%	12.23%	5.52%	20.40%	10.31%
140412696-02	4.35%	1.11%	5.19%	9.14%	9.63%	4.29%	12.01%	5.60%	20.31%	10.23%
1404126120-01	4.19%	1.22%	5.68%	8.46%	9.62%	4.27%	12.22%	5.38%	20.53%	10.66%
1404126120-02	4.25%	1.32%	5.80%	8.37%	9.64%	3.89%	12.25%	5.37%	20.54%	10.63%
1404129030h	8.52%	0.96%	11.70%	8.47%	6.84%	3.95%	8.25%	3.34%	11.79%	5.25%
1404129040h	8.50%	0.97%	11.56%	8.51%	6.93%	3.50%	8.32%	3.40%	11.92%	5.27%
Cont4129-01b	9.39%	1.26%	11.73%	9.16%	8.06%	4.04%	9.22%	3.77%	13.11%	5.97%
Cont4129-01	8.17%	0.89%	9.92%	8.48%	7.96%	2.06%	8.83%	3.44%	12.81%	5.86%
Cont4129-02	8.99%	1.23%	9.58%	8.89%	7.31%	3.36%	8.85%	3.27%	11.86%	5.58%
804129120-01	8.87%	1.22%	10.61%	8.55%	7.31%	2.88%	8.71%	3.55%	12.07%	5.41%

Appendix 4.2 continued.

ID	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
1104126240-01	0.475	0.142	0.141	0.104	0.116	0.113	0.039	0.114	0.076	0.066
1104126240-02	0.479	0.139	0.143	0.100	0.106	0.114	0.043	0.119	0.076	0.052
1104126480-01	0.337	0.143	0.149	0.120	0.119	0.111	0.046	0.138	0.079	0.040
1104126480-02	0.342	0.145	0.147	0.122	0.124	0.116	0.047	0.144	0.086	0.064
140412601-01	0.197	0.045	0.020	0.037	0.033	0.046	0.017	0.038	0.041	0.029
140412601-02	0.203	0.049	0.022	0.044	0.051	0.040	0.018	0.041	0.041	0.019
140412602-01	0.358	0.057	0.039	0.043	0.039	0.042	0.019	0.042	0.043	0.031
140412602-02	0.354	0.056	0.036	0.041	0.037	0.041	0.020	0.044	0.043	0.038
140412604-01	0.615	0.095	0.087	0.062	0.074	0.062	0.039	0.061	0.055	0.044
140412604-02	0.567	0.084	0.073	0.058	0.065	0.066	0.027	0.059	0.052	0.035
140412606-01	0.668	0.123	0.106	0.070	0.083	0.075	0.031	0.074	0.064	0.042
140412606-02	0.638	0.108	0.098	0.065	0.071	0.067	0.030	0.068	0.058	0.043
140412608-01	0.627	0.126	0.107	0.071	0.083	0.081	0.033	0.079	0.061	0.044
140412608-02	0.659	0.127	0.114	0.075	0.090	0.092	0.034	0.082	0.064	0.044
140412624-01	0.459	0.201	0.184	0.121	0.149	0.125	0.051	0.141	0.092	0.059
140412624-02	0.492	0.196	0.163	0.117	0.141	0.122	0.046	0.132	0.090	0.064
14041260148h	0.336	0.206	0.168	0.145	0.171	0.134	0.059	0.174	0.108	0.065
14041260248h	0.339	0.193	0.139	0.141	0.175	0.130	0.058	0.175	0.106	0.061
140412648-01	0.371	0.174	0.129	0.129	0.151	0.126	0.051	0.156	0.099	0.070
140412648-02	0.319	0.187	0.161	0.142	0.161	0.133	0.055	0.171	0.103	0.072
140412672-01	0.272	0.171	0.116	0.154	0.173	0.134	0.056	0.187	0.108	0.064
140412696-01	0.241	0.171	0.119	0.199	0.180	0.159	0.064	0.211	0.122	0.097
140412696-02	0.279	0.180	0.136	0.225	0.183	0.170	0.065	0.212	0.120	0.094
1404126120-01	0.254	0.175	0.107	0.211	0.186	0.163	0.071	0.234	0.124	0.076
1404126120-02	0.251	0.173	0.109	0.205	0.180	0.155	0.068	0.220	0.118	0.068
1404129030h	0.081	0.045	0.009	0.040	0.030	0.034	0.015	0.041	0.047	0.027
1404129040h	0.084	0.046	0.008	0.039	0.030	0.034	0.014	0.039	0.047	0.026
Cont4129-01b	0.080	0.042	0.010	0.043	0.045	0.032	0.022	0.038	0.054	0.044
Cont4129-01	0.165	0.052	0.022	0.078	0.050	0.000	0.027	0.065	0.031	0.000
Cont4129-02	0.077	0.038	0.008	0.040	0.031	0.035	0.015	0.033	0.030	0.008
804129120-01	0.107	0.044	0.017	0.039	0.039	0.035	0.021	0.037	0.037	0.009

Appendix 4.2 continued.

ID	C%wtEA	N%wtEA	H%wtEA	O%wtEA	S%wtEA	C%wtAA	N%wtAA	H%wtAA	O%wtAA
1104126240-01	48.49	14.02	6.87	26.50	2.79	52.20	17.49	7.23	23.08
1104126240-02	48.60	14.64	7.23	27.11	2.91	52.22	17.50	7.25	23.03
1104126480-01	51.66	15.18	6.66	26.45	2.09	53.28	17.24	7.39	22.09
1104126480-02	51.41	15.19	6.79	25.60	2.66	53.43	17.20	7.41	21.96
140412601-01	44.88	15.25	6.80	28.51	2.05	50.68	17.80	6.94	24.59
140412601-02	44.65	15.14	6.82	28.38	1.80	51.01	17.65	6.94	24.40
140412602-01	44.25	14.65	6.63	27.43	2.34	50.66	17.86	6.94	24.53
140412602-02	44.60	15.63	6.50	27.91	2.42	50.61	17.84	6.96	24.59
140412604-01	45.58	13.72	6.80	29.71	2.00	50.97	17.76	6.95	24.32
140412604-02	44.80	14.08	6.74	28.34	2.12	50.75	17.89	6.96	24.40
140412606-01	45.15	12.60	6.31	30.44	2.22	51.01	17.76	7.00	24.23
140412606-02	45.24	14.21	6.46	30.40	2.32	50.95	17.78	6.99	24.29
140412608-01	45.53	13.18	6.56	29.09	2.54	50.97	17.80	6.99	24.25
140412608-02	44.96	13.89	6.26	8.12	2.72	51.32	17.58	7.06	24.04
140412624-01	41.60	12.10	5.25	34.30	2.07	52.85	17.16	7.28	22.71
140412624-02	45.71	12.97	5.89	32.51	1.61	52.82	17.16	7.25	22.77
14041260148h	-	-	-	-	-	54.15	16.75	7.41	21.69
14041260248h	-	-	-	-	-	54.06	16.87	7.43	21.64
140412648-01	47.96	12.85	5.93	29.67	1.59	53.72	16.94	7.39	21.95
140412648-02	46.50	12.17	5.48	-	0.90	54.18	16.85	7.45	21.51
140412672-01	-	-	-	-	-	54.46	16.76	7.51	21.27
140412696-01	-	-	-	-	-	55.02	16.67	7.58	20.72
140412696-02	-	-	-	-	-	54.94	16.77	7.57	20.73
1404126120-01	-	-	-	-	-	55.07	16.68	7.60	20.65
1404126120-02	-	-	-	-	-	55.01	16.71	7.60	20.68
1404129030h	-	-	-	-	-	50.73	17.74	6.88	24.65
1404129040h	-	-	-	-	-	50.70	17.77	6.89	24.65
Cont4129-01b	44.53	15.16	6.68	24.05	3.16	50.94	17.69	6.93	24.44
Cont4129-01	44.53	15.16	6.68	24.05	3.16	50.85	17.70	6.98	24.46
Cont4129-02	44.88	15.12	6.88	27.42	2.64	50.82	17.70	6.94	24.53
804129120-01	45.22	15.70	6.89	26.68	3.06	50.79	17.75	6.93	24.53

Appendix 4.2 continued.

ID	C%wtAA (deamid)	N%wtAA (deamid)	H%wtAA (deamid)	O%wtAA (deamid)
1104126240-01	52.37	16.28	7.19	24.15
1104126240-02	52.40	16.28	7.20	24.12
1104126480-01	53.48	15.98	7.35	23.18
1104126480-02	53.64	15.97	7.37	23.02
140412601-01	50.81	16.63	6.89	25.66
140412601-02	51.15	16.48	6.90	25.47
140412602-01	50.80	16.71	6.90	25.60
140412602-02	50.75	16.66	6.91	25.68
140412604-01	51.10	16.68	6.90	25.32
140412604-02	50.88	16.77	6.91	25.44
140412606-01	51.14	16.67	6.96	25.23
140412606-02	51.08	16.64	6.94	25.34
140412608-01	51.10	16.67	6.94	25.29
140412608-02	51.46	16.43	7.02	25.08
140412624-01	53.03	15.98	7.24	23.75
140412624-02	52.99	16.01	7.21	23.79
14041260148h	54.38	15.52	7.37	22.73
14041260248h	54.29	15.64	7.39	22.69
140412648-01	53.93	15.75	7.35	22.97
140412648-02	54.39	15.68	7.42	22.50
140412672-01	54.68	15.61	7.47	22.24
140412696-01	55.24	15.60	7.55	21.61
140412696-02	55.16	15.68	7.54	21.62
1404126120-01	55.28	15.63	7.57	21.51
1404126120-02	55.22	15.66	7.57	21.55
1404129030h	50.87	16.54	6.83	25.76
1404129040h	50.84	16.55	6.84	25.77
Cont4129-01b	51.08	16.54	6.89	25.49
Cont4129-01	51.00	16.46	6.94	25.60
Cont4129-02	50.97	16.51	6.89	25.63
804129120-01	50.93	16.56	6.89	25.62

Appendix 4.2 continued.

ID	C%wtAA (oxid)	N%wtAA (oxid)	H%wtAA (oxid)	O%wtAA (oxid)	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$
1104126240-01	52.13	13.94	6.81	27.12	-25.69	5.04	-
1104126240-02	52.18	13.91	6.83	27.08	-25.60	5.14	-129.07
1104126480-01	53.16	13.52	6.98	26.33	-	-	-
1104126480-02	53.29	13.50	7.00	26.22	-	-	-
140412601-01	50.60	14.41	6.51	28.48	-	-	-
140412601-02	50.84	14.28	6.52	28.36	-	-	-
140412602-01	50.59	14.50	6.52	28.39	-	-	-
140412602-02	50.59	14.45	6.53	28.43	-	-	-
140412604-01	50.80	14.48	6.52	28.19	-	-	-
140412604-02	50.67	14.54	6.54	28.26	-	-	-
140412606-01	50.91	14.52	6.58	27.99	-	-	-
140412606-02	50.84	14.45	6.57	28.13	-	-	-
140412608-01	50.87	14.48	6.57	28.09	-25.24	4.48	-117.74
140412608-02	51.24	14.19	6.63	27.94	-	-	-
140412624-01	52.66	13.80	6.87	26.67	-	-	-
140412624-02	52.57	13.83	6.84	26.75	-25.99	4.67	-131.32
14041260148h	53.77	13.36	7.02	25.84	-	-	-
14041260248h	53.72	13.44	7.05	25.79	-	-	-
140412648-01	53.41	13.54	7.00	26.06	-	-	-
140412648-02	53.82	13.43	7.07	25.68	-	-	-
140412672-01	54.10	13.43	7.14	25.33	-	-	-
140412696-01	54.59	13.28	7.21	24.92	-26.79	5.11	-
140412696-02	54.51	13.30	7.19	25.00	-	-	-162.27
1404126120-01	54.61	13.37	7.23	24.78	-	-	-
1404126120-02	54.56	13.40	7.24	24.81	-	-	-
1404129030h	50.59	14.33	6.46	28.63	-26.19	4.38	-119.35
1404129040h	50.58	14.33	6.47	28.63	-	-	-
Cont4129-01b	50.78	14.30	6.50	28.42	-	-	-
Cont4129-01	50.81	14.27	6.57	28.35	-	-	-
Cont4129-02	50.73	14.18	6.50	28.58	-	-	-
804129120-01	50.67	14.29	6.50	28.54	-	-	-

Appendix 4.2 continued.

ID	$\delta^{18}O$/‰	$C:N_{atomISOT}$
1104126240-01	-	4.03
1104126240-02	11.09	4.04
1104126480-01	-	-
1104126480-02	-	-
140412601-01	-	-
140412601-02	-	-
140412602-01	-	-
140412602-02	-	-
140412604-01	-	-
140412604-02	-	-
140412606-01	-	-
140412606-02	-	-
140412608-01	9.78	3.79
140412608-02	-	-
140412624-01	-	-
140412624-02	10.02	4.11
14041260148h	-	-
14041260248h	-	-
140412648-01	-	-
140412648-02	-	-
140412672-01	-	-
140412696-01	-	4.97
140412696-02	8.84	-
1404126120-01	-	-
1404126120-02	-	-
1404129030h	11.41	3.50
1404129040h	-	-
Cont4129-01b	-	-
Cont4129-01	-	-
Cont4129-02	-	-
804129120-01	-	-

Appendix 4.2 continued.

ID	RP-HPLC run	Sample	Temperature/°C	Time/h	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]
804129120-02	H398	4129	80	120	216986	427927	356904	226281	30544
804129720-02	H398	4129	80	720	198477	401285	284537	192715	21247
804129720-01	H420	4129	80	720	108048	214541	156941	106889	11560
8041291440-02	H398	4129	80	1440	536368	1149559	688307	517529	54001
8041291440-01	H398	4129	80	1440	670258	1433794	878817	656477	69744
1104129120-01	H398	4129	110	120	296681	775014	453657	339195	39612
1104129120-02	H398	4129	110	120	110308	284257	178439	130875	20130
1104129240-01	H398	4129	110	240	40536	132701	55202	45082	10762
1104129240-01b	H402	4129	110	240	75113	235044	99294	83951	12954
1104129240-02	H398	4129	110	240	56590	188042	93238	78445	13679
1104129480-02	H420	4129	110	480	180849	689120	209308	209370	33204
1104129480-01	H398	4129	110	480	47739	185110	59084	54667	12923
1104129480-02	H398	4129	110	480	15498	58020	21594	16810	5786
140412901-01	H398	4129	140	1	223740	452380	378579	232930	23954
140412901-02	H398	4129	140	1	156820	306407	241886	149713	15384
140412902-01	H398	4129	140	2	317987	875719	889155	523615	0
140412902-02	H398	4129	140	2	213355	431724	336749	221452	25478
140412904-01	H398	4129	140	4	329920	712856	564002	367261	49788
140412904-02	H398	4129	140	4	478317	1040226	836440	545400	63061
140412906-01	H398	4129	140	6	215648	504105	372271	249902	30143
140412906-02	H398	4129	140	6	453522	1037684	810694	550002	68167
140412908-01	H398	4129	140	8	271866	710299	545589	381404	47848
140412908-02	H398	4129	140	8	342321	833824	615143	422887	46617
140412924-01	H398	4129	140	24	78589	308739	134935	114831	23905
140412924-02	H398	4129	140	24	111132	418926	187155	163631	28749
14041290148h	G483	4129	140	48	314585	1497148	367300	414170	82208
14041290248h	G483	4129	140	48	387781	1794839	469628	496472	99702
140412948-01	H398	4129	140	48	47933	219736	67856	64493	18966
140412948-02	H398	4129	140	48	167489	772663	205047	217130	45121
140412972-01	H398	4129	140	72	241627	993204	333669	310701	69475
140412972-02	H398	4129	140	72	195496	649960	149395	170400	50811

Appendix 4.2 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx] %	[Glx] %	[Ser] %
804129120-02	273998	214704	187742	82732	221568	86047	309549	141897	8.47%	16.70%	13.93%
804129720-02	242253	191387	173441	45757	201724	77922	294935	128908	8.77%	17.73%	12.57%
804129720-01	117648	102011	97115	32217	109083	39663	158596	72505	8.82%	17.52%	12.81%
8041291440-02	589981	521021	498024	95838	558239	203616	842284	363365	8.80%	18.85%	11.29%
8041291440-01	773344	659180	623422	106767	701906	256197	1049077	453595	8.73%	18.69%	11.45%
1104129120-01	448179	343483	332778	70838	394583	155036	566415	263046	7.17%	18.74%	10.97%
1104129120-02	169147	130119	119516	51863	146728	54399	200487	94712	7.07%	18.21%	11.43%
1104129240-01	64406	56250	57796	21767	67695	27490	107291	48913	5.96%	19.53%	8.12%
1104129240-01b	102248	106220	103372	36332	123550	47927	188195	89394	6.27%	19.63%	8.29%
1104129240-02	97123	87873	80828	28223	98876	36405	141671	68574	5.76%	19.15%	9.50%
1104129480-02	208164	304259	301128	90450	356583	135710	575384	282433	5.53%	21.06%	6.40%
1104129480-01	63979	81071	79814	34670	96195	37828	154808	76649	5.28%	20.49%	6.54%
1104129480-02	24266	24253	26691	11715	29419	12159	52289	25061	5.18%	19.38%	7.21%
140412901-01	241535	230416	191885	56407	234888	92228	323236	146147	8.61%	17.41%	14.57%
140412901-02	164191	151361	133327	35796	156788	65434	227960	100996	8.94%	17.46%	13.78%
140412902-01	1833864	573891	454972	99619	463419	206542	758152	294864	4.73%	13.04%	13.24%
140412902-02	429898	211041	189161	55899	225155	92653	318186	141287	7.96%	16.10%	12.56%
140412904-01	544180	347650	316137	106480	385002	157668	528381	240689	7.67%	16.57%	13.11%
140412904-02	808500	515951	458059	166074	560898	227186	754931	353977	7.60%	16.53%	13.29%
140412906-01	384343	232698	223130	82685	270608	114461	369281	172113	7.22%	16.87%	12.46%
140412906-02	821404	513928	472603	200468	574734	237651	765387	367961	7.13%	16.32%	12.75%
140412908-01	552628	334133	312746	123648	390962	152457	503573	248021	6.41%	16.75%	12.86%
140412908-02	628174	398497	374904	111942	464860	193420	620896	293893	6.92%	16.85%	12.43%
140412924-01	182457	129461	146732	62015	174569	75058	257393	126171	4.66%	18.32%	8.01%
140412924-02	262473	185499	201317	72831	242877	101432	348179	171557	4.81%	18.13%	8.10%
14041290148h	679809	634606	749262	284508	918891	430750	1477821	752859	3.95%	18.79%	4.61%
14041290248h	777605	708852	887679	346204	1067173	473237	1694738	865332	4.14%	19.17%	5.02%
140412948-01	109217	97093	112606	52175	130918	61891	208313	102007	4.01%	18.37%	5.67%
140412948-02	338015	338114	377168	167846	443039	206297	731221	362130	4.15%	19.16%	5.08%
140412972-01	459834	455408	492130	207933	594533	280213	964827	491428	4.44%	18.26%	6.13%
140412972-02	266533	305684	341030	149859	416914	214584	705590	362472	5.32%	17.70%	4.07%

Appendix 4.2 continued.

ID	[L-Thr] %	[L-His] %	[Gly] %	[L-Arg] %	[Ala] %	[Tyr] %	[Val] %	[Phe] %	[Leu] %	[Ile] %
804129120-02	8.83%	1.19%	10.69%	8.38%	7.33%	3.23%	8.65%	3.36%	12.08%	5.54%
804129720-02	8.52%	0.94%	10.70%	8.46%	7.66%	2.02%	8.91%	3.44%	13.03%	5.70%
804129720-01	8.73%	0.94%	9.61%	8.33%	7.93%	2.63%	8.91%	3.24%	12.95%	5.92%
8041291440-02	8.49%	0.89%	9.68%	8.55%	8.17%	1.57%	9.16%	3.34%	13.81%	5.96%
8041291440-01	8.56%	0.91%	10.08%	8.59%	8.12%	1.39%	9.15%	3.34%	13.67%	5.91%
1104129120-01	8.20%	0.96%	10.84%	8.31%	8.05%	1.71%	9.54%	3.75%	13.70%	6.36%
1104129120-02	8.38%	1.29%	10.84%	8.34%	7.66%	3.32%	9.40%	3.49%	12.84%	6.07%
1104129240-01	6.63%	1.58%	9.48%	8.28%	8.50%	3.20%	9.96%	4.04%	15.79%	7.20%
1104129240-01b	7.01%	1.08%	8.54%	8.87%	8.63%	3.03%	10.32%	4.00%	15.72%	7.47%
1104129240-02	7.99%	1.39%	9.89%	8.95%	8.23%	2.87%	10.07%	3.71%	14.43%	6.99%
1104129480-02	6.40%	1.01%	6.36%	9.30%	9.20%	2.76%	10.90%	4.15%	17.59%	8.63%
1104129480-01	6.05%	1.43%	7.08%	8.97%	8.83%	3.84%	10.65%	4.19%	17.13%	8.48%
1104129480-02	5.62%	1.93%	8.11%	8.10%	8.92%	3.91%	9.83%	4.06%	17.47%	8.37%
140412901-01	8.97%	0.92%	9.30%	8.87%	7.39%	2.17%	9.04%	3.55%	12.44%	5.63%
140412901-02	8.53%	0.88%	9.36%	8.63%	7.60%	2.04%	8.94%	3.73%	12.99%	5.76%
140412902-01	7.79%	0.00%	27.30%	8.54%	6.77%	1.48%	6.90%	3.07%	11.29%	4.39%
140412902-02	8.26%	0.95%	16.04%	7.87%	7.06%	2.09%	8.40%	3.46%	11.87%	5.27%
140412904-01	8.54%	1.16%	12.65%	8.08%	7.35%	2.47%	8.95%	3.66%	12.28%	5.59%
140412904-02	8.67%	1.00%	12.85%	8.20%	7.28%	2.64%	8.91%	3.61%	12.00%	5.62%
140412906-01	8.36%	1.01%	12.86%	7.79%	7.47%	2.77%	9.05%	3.83%	12.36%	5.76%
140412906-02	8.65%	1.07%	12.91%	8.08%	7.43%	3.15%	9.04%	3.74%	12.03%	5.79%
140412908-01	8.99%	1.13%	13.03%	7.88%	7.37%	2.92%	9.22%	3.59%	11.87%	5.85%
140412908-02	8.55%	0.94%	12.69%	8.05%	7.58%	2.26%	9.39%	3.91%	12.55%	5.94%
140412924-01	6.81%	1.42%	10.83%	7.68%	8.71%	3.68%	10.36%	4.45%	15.27%	7.49%
140412924-02	7.08%	1.24%	11.36%	8.03%	8.71%	3.15%	10.51%	4.39%	15.07%	7.43%
14041290148h	5.20%	1.03%	8.53%	7.96%	9.40%	3.57%	11.53%	5.41%	18.54%	9.45%
14041290248h	5.30%	1.07%	8.31%	7.57%	9.48%	3.70%	11.40%	5.06%	18.11%	9.24%
140412948-01	5.39%	1.59%	9.13%	8.12%	9.41%	4.36%	10.95%	5.17%	17.42%	8.53%
140412948-02	5.38%	1.12%	8.38%	8.38%	9.35%	4.16%	10.98%	5.12%	18.13%	8.98%
140412972-01	5.71%	1.28%	8.45%	8.37%	9.05%	3.82%	10.93%	5.15%	17.74%	9.03%
140412972-02	4.64%	1.38%	7.26%	8.32%	9.28%	4.08%	11.35%	5.84%	19.21%	9.87%

Appendix 4.2 continued.

ID	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
804129120-02	0.105	0.043	0.020	0.040	0.040	0.037	0.020	0.032	0.040	0.031
804129720-02	0.194	0.050	0.031	0.043	0.040	0.065	0.023	0.046	0.042	0.032
804129720-01	0.189	0.047	0.030	0.048	0.048	0.069	0.019	0.041	0.042	0.036
8041291440-02	0.251	0.059	0.044	0.046	0.038	0.049	0.026	0.059	0.043	0.031
8041291440-01	0.237	0.058	0.045	0.047	0.041	0.062	0.027	0.058	0.043	0.031
1104129120-01	0.558	0.111	0.104	0.069	0.069	0.091	0.032	0.079	0.058	0.045
1104129120-02	0.571	0.106	0.108	0.072	0.073	0.097	0.030	0.077	0.056	0.022
1104129240-01	0.454	0.140	0.130	0.100	0.097	0.126	0.034	0.101	0.073	0.077
1104129240-01b	0.470	0.140	0.128	0.101	0.098	0.105	0.035	0.114	0.070	0.058
1104129240-02	0.491	0.148	0.149	0.098	0.100	0.094	0.037	0.102	0.073	0.059
1104129480-02	0.343	0.140	0.161	0.108	0.115	0.096	0.047	0.133	0.075	0.051
1104129480-01	0.338	0.138	0.130	0.125	0.122	0.157	0.044	0.111	0.077	0.081
1104129480-02	0.340	0.143	0.126	0.158	0.148	0.098	0.042	0.128	0.118	0.113
140412901-01	0.223	0.047	0.030	0.041	0.037	0.041	0.017	0.036	0.034	0.012
140412901-02	0.292	0.053	0.029	0.047	0.045	0.045	0.020	0.037	0.044	0.034
140412902-01	0.381	0.060	0.046	0.041	0.032	0.045	0.017	0.037	0.035	0.020
140412902-02	0.379	0.059	0.041	0.047	0.045	0.037	0.018	0.038	0.041	0.030
140412904-01	0.597	0.085	0.080	0.054	0.052	0.054	0.023	0.051	0.050	0.038
140412904-02	0.611	0.086	0.087	0.056	0.051	0.053	0.028	0.053	0.049	0.037
140412906-01	0.655	0.114	0.094	0.067	0.067	0.067	0.029	0.068	0.060	0.042
140412906-02	0.689	0.112	0.113	0.066	0.066	0.065	0.030	0.063	0.054	0.037
140412908-01	0.678	0.134	0.122	0.072	0.078	0.082	0.030	0.072	0.061	0.049
140412908-02	0.689	0.133	0.118	0.072	0.076	0.080	0.036	0.073	0.060	0.049
140412924-01	0.485	0.213	0.177	0.119	0.136	0.122	0.043	0.118	0.084	0.067
140412924-02	0.530	0.217	0.200	0.119	0.132	0.118	0.047	0.122	0.082	0.061
14041290148h	0.379	0.235	0.207	0.162	0.169	0.140	0.063	0.171	0.110	0.069
14041290248h	0.377	0.229	0.208	0.147	0.162	0.130	0.060	0.157	0.102	0.064
140412948-01	0.356	0.199	0.171	0.152	0.143	0.138	0.050	0.154	0.093	0.051
140412948-02	0.338	0.193	0.186	0.141	0.131	0.124	0.053	0.145	0.089	0.066
140412972-01	0.338	0.169	0.129	0.144	0.132	0.122	0.052	0.144	0.090	0.070
140412972-02	0.313	0.191	0.178	0.186	0.147	0.146	0.056	0.169	0.102	0.080

Appendix 4.2 continued.

ID	C%wtEA	N%wtEA	H%wtEA	O%wtEA	S%wtEA	C%wtAA	N%wtAA	H%wtAA	O%wtAA
804129120-02	45.67	15.66	7.05	26.28	2.65	50.83	17.70	6.93	24.54
804129720-02	44.94	14.87	6.83	27.48	3.39	50.88	17.74	6.99	24.39
804129720-01	43.70	14.27	6.73	26.88	3.33	51.01	17.61	7.00	24.38
8041291440-02	44.42	14.25	6.70	26.89	3.02	51.09	17.69	7.05	24.18
8041291440-01	45.07	14.51	6.46	26.78	2.94	51.00	17.75	7.04	24.22
1104129120-01	45.38	14.37	6.64	30.20	2.58	51.35	17.67	7.07	23.91
1104129120-02	45.58	14.66	6.66	28.05	2.37	51.37	17.64	7.02	23.98
1104129240-01	48.78	14.78	6.47	27.81	3.19	52.50	17.43	7.19	22.87
1104129240-01b	48.78	14.78	6.47	27.81	3.19	52.50	17.40	7.22	22.88
1104129240-02	49.31	14.76	7.39	26.49	2.79	52.00	17.61	7.15	23.24
1104129480-02	50.73	16.30	6.49	23.73	2.28	53.24	17.21	7.37	22.18
1104129480-01	50.57	15.35	6.81	14.59	2.38	53.31	17.20	7.33	22.16
1104129480-02	50.73	16.30	6.49	23.73	2.28	53.24	17.22	7.30	22.25
140412901-01	46.12	14.90	6.89	28.01	2.01	50.79	17.68	6.98	24.55
140412901-02	45.49	15.04	6.79	28.65	1.95	50.94	17.64	6.99	24.43
140412902-01	45.21	15.70	6.74	27.59	2.51	49.31	19.02	6.76	24.92
140412902-02	44.71	14.27	6.80	28.02	1.97	50.39	18.09	6.88	24.64
140412904-01	45.92	13.13	6.31	30.51	2.44	50.85	17.81	6.95	24.40
140412904-02	45.73	13.98	6.91	28.68	2.28	50.79	17.82	6.94	24.45
140412906-01	45.92	13.83	6.96	30.04	2.41	51.04	17.71	6.96	24.28
140412906-02	46.34	13.35	6.92	26.49	2.35	51.02	17.76	6.95	24.27
140412908-01	44.20	12.79	6.09	29.94	1.98	50.98	17.74	6.96	24.31
140412908-02	46.32	13.51	6.79	26.41	2.83	51.08	17.74	7.00	24.18
140412924-01	56.03	16.14	7.74	30.84	2.58	52.74	17.33	7.20	22.72
140412924-02	48.34	14.20	6.03	30.91	1.60	52.55	17.45	7.20	22.79
14041290148h	-	-	-	-	-	54.21	16.94	7.45	21.40
14041290248h	-	-	-	-	-	54.04	16.90	7.42	21.64
140412948-01	50.98	13.48	6.75	-	1.77	53.84	17.12	7.35	21.69
140412948-02	50.86	14.67	6.49	30.26	1.20	53.98	17.03	7.40	21.59
140412972-01	-	-	-	-	-	53.80	17.07	7.38	21.74
140412972-02	-	-	-	-	-	54.56	16.89	7.47	21.09

Appendix 4.2 continued.

ID	C%wtAA (deamid)	N%wtAA (deamid)	H%wtAA (deamid)	O%wtAA (deamid)
804129120-02	50.97	16.53	6.89	25.62
804129720-02	51.03	16.51	6.94	25.52
804129720-01	51.17	16.37	6.95	25.51
8041291440-02	51.25	16.40	7.00	25.35
8041291440-01	51.15	16.47	6.99	25.38
1104129120-01	51.50	16.47	7.03	25.00
1104129120-02	51.51	16.47	6.97	25.04
1104129240-01	52.68	16.25	7.15	23.92
1104129240-01b	52.68	16.20	7.18	23.93
1104129240-02	52.16	16.47	7.11	24.26
1104129480-02	53.44	15.99	7.34	23.24
1104129480-01	53.51	16.02	7.29	23.18
1104129480-02	53.43	16.08	7.26	23.24
140412901-01	50.93	16.47	6.93	25.66
140412901-02	51.09	16.41	6.95	25.56
140412902-01	49.37	18.23	6.72	25.68
140412902-02	50.51	16.97	6.83	25.68
140412904-01	50.98	16.68	6.90	25.43
140412904-02	50.92	16.70	6.89	25.49
140412906-01	51.18	16.59	6.92	25.31
140412906-02	51.15	16.67	6.91	25.27
140412908-01	51.11	16.67	6.92	25.30
140412908-02	51.22	16.64	6.95	25.19
140412924-01	52.91	16.27	7.17	23.66
140412924-02	52.71	16.40	7.16	23.73
14041290148h	54.40	15.88	7.42	22.30
14041290248h	54.24	15.81	7.39	22.57
140412948-01	54.02	16.09	7.31	22.58
140412948-02	54.17	15.95	7.36	22.51
140412972-01	53.99	16.03	7.35	22.64
140412972-02	54.77	15.81	7.44	21.98

Appendix 4.2 continued.

ID	C%wtAA (oxid)	N%wtAA (oxid)	H%wtAA (oxid)	O%wtAA (oxid)	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$
804129120-02	50.70	14.30	6.51	28.49	-	-	-
804129720-02	50.84	14.31	6.57	28.29	-	-	-
804129720-01	50.95	14.21	6.57	28.27	-	-	-
8041291440-02	51.09	14.20	6.62	28.09	-25.38	4.68	-120.18
8041291440-01	51.01	14.25	6.61	28.12	-25.33	4.33	-114.92
1104129120-01	51.27	14.29	6.66	27.77	-	-	-119.39
1104129120-02	51.20	14.23	6.59	27.97	-	-	-
1104129240-01	52.23	13.97	6.79	27.01	-25.83	4.72	-
1104129240-01b	52.33	13.89	6.82	26.96	-	-	-
1104129240-02	51.86	14.09	6.73	27.31	-	-	-132.05
1104129480-02	53.09	13.60	6.97	26.33	-25.46	4.30	-
1104129480-01	53.04	13.62	6.93	26.41	-	-	-
1104129480-02	52.87	13.77	6.92	26.44	-	-	-
140412901-01	50.76	14.20	6.55	28.50	-	-	-
140412901-02	50.88	14.19	6.57	28.37	-	-	-
140412902-01	49.44	16.20	6.39	27.96	-	-	-
140412902-02	50.30	14.89	6.48	28.33	-	-	-
140412904-01	50.71	14.52	6.53	28.24	-	-	-
140412904-02	50.67	14.54	6.52	28.26	-	-	-
140412906-01	50.86	14.52	6.55	28.07	-	-	-
140412906-02	50.84	14.52	6.54	28.10	-	-	-
140412908-01	50.82	14.56	6.55	28.07	-25.20	4.68	-127.80
140412908-02	50.95	14.53	6.58	27.94	-25.48	4.44	-121.38
140412924-01	52.38	14.13	6.81	26.68	-	-	-
140412924-02	52.26	14.23	6.81	26.70	-	-	-
14041290148h	53.77	13.75	7.08	25.39	-	-	-
14041290248h	53.61	13.76	7.05	25.58	-	-	-
140412948-01	53.34	13.83	6.97	25.85	-	-	-
140412948-02	53.57	13.72	7.02	25.69	-	-	-
140412972-01	53.39	13.77	7.00	25.84	-	-	-
140412972-02	54.03	13.54	7.09	25.34	-	-	-

Appendix 4.2 continued.

ID	$\delta^{18}O$/‰	$C:N_{atomISOT}$
804129120-02	-	-
804129720-02	-	-
804129720-01	-	-
8041291440-02	12.16	3.73
8041291440-01	11.49	3.67
1104129120-01	10.86	-
1104129120-02	-	-
1104129240-01	-	3.94
1104129240-01b	-	-
1104129240-02	10.55	-
1104129480-02	-	3.74
1104129480-01	-	-
1104129480-02	-	-
140412901-01	-	-
140412901-02	-	-
140412902-01	-	-
140412902-02	-	-
140412904-01	-	-
140412904-02	-	-
140412906-01	-	-
140412906-02	-	-
140412908-01	10.49	3.75
140412908-02	10.39	3.77
140412924-01	-	-
140412924-02	-	-
14041290148h	-	-
14041290248h	-	-
140412948-01	-	-
140412948-02	-	-
140412972-01	-	-
140412972-02	-	-

Appendix 4.2 continued.

ID	RP-HPLC run	Sample	Temperature/°C	Time/h	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]
140412996-01	H398	4129	140	96	72250	377134	82693	96805	29364
140412996-02	H398	4129	140	96	77974	424595	91779	109849	32745
1404129120-01	H398	4129	140	120	174027	971809	203287	253051	70326
1404129120-02	H398	4129	140	120	45641	247580	58545	66567	19211

Appendix 4.2 continued.

ID	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]	[Ile]	[Asx] %	[Glx] %	[Ser] %
140412996-01	154052	185610	211175	94823	262644	140491	452126	233732	3.27%	17.09%	3.75%
140412996-02	179217	209626	245978	116229	312333	166325	530405	275305	3.04%	16.57%	3.58%
1404129120-01	416440	488315	594094	234740	760898	426411	1318045	698025	2.84%	15.88%	3.32%
1404129120-02	102815	113823	152720	59950	191656	102512	331593	173467	2.94%	15.95%	3.77%

Appendix 4.2 continued.

ID	[L-Thr] %	[L-His] %	[Gly] %	[L-Arg] %	[Ala] %	[Tyr] %	[Val] %	[Phe] %	[Leu] %	[Ile] %
140412996-01	4.39%	1.33%	6.98%	8.41%	9.57%	4.30%	11.90%	6.36%	20.48%	10.59%
140412996-02	4.29%	1.28%	6.99%	8.18%	9.60%	4.54%	12.19%	6.49%	20.70%	10.74%
1404129120-01	4.13%	1.15%	6.80%	7.98%	9.71%	3.83%	12.43%	6.97%	21.53%	11.40%
1404129120-02	4.29%	1.24%	6.62%	7.33%	9.84%	3.86%	12.35%	6.60%	21.36%	11.18%

Appendix 4.2 continued.

ID	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
140412996-01	0.303	0.193	0.161	0.226	0.148	0.162	0.060	0.177	0.106	0.080
140412996-02	0.318	0.209	0.151	0.253	0.154	0.168	0.066	0.175	0.114	0.087
1404129120-01	0.302	0.203	0.147	0.269	0.155	0.175	0.071	0.186	0.115	0.082
1404129120-02	0.296	0.200	0.128	0.242	0.151	0.151	0.063	0.153	0.107	0.084

Appendix 4.2 continued.

ID	C%wtEA	N%wtEA	H%wtEA	O%wtEA	S%wtEA	C%wtAA	N%wtAA	H%wtAA	O%wtAA
140412996-01	-	-	-	-	-	55.23	16.72	7.58	20.47
140412996-02	-	-	-	-	-	55.43	16.63	7.60	20.34
1404129120-01	-	-	-	-	-	55.73	16.53	7.67	20.07
1404129120-02	-	-	-	-	-	55.62	16.45	7.66	20.28

Appendix 4.2 continued.

ID	C%wtAA (deamid)	N%wtAA (deamid)	H%wtAA (deamid)	O%wtAA (deamid)
140412996-01	55.42	15.78	7.55	21.25
140412996-02	55.62	15.72	7.58	21.08
1404129120-01	55.92	15.66	7.65	20.78
1404129120-02	55.81	15.56	7.63	21.00

Appendix 4.2 continued.

ID	C%wtAA (oxid)	N%wtAA (oxid)	H%wtAA (oxid)	O%wtAA (oxid)	$\delta^{13}C/‰$	$\delta^{15}N/‰$	$\delta^{2}H/‰$
140412996-01	54.63	13.50	7.21	24.65	-	-	-168.58
140412996-02	54.80	13.50	7.24	24.46	-	-	-169.91
1404129120-01	55.08	13.50	7.32	24.11	-	-	-
1404129120-02	54.96	13.52	7.31	24.21	-	-	-

Appendix 4.2 continued.

ID	$\delta^{18}O$/‰	$C:N_{atomISOT}$
140412996-01	10.25	-
140412996-02	9.80	-
1404129120-01	-	-
1404129120-02	-	-

Appendix 4.5. AA composition (of AAs recovered by RP-HPLC) of the 10 most important proteins in the wool fibre. Data from Clerens *et al*. (2010). Ordering derived by multiplying Score (combined Mascot score), M_r (molar mass) and Coverage (sequence coverage %) as a proxy for abundance.

(a) protein identity.

	Protein	Score	M_r /kDa	Coverage/%	N unique peptides	% AA residues recovered
1	IFP Type II K86	20036.2	54.8	98.2	325	85.2
2	IFP Type II K81	20490.7	55.1	89.2	332	85.4
3	IFP Type II K83	18237.1	53.6	93.1	300	85.1
4	IFP Type I K31	18627.2	46.6	98.5	307	86.2
5	IFP Type I k33b	16984.7	47.7	94.3	291	88.2
6	IFP Type II K85	14750.3	55.3	93	242	87.1
7	IFP Type I K34	15665.3	46.6	92.1	255	88.7
8	IFP Type I K33a var1	13551.3	46	93.5	234	87.3
9	IFP Type I K35	8339.7	50.4	89.5	136	84.4
10	IFP Type II K87	4799.3	52.9	39	82	87.5

Appendix 4.5 continued. (b) protein % AA content (of recovered AAs only).

	Asx	Glx	Ser	L-Thr	L-His	Gly	L-Arg	Ala	Tyr	Val	Phe	Leu	Ile
1	8.86	15.99	11.37	4.82	0.58	8.86	8.09	11.18	3.28	9.63	2.12	10.60	4.62
2	9.01	16.40	10.39	4.62	0.46	10.39	9.01	10.16	3.23	8.08	2.77	10.62	4.85
3	9.57	17.46	9.57	4.78	0.48	9.81	8.61	9.57	2.87	8.37	3.35	10.53	5.02
4	12.96	20.85	9.58	6.48	0.56	3.38	9.01	6.76	2.82	7.04	2.25	13.80	4.51
5	12.90	20.97	10.48	6.45	0.54	3.76	8.33	6.45	3.23	7.26	2.15	13.71	3.76
6	8.90	16.21	11.87	4.79	1.14	7.99	8.90	10.73	3.65	7.99	2.97	9.82	5.02
7	11.91	21.05	13.57	5.82	1.11	1.94	9.42	5.82	3.32	5.82	2.22	13.85	4.16
8	12.78	21.31	9.38	6.25	1.14	3.13	9.38	5.68	2.56	7.67	2.56	13.92	4.26
9	10.16	18.75	11.98	5.21	1.04	6.77	8.07	8.85	2.86	5.99	2.60	14.06	3.65
10	8.35	16.71	13.60	5.25	1.67	8.59	8.35	8.83	4.30	7.64	2.39	9.31	5.01

Appendix 7.1. Technical description of archaeological textiles selected for isotope and AA analysis.

ID	Site	Context date	Sf/context no	Type	Spin	Density
2894	RKH	1000-1200	2001-26-30 (i)	Yarn	S+Z	-
2895	RKH	1000-1200	2001-26-31	2/2 plain twill	ZS	8 x 8
3960	RKH	1000-1200	2001-26-30 (ii)	Staple	-	-
3961	RKH	1000-1200	2001-26-46	Cord	Z2S	-
2896ave	RKH	1200-1400	1999-18-57	2/2 plain twill	ZS	11 x 8
2897	RKH	1200-1400	2000-6-187 (a)	2/2 plain twill	ZS	10 x 9
2898	RKH	1200-1400	2000-6-187 (b)	2/2 plain twill	ZS	13 x 10
2899	RKH	1200-1400	2000-6-208 Box 1 (f)	2/2 plain twill	ZS	?
2901	RKH	1200-1400	2000-6-208 Box 2 (g)	2/2 plain twill	ZS	12 x 8
3962	RKH	1200-1400	2000-6-187 (c)	2/2 plain twill	ZS	12 x 9
3963	RKH	1200-1400	2000-6-208 Box 1 (f)	2/2 plain twill	ZS	?
3964	RKH	1200-1400	2000-6-208 Box 2 (c)	2/2 plain twill	ZS	10 x 9
3965	RKH	1200-1400	2001-26-76 (iii)	Staple	-	-
2902	RKH	1400-1600	1989-33-380 (a)	2/2 plain twill	ZS	8 x 7
2903	RKH	1400-1600	1989-33-380 (f)	Tabby	?SS	16 x 8
2904	RKH	1400-1600	1989-33-380 (g)	Yarn	Z	-
2950ave	RKH	1400-1600	1989-33-380 (iii)	Staple	-	-
3966	RKH	1400-1600	2000-6-130	Tabby	Z+S/S	10 x 8
3967	RKH	1400-1600	1989-33-380 (c)	Tabby	SS	12 x 12
3968	RKH	1400-1600	1989-33-380 (d)	Tabby	SS	10 x 10
2906	RKH	1400-1600	1989-33-380 (i) (b)	Staple	-	-
4120ave	RKH	1200-1400	2000-6-208 Box 1	2/2 plain twill	ZS	?
4329	HSS	C7-8	HE4	2/1 plain twill	ZS	14 x 10
4330	HSS	C7-8	HE21b	2/2 chevron/ diamond twill	ZS	11 x 8
4331	HSS	C7-8	HE27 weft	Tabby	ZS	3.5 x 3
4332	HSS	C7-8	HE33a	Tabby	?	?
4333	HSS	C7-8	HE41	Staple	-	-
4334	HSS	C7-8	HE50	Staple	-	-
4335	HSS	C7-8	HE69a	Staple	-	-
4336	HSS	C7-8	HE76c	Tabby (?band)	ZS	-
4337	HSS	C7-8	HE77a	2/2 diamond twill	ZS	7 x 8

Appendix 7.1 continued.

ID	Dye	Pigment	Fleece	Other	Category
2894	nt	nt	nt		typical
2895	nt	nt	nt		typical
3960	nt	nt	nt		typical
3961	nt	nt	nt		typical
2896ave	nt	nt	nt		typical
2897	nt	nt	nt		typical
2898	nt	nt	nt		typical
2899	nt	nt	nt		typical
2901	nt	nt	nt		typical
3962	nt	nt	nt	even	typical
3963	nt	nt	nt		typical
3964	nt	nt	nt		typical
3965	nt	nt	nt		typical
2902	nt	nt	nt		typical
2903	nt	nt	nt	napped	atypical
2904	nt	nt	nt		typical
2950ave	nt	nt	nt		typical
3966	nt	nt	nt		atypical
3967	nt	nt	nt	napped	atypical
3968	nt	nt	nt		unknown
2906	nt	nt	nt		typical
4120ave	nt	nt	nt		typical
4329	madder	none	HM x HM		atypical
4330	ndd	dense	HM x HM		typical
4331	ndd	dense on coarse fibres	HM		typical
4332	ndd	none	?M x ?M	open	atypical
4333	ndd	none	H		typical
4334	ndd	dense	HM		typical
4335	ndd	medium on coarse fibres	HM	?fell wool	typical
4336	ndd	dense	HM x HM	?band	typical
4337	ndd	moderate/light	HM x HM		typical

Appendix 7.1 continued.

ID	Site	Context date	Sf/context no	Type	Spin	Density
4338	HSS	C7-8	HE92	2/2 diamond twill	ZS	10 x 10
3959	YCG	930-975	Cat. no 1309 Context 32725 sf no 13517	Nålebinding	S2Z	-
4058	YCG	850-900	Cat. no 1255 Context 34882 cess pit fill Sf no 13584	Staple	-	-
4059	YCG	850-900	Cat. no 1257 Context 32722 pit fill Sf no 13499	Tabby	ZS	4 x 2-3
4060a	YCG	850-900	Cat. no 1259 Context 34910 pit fill Sf no 13382	Tabby	ZS	12 x 8
4060b	YCG	850-900	Cat. no 1259 Context 34910 pit fill Sf no 13382	Yarn	Z2S	-
4061	YCG	930-975	Cat. no 1285 Context 34558 Sf no 13020	Staple	-	-
4062	YCG	930-975	Cat. no 1289 Context 32725 Sf no 13525	Staple	-	-
4063	YCG	930-975	Cat. no 1290 Context 28432 Sf no 10519	Staple	-	-
4064	YCG	930-975	Cat. no 1295 Context 32725 Sf no 13520	Tabby, piled	ZS	5 x 4
4065	YCG	930-975	Cat. no 1295 Context 32725 Sf no 13520	Yarn	S	-
4066	YCG	930-975	Cat. no 1300 Context 28432 Sf no 10535	2/2 plain twill	ZS	14 x 7
4067	YCG	930-975	Cat. no 1302 Context 34558 pit fill Sf no 13019	2/2 chevron twill	ZS	8 x 5-6
4068	YCG	930-975	Cat. no 1303 Context 32725 Sf no 13524	2/2 chevron twill	ZS	10-11 x 6-7
4069	YCG	930-975	Cat. no 1305 Context 27093 Sf no 9633	2/2 chevron twill	ZS	16 x 12
4070	YCG	930-975	Cat. no 1306 Context 27093 Sf no 9633	2/2 chevron twill	ZS	18 x 16
4071	YCG	975-1150	Cat. no 1374 Context 1473 Sf no 407	Staple	-	-
4072	YCG	975-1150	Cat. no 1377 Context 1473 Sf no 407	Staple	-	-
4073	YCG	975-1150	Cat. no 1381 Context 1473 Sf no 12912	2/2 diamond twill	ZS	14 x 11
4074	YCG	C13-14	Cat. no 1413 Context 4829 Sf no 16063	Staple	-	-
4075	YCG	C13	Cat. no 1415 Context 10879 Sf no 2703	2/1 plain twill	Z/S+Z	11 x 6-7
4076	YCG	C13-14	Cat. no 1419 Context 10758 cess pit fill Sf no 16064	Tabby	ZS	12-14 x 12-14
4077	YCG	C13	Cat. no 1423 Context 10879 Sf no 2692	Yarn	Z	-
4078ave	YCG	Anglo-Scandinavian	Cat. no 1460 Context 2070 Sf no 247(a)	Tabby, piled	ZS	5 x 5
4079	YCG	Anglo-Scandinavian	Cat. no 1460 Context 2070 Sf no 247(b)	Tabby	ZZ	24 x 16
4080	YCG	Anglo-Scandinavian	Cat. no 1460 Context 2070 Sf no 247	Yarn	Z2S	-
4095	YCG	930-975	Cat. No 1297 Context 28432 Sf no 10519	Tabby	ZS	4 x 3-4
4081	YLB	930-1040	Cat. no 565 Context Trench II, 10 Sf no 5075	2/1 diamond twill	ZZ	22 x 11
4082	YLB	930-1040	Cat. no 569 Context Trench II, 10 Sf no 5252	2/1 diamond twill	ZZ	20 x 11
4083	YLB	930-1040	Cat. no 570 Context Trench III, 6 Sf no 5073	2/1 diamond twill	ZZ	16 x 10
4084	YLB	900-1000	Cat. no 571 Context Trench II, 7 Sf no ?5267	2/2 chevron twill	ZS	18 x 15

Appendix 7.1 continued.

ID	Dye	Pigment	Fleece	Other	Category
4338	ndd	none	H x H		typical
3959	ndd	none	nt	sock	atypical
4058	ndd	none	H		typical
4059	nt	none	H x H	fringe of knotted warps	typical
4060a	ndd	dense	H x HM	loose	typical
4060b	ndd	none	nt	sewn through 4060a	typical
4061	nt	none	H		typical
4062	ndd	none	HM		typical
4063	ndd	none	HM		typical
4064	ndd	none	H x H	ground of 4065	hybrid typical/atypical
4065	ndd	none	H	pile of 4064	hybrid typical/atypical
4066	ndd	none	GM x H		typical
4067	indigotin	none	M x H	soft uneven yarn	typical
4068	ndd	dense (warp) /none (weft)	H x HM	waðmál	atypical
4069	ndd	none	GM x HM		typical
4070	lichen purple	none	HM x M	v even	atypical
4071	nt	none	H	tips and roots present	typical
4072	ndd	none	GM		typical
4073	madder	nt	nt		typical
4074	ndd	none	SF		typical
4075	ndd	none	M x SF+HM		typical
4076	nt	none	nt	matted	typical
4077	ndd	none	H		typical
4078ave	madder	none	H x H+H	locks of loosely twisted wool darned in	hybrid typical/atypical
4079	ndd	none	nt	lining of 4078	atypical
4080	ndd	none	nt	thread joining 4078 and 4079	typical
4095	ndd	none	M x HM	uneven, loose	typical
4081	nt	nt	nt	offcut	unknown
4082	nt	nt	nt		unknown
4083	nt	nt	nt		unknown
4084	nt	nt	nt	irregular pattern	typical

Appendix 7.1 continued.

ID	Site	Context date	Sf/context no	Type	Spin	Density
4085	YLB	930-1040	Cat. no 574 Context Trench II, 10 f no 5077	2/1 chevron twill	ZS	20 x 14
4086	YLB	930-1040	Cat. no 577 Context Trench II, 10 Sf no 5076	2/2 diamond twill	Z/Z+S	14 x 9
4087ave	YLB	930-1040	Cat. no 579 Context Trench II, 16 Sf no ?5098	2/2 diamond twill, piled	ZS	12 x 7
4088	YLB	900-1000	Cat. no 580 Context Trench II, 7 Sf no 5275	Tabby(?)	ZS	4 x 3
4089	YLB	900-1000	Cat. no 582 Context Trench II, 7 Sf no 5276	Tabby	SS	5 x 3.5
4090	YLB	930-1040	Cat. no 584 Context Trench II, 10 Sf no 5078	Tabby	SS	3.5 x 3.5
4091	YLB	930-1040	Cat. no 584 Context Trench II, 10 Sf no 5078	Tabby	SS	3.5 x 3.5
4092	YLB	900-1000	Cat. no 587 Context Trench II, 10 Sf no 5281	?2/2 plain twill	Z/S+Z	6 x 5
4093	YLB	930-1040	Cat. no 588 Context Trench II, 10 Sf no 5282	?2/1 plain twill	Z/S+Z	4.5 x 5
4094	YLB	930-1040	Cat. no 591 Context Trench II, 30 Sf no 5176	Tabby repp	ZZ	22 x 12
4121	YSG	Anglo-Scandinavian	Sf 19b, context 5021	2/1 diamond	ZZ	22-24/14-16
4122	YSG	Anglo-Scandinavian	Sf 19c, context 5021	2/2 plain twill	ZS	10 x 7
4123	YSG	Anglo-Scandinavian	Sf 19e, context 5021	2/2 twill	ZS	10 x 10
4124	YSG	Anglo-Scandinavian	Sf 19h, context 5021	2/1 twill	SS	5 x 4
4125	YSG	Anglo-Scandinavian	Sf 404, context 9021	Tabby	ZS	6-8 x 4
3944	NBG	1st half C15th	BGT26, T13	Knit	Z2S	15 x 27*
3945	NBG	1st half C15th	BGT26, T11	2/2 plain twill	ZZ	14 x 12
3946	NBG	1st half C15th	BGT26, T12	Tabby	SS	5-6 x 5
3947	NBG	1st half C15th	BGT21, T6	2/2 plain twill	ZZ	14 x 84-104
3948	NBG	1st half C15th	BGT14, T4	2/2 plain twill	SS	22 x 20
3949	NBG	1st half C15th	BGT14, T5	Tabby	SS	6 x 5
3950	NBG	Beginning C16th	BGT59, T47-50	Knit	?Z2S	17 x 25*
3951	NBG	Beginning C16th	BGT59, T51-55	Knit	?Z2S	22 x 35*
3952	NBG	Beginning C16th	BGT63, T64	2/2 plain twill	ZZ	13 x 86-96
3953	NBG	Beginning C16th	BGT63, T65	Tabby	SS	11 x 8
3954	NBG	Beginning C16th	BGT59, T33	Tabby	SS	7 x 5
3955	NBG	Beginning C16th	BGT59, T41	Tabby	SS	14 x 11
3956	NBG	Beginning C16th	BGT59, T25	Tabby	SS	9 x 9
3957	NBG	Beginning C16th	BGT59, T27	Tabby	SS	8 x 8
4544	NQS	mid-late C13th	T4, context 574	2/1 plain twill	ZS	10 x 7
4545	NQS	mid-late C13th	T5, context 574	2/1 plain twill	ZS	7 x 5

Appendix 7.1 continued.

ID	Dye	Pigment	Fleece	Other	Category
4085	nt	nt	nt		typical
4086	nt	nt	nt		typical
4087ave	nt	nt	nt	S-spun thread darned in	hybrid typical/atypical
4088	nt	nt	nt	fulled/matted	typical
4089	nt	nt	nt	errors in weave	typical
4090	nt	nt	nt	dark system	typical
4091	nt	nt	nt	light system	typical
4092	nt	nt	nt		typical
4093	nt	nt	nt		typical
4094	madder	nt	nt		typical
4121	nt	moderate/light	H/HM		unknown
4122	ndd	moderate/light	nt		typical
4123	tannin	moderate/light	nt		typical
4124	ndd	none	HM x HM		typical
4125	Indigotin + tannin	none	GM x HM	shaggy pile both faces	atypical
3944	kermes	none	F		atypical
3945	nt	nt	nt	heavily fulled	typical
3946	nt	nt	nt	light-medium fulled	typical
3947	nt	nt	nt	worsted	atypical
3948	nt	nt	nt	lightly fulled	typical
3949	nt	nt	nt	medium fulled	typical
3950	nt	moderate/light	SF	cap, lightly fulled	typical
3951	nt	nt	nt	cap	typical
3952	nt	nt	nt	worsted	typical
3953	nt	nt	nt	lightly fulled	typical
3954	nt	nt	nt		typical
3955	nt	nt	nt	lightly fulled	typical
3956	nt	nt	nt	lightly fulled, scalloped edge	typical
3957	nt	nt	nt	medium fulled, ?weft-faced	typical
4544	madder	none	H/HM		typical
4545	ndd	none	HM/M		typical

Appendix 7.1 continued.

ID	Site	Context date	Sf/context no	Type	Spin	Density
4546	NQS	mid-late C13th	T7, context 630	Tabby	S2Z/S2Z	2 x 2
4547	NQS	mid-late C13th	T8, context 639	Tabby	S2Z/S2Z	2-3 x 3
5169	BKA	c. 750-850	W10 (f)	2/2 diamond	ZZ	32 x 16
5170	BKA	c. 950-end C10th	W20	2/1 diamond	ZZ	55-60 x 17
5171	BKA	c.950	W9	Tabby or 2/1 plain twill, piled	??	?
5172	BKA	c.950	W1	Tabby, piled	ZS	4 x 3
5173	BKA	c. 950-975	W6	2/1 plain twill	Z?	10 x 4-5
5174	BKA	c.950	W2	Tabby	ZS	5 x 4-5
5175	BKA	c.950	W8	Twill	ZZ	?

Appendix 7.1 continued.

ID	Dye	Pigment	Fleece	Other	Category
4546	ndd	none	nt	?wool	typical
4547	ndd	none	nt	goat hair	typical
5169	nt	nt	nt		atypical
5170	nt	nt	nt		atypical
5171	nt	nt	nt	pile (unspun)	typical
5172	nt	nt	nt	rough and thin, pile	typical
5173	nt	nt	nt		typical
5174	nt	nt	nt	regular, felted on one side	typical
5175	nt	nt	nt		typical

Appendix 7.2. Isotope ($\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$) and $C:N_{atomB}$ results of all textile samples.

ID	Site	Yield %	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomB}$
2894	RKH	72%	-24.27	1.92	-118.3	10.22	4.28
2895	RKH	30%	-24.05	3.15	-111.4	9.68	4.55
3960	RKH	-	-	-	-	-	-
3961	RKH	85%	-23.26	0.39	-93.7	17.37	4.07
2896ave	RKH	67%	-23.11	3.87	-92.5	15.20	4.25
2897	RKH	40%	-23.74	2.28	-101.7	13.19	3.95
2898	RKH	41%	-23.67	2.36	-101.6	13.57	3.95
2899	RKH	73%	-24.03	4.07	-103.0	14.03	4.36
2901	RKH	54%	-24.14	3.51	-100.8	13.40	4.26
3962	RKH	25%	-23.91	2.20	-98.9	12.33	3.55
3963	RKH	63%	-24.23	2.78	-104.1	13.79	3.86
3964	RKH	88%	-24.21	3.32	-109.3	15.28	3.72
3965	RKH	58%	-23.83	2.63	-100.5	11.70	3.32
2902	RKH	32%	-23.96	2.82	-95.0	14.51	3.79
2903	RKH	70%	-24.06	6.80	-77.8	15.81	3.87
2904	RKH	91%	-23.68	2.55	-105.9	13.53	3.88
2950ave	RKH	-	-23.86	2.40	-102.8	14.61	3.84
3966	RKH	61%	-23.64	6.01	-80.4	17.15	4.36
3967	RKH	40%	-24.36	5.50	-86.8	16.12	3.54
3968	RKH	69%	-23.88	4.86	-89.5	16.01	3.65
2906	RKH	-	-23.78	1.14	-105.8	12.42	3.43
4120ave	RKH	68%	-24.03	3.69	-104.4	12.80	4.24
4329	HSS	75%	-23.34	8.92	-94.0	10.66	3.78
4330	HSS	-	-23.52	4.69	-107.9	12.13	3.79
4331	HSS	89%	-23.24	9.43	-78.8	14.86	3.87
4332	HSS	82%	-24.30	10.67	-94.9	13.02	3.96
4333	HSS	81%	-22.20	10.40	-86.4	11.97	3.76
4334	HSS	93%	-23.46	10.26	-80.5	14.65	3.86
4335	HSS	64%	-22.89	11.11	-89.7	12.54	3.80
4336	HSS	86%	-24.38	6.22	-102.9	10.27	3.85
4337	HSS	-	-23.24	9.43	-82.4	13.01	3.87
4338	HSS	-	-22.56	9.92	-81.1	14.09	3.68
3959	YCG	72%	-23.53	6.23	-85.0	15.77	3.39
4058	YCG	-	-24.03	7.02	-104.4	12.78	3.37
4059	YCG	87%	-	-	-	-	-
4060a	YCG	-	-24.24	6.47	-95.8	14.32	3.30
4060b	YCG	90%	-25.29	11.03	-102.6	13.93	3.49
4061	YCG	91%	-	-	-	-	-
4062	YCG	92%	-23.79	4.34	-97.6	14.88	3.31
4063	YCG	-	-23.64	4.95	-89.2	13.78	3.37
4064	YCG	86%	-23.73	5.92	-88.0	15.15	3.38
4065	YCG	97%	-24.09	7.22	-98.8	14.82	3.35
4066	YCG	82%	-24.36	7.89	-89.1	15.20	3.47
4067	YCG	80%	-	-	-	-	-
4068	YCG	87%	-23.49	8.70	-88.0	14.31	3.48
4069	YCG	60%	-24.17	6.21	-89.4	13.93	3.43
4070	YCG	74%	-23.56	6.26	-85.0	14.43	3.36
4071	YCG	87%	-	-	-	-	-
4072	YCG	95%	-23.97	5.55	-98.3	13.68	3.31

Appendix 7.2 continued.

ID	Site	Yield %	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomB}$
4073	YCG	60%	-24.95	6.64	-92.3	13.63	4.38
4074	YCG	-	-23.97	7.30	-100.4	13.97	3.59
4075	YCG	94%	-24.52	4.86	-90.1	17.09	3.83
4077	YCG	85%	-23.77	5.62	-86.5	15.36	3.39
4078ave	YCG	85%	-24.24	7.45	-93.2	14.95	3.71
4079	YCG	81%	-23.22	7.09	-91.7	14.91	3.52
4080	YCG	82%	-23.85	7.57	-97.4	14.34	3.51
4095	YCG	74%	-25.23	9.63	-99.5	13.30	3.40
4081	YLB	56%	-23.66	6.87	-88.2	15.36	3.46
4082	YLB	60%	-24.08	8.42	-85.1	13.53	3.55
4083	YLB	62%	-24.06	7.03	-83.2	15.75	3.36
4076	YCG	-	-	-	-	-	-
4085	YLB	71%	-23.78	4.30	-90.0	12.88	3.33
4086	YLB	66%	-23.88	6.41	-93.2	13.62	3.36
4087ave	YLB	-	-24.03	7.16	-89.6	14.79	3.55
4088	YLB	71%	-24.11	7.94	-97.2	13.97	3.29
4089	YLB	82%	-24.08	8.08	-93.7	14.37	3.34
4084	YLB	73%	-	-	-	-	-
4090	YLB	61%	-	-	-	-	-
4092	YLB	76%	-23.99	8.78	-92.0	13.52	3.39
4093	YLB	-	-24.09	7.53	-101.4	13.31	3.28
4094	YLB	95%	-23.94	7.57	-91.9	16.65	3.54
4121	YSG	81%	-24.54	7.15	-95.2	14.17	3.58
4091	YLB	79%	-	-	-	-	-
4123	YSG	81%	-24.17	3.27	-117.4	11.55	3.72
4124	YSG	80%	-24.12	6.90	-97.0	14.95	3.65
4125	YSG	62%	-23.36	6.38	-88.8	14.43	3.51
3944	NBG	84%	-24.18	6.98	-87.9	13.64	3.73
3945	NBG	80%	-24.41	7.18	-86.9	12.85	3.56
3946	NBG	73%	-24.78	5.68	-89.3	13.06	3.68
3947	NBG	52%	-	-	-	-	-
3948	NBG	90%	-23.93	4.85	-87.5	14.63	3.57
3949	NBG	76%	-24.87	5.04	-98.4	13.70	3.69
3950	NBG	84%	-24.82	7.55	-88.7	13.87	4.09
3951	NBG	81%	-24.57	7.33	-87.2	14.06	3.75
3952	NBG	90%	-23.29	7.08	-86.5	14.84	3.63
3953	NBG	75%	-24.43	5.26	-89.2	14.22	3.60
3954	NBG	74%	-24.76	5.60	-91.4	14.24	3.72
3955	NBG	85%	-23.98	5.30	-86.5	12.67	3.74
3956	NBG	81%	-	-	-	-	-
3957	NBG	86%	-24.66	5.31	-94.8	14.00	3.60
4544	NQS	66%	-23.81	8.72	-90.1	12.80	3.81
4545	NQS	42%	-23.76	8.68	-88.5	14.28	3.95
4546	NQS	78%	-23.98	4.42	-92.5	10.72	3.85
4547	NQS	51%	-24.00	6.60	-89.3	10.92	3.68
5169	BKA	80%	-22.39	6.15	-100.2	13.49	3.90
5170	BKA	70%	-22.65	9.66	-85.0	14.56	3.98
5171	BKA	67%	-23.45	6.87	-89.2	14.50	3.99
5172	BKA	53%	-22.99	8.16	-86.2	15.03	3.85

Appendix 7.2 continued.

ID	Site	Yield %	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomB}$
5173	BKA	44%	-22.88	7.47	-85.0	15.41	4.01
5174	BKA	51%	-23.24	8.06	-90.7	15.77	3.99
5175	BKA	50%	-23.25	9.32	-110.0	10.73	3.88

Appendix 7.3. Isotope ($\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$) and $C:N_{atomB}$ results of all textile samples with multiple measurements.

ID	Site	$\delta^{13}C$/‰	$\delta^{15}N$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$C:N_{atomB}$
4120-I	RKH	-24.03	3.48	-105.4	13.22	4.16
4120-II	RKH	-23.98	3.52	-104.5	12.01	4.16
4120-III	RKH	-23.88	3.65	-106.8	11.99	4.13
4120-IV	RKH	-23.95	3.54	-101.6	11.73	4.13
4120-V	RKH	-24.01	3.62	-104.8	13.21	4.16
4120-VI	RKH	-24.13	3.63	-102.7	12.86	4.40
4120-VII	RKH	-24.12	4.05	-107.1	13.85	4.27
4120-VIII	RKH	-24.01	3.82	-101.5	12.71	4.27
4120-IX	RKH	-24.13	3.87	-105.2	13.60	4.44
2896-I	RKH	-23.15	3.92	-92.9	14.47	4.33
2896-II	RKH	-23.21	3.57	-93.6	15.54	4.18
2896-III	RKH	-22.96	4.11	-91.0	15.59	4.23
4078-I	YCG	-24.91	7.73	-94.1	15.85	3.48
4078-II	YCG	-23.89	7.74	-93.5	14.62	3.82
4078-III	YCG	-23.93	6.88	-91.9	14.38	3.84
4087-I	YLB	-24.08	7.03	-87.1	14.97	3.60
4087-II	YLB	-23.97	7.29	-92.1	14.60	3.50
2950-I	RKH	-23.56	2.75	-104.7	15.23	3.92
2950-II	RKH	-23.85	2.26	-103.7	15.23	3.80
2950-III	RKH	-23.83	2.37	-105.4	14.71	3.80
2950-IV	RKH	-23.73	2.37	-99.0	15.60	3.82
2950-V	RKH	-23.84	2.41	-105.5	14.43	3.78
2950-VI	RKH	-23.80	2.03	-102.4	14.84	3.81
2950-VII	RKH	-23.96	2.29	-99.7	15.43	3.83
2950-VIII	RKH	-24.01	2.62	-98.8	13.34	3.89
2950-IX	RKH	-24.08	2.79	-101.3	13.96	3.85
2950-X	RKH	-23.95	2.06	-107.2	13.37	3.87

Appendix 7.4. AA concentrations, % AA content, and AA racemisation data for all textile samples.

ID	Location	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]
2894	RKH	-	-	-	-	-	-	-	-	-	-	-	-
2895	RKH	171484	464286	62261	111233	15726	245372	159075	245516	41937	245382	90897	322143
3960	RKH	711809	1753002	589798	744275	75223	715194	776432	785998	157281	884964	171068	1134547
3961	RKH	557081	1101100	792386	551350	47066	549354	489686	436329	202187	541066	186070	731460
2896a	RKH	309001	736220	326797	292698	34955	260887	248755	297418	19450	312631	102436	480570
2896b	RKH	290741	704312	316044	291700	35860	276102	243033	281374	19107	309553	101051	456958
2897	RKH	285042	663906	331088	292612	35978	276025	262646	275378	7604	279518	89937	423740
2898	RKH	307837	747563	423042	397737	47459	328330	335631	299923	85716	351016	102570	460728
2899a	RKH	310418	722696	324364	302192	36414	252137	269283	292283	20374	302762	86071	449223
2899b	RKH	330156	735098	316216	269611	32697	246807	265079	316717	24423	314266	92503	477725
2901	RKH	269722	616128	281764	254544	29883	222578	238195	256005	24039	262339	79100	395942
3962	RKH	457165	1121513	585635	569889	52980	426242	475174	446155	90668	500653	135661	674474
3963	RKH	606715	1341101	537584	469329	53174	381719	495403	500026	71789	528207	151303	867139
3964	RKH	564667	1264594	576274	527060	46964	408660	501769	469667	64225	529357	153043	804330
3965	RKH	572143	1173658	966141	655865	73407	901367	586344	496297	241975	595045	220247	804483
2902	RKH	282726	600855	388792	303054	29694	335032	260212	262102	21258	277686	107377	394529
2903	RKH	410144	872763	573511	422098	52226	476688	359288	381894	12910	409773	150685	588636
2904	RKH	318499	660051	409529	310470	37689	293717	292857	276844	48701	306497	100473	444075
2950ave	RKH	-	-	-	-	-	-	-	-	-	-	-	-
3966	RKH	434183	1056653	519396	467132	29649	446690	377536	407482	72016	484163	149958	649869
3967	RKH	560285	1247605	815237	670532	0	773534	551191	533929	85818	575945	191943	827995
3968	RKH	566309	1330334	784307	672739	0	653376	547148	571111	52208	613868	183094	851947
2906	RKH	751203	1650519	1123658	796828	76955	865716	719908	677968	115425	772220	237721	1069767
4120-IX	RKH	324924	719876	278546	235366	30465	218502	261638	300336	36981	289784	85222	481497
4120-V	RKH	221447	502522	207101	171911	21618	135749	187554	194800	24792	201573	56034	326491
4120-VIII	RKH	208711	472641	190428	165368	20620	135453	175477	192601	27300	189621	52624	314163

Appendix 7.4 continued.

Lotno	[Ile]	[Asx]%	[Glx]%	[Ser]%	[L-Thr]%	[L-His]%	[Gly]%	[L-Arg]%	[Ala]%	[Tyr]%	[Val]%	[Phe]%	[Leu]%
2894	-	-	-	-	-	-	-	-	-	-	-	-	-
2895	153080	7.36%	19.94%	2.67%	4.78%	0.68%	10.54%	6.83%	10.54%	1.80%	10.54%	3.90%	13.84%
3960	549932	7.87%	19.37%	6.52%	8.22%	0.83%	7.90%	8.58%	8.69%	1.74%	9.78%	1.89%	12.54%
3961	342635	8.53%	16.87%	12.14%	8.45%	0.72%	8.42%	7.50%	6.68%	3.10%	8.29%	2.85%	11.21%
2896a	198981	8.53%	20.33%	9.03%	8.08%	0.97%	7.21%	6.87%	8.21%	0.54%	8.63%	2.83%	13.27%
2896b	193727	8.26%	20.01%	8.98%	8.29%	1.02%	7.84%	6.91%	7.99%	0.54%	8.80%	2.87%	12.98%
2897	173076	8.39%	19.55%	9.75%	8.61%	1.06%	8.13%	7.73%	8.11%	0.22%	8.23%	2.65%	12.48%
2898	209689	7.51%	18.25%	10.33%	9.71%	1.16%	8.01%	8.19%	7.32%	2.09%	8.57%	2.50%	11.24%
2899a	187914	8.73%	20.32%	9.12%	8.50%	1.02%	7.09%	7.57%	8.22%	0.57%	8.51%	2.42%	12.63%
2899b	200432	9.12%	20.30%	8.73%	7.44%	0.90%	6.81%	7.32%	8.74%	0.67%	8.68%	2.55%	13.19%
2901	166821	8.71%	19.89%	9.10%	8.22%	0.96%	7.19%	7.69%	8.27%	0.78%	8.47%	2.55%	12.78%
3962	315958	7.81%	19.16%	10.01%	9.74%	0.91%	7.28%	8.12%	7.62%	1.55%	8.56%	2.32%	11.53%
3963	351885	9.55%	21.10%	8.46%	7.38%	0.84%	6.01%	7.80%	7.87%	1.13%	8.31%	2.38%	13.64%
3964	348574	9.02%	20.20%	9.21%	8.42%	0.75%	6.53%	8.02%	7.50%	1.03%	8.46%	2.45%	12.85%
3965	347192	7.49%	15.37%	12.66%	8.59%	0.96%	11.81%	7.68%	6.50%	3.17%	7.79%	2.89%	10.54%
2902	174686	8.22%	17.48%	11.31%	8.81%	0.86%	9.74%	7.57%	7.62%	0.62%	8.08%	3.12%	11.48%
2903	250008	8.27%	17.59%	11.56%	8.51%	1.05%	9.61%	7.24%	7.70%	0.26%	8.26%	3.04%	11.87%
2904	186173	8.64%	17.91%	11.11%	8.42%	1.02%	7.97%	7.95%	7.51%	1.32%	8.32%	2.73%	12.05%
2950ave	-	-	-	-	-	-	-	-	-	-	-	-	-
3966	297984	8.05%	19.59%	9.63%	8.66%	0.55%	8.28%	7.00%	7.56%	1.34%	8.98%	2.78%	12.05%
3967	366948	7.78%	17.33%	11.32%	9.31%	0.00%	10.74%	7.65%	7.41%	1.19%	8.00%	2.67%	11.50%
3968	389459	7.85%	18.44%	10.87%	9.32%	0.00%	9.05%	7.58%	7.91%	0.72%	8.51%	2.54%	11.81%
2906	481319	8.04%	17.67%	12.03%	8.53%	0.82%	9.27%	7.71%	7.26%	1.24%	8.27%	2.55%	11.45%
4120-IX	199786	9.38%	20.79%	8.04%	6.80%	0.88%	6.31%	7.56%	8.67%	1.07%	8.37%	2.46%	13.90%
4120-V	138990	9.26%	21.02%	8.66%	7.19%	0.90%	5.68%	7.85%	8.15%	1.04%	8.43%	2.34%	13.66%
4120-VIII	132100	9.17%	20.76%	8.36%	7.26%	0.91%	5.95%	7.71%	8.46%	1.20%	8.33%	2.31%	13.80%

Appendix 7.4 continued.

Lotno	[Ile]%	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
2894	-	-	-	-	-	-	-	-	-	-	-
2895	6.57%	0.7746	0.1827	0.2268	0.1436	0.1885	0.1164	0.0573	0.1130	0.0884	0.0604
3960	6.08%	0.2978	0.0896	0.1426	0.0617	0.1193	0.0677	0.0285	0.0941	0.0637	0.0478
3961	5.25%	0.1030	0.0465	0.0110	0.0414	0.0373	0.0416	0.0167	0.0378	0.0411	0.0277
2896a	5.50%	0.1437	0.0581	0.0248	0.0769	0.0309	0.0663	0.0227	0.0493	0.0463	0.0314
2896b	5.50%	0.1531	0.0632	0.0230	0.0780	0.0336	0.0666	0.0249	0.0511	0.0507	0.0395
2897	5.10%	0.1459	0.0475	0.0988	0.0488	0.0352	0.2452	0.0212	0.0423	0.0354	0.0223
2898	5.12%	0.1607	0.0579	0.1048	0.0597	0.0412	0.0596	0.0227	0.0455	0.0419	0.0218
2899a	5.28%	0.1267	0.0552	0.1112	0.0781	0.0469	0.0758	0.0232	0.0463	0.0441	0.0258
2899b	5.53%	0.1403	0.0648	0.1131	0.0875	0.0657	0.0566	0.0250	0.0505	0.0521	0.0267
2901	5.39%	0.1395	0.0603	0.1282	0.0712	0.0668	0.0784	0.0237	0.0488	0.0483	0.0226
3962	5.40%	0.1601	0.0545	0.1013	0.0446	0.0877	0.0465	0.0182	0.0458	0.0488	0.0270
3963	5.54%	0.1290	0.0507	0.1061	0.0513	0.0521	0.0337	0.0155	0.0421	0.0434	0.0252
3964	5.57%	0.1302	0.0522	0.1017	0.0471	0.0478	0.0673	0.0159	0.0417	0.0439	0.0252
3965	4.55%	0.1095	0.0454	0.0366	0.0493	0.0559	0.0429	0.0147	0.0368	0.0545	0.0220
2902	5.08%	0.1189	0.0570	0.0240	0.0630	0.0655	0.0950	0.0211	0.0431	0.0483	0.0193
2903	5.04%	0.1077	0.0486	0.0270	0.0612	0.0405	0.0441	0.0198	0.0414	0.0388	0.0182
2904	5.05%	0.1129	0.0494	0.0231	0.0610	0.0362	0.0480	0.0224	0.0410	0.0420	0.0076
2950ave	-	-	-	-	-	-	-	-	-	-	-
3966	5.53%	0.1495	0.0593	0.0250	0.0495	0.0640	0.0610	0.0192	0.0463	0.0474	0.0316
3967	5.10%	0.1078	0.0488	0.0206	0.0494	0.0640	0.0609	0.0148	0.0406	0.0488	0.0184
3968	5.40%	0.1141	0.0523	0.0199	0.0515	0.0612	0.0506	0.0154	0.0404	0.0351	0.0185
2906	5.15%	0.1009	0.0483	0.0132	0.0412	0.0681	0.2129	0.0154	0.0485	0.0454	0.0344
4120-IX	5.77%	13.77%	4.93%	9.01%	5.48%	6.36%	3.86%	1.59%	4.33%	3.52%	1.04%
4120-V	5.81%	12.79%	5.07%	10.63%	5.11%	4.27%	3.57%	1.48%	4.77%	3.24%	1.64%
4120-VIII	5.80%	13.40%	4.84%	9.89%	5.72%	6.68%	5.05%	1.66%	4.03%	3.88%	4.07%

Appendix 7.4 continued.

ID	Location	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]
4329	HSS	545324	1080198	758776	557856	49283	568041	520570	465839	104106	535806	175285	748568
4330	HSS	327701	671265	555866	369597	30736	375983	329687	286013	71205	346873	109216	465248
4331	HSS	483423	975737	702303	484282	33101	461485	468299	437424	76446	488323	148055	666664
4332	HSS	305825	585054	387906	280111	18007	257264	272372	252957	66537	291001	99548	403732
4333	HSS	548260	1086427	761234	518728	61547	513641	551217	478214	105733	551907	172367	775069
4334	HSS	469779	969683	747957	510511	61523	543863	487387	427185	62569	501856	152006	673252
4335	HSS	444232	920823	667107	471594	41896	425139	455260	399167	63022	464647	133544	621837
4336	HSS	474626	978921	770554	548008	60354	520343	499332	421229	77793	513512	153078	642754
4337	HSS	540438	1089485	775759	520707	57145	490887	553240	478902	96745	526506	160813	717660
4338	HSS	520535	1047006	734739	510830	50836	479221	524958	438024	40858	505190	160580	698092
3959	YCG	654877	1350846	1027486	749544	81154	843349	666921	555807	167180	681003	221953	916709
4058	YCG	495785	1041869	835252	526073	58273	576499	505116	427897	92754	514602	163332	689819
4059	YCG	757046	1555560	1108875	800227	91301	887087	756075	618557	157084	763480	244664	1027222
4060a	YCG	581997	1245173	966884	738548	0	879312	610354	527550	140927	629516	205845	844420
4060b	YCG	655452	1318847	932123	700689	0	846386	615769	582253	134188	653701	222373	913330
4061	YCG	622849	1262672	887838	639218	76162	736779	609175	514025	152760	624988	206035	860401
4062	YCG	929959	1871246	1350916	958467	106855	1076972	920462	760344	210853	921970	299988	1252589
4063	YCG	542660	1137349	846831	641020	0	814441	568326	485410	183435	565318	188120	776088
4064	YCG	559658	1156647	895363	658942	0	845381	567986	508365	147777	578049	202677	796740
4065	YCG	673419	1352719	1020235	718592	82304	859248	681531	560140	186606	679308	229681	916203
4066	YCG	456381	962475	750327	573793	0	1142625	448421	411860	94826	476839	166495	636010
4067	YCG	643080	1300886	905980	696804	0	830863	610835	569093	154169	644337	225441	907644
4068	YCG	517997	1060338	828290	623012	0	1200659	517283	466682	129103	535809	194427	723887
4069	YCG	147057	284318	232111	149995	14168	214846	133995	132424	36283	146380	47678	194506
4070	YCG	723673	1471043	1101983	780588	70745	864766	711336	595087	133479	728684	218704	967601
4071	YCG	635320	1244558	909981	587782	59896	720613	624806	519064	144312	605227	204404	833334

Appendix 7.4 continued.

Lotno	[Ile]	[Asx]%	[Glx]%	[Ser]%	[L-Thr]%	[L-His]%	[Gly]%	[L-Arg]%	[Ala]%	[Tyr]%	[Val]%	[Phe]%	[Leu]%
4329	351223	8.44%	16.72%	11.74%	8.63%	0.76%	8.79%	8.06%	7.21%	1.61%	8.29%	2.71%	11.59%
4330	223114	7.87%	16.13%	13.35%	8.88%	0.74%	9.03%	7.92%	6.87%	1.71%	8.33%	2.62%	11.18%
4331	315534	8.42%	17.00%	12.23%	8.44%	0.58%	8.04%	8.16%	7.62%	1.33%	8.51%	2.58%	11.61%
4332	187486	8.97%	17.17%	11.38%	8.22%	0.53%	7.55%	7.99%	7.42%	1.95%	8.54%	2.92%	11.85%
4333	365164	8.45%	16.74%	11.73%	7.99%	0.95%	7.91%	8.49%	7.37%	1.63%	8.50%	2.66%	11.94%
4334	329511	7.91%	16.33%	12.60%	8.60%	1.04%	9.16%	8.21%	7.20%	1.05%	8.45%	2.56%	11.34%
4335	304602	8.21%	17.01%	12.32%	8.71%	0.77%	7.85%	8.41%	7.37%	1.16%	8.58%	2.47%	11.49%
4336	320602	7.94%	16.37%	12.88%	9.16%	1.01%	8.70%	8.35%	7.04%	1.30%	8.59%	2.56%	10.75%
4337	352351	8.50%	17.13%	12.20%	8.19%	0.90%	7.72%	8.70%	7.53%	1.52%	8.28%	2.53%	11.28%
4338	332370	8.61%	17.33%	12.16%	8.45%	0.84%	7.93%	8.69%	7.25%	0.68%	8.36%	2.66%	11.55%
3959	414821	7.86%	16.21%	12.33%	9.00%	0.97%	10.12%	8.00%	6.67%	2.01%	8.17%	2.66%	11.00%
4058	320807	7.93%	16.68%	13.37%	8.42%	0.93%	9.23%	8.08%	6.85%	1.48%	8.24%	2.61%	11.04%
4059	468910	8.20%	16.84%	12.01%	8.66%	0.99%	9.60%	8.19%	6.70%	1.70%	8.27%	2.65%	11.12%
4060a	385412	7.50%	16.05%	12.47%	9.52%	0.00%	11.34%	7.87%	6.80%	1.82%	8.12%	2.65%	10.89%
4060b	417713	8.20%	16.50%	11.66%	8.77%	0.00%	10.59%	7.70%	7.28%	1.68%	8.18%	2.78%	11.43%
4061	380920	8.22%	16.67%	11.72%	8.44%	1.01%	9.73%	8.04%	6.79%	2.02%	8.25%	2.72%	11.36%
4062	570920	8.28%	16.66%	12.03%	8.53%	0.95%	9.59%	8.20%	6.77%	1.88%	8.21%	2.67%	11.15%
4063	350107	7.64%	16.02%	11.93%	9.03%	0.00%	11.47%	8.01%	6.84%	2.58%	7.96%	2.65%	10.93%
4064	360371	7.69%	15.89%	12.30%	9.05%	0.00%	11.62%	7.80%	6.98%	2.03%	7.94%	2.78%	10.95%
4065	420990	8.04%	16.14%	12.17%	8.57%	0.98%	10.25%	8.13%	6.68%	2.23%	8.11%	2.74%	10.93%
4066	287879	7.12%	15.02%	11.71%	8.95%	0.00%	17.83%	7.00%	6.43%	1.48%	7.44%	2.60%	9.93%
4067	396335	8.16%	16.50%	11.49%	8.84%	0.00%	10.54%	7.75%	7.22%	1.96%	8.17%	2.86%	11.51%
4068	325120	7.27%	14.89%	11.63%	8.75%	0.00%	16.86%	7.26%	6.55%	1.81%	7.52%	2.73%	10.16%
4069	90843	8.06%	15.58%	12.72%	8.22%	0.78%	11.77%	7.34%	7.26%	1.99%	8.02%	2.61%	10.66%
4070	455601	8.20%	16.67%	12.49%	8.85%	0.80%	9.80%	8.06%	6.74%	1.51%	8.26%	2.48%	10.97%
4071	397149	8.49%	16.62%	12.16%	7.85%	0.80%	9.63%	8.35%	6.93%	1.93%	8.08%	2.73%	11.13%

Appendix 7.4 continued.

Lotno	[Ile]%	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
4329	5.44%	0.1266	0.0438	0.0523	0.0388	0.0418	0.0464	0.0177	0.0378	0.0369	0.0279
4330	5.36%	0.1105	0.0371	0.0425	0.0366	0.0240	0.0469	0.0158	0.0349	0.0333	0.0278
4331	5.50%	0.1235	0.0430	0.0587	0.0410	0.0589	0.0494	0.0157	0.0339	0.0369	0.0276
4332	5.50%	0.1359	0.0406	0.0632	0.0424	0.0284	0.0385	0.0157	0.0410	0.0320	0.0104
4333	5.63%	0.1067	0.0416	0.0447	0.0370	0.0358	0.0395	0.0198	0.0408	0.0332	0.0253
4334	5.55%	0.1113	0.0434	0.0489	0.0420	0.0474	0.0473	0.0203	0.0436	0.0489	0.0406
4335	5.63%	0.1204	0.0442	0.0465	0.0427	0.0542	0.0515	0.0176	0.0383	0.0366	0.0288
4336	5.36%	0.1221	0.0419	0.0552	0.0402	0.0386	0.0425	0.0158	0.0392	0.0310	0.0092
4337	5.54%	0.1225	0.0436	0.0574	0.0429	0.0500	0.0486	0.0157	0.0399	0.0329	0.0093
4338	5.50%	0.1060	0.0391	0.0460	0.0369	0.0294	0.0437	0.0169	0.0355	0.0305	0.0070
3959	4.98%	0.1133	0.0452	0.0519	0.0430	0.0552	0.0396	0.0156	0.0720	0.0522	0.0228
4058	5.13%	0.1127	0.0427	0.0802	0.0395	0.0480	0.0501	0.0155	0.0396	0.0395	0.0221
4059	5.08%	0.1151	0.0456	0.0533	0.0430	0.0422	0.0440	0.0164	0.0424	0.0433	0.0234
4060a	4.97%	0.1188	0.0457	0.0582	0.0409	0.0403	0.0339	0.0146	0.0426	0.0477	0.0169
4060b	5.23%	0.1203	0.0459	0.0530	0.0442	0.0413	0.0412	0.0153	0.0438	0.0364	0.0178
4061	5.03%	0.1168	0.0451	0.0534	0.0407	0.0389	0.0341	0.0167	0.0403	0.0429	0.0245
4062	5.08%	0.1091	0.0444	0.0459	0.0409	0.0379	0.0404	0.0161	0.0409	0.0426	0.0232
4063	4.93%	0.1179	0.0458	0.0522	0.0396	0.0400	0.0388	0.0136	0.0400	0.0460	0.0153
4064	4.95%	0.1165	0.0454	0.0562	0.0404	0.0440	0.0371	0.0143	0.0416	0.0476	0.0180
4065	5.02%	0.1119	0.0447	0.0475	0.0443	0.0489	0.0441	0.0150	0.0373	0.0412	0.0228
4066	4.49%	0.1286	0.0465	0.0737	0.0399	0.0358	0.0433	0.0144	0.0421	0.0381	0.0114
4067	5.03%	0.1255	0.0461	0.0611	0.0440	0.0384	0.0359	0.0142	0.0396	0.0471	0.0152
4068	4.56%	0.1141	0.0454	0.0470	0.0404	0.0348	0.0369	0.0141	0.0397	0.0349	0.0122
4069	4.98%	0.1234	0.0464	0.0566	0.0408	0.0437	0.0517	0.0185	0.0463	0.0449	0.0366
4070	5.16%	0.1278	0.0460	0.0681	0.0395	0.0389	0.0428	0.0161	0.0414	0.0448	0.0289
4071	5.30%	0.1137	0.0464	0.0795	0.0393	0.0533	0.0449	0.0154	0.0414	0.0442	0.0298

Appendix 7.4 continued.

ID	Location	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]
4072	YCG	444899	891125	720965	478371	60039	606613	448524	403551	123276	457248	172235	644886
4073	YCG	565028	1139953	897607	623060	50972	768942	488612	523050	107526	609121	182008	752695
4074	YCG	496431	970471	850976	561142	0	726192	480770	429238	105604	513163	194893	700000
4075	YCG	742369	1613173	1207562	877043	89888	986224	691197	639494	141333	830084	260036	1038380
4076	YCG	498557	1002843	758720	569806	0	696237	472812	458212	115116	518242	181932	711503
4077	YCG	552081	1120486	839419	628118	0	732144	559255	487819	119060	576949	192816	793233
4078	YCG	833910	1658382	1104173	796718	86789	940333	794980	650370	200368	792980	271101	1123927
4079	YCG	797056	1614511	1066297	795436	65518	873852	741890	633640	180797	770328	259648	1074457
4080	YCG	784356	1552484	1012076	737389	81909	833983	732299	623699	185640	747183	264134	1078403
4095	YCG	326819	590745	336823	330376	0	78619	331537	266211	71484	341134	106227	517405
4081	YLB	626469	1246229	921217	687579	0	809382	614182	548454	116523	630387	215564	877175
4082	YLB	667437	1456780	1145382	822526	67271	878548	689024	595427	176067	731400	217223	922381
4083	YLB	648761	1266171	849058	613198	56146	677239	593466	531557	130306	618009	204659	855015
4084	YLB	716404	1488850	1122827	824154	73621	894976	724493	596675	325739	740390	250326	990945
4085	YLB	722708	1467755	1038334	787036	55099	786970	680024	616250	118993	723742	226829	963507
4086	YLB	662457	1313737	922537	656027	57014	736393	616523	560201	159715	644617	217587	891403
4087a	YLB	629178	1245953	817038	613008	49716	701541	555461	513953	109269	614816	204006	845124
4087b	YLB	785985	1568344	1050782	768219	62835	902471	724329	650352	144151	764538	247252	1048857
4088	YLB	559402	1059102	657521	579830	0	293167	603721	458219	132129	595344	192920	884705
4089	YLB	804972	1602614	1148970	823913	70635	994632	773866	670145	187825	784028	258257	1077846
4090	YLB	762590	1468974	993462	698768	58496	858535	673290	638608	163773	702496	251464	995861
4091	YLB	661031	1323210	990114	690474	56084	854851	629618	569541	157589	666333	236640	913858
4092	YLB	774092	1511426	1064303	754295	76143	952056	716503	650987	211543	740429	275774	1060732
4093	YLB	293171	517657	309121	287270	0	68160	301409	236704	80387	302896	103268	486371
4094	YLB	736173	1456342	1024651	721444	69679	859369	695340	611906	143986	719211	248723	1009236
4121	YSG	768071	1536424	1060668	758543	73176	785575	710387	621413	157119	735954	227058	1012286

Appendix 7.4 continued.

Lotno	[Ile]	[Asx]%	[Glx]%	[Ser]%	[L-Thr]%	[L-His]%	[Gly]%	[L-Arg]%	[Ala]%	[Tyr]%	[Val]%	[Phe]%	[Leu]%
4072	274826	7.77%	15.56%	12.59%	8.35%	1.05%	10.59%	7.83%	7.05%	2.15%	7.98%	3.01%	11.26%
4073	371502	7.98%	16.10%	12.68%	8.80%	0.72%	10.86%	6.90%	7.39%	1.52%	8.60%	2.57%	10.63%
4074	310029	7.83%	15.31%	13.42%	8.85%	0.00%	11.46%	7.58%	6.77%	1.67%	8.10%	3.07%	11.04%
4075	505516	7.72%	16.76%	12.55%	9.11%	0.93%	10.25%	7.18%	6.65%	1.47%	8.63%	2.70%	10.79%
4076	312297	7.92%	15.93%	12.05%	9.05%	0.00%	11.06%	7.51%	7.28%	1.83%	8.23%	2.89%	11.30%
4077	348083	7.94%	16.12%	12.08%	9.04%	0.00%	10.54%	8.05%	7.02%	1.71%	8.30%	2.77%	11.41%
4078	505762	8.54%	16.99%	11.31%	8.16%	0.89%	9.63%	8.15%	6.66%	2.05%	8.12%	2.78%	11.52%
4079	483695	8.52%	17.25%	11.40%	8.50%	0.70%	9.34%	7.93%	6.77%	1.93%	8.23%	2.77%	11.48%
4080	468179	8.62%	17.06%	11.12%	8.10%	0.90%	9.16%	8.05%	6.85%	2.04%	8.21%	2.90%	11.85%
4095	213177	9.31%	16.83%	9.59%	9.41%	0.00%	2.24%	9.44%	7.58%	2.04%	9.72%	3.03%	14.74%
4081	394834	8.15%	16.21%	11.98%	8.94%	0.00%	10.53%	7.99%	7.13%	1.52%	8.20%	2.80%	11.41%
4082	448039	7.57%	16.52%	12.99%	9.33%	0.76%	9.96%	7.81%	6.75%	2.00%	8.29%	2.46%	10.46%
4083	384420	8.73%	17.05%	11.43%	8.26%	0.76%	9.12%	7.99%	7.16%	1.75%	8.32%	2.76%	11.51%
4084	450110	7.79%	16.18%	12.21%	8.96%	0.80%	9.73%	7.88%	6.49%	3.54%	8.05%	2.72%	10.77%
4085	458785	8.36%	16.98%	12.01%	9.10%	0.64%	9.10%	7.87%	7.13%	1.38%	8.37%	2.62%	11.14%
4086	403544	8.45%	16.75%	11.76%	8.37%	0.73%	9.39%	7.86%	7.14%	2.04%	8.22%	2.77%	11.37%
4087a	384263	8.64%	17.11%	11.22%	8.42%	0.68%	9.63%	7.63%	7.06%	1.50%	8.44%	2.80%	11.60%
4087b	492865	8.53%	17.03%	11.41%	8.34%	0.68%	9.80%	7.86%	7.06%	1.56%	8.30%	2.68%	11.39%
4088	0	9.30%	17.60%	10.93%	9.64%	0.00%	4.87%	10.04%	7.62%	2.20%	9.90%	3.21%	14.71%
4089	502856	8.30%	16.52%	11.84%	8.49%	0.73%	10.25%	7.98%	6.91%	1.94%	8.08%	2.66%	11.11%
4090	438447	8.76%	16.88%	11.41%	8.03%	0.67%	9.86%	7.73%	7.34%	1.88%	8.07%	2.89%	11.44%
4091	400373	8.11%	16.24%	12.15%	8.47%	0.69%	10.49%	7.73%	6.99%	1.93%	8.18%	2.90%	11.21%
4092	458315	8.37%	16.35%	11.51%	8.16%	0.82%	10.30%	7.75%	7.04%	2.29%	8.01%	2.98%	11.47%
4093	196216	9.21%	16.27%	9.71%	9.03%	0.00%	2.14%	9.47%	7.44%	2.53%	9.52%	3.24%	15.28%
4094	445202	8.42%	16.66%	11.72%	8.25%	0.80%	9.83%	7.95%	7.00%	1.65%	8.23%	2.85%	11.55%
4121	471131	8.61%	17.23%	11.89%	8.51%	0.82%	8.81%	7.97%	6.97%	1.76%	8.25%	2.55%	11.35%

Appendix 7.4 continued.

Lotno	[Ile]%	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
4072	4.80%	0.1227	0.0445	0.0790	0.0510	0.0330	0.0398	0.0110	0.0351	0.0491	0.0164
4073	5.25%	0.1591	0.0489	0.1196	0.0455	0.0570	0.0478	0.0151	0.0442	0.0476	0.0352
4074	4.89%	0.1102	0.0455	0.0309	0.0450	0.0270	0.0399	0.0176	0.0355	0.0525	0.0169
4075	5.25%	0.1833	0.0491	0.1234	0.0422	0.0438	0.0468	0.0169	0.0472	0.0445	0.0302
4076	4.96%	0.1244	0.0459	0.0643	0.0440	0.0404	0.0420	0.0189	0.0446	0.0411	0.0173
4077	5.01%	0.1209	0.0455	0.0540	0.0415	0.0283	0.0450	0.0170	0.0404	0.0516	0.0164
4078	5.18%	0.1206	0.0462	0.0466	0.0393	0.0355	0.0425	0.0168	0.0447	0.0439	0.0294
4079	5.17%	0.1256	0.0456	0.0525	0.0368	0.0363	0.0401	0.0150	0.0407	0.0477	0.0287
4080	5.14%	0.1176	0.0451	0.0459	0.0401	0.0388	0.0453	0.0156	0.0415	0.0488	0.0267
4095	6.07%	0.1293	0.0378	0.1340	0.0598	0.0950	0.0357	0.0303	0.0982	0.0088	0.0246
4081	5.14%	0.1250	0.0463	0.0673	0.0435	0.0332	0.0418	0.0156	0.0408	0.0514	0.0176
4082	5.08%	0.1258	0.0462	0.0663	0.0404	0.0518	0.0461	0.0165	0.0424	0.0492	0.0294
4083	5.18%	0.1254	0.0466	0.0643	0.0432	0.0527	0.0502	0.0164	0.0458	0.0459	0.0242
4084	4.89%	0.1170	0.0424	0.0587	0.0371	0.0347	0.0400	0.0151	0.0340	0.0393	0.0237
4085	5.31%	0.1327	0.0469	0.0744	0.0415	0.0505	0.0517	0.0169	0.0417	0.0442	0.0230
4086	5.15%	0.1297	0.0470	0.0751	0.0428	0.0655	0.0463	0.0159	0.0387	0.0445	0.0239
4087a	5.28%	0.1412	0.0490	0.0686	0.0435	0.0453	0.0522	0.0192	0.0440	0.0441	0.0266
4087b	5.35%	0.1387	0.0489	0.0631	0.0407	0.0440	0.0523	0.0175	0.0454	0.0468	0.0301
4088	0.00%	0.1195	0.0391	0.0746	0.0437	0.0318	0.0362	0.0182	0.0449	0.0217	0.0000
4089	5.18%	0.1239	0.0467	0.0634	0.0399	0.0497	0.0463	0.0157	0.0409	0.0473	0.0293
4090	5.04%	0.1299	0.0473	0.0716	0.0416	0.0615	0.0473	0.0162	0.0400	0.0504	0.0218
4091	4.91%	0.1318	0.0482	0.0650	0.0407	0.0513	0.0544	0.0162	0.0400	0.0474	0.0313
4092	4.96%	0.1229	0.0463	0.0563	0.0399	0.0466	0.0478	0.0156	0.0421	0.0495	0.0270
4093	6.17%	0.1181	0.0347	0.0545	0.0587	0.0948	0.0274	0.0328	0.1499	0.0072	0.0316
4094	5.09%	0.1212	0.0468	0.0642	0.0410	0.0470	0.0568	0.0173	0.0430	0.0521	0.0316
4121	5.28%	0.1276	0.0496	0.0653	0.0401	0.0438	0.0387	0.0174	0.0486	0.0473	0.0300

Appendix 7.4 continued.

ID	Location	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]
4122	YSG	807109	1664572	1137891	854182	87156	903436	808189	672721	189237	797789	237925	1077369
4123	YSG	318861	568970	301577	309894	0	68593	323931	261652	69487	320713	89974	481023
4124	YSG	853148	1708925	1165071	838490	80264	982640	808518	711423	210749	855129	276787	1169675
4125	YSG	725713	1484078	1090837	801855	61800	1038247	688201	606786	150492	729692	243614	991146
3944	NBG	412166	949596	863513	608401	46731	730643	412809	467737	117792	513864	133984	563186
3945	NBG	534128	1195408	992946	752684	48763	817722	552385	490712	148361	610885	175008	702926
3946	NBG	804369	1582734	1225753	826193	61524	1142177	732609	664604	205534	799958	291255	1083121
3947	NBG	715356	1716299	1428832	1160680	78492	1149338	797552	706936	146246	853718	222808	987492
3948	NBG	634454	1354310	1090452	811595	62581	1027446	636802	632255	196730	728051	215423	879224
3949	NBG	662940	1318043	1087690	740923	50237	1144931	585450	608902	180215	677929	242239	881858
3950	NBG	449808	951123	850001	577324	41783	774127	436337	460644	122322	506197	152587	604387
3951	NBG	644761	1367345	1144994	817530	61699	1071621	606914	650581	176577	699909	224984	871056
3952	NBG	504049	1117574	939482	676983	43712	804358	502283	492677	120048	590309	168839	694487
3953	NBG	598523	1330321	1245326	826506	67001	1046609	610842	584124	155596	723460	209884	839624
3954	NBG	664040	1318647	1044301	712306	57648	998672	588822	555403	147033	673171	235400	914113
3955	NBG	473867	1124860	1049760	750737	52168	914646	523241	535976	130111	625394	152670	659987
3956	NBG	608840	1297201	1092859	776097	56208	1021794	610438	544195	173138	675408	218155	839804
3957	NBG	824012	1671810	1365806	901526	77173	1344313	783208	691297	233587	850020	299781	1126864
4544	NQS	346654	670093	582680	330115	45815	709383	285162	302275	117275	321009	126394	440293
4545	NQS	715833	1371504	889006	646220	70970	647532	655933	620521	101162	679648	237673	969838
4546	NQS	415959	846909	577029	434282	39693	395269	365876	381204	69144	420503	115707	563548
4547	NQS	481980	1000925	676623	480811	39972	487537	475223	431960	116770	495010	145644	655713
5169	BKA	328212	658360	392440	309357	0	308623	294106	294185	64135	323209	96674	470817
5170	BKA	618032	1271351	739308	623928	0	596219	574643	550650	93399	628008	171791	869129
5171	BKA	560887	1146105	712623	584307	0	547678	549169	491792	103917	578020	155079	787927
5172	BKA	578003	1158239	776175	604155	0	655003	558621	513402	145002	575482	189951	840222

Appendix 7.4 continued.

Lotno	[Ile]	[Asx]%	[Glx]%	[Ser]%	[L-Thr]%	[L-His]%	[Gly]%	[L-Arg]%	[Ala]%	[Tyr]%	[Val]%	[Phe]%	[Leu]%
4122	497678	8.29%	17.10%	11.69%	8.77%	0.90%	9.28%	8.30%	6.91%	1.94%	8.19%	2.44%	11.07%
4123	203702	9.61%	17.15%	9.09%	9.34%	0.00%	2.07%	9.76%	7.88%	2.09%	9.66%	2.71%	14.50%
4124	523614	8.38%	16.78%	11.44%	8.23%	0.79%	9.65%	7.94%	6.99%	2.07%	8.40%	2.72%	11.48%
4125	452986	8.01%	16.37%	12.03%	8.85%	0.68%	11.45%	7.59%	6.69%	1.66%	8.05%	2.69%	10.93%
3944	287405	6.75%	15.55%	14.14%	9.96%	0.77%	11.96%	6.76%	7.66%	1.93%	8.41%	2.19%	9.22%
3945	361683	7.23%	16.19%	13.45%	10.19%	0.66%	11.07%	7.48%	6.65%	2.01%	8.27%	2.37%	9.52%
3946	496270	8.11%	15.96%	12.36%	8.33%	0.62%	11.52%	7.39%	6.70%	2.07%	8.07%	2.94%	10.92%
3947	507471	6.83%	16.39%	13.65%	11.08%	0.75%	10.98%	7.62%	6.75%	1.40%	8.15%	2.13%	9.43%
3948	428574	7.29%	15.57%	12.54%	9.33%	0.72%	11.81%	7.32%	7.27%	2.26%	8.37%	2.48%	10.11%
3949	409018	7.72%	15.34%	12.66%	8.63%	0.58%	13.33%	6.82%	7.09%	2.10%	7.89%	2.82%	10.27%
3950	307264	7.22%	15.26%	13.64%	9.26%	0.67%	12.42%	7.00%	7.39%	1.96%	8.12%	2.45%	9.70%
3951	416004	7.37%	15.62%	13.08%	9.34%	0.70%	12.24%	6.93%	7.43%	2.02%	8.00%	2.57%	9.95%
3952	344193	7.20%	15.97%	13.42%	9.67%	0.62%	11.49%	7.18%	7.04%	1.72%	8.43%	2.41%	9.92%
3953	412901	6.92%	15.38%	14.40%	9.55%	0.77%	12.10%	7.06%	6.75%	1.80%	8.36%	2.43%	9.71%
3954	416936	7.98%	15.84%	12.54%	8.55%	0.69%	11.99%	7.07%	6.67%	1.77%	8.08%	2.83%	10.98%
3955	345406	6.46%	15.33%	14.30%	10.23%	0.71%	12.46%	7.13%	7.30%	1.77%	8.52%	2.08%	8.99%
3956	404068	7.32%	15.59%	13.14%	9.33%	0.68%	12.28%	7.34%	6.54%	2.08%	8.12%	2.62%	10.10%
3957	534137	7.70%	15.62%	12.76%	8.42%	0.72%	12.56%	7.32%	6.46%	2.18%	7.94%	2.80%	10.53%
4544	211302	7.72%	14.93%	12.98%	7.35%	1.02%	15.80%	6.35%	6.73%	2.61%	7.15%	2.82%	9.81%
4545	453182	8.88%	17.02%	11.03%	8.02%	0.88%	8.03%	8.14%	7.70%	1.26%	8.43%	2.95%	12.03%
4546	276540	8.49%	17.28%	11.77%	8.86%	0.81%	8.06%	7.46%	7.78%	1.41%	8.58%	2.36%	11.50%
4547	313099	8.31%	17.25%	11.66%	8.29%	0.69%	8.40%	8.19%	7.45%	2.01%	8.53%	2.51%	11.30%
5169	218640	8.73%	17.52%	10.44%	8.23%	0.00%	8.21%	7.82%	7.83%	1.71%	8.60%	2.57%	12.53%
5170	409089	8.65%	17.79%	10.35%	8.73%	0.00%	8.34%	8.04%	7.71%	1.31%	8.79%	2.40%	12.16%
5171	386774	8.49%	17.35%	10.79%	8.85%	0.00%	8.29%	8.32%	7.45%	1.57%	8.75%	2.35%	11.93%
5172	393150	8.27%	16.58%	11.11%	8.65%	0.00%	9.37%	7.99%	7.35%	2.08%	8.24%	2.72%	12.02%

Appendix 7.4 continued.

Lotno	[Ile]%	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
4122	5.11%	0.1214	0.0486	0.0605	0.0397	0.0479	0.0450	0.0147	0.0436	0.0484	0.0243
4123	6.14%	0.1221	0.0375	0.0427	0.0661	0.1090	0.0307	0.0193	0.0430	0.0082	0.0423
4124	5.14%	0.1296	0.0485	0.0498	0.0407	0.0371	0.0440	0.0184	0.0490	0.0504	0.0309
4125	5.00%	0.1299	0.0482	0.0414	0.0411	0.0448	0.0582	0.0171	0.0445	0.0494	0.0290
3944	4.71%	0.1364	0.0497	0.0579	0.0425	0.0954	0.0613	0.0172	0.0404	0.0577	0.0383
3945	4.90%	0.1277	0.0493	0.0341	0.0405	0.0443	0.0565	0.0162	0.0423	0.0214	0.0359
3946	5.00%	0.1156	0.0477	0.0203	0.0382	0.0418	0.0467	0.0160	0.0414	0.0508	0.0300
3947	4.85%	0.1422	0.0487	0.0642	0.0410	0.0641	0.0765	0.0162	0.0476	0.0567	0.0372
3948	4.93%	0.1208	0.0501	0.0345	0.0409	0.0566	0.0496	0.0162	0.0517	0.0602	0.0337
3949	4.76%	0.1235	0.0486	0.0283	0.0394	0.0738	0.0432	0.0168	0.0427	0.0534	0.0265
3950	4.93%	0.1390	0.0513	0.0505	0.0419	0.0750	0.0471	0.0178	0.0431	0.0644	0.0454
3951	4.75%	0.1407	0.0500	0.0478	0.0409	0.0862	0.0454	0.0159	0.0426	0.0581	0.0357
3952	4.92%	0.1713	0.0505	0.0726	0.0429	0.0658	0.0653	0.0174	0.0459	0.0539	0.0334
3953	4.77%	0.1285	0.0484	0.0396	0.0398	0.0499	0.0496	0.0160	0.0401	0.0563	0.0367
3954	5.01%	0.1220	0.0481	0.0269	0.0408	0.0435	0.0478	0.0168	0.0442	0.0510	0.0300
3955	4.71%	0.1424	0.0506	0.0410	0.0403	0.0840	0.0490	0.0173	0.0462	0.0584	0.0278
3956	4.86%	0.1171	0.0473	0.0204	0.0381	0.0426	0.0437	0.0159	0.0415	0.0510	0.0245
3957	4.99%	0.1140	0.0464	0.0266	0.0397	0.0408	0.0407	0.0162	0.0415	0.0499	0.0281
4544	4.71%	0.1347	0.0431	0.0566	0.0476	0.0668	0.0438	0.0153	0.0368	0.0330	0.0101
4545	5.62%	0.1296	0.0455	0.0524	0.0403	0.0567	0.0376	0.0196	0.0429	0.0348	0.0081
4546	5.64%	0.1533	0.0514	0.3154	0.0521	0.0748	0.0476	0.0159	0.0503	0.0449	0.0264
4547	5.40%	0.1651	0.0519	0.3332	0.0498	0.0467	0.0474	0.0146	0.0508	0.0346	0.0100
5169	5.82%	0.0962	0.0456	0.0266	0.0461	0.0479	0.0415	0.0162	0.0339	0.0471	0.0348
5170	5.73%	0.0963	0.0465	0.0259	0.0460	0.0404	0.0384	0.0153	0.0398	0.0451	0.0279
5171	5.86%	0.0898	0.0439	0.0213	0.0400	0.0386	0.0355	0.0131	0.0337	0.0451	0.0298
5172	5.63%	0.0928	0.0470	0.0209	0.0423	0.0391	0.0357	0.0146	0.0354	0.0488	0.0343

Appendix 7.4 continued.

ID	Location	[Asx]	[Glx]	[Ser]	[L-Thr]	[L-His]	[Gly]	[L-Arg]	[Ala]	[Tyr]	[Val]	[Phe]	[Leu]
5173	BKA	124360	256537	136873	116708	0	110754	114432	115668	27431	121448	35093	185981
5174	BKA	427112	944156	597100	475023	47158	479514	432041	418778	116170	461160	140454	644910
5175	BKA	83916	162163	94253	1089	147675	7414	31647	16810	4226	17968	25895	120099

Appendix 7.4 continued.

Lotno	[Ile]	[Asx]%	[Glx]%	[Ser]%	[L-Thr]%	[L-His]%	[Gly]%	[L-Arg]%	[Ala]%	[Tyr]%	[Val]%	[Phe]%	[Leu]%
5173	86029	8.69%	17.92%	9.56%	8.15%	0.00%	7.74%	7.99%	8.08%	1.92%	8.49%	2.45%	12.99%
5174	291705	7.80%	17.24%	10.91%	8.68%	0.86%	8.76%	7.89%	7.65%	2.12%	8.42%	2.57%	11.78%
5175	54033	10.94%	21.14%	12.29%	0.14%	19.25%	0.97%	4.13%	2.19%	0.55%	2.34%	3.38%	15.65%

Appendix 7.4 continued.

Lotno	[Ile]%	Asx D/L	Glx D/L	Ser D/L	Arg D/L	Ala D/L	Tyr D/L	Val D/L	Phe D/L	Leu D/L	Ile D/L
5173	6.01%	0.0918	0.0445	0.0237	0.0501	0.0517	0.0353	0.0159	0.0371	0.0532	0.0769
5174	5.33%	0.1017	0.0499	0.0292	0.0512	0.0580	0.0367	0.0153	0.0399	0.0549	0.0421
5175	7.04%	0.0940	0.0437	0.0179	2.3635	4.1621	0.1551	0.0717	0.0421	0.0501	0.0392

Appendix 8.1. Technical description (Chapter 6) of all samples, with summary isotope results. For full analytical details see Chapter 7. Density was measured in yarns per cm, except for knitted samples (*) which are in stitches per cm. For fleece type abbreviations, see summary in Walton Rogers (1995). nt = not tested. ndd = no dye detected. Where more than one isotope is listed as an outlier, a comma between them indicates the sample was an outlier from excavation/location median in each independently; a stroke between them indicates that the sample was outlying only when both isotopes were considered together.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
2894	RKH	1000–1200	Yarn	S+Z	-	nt	nt	nt		typical	$\delta^{18}O$
2895	RKH	1000–1200	2/2 plain twill	ZS	8 x 8	nt	nt	nt		typical	$\delta^{18}O$
3961	RKH	1000–1200	Cord	Z2S	-	nt	nt	nt		typical	$\delta^{18}O$
2896ave	RKH	1200–1400	2/2 plain twill	ZS	11 x 8	nt	nt	nt		typical	-
2897	RKH	1200–1400	2/2 plain twill	ZS	10 x 9	nt	nt	nt		typical	-
2898	RKH	1200–1400	2/2 plain twill	ZS	13 x 10	nt	nt	nt		typical	-
2899	RKH	1200–1400	2/2 plain twill	ZS	?	nt	nt	nt		typical	-
2901	RKH	1200–1400	2/2 plain twill	ZS	12 x 8	nt	nt	nt		typical	-
3962	RKH	1200–1400	2/2 plain twill	ZS	12 x 9	nt	nt	nt	even	typical	-
3963	RKH	1200–1400	2/2 plain twill	ZS	?	nt	nt	nt		typical	-
3964	RKH	1200–1400	2/2 plain twill	ZS	10 x 9	nt	nt	nt		typical	-
3965	RKH	1200–1400	Staple	-	-	nt	nt	nt		typical	-
2902	RKH	1400-1600	2/2 plain twill	ZS	8 x 7	nt	nt	nt		typical	-
2903	RKH	1400-1600	Tabby	?SS	16 x 8	nt	nt	nt	napped	atypical	$\delta^{15}N$, $\delta^{2}H$
2904	RKH	1400-1600	Yarn	Z	0	nt	nt	nt		typical	-
2950ave	RKH	1400–1600	Staple	-	-	nt	nt	nt		typical	-
3966	RKH	1400–1600	Tabby	Z+S/S	10 x 8	nt	nt	nt		atypical	$\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$

Appendix 8.1 continued.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
3967	RKH	1400–1600	Tabby	SS	12 x 12	nt	nt	nt	napped	atypical	$\delta^{18}O$
3968	RKH	1400–1600	Tabby	SS	10 x 10	nt	nt	nt		unknown	$\delta^{18}O$
2906	RKH	1400–1600	Staple	-	-	nt	nt	nt		typical	-
4120ave	RKH	1200–1400	2/2 plain twill	ZS	?	nt	nt	nt		typical	-
4329	HSS	C7–8	2/1 plain twill	ZS	14 x 10	madder	none	HM x HM		atypical	$\delta^{2}H/\delta^{18}O$
4330	HSS	C7–8	2/2 chevron/ diamond twill	ZS	11 x 8	ndd	dense	HM x HM		typical	$\delta^{15}N$
4331	HSS	C7–8	Tabby	ZS	3.5 x 3	ndd	dense on coarse fibres	HM		typical	$\delta^{2}H/\delta^{18}O$
4332	HSS	C7–8	Tabby	??		ndd	none	?M x ?M	open	atypical	-
4333	HSS	C7–8	Staple	-	-	ndd	none	H		typical	-
4334	HSS	C7–8	Staple	-	-	ndd	dense	HM		typical	-
4335	HSS	C7–8	Staple	-	-	ndd	medium on coarse fibres	HM	?fell wool	typical	-
4336	HSS	C7–8	Tabby (?band)	ZS	?	ndd	dense	HM x HM	?band	typical	$\delta^{15}N$, $\delta^{18}O$
4337	HSS	C7–8	2/2 diamond twill	ZS	7 x 8	ndd	moderate/ light	HM x HM		typical	-
4338	HSS	C7–8	2/2 diamond twill	ZS	10 x 10	ndd	none	H x H		typical	-
3959	YCG	930–975	Nålebinding	S2Z	-	ndd	none	nt	sock	atypical	-

Appendix 8.1 continued.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
4058	YCG	850–900	Staple	-	-	ndd	none	H		typical	-
4060a	YCG	850–900	Tabby	ZS	12 x 8	ndd	dense	H x HM	loose	typical	-
4060b	YCG	850–900	Yarn	Z2S	-	ndd	none	nt		typical	$\delta^{15}N$
4062	YCG	930–975	Staple	-	-	ndd	none	HM		typical	-
4063	YCG	930–975	Staple	-	-	ndd	none	HM		typical	-
4064	YCG	930–975	Tabby	ZS	5 x 4	ndd	none	H x H	ground of 4065	hybrid typical/ atypical	-
4065	YCG	930–975	Yarn	S	-	ndd	none	H	pile of 4064	hybrid typical/ atypical	-
4066	YCG	930–975	2/2 plain twill	ZS	14 x 7	ndd	none	GM x H		typical	-
4068	YCG	930–975	2/2 chevron twill	ZS	10-11 x 6-7	ndd	dense (warp)/ none (weft)	H x HM	waðmál	atypical	-
4069	YCG	930–975	2/2 chevron twill	ZS	16 x 12	ndd	none	GM x HM		typical	-
4070	YCG	930–975	2/2 chevron twill	ZS	18 x 16	lichen purple	none	HM x M	v even	atypical	-
4072	YCG	975–1150	Staple	-	-	ndd	none	GM		typical	-
4073	YCG	930–975	2/2 diamond twill	ZS	14 x 11	madder	nt	nt		typical	-
4074	YCG	C13–14	Staple	-	-	ndd	none	SF		typical	-

Appendix 8.1 continued.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
4075	YCG	C13	2/1 plain twill	Z/S+Z	11 x 6-7	ndd	none	M x SF+HM		typical	$\delta^{18}O$
4077	YCG	C13	Yarn	Z	-	ndd	none	H		typical	-
4078ave	YCG	Anglo-Scand.	Tabby, piled	ZS	5 x 5	madder	none	H x H+H	locks of loosely twisted wool darned in	hybrid typical/ atypical	-
4079	YCG	Anglo-Scand.	Tabby	ZZ	24 x 16	ndd	none	nt	lining of 4078	atypical	-
4080	YCG	Anglo-Scand.	Yarn	Z2S	-	ndd	none	nt	thread joining 4078 and 4079	typical	-
4095	YCG	930–975	Tabby	ZS	4 x 3-4	ndd	none	M x HM	uneven, loose	typical	$\delta^{13}C/\delta^{15}N$
4081	YLB	930–1040	2/1 diamond twill	ZZ	22 x 11	nt	nt	nt	offcut	unknown	-
4082	YLB	930–1040	2/1 diamond twill	ZZ	20 x 11	nt	nt	nt		unknown	-
4083	YLB	930–1040	2/1 diamond twill	ZZ	16 x 10	nt	nt	nt		unknown	
4085	YLB	930–1040	2/1 chevron twill	ZS	20 x 14	nt	nt	nt		typical	$\delta^{15}N/\delta^{18}O$
4086	YLB	930–1040	2/2 diamond twill	Z/Z+S	14 x 9	nt	nt	nt		typical	-
4088	YLB	900–1000	Tabby(?)	ZS	4 x 3	nt	nt	nt	fulled/matted	typical	-

Appendix 8.1 continued.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
4089	YLB	900–1000	Tabby	SS	5 x 3.5	nt	nt	nt	errors in weave	typical	-
4092	YLB	900–1000	?2/2 plain twill	Z/S+Z	6 x 5	nt	nt	nt		typical	-
4093	YLB	930–1040	?2/1 plain twill	Z/S+Z	4.5 x 5	nt	nt	nt		typical	-
4094	YLB	930–1040	Tabby repp	ZZ	22 x 12	madder	nt	nt		typical	$\delta^{18}O$
4121	YSG	Anglo-Scand.	2/1 diamond	ZZ	22-24/14-16	nt	moderate/ light	H/HM		unknown	-
4123	YSG	Anglo-Scand.	2/2 twill	ZS	10 x 10	tannin	moderate/ light	nt		typical	$\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$
4124	YSG	Anglo-Scand.	2/1 twill	SS	5 x 4	ndd	none	HM x HM		typical	-
4125	YSG	Anglo-Scand.	Tabby	ZS	6-8 x 4	Indigotin + tannin	none	GM x HM	shaggy pile both faces	atypical	-
3944	NBG	1st half C15	Knit	Z2S	15 x 27*	kermes	none	F		atypical	-
3945	NBG	1st half C15	2/2 plain twill	ZZ	14 x 12	nt	nt	nt	heavily fulled	typical	-
3946	NBG	1st half C15	Tabby	SS	5-6 x 5	nt	nt	nt	light-medium fulled	typical	-
3948	NBG	1st half C15	2/2 plain twill	SS	22 x 20	nt	nt	nt	lightly fulled	typical	-
3949	NBG	1st half C15	Tabby	SS	6 x 5	nt	nt	nt	medium fulled	typical	-
3950	NBG	Early C16	Knit	?Z2S	17 x 25*	nt	moderate/ light	SF	cap, lightly fulled	typical	-

Appendix 8.1 continued.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
3951	NBG	Early C16	Knit	?Z2S	22 x 35*	nt	nt	nt	cap	typical	-
3952	NBG	Early C16	2/2 plain twill	ZZ	13 x 86-96	nt	nt	nt	worsted	typical	-
3953	NBG	Early C16	Tabby	SS	11 x 8	nt	nt	nt	lightly fulled	typical	-
3954	NBG	Early C16	Tabby	SS	7 x 5	nt	nt	nt		typical	-
3955	NBG	Early C16	Tabby	SS	14 x 11	nt	nt	nt	lightly fulled	typical	-
3957	NBG	Early C16	Tabby	SS	8 x 8	nt	nt	nt	medium fulled, ?weft-faced	typical	-
4544	NQS	Mid-late C13	2/1 plain twill	ZS	10 x 7	madder	none	H/HM		typical	-
4545	NQS	Mid-late C13	2/1 plain twill	ZS	7 x 5	ndd	none	HM/M		typical	-
4546	NQS	Mid-late C13	Tabby	S2Z/S2Z	2 x 2	ndd	none	nt	?wool	typical	$\delta^{18}O$
4547	NQS	Mid-late C13	Tabby	S2Z/S2Z	2-3 x 3	ndd	none	nt	goat hair	typical	$\delta^{18}O$
5169	BKA	*c.* 750–850	2/2 diamond	ZZ	32 x 16	nt	nt	nt		atypical	-
5170	BKA	*c.* 950–end C10	2/1 diamond	ZZ	55-60 x 17	nt	nt	nt		atypical	-
5171	BKA	*c.*950	Tabby or 2/1 plain twill, piled	??	?	nt	nt	nt	pile (unspun)	typical	-
5172	BKA	*c.950*	Tabby, piled	ZS	4 x 3	nt	nt	nt	rough and thin, pile	typical	-
5173	BKA	*c. 950–975*	2/1 plain twill	Z?	10 x 4-5	nt	nt	nt		typical	-

Appendix 8.1 continued.

ID	Site	Context date	Type	Spin	Density	Dye	Pigment	Fleece	Other	Character	Outlier?
5174	BKA	*c*.950	Tabby	ZS	5 x 4-5	nt	nt	nt	regular, felted on one side	typical	-
5175	BKA	*c*.950	2/1 or 2/2 plain twill, ?piled	ZZ	?	nt	nt	nt		typical	δ^2H, $\delta^{18}O$