CHAPTER 2

LITERATURE REVIEW

Strontium-isotope analysis has an established role within environmental research, as the characteristic chemical properties of strontium mean that it can be used to trace the pathways of important nutrient cations (i.e. Ca^{2+} and Mg^{2+}) through an ecosystem (Åberg 1995). This, for example, has allowed specific mineral nutrient-sources to be characterised within base-depleted environments (e.g. Blum *et al.* 2002). Strontium is also used to identify water sources in aquifers and surface catchments (e.g. Negrel *et al.* 2004; Shand *et al.* 2007). Essentially, these studies are recent adjuncts to the primary role that $^{87}Sr/^{86}Sr$ analysis has played in dating the age of the earth, and in unpicking the metamorphic history of sedimentary rocks. The development of the instrumentation and analytical methods, which allow accurate and precise isotope measurements of the natural stable isotopes of strontium – ^{84}Sr (0.56 %), ^{86}Sr (9.86 %), ^{87}Sr (7.00 %), ^{88}Sr (82.58 %) – to be made as a matter of routine, are summarised in widely available texts, such as Dickin (1995) and Faure and Mensing (2005).

One of the earliest uses of $^{87}Sr/^{86}Sr$ analysis in archaeology was in establishing the provenance of Mediterranean obsidian (Gale 1981). However, Ericson (1985) is widely credited with bringing the potential of $^{87}Sr/^{86}Sr$ analysis to the attention of archaeologists as a tool in the study of human mobility and migration. Figure 2.01 (overleaf) provides an indication of how, since then, the number of publications referring to $^{87}Sr/^{86}Sr$ analysis began to expand rapidly during the mid–late 1990s. This increase in activity is marked by the publication of a series of now highly cited papers (Price *et al.* 1994; Ezzo *et al.* 1997; Grupe *et al.* 1997; Price *et al.* 1998; Price *et al.* 2000), generated by a research-group lead by T. Douglas Price and James H. Burton. These authors established a general framework for the interpretation of human data, within which the originating population of an archaeological skeletal assemblage is assumed to have been in a state of equilibrium with the strontium provided by its local resource catchment.

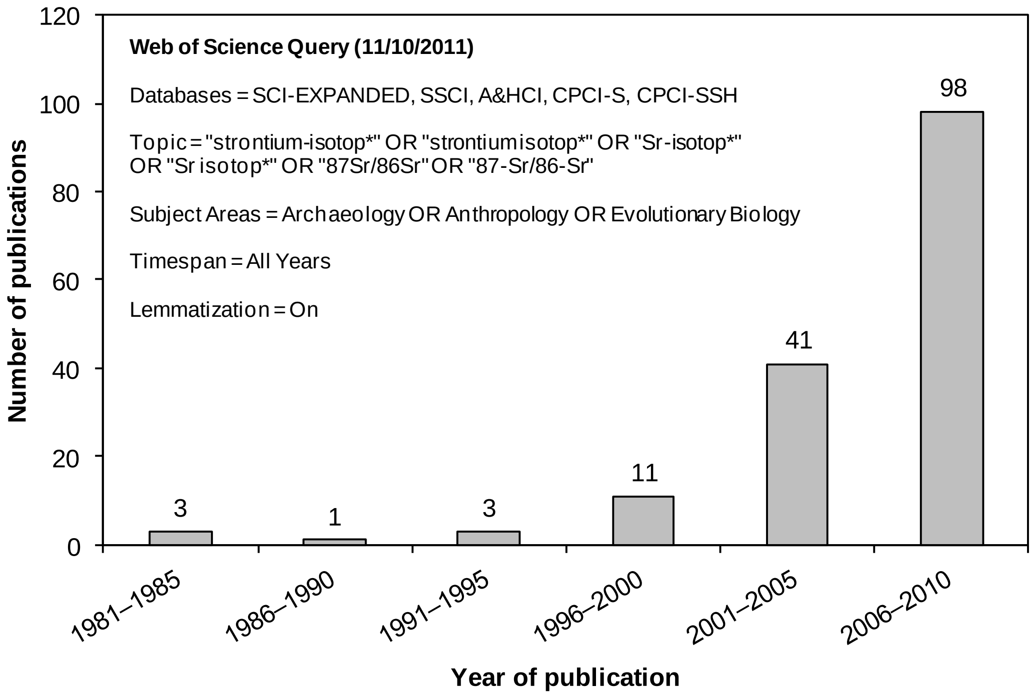


Figure 2.01: Bar chart indicating the rapid increase in publications relating to the use of $^{87}Sr/^{86}Sr$ analysis within archaeology, anthropology and evolutionary biology, derived from Web of Science database query (Web of Knowledge 2011).

Despite the fact that bone is known to be a geochemically open system, with respect to strontium (Schoeninger *et al.* 1984), early archaeological studies tended to make intensive use of this material. However, following Horn and Müller-Söhnius's (1999) review of the work of Grupe *et al.* (1997), the applications of $^{87}Sr/^{86}Sr$ analysis have been advanced substantially by the investigation of the relative levels of preservation of biogenic strontium in different skeletal tissues (Beard and Johnson 2000; Budd *et al.* 2000; Hoppe *et al.* 2003; Trickett *et al.* 2003). Most significantly, the ground-breaking work undertaken by Montgomery (2002) and similar comparisons made by Chiaradia *et al.* (2003), both demonstrate the robustness of highly mineralised core dental enamel to diagenesis, compared even to dentine. Accordingly, bone-based studies have been largely superseded by research based solely on the analysis of archaeological dental enamel.

The theoretical background and many of the applications of $^{87}Sr/^{86}Sr$ analysis within archaeology have been reviewed by Bentley (2006). All are predicated on the assumption that a substantial systematic component of the geographic variation in $^{87}Sr/^{86}Sr$ composition, which can be observed between biota from different regions, is under geological control. Conventionally, archaeological assemblages have been analysed in an attempt to identify a core range of innate local $^{87}Sr/^{86}Sr$ values. Most commonly, extreme values defined by some statistical measure of dispersion have been used to identify non-locals. In addition, human control groups have been established on the basis of cultural associations within cemeteries (Evans *et al.* 2006), and mixing models have been applied to characterise different groups that fall within a common range of $^{87}Sr/^{86}Sr$ values (Montgomery *et al.* 2007).

Biosphere $^{87}Sr/^{86}Sr$ values are thought to be indicative of the age and geochemical characteristics of different geological substrates (Beard and Johnson 2000). However, one of the earliest insights into the application of $^{87}Sr/^{86}Sr$ analysis within archaeology was that biosphere $^{87}Sr/^{86}Sr$ ranges do not resemble whole-rock values. Bioavailable strontium can comprise a complex mixture of strontium provided by rock weathering-products and atmospheric inputs, often with distinctive $^{87}Sr/^{87}Sr$ fingerprints of their own (Ericson 1985). This means that, whether or not non-local individuals can be identified within an assemblage by statistical methods, archaeologists are ultimately dependent on independent empirical environmental data to attach geographic meaning to a given range of $^{87}Sr/^{86}Sr$ values. The first archaeological review paper, dealing specifically with the issues surrounding the geographic characterisation of $^{87}Sr/^{86}Sr$ in the biosphere, was published by Price *et al.* (2002). Based largely on the success of the Grasshopper Pueblo study in Arizona (USA) (Ezzo *et al.* 1997), this popularised the use of modern faunal material to recover site specific $^{87}Sr/^{86}Sr$ biosphere ranges.

The faunal approach to biosphere characterisation has also been applied using archaeological material, in attempt to circumvent the perception that recent anthropogenic inputs may invalidate the use of modern sample media (Bentley 2003; Bentley *et al.* 2004). The approach is encapsulated by Bentley and Knipper (2005), who state that:

> *"Through a lifetime of feeding, herbivores obtain a remarkably consistent average $^{87}Sr/^{86}Sr$ ratio that is representative of their catchment area."* (Bentley and Knipper 2005: 632)

Thus, the narrowing of the variance associated with a theoretical underlying biosphere distribution is often cited as a positive attribute of faunal reference data. This makes the use of animal tissues to obtain a spatial and temporal biosphere average an appealing option, as it appears to circumvent the need for labour-intensive programs of environmental sampling.

However, by 2002 it had already been shown that the high-crowned teeth of domestic sheep and cattle could contain significant time-related changes in $^{87}Sr/^{86}Sr$ composition (Balasse 2002). And indeed, $^{87}Sr/^{86}Sr$ analysis has emerged as a powerful method with which to investigate the use of animals by humans (Bendrey *et al.* 2009; Towers *et al.* 2010; Viner *et al.* 2010; Britton 2011). Although examples from wild fauna are available, which suggest that in some circumstances a consistent dietary average may be achieved (Pellegrini *et al.* 2008), widespread reports of enamel heterogeneity make the general concept of a single site-specific average faunal $^{87}Sr/^{86}Sr$ value somewhat redundant. Perhaps more importantly, these data indicate that distinctive and possibly functionally-discrete $^{87}Sr/^{86}Sr$ biosphere domains were present in the past (Montgomery *et al.* 2010). Studies of migratory species confirms that isotopic differentiation occurs on a sub-continental scale (Britton 2009), but it may also be present on a regional or even local scale commensurate with livestock management (Balasse 2002; Bentley and Knipper 2005; Evans *et al.* 2007).

While it would be naive to assume that a detailed biosphere map would allow geographic provenance to be attributed on an individual basis, even the most basic interpretations of archaeological data make profound assumptions regarding the character of biosphere variation. Even the use of a mean as a measure of central tendency implies that the local individuals contributing to an assemblage provide a representative sample of a uni-modal, and symmetrical biosphere distribution. In contrast, the available faunal data imply that there may be significant variations across the landscape within which livestock are managed. From a practical perspective, it is unlikely that any given range of biosphere $^{87}Sr/^{86}Sr$ values would be geographically unique. However, it is important to attempt to understand the geographic implications of different ranges of $^{87}Sr/^{86}Sr$ values provided by archaeological data. Conceptual models are needed to understand the potential effects of geographic variables on ambient biosphere variation and the character of biosphere variation in different geographic settings.

2.1 The characterisation of biosphere $^{87}Sr/^{86}Sr$ values for archaeological applications

Detailed ecological studies that focus on specific experimental ecosystems provide evidence that strontium with a characteristic $^{87}Sr/^{86}Sr$ composition is passed through the food-chain with some fidelity (Blum *et al.* 2000; Blum *et al.* 2001). In addition, continent-wide food-provenance surveys, such as European TRACE project (TRACE 2009), lend support to the assertion that there is a significant degree of systematic geographic variation in the composition of bioavailable strontium related to underlying geology (Voerkelius *et al.* 2010). However, neither scale of study provides access to the spatial resolution which current interpretations imply may be important in determining the isotopic characteristics of human and faunal archaeological assemblages.

Hodell *et al.* (2004) are amongst the first authors to have published a regional survey of the strontium $^{87}Sr/^{86}Sr$ composition of fully geo-referenced environmental samples. Over 200 samples comprising bedrock, soil, water, and plant material were collected within the Maya region of Mesoamerica (Mexico, Guatemala and Honduras). The authors (*ibid.*) clearly state that they did not intend to achieve equal area coverage of the study region and do not present their findings as a mapping exercise *per se*. Rather, this work represents a systematic ground-truthing exercise, and a vital orientation study for archaeologists working in the Maya region. The authors found that geologic provinces with distinctive $^{87}Sr/^{86}Sr$ distributions are coincident with culturally meaningful geographic subdivisions of the region.

The first explicit attempt to compile a biosphere $^{87}Sr/^{86}Sr$ map of a coherent region of the UK was undertaken on the Isle of Skye by Evans *et al.* (2009). In this study, vegetation and stream waters were collected above a number of distinctive geological divisions of the biosphere. These included a mountainous central granite region, bounded to the north by spatially dominant basalt and ultra-basic rocks and to the south by Lower Palaeozoic and Precambrian meta-sediments. The vegetation data cover a substantial $^{87}Sr/^{86}Sr$ range, from 0.7049–0.7200, reflecting the presence of a number of highly contrasting lithologies. However, although basalt rocks provided the lowest $^{87}Sr/^{86}Sr$ biosphere values, a sample collected directly above the central granite formation provided a value of only 0.7101. Some of the highest values (0.7165–0.7200) were obtained from the foot-hills surrounding the areas of elevated, mountainous topography.

A number of key conclusions are drawn from this paper (Evans *et al.* 2009), which are relevant more widely to biosphere $^{87}Sr/^{86}Sr$ characterisation within the UK. It is suggested that, under high rainfall conditions, seawater-strontium may be an important biosphere end-member. However, there is no evidence of any pronounced, systematic, gradational change in $^{87}Sr/^{86}Sr$ composition. Accordingly, the authors (*ibid.*) dismiss the use of contoured maps in areas of varied and contrasting geology. Rather, distinctive, although overlapping ranges of biosphere $^{87}Sr/^{86}Sr$ values are attributed to discrete, geologically grouped ‘biosphere packages’. The aureole of high $^{87}Sr/^{86}Sr$ values surrounding the mountainous granitic region on Skye, suggest that topographic contrasts between adjacent geological divisions of the biosphere are an important factor in determining the character of the transition between those divisions, and that recent superficial deposits may themselves represent distinctive $^{87}Sr/^{86}Sr$ domains.

The only UK-wide attempt to characterise $^{87}Sr/^{86}Sr$ variation within the biosphere is provided by Evans *et al.* (2010b). To maximise geographic coverage the authors made use of published and unpublished data obtained from vegetation, mineral waters and un-confined stream waters, soil-leaches, and archaeological bone and dentine as a soil-leach proxy. These included data from Evans *et al.* (2009) and Evans and Tatham (2004), but the majority were provided by archaeological studies with a site-specific focus, where biosphere samples were collected on an opportunistic, *ad-hoc* basis. The national biosphere map contained by the publication, is compiled by using the BGS 1:625000 map of bedrock geology (BGS 2008) to extrapolate predicted $^{87}Sr/^{86}Sr$ ranges across large areas of the country. The authors present an interpretive framework for the limited, low-density national data-set, based on the assumption – *a priori* – that underling geology drives systematic biosphere $^{87}Sr/^{86}Sr$ variation.

Using a similar approach, an initial attempt has been made to characterise biosphere variation across the Aegean (Nafplioti 2011); a region where intense tectonic activity has resulted in very great geological complexity. The author (*ibid.*) simplifies this by dividing the study area into fault-bounded structural zones, each comprising rocks that possess a similar geological history. The $^{87}Sr/^{86}Sr$ compositions of samples of archaeological dental enamel from cattle, sheep/goats and pigs/wild boar ($n = 34$), archaeological human and animal bone ($n = 17$), composite samples of modern snail shells ($n = 21$), and one sample of modern rabbit enamel are reported from 26 sites within eight geo-tectonic packages. Where more than one sample medium was available within a geo-tectonic package, these generally provided overlapping ranges of $^{87}Sr/^{86}Sr$ values. Although all bone is highly susceptible to diagenesis, and may largely reflect the $^{87}Sr/^{86}Sr$ composition of labile strontium within the burial environment, the author expresses some doubt concerning the presumed local origin of the human material and chooses exclude these values from their final map (Nafplioti 2011: Figure 3).

Theoretically, the major divisions of the biosphere proposed by Nafplioti (2011) suggest that distinctive geological units, such the granitic rocks of the Attic-Cycladic Massif, have some potential to provide distinctive biosphere $^{87}Sr/^{86}Sr$ values. However, it is apparent form the site descriptions given by author (*ibid.*) that the samples were generally obtained from areas dominated locally by Pleistocene alluvium, Neogene marine sediments, or various Triassic, Jurassic and Cretaceous formations that included limestone and marl members. Excluding two outlying $^{87}Sr/^{86}Sr$ values of 0.7100 and higher, seven out of the eight packages defined by Napfoliti provided samples that varied in $^{87}Sr/^{86}Sr$ composition from around 0.7081–0.7097, with evidence for some degree of systematic geographic variation within this range. The most distinctive values were obtained from three enamel samples from the island of Chios in the NE Aegean (0.7105, 0.7111, 0.7119), but no clear argument is made for why this should be the case.

The majority of the data reported by Nafplioti (2011) resemble the predicted range of biosphere $^{87}Sr/^{86}Sr$ values associated with Mesozoic rocks in the UK suggested by Evans *et al.* (2010b). This may reflect the combined influence of geological marine carbonates and the varied sources of detrital minerals likely to have contributed to the geologically recent sediments present at many of the sample sites. Accordingly, due to the nature of sample collection it is difficult to assess the extent to which the reported values relate to a local environmental context, associated with good preservation of skeletal tissues, or whether the ranges of $^{87}Sr/^{86}Sr$ values are more widely applicable to the much larger geo-tectonic packages defined by the author. Although the use of faunal dental enamel could be considered to be an attempt to overcome this site-specific focus (cf. Bentley *et al.* 2004), no serial sampling was undertaken. This make it difficult assess local variability.

As outlined by Beard and Johnson (2000) the use of geologically-defined biosphere mapping, relies on the assumption that geological map-units define ecologically and culturally meaningful isotope domains. However, in many parts of the world the solid geology is sealed beneath recent superficial deposits. For example, substantial glacial deposits are present across Northern continental Europe, Scandinavia, and the British Isles. In this geographic context, Frei and Frei (2011) report a low-density, survey of stream waters from mainland Denmark, rendered as a national biosphere $^{87}Sr/^{86}Sr$ map. The Danish landscape is dominated by a variety of Pleistocene glacial sediments, which extend from the quaternary plains of the Swedish, Scandinavian Peninsula (Scandia) and into northern Germany and Poland. Rather than attempting to characterise specific geological divisions of the biosphere, the authors (*ibid.*) generate continuous interpolated maps of $^{87}Sr/^{86}Sr$ variation across Denmark, using geo-statistical methods. It is suggested that these reveal more detail than the raw data.

The $^{87}Sr/^{86}Sr$ values reported by Frei and Frei (2011: Table 1) range from 0.7079–0.7206, with a median of 0.7096 (n = 193). The central 50 % of the data fall between 0.7092–0.7100. Over half of the data below the lower quartile are located in Jutland, surrounding Limfjord (an area of open water that separates North Jutland Island from the rest of the Jutland Peninsula). Two samples, with high $^{87}Sr/^{86}Sr$ compositions (0.7160 and 0.7206) were collected on the Danish Island of Bornholm, where Precambrian basement rocks are exposed. The samples from this region are excluded from the authors' statistical treatment. However, due to uneven sampling density and the widespread distribution of occasional high $^{87}Sr/^{86}Sr$ values across the study area, it is difficult to exclude the possibility that many of the 'details' of biosphere variation alluded to by Frei and Frei (2011) are statistical artefacts. Nonetheless, the presented maps do identify the northern region of the Jutland peninsula as a potentially distinctive biosphere domain.

Notably, despite being collected above thick superficial deposits, which frequently contain clasts derived from the Scandinavian shield, Danish stream waters do not generally indicate the widespread presence of high, radiogenic biosphere $^{87}Sr/^{86}Sr$ values. This finding is corroborated by a compilation of archaeological and modern skeletal data reported by Price *et al.* (2011: Figure 4). Although not presented as a biosphere map, these samples were obtained from Denmark and Northern Germany (n = 60), the upland zone of southern Sweden (n = 4) and the lower lying Scandia region (n = 4). Within the Danish data-set, the authors (*ibid.*) include radiogenic values of 0.7114–0.7231 from Island of Bornholm (n = 5), which are consistent with the stream water values reported by Frei and Frei (2011). This range also encompasses the upland Swedish data (0.7128–0.7164) presented by Price *et al.* (2011). However, apart from one sample (0.7160), the data from the Scandia region (0.7104–0.7108) fall within range of the values shown across the rest of Denmark and Northern Germany (0.7073–0.7109); excluding the samples from Bornholm, the central 50 % of these fall between 0.7085–0.7099, but all of the data below the lower quartile were obtained from the Jutland Peninsula.

The data provided by Frei and Frei (2011), in conjunction with those of Price *et al.* (2011), show that it cannot be assumed that glacial deposits containing Precambrian clasts will lead necessarily to the widespread occurrence of biosphere $^{87}Sr/^{86}Sr$ values resembling those seen in areas where radiogenic basement rocks are exposed. This presumably reflects the combined influence of other parent materials – such as the Upper Cretaceous strata, or the Eocene volcanic sentiments that underlie some parts of Denmark – and regional patterns of glacial out-wash. Although the presence of thick, quaternary deposits makes it difficult to establish biosphere packages based on solid geology, Frei and Frei (2011) identify at least one distinctive biosphere domain; In Denmark, biosphere values of 0.7085 and lower (stream water and skeletal data) are reported only within the Jutland Peninsula. However, over 20 % of the available data (skeletal and stream water) from Jutland fall between 0.7086–0.7128, which is similar to the 0.7086–0.7118 range of values reported across the reset of the mainland (i.e. Funen and Zealand). It remains to be seen how broad regional contrasts of this type may be reflected in archaeological data.

At a national scale, biosphere values may by quite variable, but it may still be possible to further resolve regional differences in biosphere $^{87}Sr/^{86}Sr$

variation. Local-scale biosphere $^{87}Sr/^{86}Sr$ variation was investigated in more detail by Sillen *et al.* (1998) in a paleontological study that highlighted the significance of identifying the potential for environmentally controlled differences within one geological province. The authors (*ibid.*) found that the $^{87}Sr/^{86}Sr$ values obtained from comparable sample media were very different in two contrasting but proximate modern environments; that is, in arid grassland (the xeric veldt) and river-side (riparian) habitats. Soil extracts and bulk soils were analysed, along with their associated flora and fauna. When data from hominid fossils were compared with these, it was found that all but one individual closely matched the $^{87}Sr/^{86}Sr$ range obtained from the grassland (veldt) environment. The authors (*ibid.*) acknowledge that, without the modern survey information, it had not been previously possible to interpret the skeletal data (Sillen *et al.* 1995).

Porder *et al.* (2003) also used modern vegetation to obtain estimates of biosphere $^{87}Sr/^{86}Sr$ compositions, but as a geographic control for the characteristic ranges of values obtained from the remains of small mammals recovered from fossil raptor middens. A significant part of their findings relates to the statistical constraint that modern material provided for each fossil site and, in turn the estimated size of the distinct feeding territory of the predators responsible for the accumulation of the fossil assemblages. These constraints were based on a number of key assumptions stated within the paper:

- Bedrock geology and geomorphology determine the boundaries between soils associated with different characteristic $^{87}Sr/^{86}Sr$ ranges in vegetation.
- Strontium-isotope ratios in vegetation on a given rock type have not changed significantly as a result of Holocene soil formation process.
- Strontium is passed from vegetation to the species feeding on that vegetation.
- Skeletal strontium signatures are not the result of diagenetic change.
- Predators pick prey at random over a circular range.

The use of an explicitly defined home-range to render site-specific local biosphere $^{87}Sr/^{86}Sr$ values is not widespread within the archaeological literature. However Chenery *et al.* (2010) do attempt this for Roman Gloucester, located in SW England close to the Welsh boarder. Vegetation collected within a 30 km radius of the city varied in $^{87}Sr/^{86}Sr$ composition from 0.7077–0.7162, and provided a mean value of 0.7109 ± 0.0045 (2 SD, n = 34). Within a 10 km radius of Gloucester, an attenuated biosphere range of approximately 0.708–0.711 is used by the authors (*ibid.*) as a more precise indication of local values (Chenery *et al.* 2010: Figure 5). This reflects the location of the city above lower Jurassic sediments, which include limestone strata that are likely to represent a rich source of geological marine carbonates.

The mean $^{87}Sr/^{86}Sr$ composition of samples collected by Chenery *et al.* (2010) above rocks of Jurassic age is 0.7091 ± 0.0020 (2 SD n = 16), compared with those collected above older rocks (dominated by Palaeozoic sandstones and Triassic mudstones), which provide a mean of 0.7125 ± 0.0037. (2 SD, n = 18). Accordingly, the overall biosphere average is affected by variable sample density within the study area. Rather than using the arithmetic mean, an alternative approach would be to generate a weighted local average based on the exposure of the various outcrops. This would require the additional assumption that the each of the geological formations within the study area could contribute uniformly to dietary strontium, both in terms of overall productivity and the dietary components produced above them. In addition, it would be difficult to determine appropriate confidence limits for such a weighted estimate (Gatz and Smith 1995a; 1995b).

Nonetheless, as part of a review of strontium isotope analysis within archaeological research, Bentley (2006) emphasises the need to characterise local $^{87}Sr/^{86}Sr$ values in relation to specific archaeological sites, advocating the use of faunal material to obtain a representative average for different feeding territories. As an example, Bentley (2006) cites the work of Hoppe *et al.* (1999) as an attempt to:

> *"…help map the biologically-available $^{87}Sr/^{86}Sr$ across Florida and Georgia."* (Bentley 2006: 155)

However, in their study of mammoth migration, Hoppe *et al.* (1999) used plants and surface water to characterise the modern bioavailable isotope-ratios at three fossil quarry sites. Four plant specimens were combined to produce a mean $^{87}Sr/^{86}Sr$ value, which was compared with one water sample at each site. The bones and teeth from three modern rodents were used to provide supplemental local estimates at each of four additional sites. Water values were found to be similar to those provided by vegetation.

In both the faunal and the vegetation data-sets the samples with the lowest quoted confidence intervals were collected from locations that are proximal the coast. That is, summary data for the rodent teeth and plant material area reported to four significant figures as 0.7092 ± 0.0000 and 0.7090 ± 0.0001 respectively (Hoppe *et al.* 1999: Figure 1). These are similar to the composition of modern seawater at 0.70917 ± 0.00001 (Hodell *et al.* 1990; Davis *et al.* 2003), suggesting that the least variable sites may be influenced by a modern marine-strontium contribution. Hoppe *et al.* (1999) assert that the plants provided a measure of biosphere heterogeneity, while the rodents provided an average of a local area. However, the authors (*ibid.*) did not collect comparable numbers of samples systematically at each site, making it difficult to verify whether this is reflected by any difference in variance.

There have been a number of further attempts to estimate local biosphere values using archaeological faunal material. For example, Bentley *et al.* (2004) focus on the use of archaeological pig enamel as a trophic-level proxy for human teeth and Price *et al.* (2002) advocate the use of small rodents. This approach is based on the observation that faunal remains recovered from archaeological sites, or modern animals occupying a given study area, tend to provide a relatively narrow range of strontium isotope values compared to other sample media (Bentley 2006). Its application is exemplified by the Grasshopper Pueblo study of Ezzo *et al.* (1997). The experimental design relies on the assumption that a faunal ‘isotope signature’ provides a suitable proxy for humans, that is closely related to the specific archaeological assemblage being studied. Price *et al.* (2002) recommend the use of archaeological material for the purpose, suggesting that modern sample media may incorporate exotic strontium introduced imported food-stuffs and nutritional supplements.

Bentley and Knipper (2005) attempted to combine the use of archaeological material with the geographic coverage of a survey, to map biosphere variation using archaeological pig enamel. This paper incorporates 22 site-specific characterisation studies that confirm the anticipated contrast between upland and lowland sites. However, any spatial measure of local variation is limited by the distribution of appropriate archaeological sites. Moreover, the reported values are consistent with those available for stream waters (Tricca *et al.* 1999; Eikenberg *et al.* 2001; Aubert *et al.* 2002) or sample media such as snail shells (Bentley 2003), which Bentley and Knipper (2005) use to support the local origin of the archaeological $^{87}Sr/^{86}Sr$ signatures. Similar work undertaken across Midwestern United States has confirmed the presence of significant differences between major geological provinces (Hedman *et al.* 2009). In effect, the geographic controls for this type of study are provided by geological maps.

Haverkort *et al.* (2008) made use of the averaging properties of modern fauna to estimate the range of $^{87}Sr/^{86}Sr$ values associated with three pre-determined and well defined geological provinces in the region of Lake Baikal (Siberia). This study aimed to test two model food-procurement strategies suggested by light isotope studies of Neolithic and Bronze-Age foragers (see Haverkort *et al.* 2008, and references therein). Multiple land mammals and fish were analysed to characterise terrestrial and aquatic resources respectively, within each province. In general the aquatic species were found to be less variable than the terrestrial species, except for Northern Pike; this fish species provided highly radiogenic values in an area that was also associated with the highest terrestrial faunal values.

The data reported by Haverkort *et al.* (2008) suggest that animals associated with the most radiogenic geological provinces provide the highest and most varied range of strontium isotope ratios. The association between radiogenic biosphere $^{87}Sr/^{86}Sr$ values and relatively high levels of sample variance is consistent with the observations made by Evans *et al.* (2009), regarding the relative standard deviations associated with archaeological human assemblages recovered from the British Isles, and biosphere data presented by Chenery *et al.* (2010). This is an important finding as regards the interpretation of archaeological data, especially when comparing skeletal assemblages recovered in different geological settings; that is, does a high level of variance indicate a high level of immigration, the presence of geological divisions of the biosphere that display high levels of ambient variation, or the use of a landscape comprising multiple, isotopically contrasting domains? Either modern, or archaeological faunal data may supply some form of average local reference value, but it may be that only survey methods that make use of fully geo-referenced samples are capable of resolving this issue.

2.2 Systematic geochemical mapping within the British Isles

Although methods of mapping isotopic variation within the biosphere are in their infancy, geochemical mapping is a mature area of research. The concepts and techniques employed today were developed as prospection methods within the field of exploration geochemistry, with a focus on heavy minerals concentrated from stream sediments (Rose *et al.* 1979). The greater number of determinands that can now be measured at lower concentrations, and increased levels of automation, mean that large numbers of samples can now be analysed as a matter of routine (Johnson *et al.* 2008a). Improved analytical techniques have also added to the range of samples that can be used for environmental monitoring. Accordingly, systematic multi-media geochemical surveys can be undertaken at a sufficient scale and sample density to provide detailed geochemical information for a range of purposes (Stone et al. 2003). International initiatives such as the Forum of European Geological Surveys' (FOREGS) '*Geochemical Atlas of Europe'* (Salminen *et al.* 2005) describe a pressing need for basic environmental geochemical data, driven by legislative requirements.

Geochemical mapping exercises are predicated on the assumption that the dominant controls on the distribution inorganic elements in the surface environment are related to underlying geology. Environmental surveys often record 'geochemical baselines', synonymous with the 'ambient background' described by authors such as Reimann and Garrett (2005). These terms are used to describe the total observed geochemical heterogeneity associated with any given surface environment (Salminen and Gregorauskiene 2000). This incorporates the effects of spatially-dependent processes such as weathering, anthropogenic contamination and sea spray enrichment, which are invariably superimposed on any lithogenic distribution (Reimann and Filzmoser 2000). In contrast, the term 'geochemical background' has been used to differentiate 'normal' variation from that associated with an 'anomaly' (Matschullat *et al.* 2000). A geochemical anomaly is conventionally defined as lying above the upper limit of normal variation (Garrett 1991). In the context of exploration geochemistry this may indicate the influence of a point-source, such as an ore deposit. The difference in emphasis reflects the environmental applications of modern geochemical data (Darnley *et al.* 1995).

There are a range of long-established environmental sample media used for geochemical mapping, some of the most commonly used of which are detailed in Table 2.01 (overleaf). These are dominated by materials derived at or immediately adjacent to drainage locations (streams and rivers). This reflects the capacity of such sites to integrate material from a wider, up-stream catchment area (Hawkes and Bloom 1955). For example, overbank sediments, deposited in periods of spate, are used in low density surveys to provide samples related to a substantial catchment area (for example, see floodplain maps in Salminen *et al.* 2005). In comparison – when collected beyond an alluvial setting – soil and vegetation may only represent a small spot-sample, relating the vicinity of the area covered by an artificial composite.

Table 2.01: Characteristics of the sample media used commonly in geochemical mapping exercises.

Sample Medium	Processual Context	Mineral Fraction	Indicative reference
Stream water	Chemical transport within catchment	Water-soluble fraction	Simpson et al. (1993)
Stream sediment	Physical transport within catchment	Less-soluble sediment fraction	Ottesen and Theobald (1994)
Heavy mineral panned concentrate	Physical transport within catchment	Concentrated, robust detrital minerals	Stendal and Theobald (1994)
Flood-plain sediment	Large scale physical transport within catchment	Less-soluble sediment fraction	Ottessen et al. (1989)
Soil	Localised spot sample or area composite	Reservoir of metals	Rawlins et al. (2003)
Vegetation	Plant nutrient uptake through root network	Bioavailable metals	Lax and Selinus (2005)

The geochemical baselines associated with different sample media can vary substantially, both in terms of concentration and the relative abundance of different elements. For example, the concentrations of strontium in stream waters are at least an order of magnitude lower than those in topsoils and stream sediments (Table 2.02, overleaf). Similar observations are applicable to direct biosphere samples; within southern Norway, Reimann *et al.* (2007a) found that the median concentrations of strontium in plant foliage varied from 19 mg/kg (n = 40) in spruce needles to 70 mg/kg (n = 33) in fern leaves (bracken). Even within the same species, different plant tissues can provide different baseline values, and can respond differently under varying environmental conditions (Reimann *et al.* 2007b). In fact, the concentrations and relative abundance of trace elements in plants are influenced by a wealth of interacting factors (Kabata-Pendias and Pendias 2001: 73–98). Accordingly, for the purposes of geochemical mapping it is important to validate collection procedures that can return internally consistent data-sets across a wide variety of geographic settings (e.g. Lax and Selinus 2005). Once an appropriate sample medium has been established, it is also necessary to determine an appropriate sampling density, based on the level of detail required (Plant 1971; Plant and Moore 1979; Fordyce et al. 1993; Hale 1994).

Table 2.02: Strontium concentrations in water, humus, topsoil and stream sediment reported in the "Statistical data of analytical results" provided in the Geochemical Atlas of Europe (Salminen *et al.* 2005: 99–108).

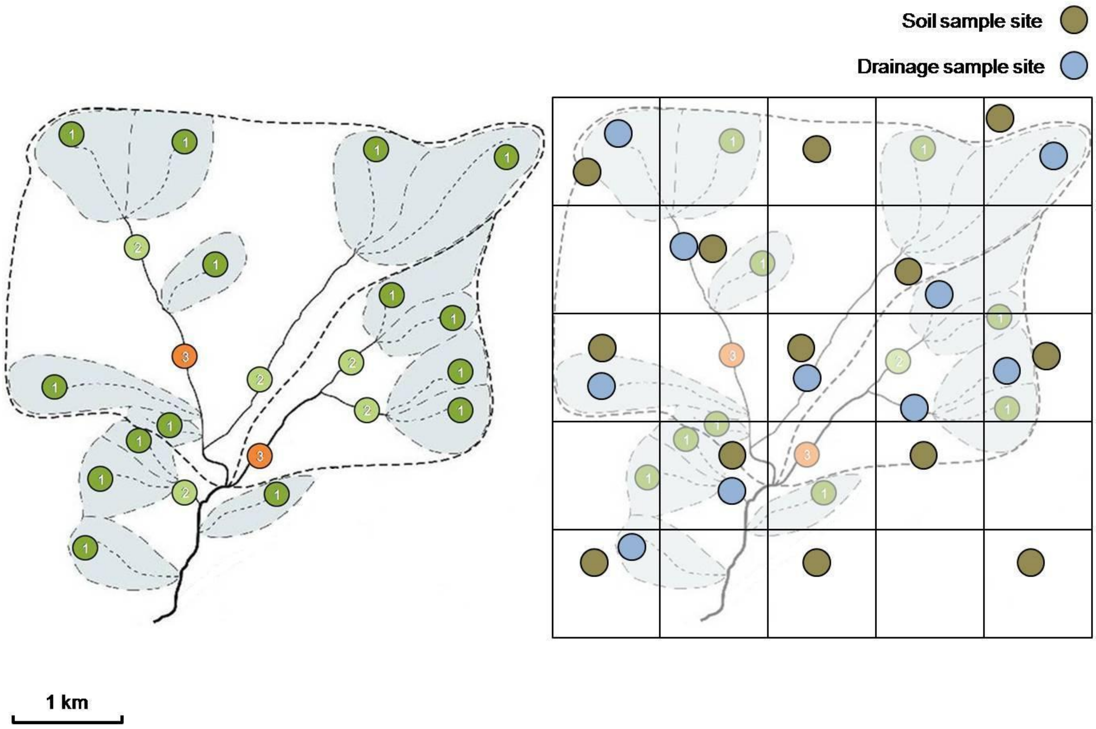
	n	Units	Min	Median	90th percentile	Max
Water	808	mg/l	0.001	0.110	0.494	13.6
Humus	367	mg/kg	1.10	17.4	40.7	205
Topsoil	845	mg/kg	8.00	89.0	249	3120
Stream sediment	852	mg/kg	31.0	126	3144	1352

The first national-scale systematic geochemical mapping exercise to be completed in the British Isles was carried out by the Applied Geochemistry Research Group at Imperial College to produce '*The Wolfson Geochemical Atlas of England and Wales'* (Webb *et al.* 1978). This publication consists of maps showing the concentrations of 21 elements in nearly 50000 stream-sediment samples, plotted at a scale of 1:2000000. Based on sampling small-catchment streams at road intersections in non-urban areas, one sample was collected for approximately every 3 km^2. However, there is no surviving sample archive. A '*Soil Geochemical Atlas for England and Wales'* (McGrath and Loveland 1992) is also available. This is a lower density survey of agricultural land based on the National Soil Inventory (NSI) and provides one soil sample for every 25 km^2, again from non-urban areas. The data and archive from this survey are curated by the National Soil Resources Institute (Cranfield University).

The British Isles are also included within the '*Geochemical Atlas of Europe'* (Salminen *et al.* 2005), which adopted catchment-based sampling strategy at a density appropriate to the sub-continental scale of its remit. Stream waters and sediments were collected at only 60 locations across the United Kingdom (UK), each representing a catchment area of up to 100 km^2. Soils were also collected at 60 locations proximal each drainage site, as were 51 floodplain sediments intended to represent much larger catchments. The published maps illustrate continent-wide patterns of geochemical variation. However, this project did not aim to capture the intense level of regional–local variation associated with the diverse geological history of the British Isles. This scale-related issue is illustrated amply when the European strontium data (Salminen *et al.* 2005) are compared to the British Geological Survey's regional geochemistry atlases of Wales (BGS 1999 and 2000) generated by the Geochemical Baseline Survey of the Environment (G-BASE), which provides a much greater level of detail.

The G-BASE project is the only systematic, high-resolution, multi-media geochemical survey that is currently active within the UK (Johnson *et al.* 2005). It was initiated in the Scottish highlands in the late 1960s, primarily as a tool for mineral prospection. Samples of washed and panned mineral concentrates, recovered from active stream beds were used to highlight the presence of economically important heavy minerals (Stendal and Theobald 1994). As mapping progressed southwards and the remit of the survey was extended, soil samples and stream waters were also collected, to provide a more widely applicable range of environmental data. The project now aims to provide full coverage of Scotland, England and Wales before the year 2020. Significantly, the sampling conditions are optimised to capture the level of geochemical variation known to exist within the British Isles, both within and between mapped geological units (Plant and Moore 1979).

Where local conditions allow, the G-BASE project collects both soils and drainage samples at a density of approximately one sample every 2 km^2, using British Ordnance Survey (OS) National Grid (BNG) to achieve even and unbiased sample coverage (Figure 2.02, overleaf). Under ideal field conditions the G-BASE project aims to collect drainage samples from, small first- and second-order catchment locations that integrate material from an area of no more than a few square kilometres. The pre-selected sites are checked in the field for evidence of localised sources of contamination before samples are collected, and modified accordingly (Johnson 2005). Soil samples are obtained independently, but at the same density, subject to the avoidance of disturbed or made-ground. At each soil site a surface A-horizon soil (5–15 cm, measured below the O-horizon) is collected from five holes augured at the corners and the centre of a 20 × 20 m square. These are combined to form a composite sample of around 1 kg. Where possible, deeper soils (35–50 cm) are also collected from the same auger holes, providing a second composite soil-samples of equivalent size.



Shaded areas indicate the watersheds for the drainage basins of 1st order streams (1). First order basins are components of a larger drainage system (3rd order basin) identified by the bold dashed line: two 1st order streams (1) merge to form a 2nd order stream (2); two 2nd order streams join to form a 3rd order stream (3) and so on. Two streams of any given order must join to form a stream of the next highest order.

Figure 2.02: Schematic diagram showing the delineation of a drainage basin by watershed and the 1×1 km Ordnance Survey (OS) grid-based system used by the G-BASE project to achieve consistent sample density, after Johnson *et al.* (2008b: Figure 4.1), with modifications.

The G-BASE project is not a targeted survey. That is, it aims to achieve consistent and un-biased coverage across the UK, at a density which means that the data are applicable to as wide a range of current and future users as possible. Considerable planning, logistical support and rigorous quality control procedures ensure consistency within and between sampling campaigns (Johnson *et al.* 2008a). At present, the area covered by the G-BASE archive extends from the Shetland Islands down to southern England, excluding urban areas as defined using the 1:50000 OS Landranger map series.

A the time of writing, the most recently analysed samples were collected from an area, partly within the Chiltern Hills, that extends down a section of the Cretaceous Chalk Escarpment and across the lower lying rocks of the Upper Jurassic to the Oolitic Limestones at the north eastern limit of the Cotswold Hills. Collected during the field season of 2007, the archive for this region includes vegetation samples, which consist of the woody twigs of mature shrubby trees found at locations proximal to each drainage site. These were collected specifically to support the aims of this thesis (cf. Chapter 3). The high sample density makes the physical, sample archive amenable to targeted re-sampling for developing applications. This material is held in the custody of BGS at the National Geosciences Data Centre (Keyworth) and is readily available to BGS staff and academics.

National projects, such as G-BASE provide high-quality, detailed geochemical data. However, when attempting to produce effective international legislation it may be difficult to reconcile existing data-sets produced to different standards and intended for use at different spatial scales. This issue lead to the establishment of the European project Geochemical Mapping of Agricultural Soils of Europe (GEMAS), a low-density exercise coordinated by the EuroGeoSurvey's Geochemistry Expert Group (EGS GEG). This was designed to generate a harmonised data-set, primarily targeted at addressing legislative requirements related to the introduction of the European Chemicals Regulation, REACH1 (Registration, Evaluation and Authorisation of Chemicals) as well as the pending EU Soil Protection Directive, which pertains to the assessment of soil quality in terms productivity, food quality and its impacts on human health.

The GEMAS field methodology is fully documented in Geological Survey of Norway (NGU) report 2008.038 (Reimann 2008) and the UK contribution is recorded in the British Geological Survey (BGS) report IR/08/081 (Scheib 2011). Soil samples were collected across the European Union, at a consistent density of approximately one sample for every 2500 square kilometres. Within the UK the even distribution of samples was achieved by using the Ordinance Survey British National Grid (BNG) to define 138 50 x 50 km (i.e. 2500 km^2) cells covering England, Scotland (including the Western and Northern Isles), Wales and Northern Ireland, making it flexible enough to allow appropriate sampling locations to be identified, even in areas of low agricultural activity. The arable samples were collected from regularly ploughed and cultivated agricultural fields, but avoiding plots that had been recently fertilised. Permanent grassland was defined by the project as any plot with undisturbed permanent vegetation that had not been ploughed within the last ten years. By specifically targeting these resources, the GEMAS project provided an unprecedented opportunity to collect vegetation samples from permanent grassland across the UK, which contribute to this thesis (Chapter 5).

2.4 Sample media available for biosphere $^{87}Sr/^{86}Sr$ mapping

The spatial and temporal averaging properties of faunal feeding patterns suggest that both wild and domestic animals could provide useful biosphere $^{87}Sr/^{86}Sr$ characterisation media. For example, if faunal remains were recovered from a domestic context, in an agro-pastoral setting they might well provide a proxy for other domestic mammals, or even human remains recovered from associated archaeological sites (Benson *et al.* 2008). It is this level of association which allows some authors to argue that site-specific $^{87}Sr/^{86}Sr$ signatures can be constructed (Price *et al.* 2002).

Unfortunately, the geographic distribution of archaeological sites may restrict the extent to which it is possible to determine the geographic characteristics of variation in the $^{87}Sr/^{86}Sr$ composition of biologically-available strontium. Thus, it may be also be necessary to make use of the concepts and sample collection methods developed for geochemical mapping to help define ambient levels of biosphere $^{87}Sr/^{86}Sr$ variation.

As an example of biosphere $^{87}Sr/^{86}Sr$ characterisation using animals, Haverkort *et al.* (2008) achieve some degree of geographic coverage within their study area (Baikal region of Russian Siberia) by collecting a range of modern terrestrial and aquatic fauna. However, the authors have difficulty in replicating the same suite of species within each of the geological sub-regions that they seek to characterise. For example, arctic ground squirrels (*Spermophilus major*) – a small mammal, presumably with a small home-range – provide nearly a quarter of all samples, but over 71 % of the individuals were collected within one sub-region. In contrast, nearly a third of the data were provided by various deer species – larger animals, with a substantial home range – 90 % of which were collected outside the sub-region from which the majority of ground squirrels were obtained. This is significant, because the levels of dispersal in $^{87}Sr/^{86}Sr$ composition associated with the two biota are different (Haverkort *et al.* 2008: 1273). Because of the imbalance in sample coverage it is impossible to test whether this is a geographic phenomenon, or whether it is related to the ecological niche occupied by each species.

Accordingly, for reasons of geographic coverage it may be prudent to target sample media that can be widely and predictably collected, and which avoid potential ethical objections related to the widespread trapping of wild animals. These issues are identified by Evans and Tatham (2004), who tabulate the advantages and disadvantages of a selection of sample media. This information is reproduced in Table 2.03 (overleaf). Although Evans and Tatham (2004) do not attempt to undertake as detailed a survey as Haverkort *et al.* (2008) the authors identify the level of uncertainty associated with the collection of animal material. Accordingly, Evans and Tatham (2004) rely on the more traditional sample media collected by geochemical surveys, consisting of stream waters, soils, and plant material. These are ubiquitous and easy to collect, and unlike faunal material have the potential to provide a high degree of spatial resolution. Potentially, they could provide an indication of the level of 'ambient background' isotopic variation, as defined in Section 2.2 (above).

Table 2.03: Potential sample media for use in the characterisation of biosphere $^{87}Sr/^{86}Sr$ values, after Evans & Tatham (2004: Table 1) with modifications.

Sample medium	Biosphere compartment	Advantages	Disadvantages
Soil-leach	Reservoir of labile strontium	• Analytical simplicity • Known provenance	• Operationally-defined value • Localised point-sample or artificial composite • Vertical variation through soil Profile
Stream water	Weathering solution run-off	• Bulk measurement • Spatial averaging • Analytical simplicity • Known provenance	• Biased by most soluble minerals • Seasonal change • Weather-related variation
Domestic animals	Biomass	• Temporal buffering • Biosphere measurement • Spatial averaging • Known provenance	• Imported feed and nutritional supplements (non-local food sources) • Livestock management Movements
Wild animals		• Biosphere measurement • Temporal buffering • Spatial averaging	• Uncertain provenance • Uncertain feeding range • Non-local food sources and nutritional supplements • Ethical consent
Vegetation		• Biosphere measurement • Bulk measurement • Temporal buffering • Trophic position (base of food-chain) • Known provenance	• Character of point-sample sample determined by scale and character of nutrient uptake by plant • Challenging sample Preparation

Soil samples appear to have some potential to provide an accurate estimate of the strontium isotope composition of the biosphere. Soils sit at the interface between the geosphere and the biosphere and represent the primary growth medium for terrestrial plants, which sit at the base of the food chain. However, bulk soil analyses do not provide information that is directly applicable to the biosphere, because of differences in the $^{87}Sr/^{86}Sr$ composition, strontium concentration, and the stability of different soil-forming minerals. Horn and Müller-Sohnius (1999) point out that the bulk soil data reported by Grupe *et al.* (1997) do not represent labile strontium and cannot be used to characterise bone diagenesis or characterise local biosphere values. To this end they suggest that aqueous soil extracts could be analysed instead (Horn and Müller-Söhnius 1999: 263). Moreover, Sillen *et al*. (1998) have shown that bulk soil may be considerably more radiogenic and more variable (0.7188–0.9006) than soil leaches (0.7232–0.7556). Their data also suggest that the most radiogenic plant material may not consistently be associated with the most radiogenic bulk-soil values.

In environmental studies, sequential extraction procedures are often used to examine the distribution of trace elements in soils and sediments (Table 2.04, overleaf). The two most commonly applied methods are those referred to as '*Tessier's Scheme'* (Tessier *et al.* 1979) and the '*BCR Scheme'* (Rauret *et al.* 1999), where Chemical extractants are applied in order of increasing activity so that the successive extracts correspond to less mobile metal associations. Owing to their operationally-defined character, some authors choose to develop their own methods to address specific questions related to specific soil-forming environments. For example, carbonate soils with a significant organic component (Breward *et al.* 1996), or those developed in a base-depleted granitoid alluvium (Nezat *et al.* 2007). The latter supports a substantial body of work carried out at Hubbard Brook Experimental Forest (New Hampshire, USA), and was used to identify the mineral sources of nutrient cations in the soils within that region (see Dasch *et al.* 2006 and references therein). Unlike the other schemes detailed in Table 2.04, it is targeted at specific minerals with different solubility profiles.

Single-step extraction schemes have also been developed that divide Tessier's fractions into a 'labile' and a 'non-labile' categories (Ure 1996). These make use of powerful complexing agents such as, ethylene-diamine-tetraacetic acid (EDTA) and dilute weak acid (acetic acid) to extract sufficient material for analysis. Such procedures may be suitable for extracting bioavailable strontium from soils for isotope analysis, but care must be taken to choose sufficiently selective reagents that are appropriate to the soil-type. For example, even weak acids will have a pronounced solvent effect on both the primary carbonates and secondary pedogenic carbonates that present in calcareous soils.

Table 2.04: Examples of soil-leach methods used to characterise the distribution and relative mobility of metals in soils.

<table>
<tr><th colspan="3"></th><th colspan="4">Extraction procedures</th></tr>
<tr><th colspan="3"></th><th>Tessier et al. (1979)</th><th>Rauret et al. (1999)</th><th>Breward et al. (1996)</th><th>Nezat et al. (2007)</th></tr>
<tr><td rowspan="7">Operationally-defined metal fractions</td><td rowspan="2">Labile pool</td><td>Exchangeable</td><td>1 M magnesium chloride solution at pH 7</td><td rowspan="2">0.11 M acetic acid solution at pH 2.85</td><td>1 M ammonium acetate solution at pH 7</td><td>1 M ammonium chloride solution at pH 7</td></tr>
<tr><td>Carbonate-bound</td><td>1 M sodium acetate solution with acetic acid at pH 5</td><td>1 M sodium acetate solution with acetic acid at pH 5</td><td rowspan="5">1 M nitric acid extraction at 20 °C
followed by
1 M nitric acid extraction at 200 °C</td></tr>
<tr><td></td><td>Organic-bound</td><td>NA</td><td>NA</td><td>1 M ammonia solution</td></tr>
<tr><td rowspan="4">Non-labile pool</td><td>Secondary Mn oxides</td><td rowspan="2">0.04 M hydroxylamine hydrochloride solution with 25 % v/v acetic acid at pH 2</td><td rowspan="2">0.5 M hydroxylamine hydrochloride solution with nitric acid at pH 1.5</td><td>0.1 M hydroxylamine hydrochloride solution</td></tr>
<tr><td>Secondary Fe oxides</td><td>0.175 M ammonium oxalate with 0.1 M oxalic acid at pH 3 (Tam's Reagent)</td></tr>
<tr><td>Sulphide and residual organic-bound</td><td>Hydrogen peroxide and nitric acid followed by 0.8 M ammonium acetate and nitric acid at pH 2</td><td>Hydrogen peroxide and nitric acid followed by 1 M ammonium acetate and nitric acid at pH 2</td><td rowspan="2">Hot hydrofluoric acid</td></tr>
<tr><td>Residual silicate-bound</td><td>Hot hydrofluoric acid</td><td>Aqua Regia</td><td>Hot hydrofluoric acid</td></tr>
</table>

Montgomery *et al.* (2000) report dilute acetic acid leaches of Chalk rock and Chalky grave fill (i.e. soil) which each have $^{87}Sr/^{86}Sr$ compositions of 0.7075. This value is approximately equivalent to the composition of Upper Cretaceous marine carbonate (cf. McArthur *et al.* 2001), and is therefore cited as a likely diagenetic end-member (Montgomery *et al.* 2000); a $^{87}Sr/^{86}Sr$ value of 0.7075 It is not considered by the authors (*ibid.*) to be representative of the local biosphere range. Evans and Tatham (2004) addressed this issue by using a dilute acetic acid leach and a de-ionised water leach, and comparing these results directly with the $^{87}Sr/^{86}Sr$ composition of vegetation from the same area. In this paper (*ibid.*), deionised water was found to provide a close approximation of the direct biosphere $^{87}Sr/^{86}Sr$ measurements (vegetation) and archaeological sample media, whereas the acetic acid soil extracts were dominated by the dissolution of endogenous carbonate minerals.

In addition to the operationally-defined biases and errors introduced by different leaching methods, soil-leach $^{87}Sr/^{86}Sr$ values have been found to vary substantially with depth (e.g. Blum and Erel 1997; Poszwa *et al.* 2004; Shand *et al.* 2007; Castorina and Masi 2008). These differences can be explained by soil-forming processes that involve the redistribution of minerals, solutions and colloids between different soil horizons. In contrast, it is possible to make a direct bulk measurement of stream water that is biologically meaningful. By definition this medium represents strontium that is soluble under ambient surface conditions, which can make a direct contribution to the food chain. The range of $^{87}Sr/^{86}Sr$ values recorded in stream waters have been shown to be characteristic of their landscape setting (Shand *et al.* 2009), such that it is possible to use surface water as an indicator of mineral weathering within specific catchments (Bain and Bacon 1994; Negrel *et al.* 2004). The degree to which bedrock type and age controls the $^{87}Sr/^{86}Sr$ compositions is well established (Wadleigh *et al.* 1985) and in some cases these data have been interpreted in relation to mixing lines extended between rain water and groundwater (Shand *et al.* 2007). Accordingly, unconfined surface water and shallow groundwater may provide useful baseline data that are relevant to the extended ecosystem (Capo *et al.* 1998; Blum *et al.* 2000).

Together with the data published by Evans and Tatham (2004), recent biosphere characterisation exercises (Montgomery *et al.* 2003; Evans *et al.* 2009) strongly suggest that plant materials are also capable of providing a direct estimate of modern biologically-available isotope values. Indeed, plant materials have long been used to map the geochemical properties of the surface environment. Lax and Selinus (2005) describe geochemical mapping activities using mosses and the roots of water-tolerant plants collected at riverside locations as part of a systematic, catchment-based national survey of Sweden. These specific materials were selected because they buffer against the short term and seasonal variations in trace element concentrations that influence the riparian environment (Brundin *et al.* 1988).

In terms of isotopic analysis, food provenance studies also indicate that plants and plant-based products possess characteristic strontium isotope ratios that are closely related to their geographic origin (García-Ruiz *et al.* 2007). Living trees have been used to provide geographic control for the provenance of archaeological architectural timber (Reynolds *et al.* 2005). Tree foliage may even record sufficient information to relate the strontium it contains to specific mineral sources (Blum *et al.* 2002; Blum *et al.* 2008). These studies indicate that plant material, including important human food resources (Benson *et al.* 2008) are capable of recording characteristic, regionally defined and geologically controlled strontium isotope signatures. These are independent of strontium concentration, and are transmitted through the food chain with some degree of fidelity (Blum *et al.* 2000; Blum *et al.* 2001).