

CHAPTER TWO

STRONTIUM AND LEAD IN THE BIOGEOSPHERE

2.1 Introduction

The application of Sr and Pb isotope analysis to questions of archaeological migration relies on the fundamental principles of radioactive decay that produces isotope variation within individual rock types. No subsequent modification of these isotope fingerprints of heavy elements occurs in the low temperature processes of weathering, soil production and transferral through the food chain. Thus, Pb and Sr extracted from plants, animals and humans can be traced back to its original geological source by the analysis of the isotope ratios contained within these biological organisms. Recent extensive reviews that explain the use of isotopes as environmental tracers have been published by Åberg (1995) and Capo *et al.* (1998) for Sr and Gulson *et al.* (1994) for Pb. Faure (1986) also covers the subject in considerable depth.

2.2 Strontium and lead in the geosphere

The isotope systems of both Pb and Sr and the possibility of using them as environmental tracers arises from radioactive decay and the formation of crustal rocks. However, their radiogenic isotopes (i.e. ^{87}Sr , ^{206}Pb , ^{207}Pb and ^{208}Pb) are produced by parent isotopes (^{87}Rb , ^{238}U , ^{235}U , ^{232}Th) that have extremely long half-lives, and thus there is negligible change as a result of radioactive decay over archaeological timescales. The Sr and Pb isotope ratios referred to, and presented, in this study (i.e. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$; henceforth referred to as Sr and Pb isotope ratios) are, therefore, essentially being utilised as stable isotope systems. Nevertheless, Pb and Sr are unrelated systems and may vary independently and for different reasons and they have been considered separately in the following sections.

2.2.1 *Strontium geochemistry*

Sr, like calcium (Ca), is an alkaline earth metal (Group IIA) with a slightly larger ionic radius (1.13 Å or 113pm) than that of Ca²⁺ (0.99 Å or 99pm). Sr has four naturally occurring stable isotopes: ⁸⁸Sr, ⁸⁷Sr, ⁸⁶Sr and ⁸⁴Sr, and their abundances are approximately 82.53%, 7.04%, 9.87% and 0.56% respectively. The abundances of ⁸⁸Sr, ⁸⁶Sr and ⁸⁴Sr are constant through time but the amount of ⁸⁷Sr is continually increasing due to the production of radiogenic ⁸⁷Sr from the slow (half-life: 4.88 x 10¹⁰ years) radioactive decay of ⁸⁷Rb, one of the naturally occurring isotopes of rubidium (Rb) (Faure 1986, 119). On archaeological time-scales, however, the decay rate of Rb is negligible. The convention is to measure ⁸⁷Sr relative to ⁸⁶Sr (⁸⁷Sr/⁸⁶Sr), because these two isotopes are most similar in abundance and only one atomic mass unit apart thus reducing measurement errors. ⁹⁰Sr is an artificial radionuclide (half-life: 28 years) produced by nuclear reactions. It has little relevance to archaeological studies but concern over ⁹⁰Sr fallout and exposure coupled with its long residence time in bone, has produced a large corpus of work on Sr movement through the biosphere and incorporation into skeletal tissues.

Sr is classified as a lithophile (silicate loving) element along with Ca and barium (Ba) and all three exhibit similar laser ablation characteristics (Longerich *et al.* 1996, 541). Sr often replaces Ca in many minerals such as apatite and calcium carbonate, although the larger radius of Sr²⁺ prevents it substituting at some Ca²⁺ lattice sites. Rb (ionic radius 1.48 Å or 148pm) substitutes for potassium (K) (ionic radius 1.33 Å or 133pm) in K-bearing minerals such as micas and K-feldspars. The Rb/Sr ratio of minerals may vary considerably, being as low as 0.005 in high-Ca deep sea carbonate to 1.7 in low-Ca granites (Faure 1986, 118). The exact Sr isotope composition of a rock will, therefore, depend on the original Rb/Sr ratio of the rock at crystallisation, its age and hence, how much radiogenic ⁸⁷Sr has evolved, as well as any subsequent mixing, fluid-mineral interaction or metamorphic activity that has occurred. Consequently, older Rb-bearing rocks will tend to contain more radiogenic ⁸⁷Sr than younger rocks whereas if no Rb was incorporated into the rock at formation, it will retain its original, unradiogenic Sr isotope ratio. The estimated ⁸⁷Sr/⁸⁶Sr ratio for “primordial” Sr is 0.699 and, as ⁸⁷Sr has been continually increasing since the Earth was formed, that of the present day mantle is 0.704 ± 0.002. Thus, the Sr isotope ratio in terrestrial whole rocks

can vary from ~ 0.703 for young, volcanic island rocks to >0.750 for K-rich (and hence Rb-rich), igneous granites formed from older, crustal rocks (Graustein 1989, 495). Although these variations may appear to be small, modern thermal-ionisation mass spectrometers can routinely measure Sr isotope ratios to an internal precision of ± 0.000007 (1SE) (Royse *et al.* 1998, 21).

Sr is released from rocks primarily through chemical weathering. Any subsequent alteration of the Sr isotope ratio (i.e. fractionation) that occurs during this and ensuing low-temperature geological or biological processes is negligible (Blum *et al.* 2000, 95; Capo *et al.* 1998, 215; Faure 1986, 186; Graustein 1989, 494; Miller *et al.* 1993, 438). This lack of mass-dependent fractionation in biogeochemical processes results from the comparatively small differences between the isotope masses of heavy elements and contrasts with the ready fractionation that occurs in lighter elements such as oxygen, carbon and nitrogen. Increasing numbers of neutrons can depress chemical reaction rates (Hoefs 1997, 4/5) and there is, for example, a much greater relative difference between ^{16}O and ^{18}O than between ^{87}Sr and ^{86}Sr . Consequently, the isotope abundances that characterise a particular rock move unaltered from the source rock into soils, groundwater, plants and animals.

This does not imply, however, that the Sr isotope ratio measured in, for example, tooth enamel or river water is exactly the same as that of the underlying whole rock. Two factors may complicate the process. Firstly, the Sr isotope ratio released from a heterogeneous, polymineralic rock may not match the ratio of the whole rock. Different components may weather more readily than others, resulting in Sr isotope ratios that are *characteristic* of, but not an *exact* reflection of, the whole parent rock. Furthermore, the Sr isotope ratio of the released Sr tends to be less radiogenic (i.e. smaller) than that of the whole rock because the Rb-bearing minerals, such as micas and K-feldspar, are generally more resistant to weathering than the Sr-bearing plagioclase and calcite minerals. Thus, over time, the remaining source rock becomes increasingly enriched in radiogenic ^{87}Sr (Faure 1986, 183/4), although on recently exposed rock surfaces (e.g. $<10,000$ years) preferential weathering of radiogenic biotite can produce the opposite effect (Blum *et al.* 1994, 5024).

The second process that may alter a given Sr isotope ratio of, for example, stream water, is mixing of two or more sources. Sr released from local rocks into soil and water may be modified by existing non-local Sr derived from other rock types through the mechanisms of wind-blown dust, river-water and precipitation (Blum *et al.* 2000, 91; Capo *et al.* 1998, 203; Miller *et al.* 1993, 438). The Sr isotope ratio of rainwater has seawater as its source. The Sr isotope ratio in modern seawater is extremely homogeneous due to the long residence time of Sr in the oceans ($\sim 2 \times 10^7$ years) relative to the mixing rate (~ 1000 years) (Åberg 1995, 310). The amount by which the local rock Sr isotope ratio is altered will depend upon the concentration of Sr and its isotope ratio in both the local and introduced source. For example, if local radiogenic stream water is mixed with a large amount of glacial melt water which has a marine Sr isotope ratio and very low Sr concentration, the Sr concentration in the resulting mix will fall considerably but the original Sr isotope ratio will drop only slightly. The resulting Sr isotope ratio will lie on a mixing line between the two end members (the local and the introduced Sr isotope ratio).

Although it has changed considerably over geological time going both up and down, the changes to the marine Sr isotope ratio result from variations in the types of rocks exposed to chemical weathering rather than radiogenic ^{87}Sr evolution (Faure 1986, 187). The Rb/Sr of seawater is only 0.0012 and, therefore, the contribution of radiogenic ^{87}Sr negligible (DePaolo & Ingram 1985, 939). This long-term temporal variation is relevant when determining the Sr isotope ratio of marine-derived sedimentary rocks such as Cretaceous chalk ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7073\text{-}0.7076$) (Veizer 1989, 157, and results in Table A4, Appendix I), but the Sr isotope ratio can be considered a constant throughout the Holocene, i.e. the last 10,000 years. All teeth samples in this study fall into this time period. The accepted value for contemporary Atlantic seawater (the international standard) is 0.7092 (Veizer 1989, 142). Although measurements of higher precision have been determined by various authors (DePaolo & Ingram 1985, 939; Faure 1986, 186), the value of 0.7092 is considered sufficiently precise to distinguish marine signatures in samples analysed in this study.

The Sr isotope ratio of rainwater or snow in coastal regions is very similar to seawater, although Sr concentration, usually $< 1\text{ppb}$ in precipitation compared to 7.7ppm in seawater, is much less (Capo *et al.* 1998, 207; Faure 1986, 188). Over landmasses, the

incorporation of terrestrial dust aerosols will progressively alter the original marine signature. The resulting change in Sr isotope ratio will depend on distance from the coast and the Sr isotope ratio and Sr concentration in the dust sources (Åberg 1995, 311; Andersson *et al.* 1990 p2607; Bacon & Bain 1995, 45; Land *et al.* 2000, 315; Miller *et al.* 1993, 438). The total input of marine-derived Sr into an ecosystem may, however, be negligible due to the very low Sr concentration in rainwater; it may only alter the terrestrial signature substantially on the coast, in areas of consistently high rainfall (Capo *et al.* 1998, 214) or seasonally during periods of thawing (Åberg 1995, 311). The Sr isotope ratio of river and stream waters has been shown to reflect the bedrock geology of the area being drained (Åberg 1995, 313; Bacon & Bain 1995, 46; Faure 1986, 184; Graustein 1989, 495; Miller *et al.* 1993, 439). Nevertheless, not all lithologies will contribute equally; marine carbonate rocks provide a high Sr concentration and low Sr isotope ratio and may thus dominate the isotope signature whilst the opposite scenario is more likely for sandstones, shales and granites (Faure 1986, 184).

The Sr isotope ratio of whole soils is primarily derived from the underlying parent bedrock modified to a variable extent with locality, and within the soil profile itself, by atmospheric deposition (Bain & Bacon 1994, 208; Blum *et al.* 2000, 91; Miller *et al.* 1993, 439). Where the outcropping geology is covered by unrelated drift deposits such as glacial till or alluvium, this will influence the Sr isotope ratio also. Soils are complex, evolving systems and, as with bedrock, whole soil Sr isotope ratio is not necessarily indicative of the mobile Sr that is available to enter the food chain (Pate & Hutton 1988, 736). Soil analyses are, therefore, problematic and it is not clear exactly what method should be used to characterise the Sr isotope ratio of weathered bedrock, anthropogenic contamination or the Sr isotope ratio available to plants (Bain & Bacon 1994, 212). Leaches of whole soils or soil fractions designed to replicate environmental processes and thereby extract the soluble and exchangeable, i.e. available, cations are frequently used. However, there is currently no standard reagent or leaching time. Researchers have used one-stage leaching processes with distilled H₂O (Pate & Hutton 1988, 732), 1M ammonium acetate buffered at pH 7 (Blum *et al.* 2000, 90), 0.1M HCl (Miller *et al.* 1993, 438), 0.6M HCl (Erel *et al.* 1994, 5301), 2.5N HCl (Sillen *et al.* 1998, 2464) or sequential extractions using 1N acetic acid, 1N HCl and 1N HNO₃ (Steinmann & Stille 1997, 615). Despite the lack of a proven method, it is clear that the

Sr isotope ratio extracted by various leaching methods is still far more representative of the mobile Sr isotope ratio than analyses of whole soil or bedrock samples (Blum *et al.* 2000, 5; Burton *et al.* 1999, 610; Sillen *et al.* 1998, 2466).

The Sr isotope ratio of soil profile leaches changes systematically with depth and this is most marked within the humic layer where atmospheric contribution has been estimated at 59% (Miller *et al.* 1993, 439). Below ~20cm, however, Sr isotope ratios exhibit considerable stability and similarity to the underlying bedrock (Åberg 1995, 317; Miller *et al.* 1993, 439; Steinmann & Stille 1997, 616). Studies of ^{90}Sr fallout indicate that a large proportion is retained within the upper 5cm and is very resistant to downward movement (Comar *et al.* 1957, 487).

There is some evidence that the Sr and Pb isotope ratios can change within a soil over time (Åberg 1995, 318; Blum *et al.* 1994, 5024; Erel *et al.* 1994, 5305) due to changes in weathering patterns of bedrock, nutrient depletion and atmospheric inputs. In archaeological studies, it is necessary, therefore, to consider whether analysis of modern soils is, in any way, representative of either the soil at the time of burial or the mobile Sr and Pb since burial. Human activities such as land-use change, landscaping, manuring, fertilising and liming as well as pollution, may have occurred and altered the soil signature. Such activities need to be considered where the analysis is performed to characterise the local Sr and Pb available for incorporation into the food chain or for post-mortem contamination.

2.2.2 Lead geochemistry

Pb is a post-transition heavy metal element with an ionic radius of 1.2 Å / 120pm. Although there are other radioactive Pb isotopes, such as ^{210}Pb , and man-made stable isotopes, such as ^{202}Pb and ^{205}Pb , four occur naturally: ^{208}Pb , ^{207}Pb , ^{206}Pb and ^{204}Pb and make up the bulk of terrestrial Pb. Their abundances are approximately: 52.3%, 22.6%, 23.6% and 1.48% respectively. ^{204}Pb is non-radiogenic and its abundance has remained virtually constant over time. Conversely, the common-Pb abundances of ^{208}Pb , ^{207}Pb , ^{206}Pb have been continually increasing since the formation of the earth from the slow radioactive decay of thorium and uranium, ^{232}Th , ^{235}U and ^{238}U respectively. However, these have very long half-lives: $^{232}\text{Th} = 14.010 \times 10^9$, $^{235}\text{U} = 0.7038 \times 10^9$ and $^{238}\text{U} =$

4.467×10^9 (Faure 1986, 284) and will show negligible change over archaeological time scales. Pb isotopes are conventionally presented as ratios rather than abundances, to the non-radiogenic ^{204}Pb : $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$.

Pb is found in many types of rocks both as a major constituent and as a trace element, not only in association with U and Th-bearing minerals but also by forming its own minerals, principally galena, from which U and Th are excluded. Pb^{2+} is known to replace K^{1+} in K-feldspar but, unlike Sr, there is no striking geological correlation with Ca-bearing minerals (Elias *et al.* 1982, 2574). For example, Pb demonstrates the laser ablation characteristics of other chalcophile (sulphide loving) elements whereas Sr, like Ca, correlates with lithophile (silicate loving) elements (Longerich *et al.* 1996, 541). It accumulates with the transition metals zinc (Zn), cadmium (Cd) and trace amounts of silver (Ag) in ore deposits. Pb isotope composition can vary considerably from the common-Pb found in low U/Pb and Th/Pb minerals such as galena, plagioclase and K-feldspar to the highly radiogenic Pb in ancient accessory minerals such as zircon and apatite or rocks like U and Th-rich granites (Erel *et al.* 1994, 5299; Faure 1986, 309). Although U and Th have many chemical similarities and can substitute readily for each other, most Th compounds are insoluble in water whereas those of U are soluble under oxidising conditions. These differences, together with the choice of Pb isotope ratios, offer a range of variables with which to differentiate between sources but make the interpretation of Pb isotope data considerably more complex than that of the single parent-daughter system of Rb/Sr (Gulson 1986, 14).

As with Sr, the Pb isotope ratios of a given country rock or ore deposit may not be simply a function of age and the concentrations of Pb, U and Th incorporated at formation. Rocks that do meet this simple “single-stage” model of formation and have remained closed to subsequent mixing are known as ordinary or conformable Pb and their isotope ratios lie on a Pb ore growth curve. Anomalous Pb, which does not lie on the growth curve, and may even plot in the future, does so because it has been mixed with radiogenic U and Th-rich crustal lead at some time in its formation history (Faure 1986, 316). The growth curve used on graphs in this thesis is the Stacey and Kramers two-stage growth curve of conformable ore deposits (Ludwig 1994; Stacey & Kramers 1975).

In the oceans, Pb has a much shorter residence time (80-100 years) compared to Sr, and as a result, does not attain the same homogeneous distribution. It is quickly removed by incorporation into sediments and marine organisms (Libes 1992, 683). Today, the main marine input comes from terrestrial run-off and atmospheric deposition, and seawater Pb concentration profiles exhibit surface enrichment with depletion at depth (Libes 1992, 182). As in the geosphere, there is no correlation with the homogeneous Ca depth profile nor its residence time of 8×10^5 years (Libes 1992, 151). Pb concentration is extremely low in the marine environment, and consequently the Pb isotope ratio of prehistoric ocean waters would have reflected the land being drained (von Blanckenburg *et al.* 1996, 4959), i.e. it would have varied depending on the geology of the proximal land masses. In contrast to Sr, there is, therefore, no constant marine or characteristic rainwater signature for Pb (Bacon & Bain 1995, 48) and coastal, river and rain waters would have varied with locality during the Holocene. In modern times increasing atmospheric deposition coupled with long range transport of pollutant aerosols may blur the geographical variation (Hamelin *et al.* 1997, 4427; Veron *et al.* 1992, 345). Pb in modern rainwater appears to be mainly suspended particulate matter derived from petrol or industrial aerosols, most of which appears to be scavenged by surface soils as its signature is not directly reflected in stream waters (Bacon & Bain 1995, 48).

There is no fractionation of the Pb isotope ratios in low-temperature biogeochemical processes due to the small variations between the atomic masses (Gulson 1986, 14; Hoefs 1997, 21), so the Pb isotope ratios that characterise a particular country rock, ore or locality are transferred unaltered to soil and groundwaters by natural weathering processes. Isotope variations, which can originate from small spatial differences within one ore field or preferential weathering of heterogeneous rock phases, are mixed within the soil and groundwater to create an homogeneous reservoir representative of the local underlying geology (Erel *et al.* 1994, 5305). As with Sr, researchers have used a variety of methods to characterise the isotope ratio of mobile soil-Pb but weak acid or water leaches, rather than bulk soil analysis, are considered to extract the soluble and exchangeable fractions (Erel *et al.* 1994, 5301; Gulson *et al.* 1994b, 904; Li *et al.* 1995, 121; Steinmann & Stille 1997, 615).

Soil-Pb accumulates in the organic fraction, i.e. the humic horizon, and soil depth profiles show that, whether natural or anthropogenic, Pb is relatively immobile within the upper 15-20cm (Adriano 1986, 227; Sheppard & Thibault 1992, 421). Pb²⁺ generally becomes more mobile as acidity increases and in the organic-rich groundwaters of saturated peat (MacKenzie *et al.* 1998, 33; Stewart & Fergusson 1994, 245; Urban *et al.* 1990, 3338) but can also be mobilised in neutral and alkaline soils containing high dissolved organic matter (Steinmann & Stille 1997, 621). Nevertheless, modern surface soils have been shown to retain historical inputs of pre-petrol Pb over considerable periods of time (Bacon *et al.* 1996, 2516). Below the organic horizon the isotope ratios shift continuously towards natural bedrock ratios (Bacon *et al.* 1996, 2516; Steinmann & Stille 1997, 615).

Source-tracing applications of prehistoric archaeological material can use and interpret Pb isotopes in a manner analogous to those of Sr. However, a Pb necklace found in an Early Bronze Age Scottish cist burial indicates that the technology to mine and smelt Pb had been acquired by this time (Hunter & Davis 1993). Metallurgy did not expand linearly with time and during some periods and within certain societies metal use was variable. During the Roman period unprecedented, large-scale Pb mining was underway in the Mendips by 49AD, Flintshire before 100AD and in Derbyshire by 117-138AD, both as a by-product of silver extraction and apparently in the case of the virtually silver-free Derbyshire ore, in its own right (Tylecote 1992, 71). Pb was exported through France during this time (Tylecote 1992, 71) and Britain was still regarded as a source of Pb during the Early Mediaeval period (Bayley 1992, 6). It is highly likely that a considerable amount of Pb remained in circulation and was recycled during the early Mediaeval period although production was considered to be small-scale (Bayley 1992, 6)

Pb exposure, therefore, becomes less dependent on geological origin and natural, baseline levels and more of an indicator of status, i.e. what access to Pb and its products was available within a society, geographical location or just to a specific individual. A further complication to archaeological studies occurs when and if the accumulating anthropogenic pollution becomes sufficient to sever the link between the locality and the bio-available Pb isotope signature. Modern large-scale atmospheric pollution only becomes a major complicating factor during the Industrial Revolution and prior to this,

trade of Pb products was the dominant mechanism for Pb movement. For example, Pb fall-out concentrations recovered from Greenland ice cores show that background atmospheric Pb deposition starts to rise *c.*2,500 BP, falls to almost background *c.*500AD and then continues its rise (Hong *et al.* 1994, 1842). Analysis of Swedish varve sediments which correlate the change in isotope ratios with the increases in concentration, confirms a small peak *c.*2000 BP followed by a long “clean” period between 400 and 900 AD. Atmospheric pollution then appears to peak *c.*1200 AD followed by four more larger rises in the 16th, 18th, 19th and 20th centuries, all of which exceed current day deposition (Brännvall *et al.* 1999, 4392/3). Increases in tropospheric Pb aerosols may result from accelerated land clearances and soil erosion and such natural or anthropogenic pollution may, over time, have contaminated burial sites and samples.

Table 2.1 Estimated range of Pb isotope ratios for anthropogenic English Pb

Pb isotope ratio	Estimated range of English ore values
$^{206}\text{Pb}/^{204}\text{Pb}$	18.1 – 18.6
$^{207}\text{Pb}/^{204}\text{Pb}$	15.60 – 15.75
$^{208}\text{Pb}/^{204}\text{Pb}$	38.0 – 38.7
$^{207}\text{Pb}/^{206}\text{Pb}$	0.840 – 0.858
$^{208}\text{Pb}/^{206}\text{Pb}$	2.065 – 2.085
$^{206}\text{Pb}/^{207}\text{Pb}$	1.165 – 1.190

Sources of data: (Bacon *et al.* 1996; Haggerty *et al.* 1996; Rohl 1996)

The Pb ore deposits in Great Britain occur in the west and north of the country mainly in association with marine sedimentary formations dating from the Palaeozoic. Since the Roman period lead has been mined in many areas including the Mendips, Derbyshire, Yorkshire Dales, Wales, Shropshire, Cumbria and Scotland. Although there is considerable isotope variation and overlap between and within these Pb deposits, it is possible to delineate a Pb isotope field that contains all the ores found at these sites and thus characterises a British ore Pb signature. Anthropogenic Pb isotope ratios can also be obtained from the analysis of archaeological Pb artefacts, such as Pb coffins.

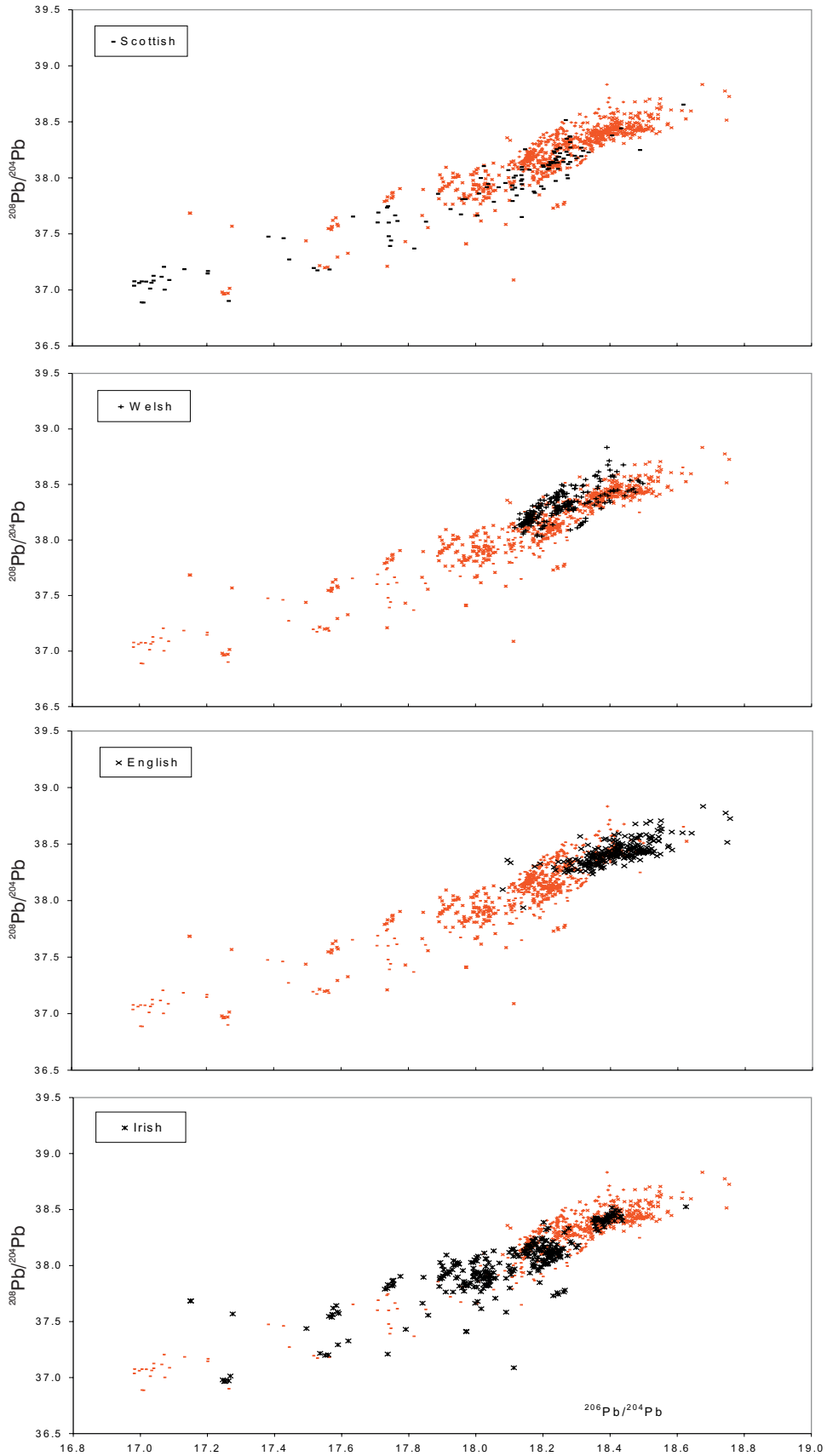


Figure 2.1 Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ showing the relative fields for Pb ores from Scotland, Wales, England and Ireland. Data from Rohl 1996 and sources quoted therein.

The normal range exhibited by English ores is listed in Table 2.1, but does not include data from geological formations lacking Pb ore mineralisation, where Pb is present as only a trace element. Furthermore, minor ore mineralisations or occasional outliers may exist outside the English ore Pb signature. However, these are unlikely to produce comparable dietary Pb isotope ratios *unless* the diet was completely dominated by food and water bearing this particular isotope ratio *or* if it resided in a concentrated source of Pb such as Pb-lined cooking pots and pewter tableware. The relationship between English, Scottish, Welsh and Irish Pb ores is illustrated in Figure 2.1.

This anthropogenic Pb isotope signature prevailed in Great Britain until around the mid-nineteenth century when imports started to exceed domestic production. Imported Pb was, and still is, predominantly of Australian Precambrian origin and hence, considerably less radiogenic than British Pb. Since the mid 19th century, therefore, the domestic signature has become gradually less radiogenic as an increasing proportion of Australian Pb was introduced. Two exceptions to this gradual decrease are evident. The first is an extremely marked fall in the five years subsequent to the Second World War when all anthropogenic Pb appears to have been imported. The second is a sharp rise back towards British Pb isotope ratios (e.g. that of Victorian Pb water pipes) in the 1990's following the reduction in leaded petrol (Bacon *et al.* 1996, 2515). This situation effectively provides two endpoints between which the domestic Pb burden fluctuates depending on the relative inputs. It is possible that contamination of soil and enamel samples may occur through more recent pollution but soil Pb isotope ratios still appear to be dominated by pre-20th century Pb rather than more recent petrol-Pb sources (Bacon *et al.* 1996, 2516).

2.3 Strontium and lead in the biosphere

Pb and Sr are found as trace constituents in plants and animals and, whilst both are considered non-essential elements, the possibility that they perform some vital function at low levels cannot be entirely ruled out (Underwood 1977, 410/445). In geochemical studies they are regarded as chemically unrelated elements: "*Chemical reactions involving lead and calcium during rock weathering and soil formation are more*

dissimilar than similar; furthermore, relationships between lead and calcium in biochemical processes are not well known.” (Elias *et al.* 1982, 2574). Nevertheless, their uptake in biological organisms through passive substitution for Ca and incorporation into the mineral phase at levels directly reflecting those available in an individual’s environment is widely accepted. Elias *et al.* (1982, 2574) justify their use of Pb/Ca ratios in an analogous manner to those of Sr/Ca by stating that “*we use the similar distributions of lead and calcium in different organs of plants and animals coupled with the fact that lead is transferred less efficiently than calcium in nutrient-consumer relations*”. *In vitro* studies using synthetic hydroxyapatite indicate that the lattice structure can readily distort in order to incorporate cations of larger ionic radii than Ca^{2+} (99pm), such as Pb^{2+} (120pm) and Sr^{2+} (112pm), at Ca^{2+} sites (Blumenthal 1990, 310). Certainly the vast majority of Sr (~99%) (Underwood 1977, 445) and Pb (>90%) (Gross *et al.* 1975, 649; Wallach & Chausmer 1990, 240) in mammalian tissues is, like Ca, found in the hard tissues of the skeleton. Because of this and their divalency, it is often claimed that Pb^{2+} and Sr^{2+} substitute in an identical manner for Ca^{2+} in the apatite structure of the carbonated hydroxyapatite of skeletal tissues (McConnell 1973, 23).

However, in animals, Sr is relatively non-toxic with a wide safety margin between dietary levels and toxicity, whereas Pb is toxic at much lower concentrations that, in children especially, are quite easy to exceed (Bowen 1979, 136/141). The effects of Ca substitution by Sr, both alkaline earth metals, appears therefore, benign whereas that of Pb is harmful. This would suggest that Sr^{2+} and Pb^{2+} do not behave in a similar manner biochemically and that their “bone-seeking” behaviour may have a different mechanism. Ca, Sr and Pb are known to concentrate in areas of active bone mineralisation. This is also true for zinc (Zn), for example, but its presence is as part of the mineralising mechanism rather than contributing to structural bone formation (Vincent 1963, 171). Furthermore, Pb has also been shown to interfere with the activity of essential transition metals. It is known, for example, to limit iron (Fe) absorption in children (Watson *et al.* 1986, 255), anaemia being one of the symptoms of Pb poisoning. There is also evidence of a mutual metabolic antagonism with copper (Cu) (Underwood 1977, 414). It is of interest to note that Pb is concentrated in red blood cells (the same is true for Zn), whereas Sr and Ca exhibit the opposite trend and are heavily concentrated in plasma (Bowen 1979, 106). Clearly, there are some similarities

to the distribution and behaviour of Ca, Sr and Pb but there are also important differences that should not be disregarded.

Some researchers believe that it is imperative to understand what an acceptable *in vivo* concentration is and the variability exhibited by trace elements and isotope ratios in modern skeletal analogues before it is possible to make sensible interpretations from archaeological remains (Hancock *et al.* 1989; Tuross *et al.* 1989). Not all researchers agree with this principle of uniformitarianism (Ezzo 1994, 12; Radosevich 1993, 278), insisting that modern populations have neither the same diet nor culture, even if they live in the same locality, and thus cannot provide comparative data. However, whilst exposure to sources and amounts of Pb and Sr may have changed greatly over archaeological time, biological and physiological systems are unlikely to have altered significantly within this relatively short evolutionary period and as shall be demonstrated below, increasing environmental concentrations do not necessarily produce increasing body burdens. Knowledge of modern analogues is, therefore, vital as a starting point to understand the tissue under analysis, how it is formed, how it behaves *in vivo* and what variation is physiologically credible before it becomes possible to identify diagenetic change.

2.3.1 Strontium uptake in plants

Bioavailable Sr is transferred isotopically unaltered through the food chain and successive trophic levels. The Sr isotope ratio of modern plants has been shown to correspond to the Sr isotope ratios obtained from soil leaches (Blum *et al.* 2000, 91; Sillen *et al.* 1998, 2466) although atmospheric deposition can dominate in aerial foliage (Graustein & Armstrong 1983, 291; Miller *et al.* 1993, 439). The primary mechanism for Sr²⁺ uptake, incorporation and excretion in plants is, as with rocks, through Ca²⁺ substitution. However, in an analogous manner to Sr²⁺ competition for Ca²⁺ lattice sites in minerals, there is a controlling mechanism that ensures biological organisms favour Ca²⁺ over Sr²⁺. This discrimination (or biopurification) against the non-nutrient Sr²⁺ in favour of Ca²⁺ (Elias *et al.* 1982, 2561) leads to gradual suppression of Sr uptake in plants in increasingly Ca rich environments (Roca & Vallejo 1995). Although this has no effect on the Sr isotope ratio, there is no clear relationship between the concentration of Sr in plants and the concentration available within the soil. Concentrations can vary

in different parts, e.g. roots and foliage, of one plant and increase with age (Elias *et al.* 1982, 2567). There is, therefore, no “normal” Sr concentration for plants (Radosevich 1993, 272) nor, as a consequence, for the diet of plant eaters, but plant Sr isotope ratios will be representative of the local environment.

2.3.2 Lead uptake in plants

Bioavailable Pb, like Sr, is transferred, with negligible fractionation from soils into all plants and through successive trophic levels. Modern plants exhibit similar Pb isotope profiles throughout a region as the soils, and consequently have been used in mineral exploration as a biogeochemical indicator to pinpoint underlying mineralisation (Gulson 1986, 114). Pb uptake is primarily non-metabolic and unrelated to Ca availability and transport (Peterson 1978, 371). Neither is it readily taken up from soils by plant roots and tends to accumulate and remain mainly in the root system, with significantly lower levels in the tuber, stem, grain and foliage (Adriano 1986, 233). Although higher soil Pb concentrations have been observed to produce correspondingly higher concentrations in plants, the concentration of Pb in the edible parts tends to be <5% of the total soil concentration (Adriano 1986, 234). Soils with high organic or clay contents restrict Pb bioavailability (Tack & Verloo 1996, 38). Atmospheric particulate Pb deposited on plant foliage may, however, circumvent the natural exclusion of Pb by the roots (Elias *et al.* 1982, 2562) and thus dominate the isotope signature of the food source (Bacon *et al.* 1996, 2514). In archaeological periods, atmospheric deposition would have resulted primarily from natural sources such as rainwater and wind-blown dusts whilst anthropogenic pollution would have been more localised and significant on a smaller geographical scale.

2.3.3 Strontium metabolism and uptake in mammals

Sr is a non-nutrient trace element that is ingested and metabolised into mammalian tissues principally from food and drink. The mechanism of incorporation is a passive and apparently benign substitution between two alkali earth divalent cations, i.e. Sr²⁺ for Ca²⁺, during nutrient uptake, internal distribution and excretion. During active ion movement across cell membranes, Sr²⁺ is actively transported in place of Ca²⁺ (Bowen 1979, 123) enabling Sr to be successfully used as a tracer in Ca-related clinical studies

(Rokita *et al.* 1996). In laboratory studies, the amount of Sr incorporated by animals is considered to reflect the amount available from the diet and environment, i.e. it is dose-dependent (Boivin *et al.* 1996, 1311), as there are no known homeostatic mechanisms that specifically regulate levels of such non-nutrients (Parker & Toots 1980, 203).

It is incorporated into the carbonate hydroxyapatite lattice at four-fold Ca^{2+} sites (Rokita *et al.* 1993, 550; Vukovic *et al.* 1998, 392) and also by adsorption onto the crystal surface (Parker & Toots 1980, 202). Sr is distributed relatively homogeneously in the skeleton and concentrations of Sr in skeletal tissues from a single individual are very similar, with bone and dentine containing slightly more than enamel (Aufderheide 1989, 243; Parker & Toots 1980, 202; Turekian & Kulp 1956, 406; Underwood 1977, 446). This may result from the smaller carbonate hydroxyapatite crystals of bone and dentine providing larger surface areas available for cation adsorption (Parker & Toots 1980, 202). Alternatively, it appears that Sr is more readily incorporated into smaller, immature crystals as increased discrimination against Sr in favour of Ca occurs in mature, large crystals of synthetic hydroxyapatite (Brudevold & Söremark 1967, 260; Likins *et al.* 1960, 2156). However, the difference may simply result from post-formation increases due to bone remodelling or secondary dentine formation, given that bone Sr concentrations are believed to increase with age (Underwood 1977, 446).

As with Sr isotope ratios, *in vivo* Sr concentrations in bone and teeth also appear to vary geographically (Brudevold & Söremark 1967, 260; Turekian & Kulp 1956, 406; Underwood 1977, 445). This could be due to regional variations in bedrock geology, water and food or cultural differences in subsistence strategies and the types of diet. Reported values for modern human skeletal and dental tissues are typically 50-300ppm (Brudevold & Söremark 1967, 260; Elliott & Grime 1993, 545; Hancock *et al.* 1989, 175; Underwood 1977, 445/6). Animal tissues exhibit a similar range, although herbivores tend to have higher concentrations than carnivores because plants are Sr-rich and meat Sr-poor (Bocherens *et al.* 1994, 784; Tuross *et al.* 1989, 661). Nevertheless, it is extremely rare for any mammalian tissues to exceed 1000ppm (Radosevich 1993, 283).

The ratio of Sr/Ca is widely used in archaeological and modern food chain studies to identify the trophic level, and hence food sources, that an individual exploited (Blum *et*

al. 2000; Burton & Price 1999; Burton *et al.* 1999; Burton & Wright 1995; Elias *et al.* 1982; Sealy & Sillen 1988; Sillen *et al.* 1995). There is a progressive biopurification, i.e. discrimination against Sr^{2+} in favour of Ca^{2+} , at each successive trophic level in both marine and terrestrial environments (Burton & Price 1999, 233; Comar *et al.* 1957, 492; Elias *et al.* 1982, 2561). This works well with single-component diets but, in practice, has proved difficult with multi-component diets (Burton & Wright 1995). Mineral metabolism is an extremely complex interaction between a range of variables that affect trace element bioavailability, not just the single biopurification factor of preferential ingestion. Some are physiological and intrinsic to the individual such as health status and age and some are intrinsic to the specific composition of ingested foods. Individual Sr metabolism is, therefore, dependent upon many factors and synergisms/antagonisms, only one of which is the amount of Ca in the diet. Controlled animal feeding experiments have produced no correlation between Sr concentrations in various diets and those of the resulting bone (Lambert & Weydert-Homeyer 1993, 89), and these results have been re-interpreted as indicating the amount of Ca in the diet rather than the amount of Sr (Burton & Wright 1995, 275). For example, Sr-uptake is suppressed in high-Ca or protein-rich diets (Aufderheide 1989, 243; Burton & Wright 1995, 275; Lambert & Weydert-Homeyer 1993, 90; Underwood 1977, 447), and due to the very low levels in milk, by consumption of dairy produce (Ezzo 1994, 12). Sr-uptake is increased in high fibre diets which actively reduce Ca absorption (Lambert & Weydert-Homeyer 1993, 90) and accordingly, herbivorous diets (Underwood 1977, 447). Consequently, the Sr concentration measured is not an indicator of the amount of Sr that is ingested but an indicator of the amount of Ca.

These factors, whilst not altering the Sr isotope ratio of the Sr ingested, may result in one dietary component contributing an unequal amount of Sr and thus greatly influence the resulting Sr isotope ratio of the diet. Dietary change over time is likely to be a bigger consideration with human populations than animals and it may be difficult to separate from changes due to migration. It has been demonstrated that modern marine and terrestrial animals have isotope compositions that reflect the environment in which they live (Åberg 1995, 311; Capo *et al.* 1998, 216; Christensen *et al.* 1995, 81; Hall-Martin *et al.* 1991, 123; Nelson *et al.* 1986, 1943; van der Merwe *et al.* 1990, 746; Vogel *et al.* 1990, 747) although migratory animals may be more difficult to interpret

using Sr isotope ratios alone (Blum *et al.* 2000, 95; Chamberlain *et al.* 1997, 138; Koch *et al.* 1992, 285; Koch *et al.* 1995, 1340).

2.3.4 Lead metabolism and uptake in mammals

Pb is a non-nutrient trace element that is ingested and metabolised into mammalian tissues principally from food and drink although inhalation can be an important pathway when atmospheric particulate pollution is prevalent. Adult humans absorb only 5-10% via the digestive system but retain 30-50% of inhaled Pb (Underwood 1977, 413). Pb is unusual in that infants and children absorb it much more efficiently across the gut wall than do adults and as a result are far more susceptible to Pb poisoning (Bowen 1979, 125). As a divalent cation, Pb^{2+} is believed to replace Ca^{2+} in nutrient uptake, internal distribution and excretion, although such substitution has several toxic effects and blocks normal Ca^{2+} messenger functions in both nerve and bone cells (Büsselberg *et al.* 1998, 372).

The vast majority of Pb^{2+} is located in the hard tissues of the skeleton where it is believed to occupy Ca^{2+} sites within the carbonate hydroxyapatite lattice (Wallach & Chausmer 1990, 240). Unlike Sr^{2+} , however, Pb^{2+} appears to favour the six-fold positions in the crystal lattice possibly because there is less space available at the four-fold sites (Verbeeck *et al.* 1981, 245). The incorporation of Pb^{2+} in place of Ca^{2+} is thermodynamically more favourable: a phosphate phase with Pb^{2+} is more stable than phosphate with Ca^{2+} ($\text{p}K_{\text{sO}}$ values: Pb = 11.4, Ca = 6.6). This would imply that, if present, Pb^{2+} would be preferentially incorporated into carbonate hydroxyapatite, as free energy differences favour Pb^{2+} over Ca^{2+} by about 27kJ mol^{-1} (Patterson *et al.* 1991, 218) and once there, would be harder to re-metabolise than Ca^{2+} . However, it has been demonstrated that whilst Pb^{2+} is readily removed from solution in the presence of hydroxyapatite, it does so by promoting the dissolution of hydroxyapatite and the subsequent precipitation of hydroxypyromorphite not through incorporation in the hydroxyapatite lattice (Lower *et al.* 1998a, 1779; Lower *et al.* 1998b, 155; Ma *et al.* 1993, 1810). Verbeeck *et al.* (1981, 246) are frequently quoted as proof that Pb^{2+} can substitute for Ca^{2+} in the carbonate hydroxyapatite lattice, yet they prepared Pb-hydroxyapatite in the laboratory at 800°C and conclude their study by casting doubt on

whether synthetic hydroxyapatite can realistically be compared to biologically mediated *in vivo* bone and tooth mineral.

Pb is not distributed homogeneously throughout the skeleton and concentrations can vary substantially between different bones (Aufderheide 1989, 249; Erkkilä *et al.* 1992, 639) but typical modern adult Pb concentrations are usually at least an order of magnitude lower than Sr concentrations, i.e. ~3-60ppm (Arnay-De-La-Rosa *et al.* 1998, 109; Drasch 1982, 211; Gross *et al.* 1975, 645; Jaworowski *et al.* 1985, 116; Manea-Krichten *et al.* 1991, 186; Yoshinaga *et al.* 1998, 406). Skeletal-Pb concentration appears to accumulate, most notably in cortical bone, until ~50-60 years of age and also increases with increasing exposure (Barry 1978, 102; Drasch 1982, 224; Erkkilä *et al.* 1992, 640; Underwood 1977, 410/1). However, Gross *et al.* (1975, 650) concluded this only occurs in higher exposure individuals (i.e. >15ppm) who continually ingest more than they excrete.

As with Sr, however, increases are not always directly correlated with exposure and may result from a host of nutritional and metabolic variables. High dietary Ca, particularly when supplemented with phosphorus (P), drastically reduces the absorption of Pb whilst excess dietary Zn has provided protection against Pb absorption in rats (Underwood 1977, 414). Modern studies have shown that inhabitants of urban hard water, and hence high-Ca, regions have lower Pb burdens than those in rural soft water regions, even when the hard water areas are extensively polluted (Jaworowski 1990, 185; Jaworowski *et al.* 1985, 121; Stack *et al.* 1974, 64). Diets rich in phytate (e.g. cereal grains and pulses) and Ca and P, also restrict Pb absorption whereas low-Fe intake and status can produce substantial increases in Pb uptake, as can Ca and P deficient diets (Jaworowski *et al.* 1985, 121; WHO 1996, 30). Pb is also much more efficiently taken up by animals fed an entirely liquid diet which implies the same may also be true for human infants (WHO 1996, 198). Soil is known to be a significant, if not the principle, source of blood Pb in children both through soil pica and general hand-to-mouth activity (Jaworowski *et al.* 1985, 121; Mielke & Reagan 1998, 227; Yaffe *et al.* 1983, 244). Moreover, drier conditions, finer dust and a more outdoor lifestyle may explain the acknowledged increases (20-30%) in children's blood Pb levels during the summer months (Mielke & Reagan 1998, 224). There is no reason to suspect that this route of Pb ingestion would have been any less important amongst

archaeological populations who may also have had restricted access to, or no desire for, washing facilities for themselves and their food. Furthermore, the introduction of rock particles directly into food during milling and grinding may have increased Pb ingestion and, crucially, non-local Pb ingestion if the millstones were imported.

As with Sr, the Pb isotope ratio that characterises an individual is a product of several dietary sources. If they are all obtained locally their ratios may be very similar. However, if inputs from water, crops and animal produce have different isotope ratios, their relative contributions to the resulting Pb isotope ratio of the individual will depend on the type of food or drink and the nutritional status, metabolic health and age of the individual. Nevertheless, it has been demonstrated that modern marine and terrestrial animals have Pb isotope compositions that reflect the dietary environment in which they live whether entirely natural or polluted with anthropogenic Pb (Hall-Martin *et al.* 1991, 127; Outridge *et al.* 1997, 212; Outridge & Stewart 1999, 111; Smith *et al.* 1990, 1519; Vogel *et al.* 1990, 748).

2.4 Biokinetics of strontium and lead in skeletal tissue

Bone is a living, constantly evolving tissue and subject to modelling (formation) and remodelling (turnover) processes throughout its lifetime. Both processes are functionally different and proceed at different rates and at different times in the skeleton (Priest & Van de Vyver 1990, 128). Remodelling processes result in the release of previously incorporated Sr and Pb and the incorporation of new, or reincorporation of old, Sr and Pb (Priest & Van de Vyver 1990, 93). As a result, bone isotope ratios may change gradually throughout life and so offer the prospect of comparing enamel formed during childhood with bone formed mainly in later life.

Sr and Pb are incorporated into enamel and primary dentine during mineralisation of the two tissues and neither tissue reforms nor remodels (Brudevold *et al.* 1977, 1171; Veis 1989, 189). Thus, the Sr and Pb isotope ratios and concentrations will reflect those of the diet during the period of mineralisation, irrespective of the age of the human or animal under investigation (Koch *et al.* 1997, 425; Underwood 1977, 446; Wieser *et al.*

1996, 415). Age at mineralisation will vary with tooth type. Breastfeeding, weaning and the independent childhood diet may all supply different Sr and Pb isotope ratios. Human teeth as archaeological, analytical samples will be considered in detail in Chapter Three.

Whilst no bone analyses have been attempted in this study, bone turnover rates can be used to indicate the rate of uptake and retention of heavy metals into the skeleton and hence, the relative contribution they may make to teeth forming during certain periods of an individual's lifetime. There is considerable evidence that uptake of heavy metals such as Sr and Pb can vary considerably with age and not just exposure. In humans, metabolic rates, bone turnover rates and skeletal formation rates vary enormously both during childhood and between bone elements, e.g. rib and femur (Erkkilä *et al.* 1992, 639; Grynepas 1993, S57; Papworth & Vennart 1984, 1057). However, unlike the lighter elements, any differential fractionation of Pb or Sr resulting from variations in these biological processes is negligible, enabling skeletal elements formed at different times of life to be compared. In contrast to adults, metabolism and growth in children is rapid; not only is their existing bone turning over, new bone is also being formed and their demand for Ca is great. In addition, young bone is more vascular and hydrated and mineral acquisition or exchange is elevated compared to the more highly mineralised, and hence comparatively inert, adult bone (Leggett *et al.* 1982, 311). As a general rule of thumb: *“The higher the rate of turnover the greater the hypomineralisation; similarly the lower the rate of turnover the greater the hypermineralisation.”* (Grynepas 1993, S62).

Sr and Pb concentrations are highest in areas of active bone modelling or remodelling (Aufderheide & Wittmers 1992, 811; Boivin *et al.* 1996, 1311; Rokita *et al.* 1996, 158) which indicates that Sr²⁺ and Pb²⁺ are preferentially deposited in the parts of the skeleton undergoing active mineralisation at the time of ingestion. It has been suggested that both Sr²⁺ and Pb²⁺ bind more strongly to osteoid matrix than to mature bone mineral (Aufderheide & Wittmers 1992, 813; Brudevold & Söremark 1967, 260; Likins *et al.* 1960, 2156) and this may be related to the larger carbonate hydroxyapatite crystals and denser structure of mature bone (Grynepas 1993, S62; Neuman & Neuman 1953, 30). Sr incorporation in this manner is rarely harmful but Pb deposition at the epiphyseal growth plates in children can seriously impair the function of bone forming

cells (osteoblasts). Instead of normal mineralised bone being formed, the osteoblasts produce a band of calcified cartilage across the epiphysis which is visible as an opaque “lead-line” on radiographs (Aufderheide & Wittmers 1992, 814).

Bone turnover rates are extremely difficult to quantify and vary between individual bones, types of bone, age, sex, health status and nutrition. Quoted rates in archaeological studies for adults, mainly for Sr in cortical bone, vary from complete replacement of its chemical constituents within 6 years (cortical not specified) (Ericson 1985, 507), 7-10 years (Price *et al.* 1994a, 414) or 5-10 years (Grupe *et al.* 1997, 518), to ~20 years (Horn & Müller-Sohnius 1999, 263). In modern adults, Rabinowitz *et al.* (1973, 726) concluded that the residence time of Pb in bone was ~27 years and Priest & Van de Vyver (1990, 130) estimated bone turnover rates at 3% per year for cortical and 22% per year for trabecular. Gulson & Gillings (1997, 823) proposed 6% per year for trabecular bone and ~1% per year for permanent dentine. However, since dentine does not turnover, this change may result from addition via secondary dentine formation; circumpulpal dentine was not removed in the analyses. Whilst many researchers have given rates for adults, they cannot be regarded as anything other than extremely imprecise estimates, particularly when applied to archaeological individuals about whom many of the necessary variables cannot be deduced. In infants and children, bone turnover rates can vary enormously with age and may exceed 100% per year in both cortical and trabecular bone during periods of rapid growth (Aufderheide & Wittmers 1992, 814; Stamoulis *et al.* 1999, 177).

In studies of ⁹⁰Sr uptake and retention, it has been shown that incorporation is greatest during periods when maximum bone formation occurs, i.e. infancy and the two years prior to puberty (about 2.5 years earlier in girls than boys) (Tolstykh *et al.* 1997, 27). Likewise, the maximum loss occurs during periods of greatest bone resorption, i.e. post-menopausal women and old age. In view of this, it is particularly important to consider what happens during periods of metabolic stress such as pregnancy and breastfeeding and how this may affect deciduous teeth mineralisation. Ca demand on the mother during this time is so high that re-mobilisation of skeletal Ca increases considerably during pregnancy and especially during breastfeeding (Gulson *et al.* 1997b, 61; Gulson *et al.* 1998, 329). This has been shown to increase blood-Pb by releasing Pb²⁺ that was incorporated into the skeleton during previous years (Gulson *et*

al. 1995, 711). Ca supplementation reduces the amount released but trabecular bone turnover rates may exceed 50% in women with insufficient Ca intake resulting in half the mother's blood-Pb being derived from old skeletal stores (Gulson *et al.* 1999, 636). Blood-Pb concentrations have been shown to be very similar in both the mother and the foetus as Pb^{2+} freely crosses the placenta (Mahaffey 1991, 15; Underwood 1977, 416). Moreover, in a recent study on mammary transfer in rats, Pb in milk was found to be 10 times more concentrated than blood-Pb from the same animal (Watson *et al.* 1997, 1024). This finding casts doubt on the progressive biopurification of Pb with respect to Ca at each trophic level.

Consequently, the deciduous dentition and the earlier forming permanent teeth may represent not only Pb ingested by the mother whilst they were mineralising but also a considerable amount of non-contemporaneous, re-mobilised Pb^{2+} from her skeleton. Sr^{2+} is very likely to be re-mobilised in the same manner when Ca demand is high. However, due to the discrimination against Sr at each successive trophic level, Sr is reduced relative to Ca in both placental and mammary transfer (Underwood 1977, 447). If the mother had recently migrated her skeletal Sr and Pb isotope ratios might be very different from her new place of residence. **This suggests that deciduous teeth and early forming permanent teeth may not be a good indicator of place of residence during infancy but may inherit isotope signatures that actually derive from the years preceding pregnancy.** Analysing teeth that formed post-weaning will, therefore, give a better indication of the environment occupied by the child.

2.5 Conclusions

Sr and Pb are present as non-essential trace elements in the geosphere and biological organisms. Although geochemically dissimilar (Sr, like Ca, is a lithophile element whereas Pb is a chalcophile element), they are both considered to substitute for Ca in animals by virtue of being bone-seeking, divalent cations. They do not, however, behave biochemically in the same manner as each other. Sr is non-toxic except at extremely high doses whereas Pb is highly toxic at doses that are relatively easy to exceed and interferes with normal Ca activity as well as that of essential transition metals.

Isotope fractionation of Pb and Sr is negligible in low temperature geological and biological processes. In a given ecosystem the Sr and Pb isotope ratios of soils, waters, plants and animals are, therefore, derived from the local geology but vary independently of each other. They will reflect, but may not be exactly the same as, the whole rock ratios due to differential weathering and mixing of sources. Nevertheless, the isotope ratios of these two elements in animal tissues provide a means of linking the animal to the geological locality it inhabits. Humans may be considerably more difficult to interpret. There may be many confounding variables such as movement of food (trade or animal grazing patterns), choice of water sources (hard/soft water), changing synergisms and antagonisms with different dietary strategies (high-dairy, high-Ca, low-Fe), that may lead to one dietary component contributing disproportionately to the Sr or Pb intake. This may mask or sever the simple link between locality and the person. It is particularly difficult with archaeological populations for whom it is rarely possible to reconstruct diet and cultural practices with certainty.

Although subsistence strategies may change through time and localities, a high degree of homogeneity in values is to be expected in a temporally restricted population living in the same locality. This is especially so because the analysis of tooth enamel ensures the isotope ratios obtained are all from a specific period during childhood. However, the dietary signatures obtained from the mother *in utero* and during breastfeeding may not directly reflect the child's place of birth but rather where the mother had been living prior to pregnancy. Teeth mineralised after weaning may thus be a better indicator of childhood residence of the individual. It is crucial to understand when skeletal tissue is most susceptible to Pb and Sr incorporation, how long these metal ions are likely to remain *in situ* and whether subsequent large intakes can alter the Sr and Pb isotope ratios during the lifetime of an individual. At the fundamental level, different isotope signatures indicate access to different dietary sources. Whether this can be clearly assigned to migration of people rather than movement of food will depend to a great extent on the integration of the isotope data with the archaeology, but in either case, the results will provide information on the subsistence strategies of archaeological burial populations.