CHAPTER FOUR

STRONTIUM AND LEAD ISOTOPE SOURCE-TRACING STUDIES OF SKELETAL REMAINS

4.1 Introduction

The isotope systems of Pb and Sr have been used individually in both archaeological and modern source tracing studies. However, Sr isotope ratios are employed far more frequently in investigations of archaeological bone and the application, often combined with that of light stable isotopes such as C, N and O, is considerably better established than that of Pb. This imbalance may stem from the fact that since the warnings by Waldron (1981; 1982; 1983), archaeologists regard the integrity of Pb in archaeological bone with significantly more suspicion than that of Sr, which is frequently accepted unquestioningly in many studies. Furthermore, the lengthier sample preparation required for Pb analysis and the ultra-clean facilities and procedures necessary to minimise laboratory and modern atmospheric contamination, makes Pb isotope analysis more difficult, expensive and time consuming by comparison. The need to minimise laboratory contamination is crucial when analysing enamel from individual teeth because samples sizes are usually very small (e.g. 20-140mg) and, as can be seen from the results Tables A1-A3 (Appendix I), Pb is considerably less abundant than Sr in tooth enamel (Pb concentrations ~0.05 - 5ppm; Sr concentrations ~150ppm). A 50mg sample of enamel with Pb concentrations ranging from 0.05 – 5ppm would contain only 2.5 – 250ng of Pb; 2.5ng of Pb being an extremely small sample for TIMS analysis.

Published studies that utilise archaeological skeletal remains tend to fall into two categories: those that harness Sr or Pb isotope analysis to answer a specific archaeological question such as diagenesis or migration, and those that utilise archaeological remains as a resource to illustrate an analytical technique or provide time-depth to an environmental or geochemical investigation. Both approaches have drawbacks. The first tend to be rich in contextual detail but may over- or misinterpret

the isotope data due to its complex nature or limitations, whilst the second group tend to be contextually inadequate with insufficient consideration for the nature or limitations of the archaeological resource they are utilising. Clearly, investigations that apply techniques developed in one discipline to material of another, benefit immeasurably from a collaborative inter-disciplinary approach.

4.2 Methods of analysis

Sr and Pb isotopes are analysed by mass spectrometry. This instrument separates and counts the ions of individual isotopes of each element, on the basis of the mass to charge ratio of the ions. Different combinations of ion source, mass analyser and ion collectors are available but the standard analytical method that has provided the highest precision measurements and resolution necessary for radiogenic isotope geochemistry for over half a century is thermal ionisation mass spectrometry (TIMS) (Halliday *et al.* 1998, 936). TIMS allows the measurement of istope ratios in samples containing a very small number of the atoms of interest with considerable accuracy and precision but requires lengthy laboratory purification of Pb and Sr and has a slow sample throughput. The majority of studies discussed in this chapter were carried out using this technique.

Less precise but with much quicker sample throughput is inductively coupled plasma-mass spectrometry (ICP-MS) which became available in 1984 and a few papers are discussed which have used this instrument to obtain Sr and Pb isotope measurements on skeletal remains. ICP-MS can provide simultaneous multi-element concentration analysis and also isotope analysis without the need for Pb or Sr separation in many samples. However, in the case of dental enamel, where the concentration of the elements of interest is very low in comparison to the high Ca/P matrix, separation may still be necessary to avoid suppression of the Pb and Sr signal (Yoshinaga *et al.* 1998, 407, J. Evans unpublished observations). Furthermore, for low-Pb samples particularly, resolution can be relatively poor, leading to large errors that in some applications may preclude separation of data. Nevertheless, this instrument has been used in environmental and archaeological studies where the resolution required in geochemistry is not vital and where meaningful interpretations can perhaps be made

using, for example, $^{206}Pb/^{207}Pb$ ratios, thus avoiding the larger errors involved in the measurement of the low abundance ^{204}Pb isotope.

The new generation multi-collector ICP-MS offers greatly increased resolution and precision with the combined advantages of both TIMS and ICP-MS. It is more versatile and user-friendly than TIMS, particularly when coupled with laser-ablation sample introduction method and may eventually replace TIMS in all but the most specialised geochemical applications (Halliday *et al.* 1998, 936). It is, however, still a relatively new instrument, not widely available and has been used in very few archaeological studies (e.g. Montgomery *et al.* 2000). Instrumental techniques used in this thesis are discussed in more detail in section 5.3.

4.3 Combined Pb and Sr isotope studies

There have been few modern or archaeological migration studies that have combined Sr and Pb isotope analysis. However, attempts to source trace modern ivory and rhinoceros horn to specific African National Parks (Hall-Martin *et al.* 1991; Vogel *et al.* 1990), have illustrated the complementary information that can be obtained by combining Pb and Sr along with other light stable isotope systems. Vogel *et al.* (1990, 748) concluded that the more isotope systems used, the better the resulting distinction between samples, but in their study Pb isotopes did not prove particularly diagnostic.

Pb isotopes have been used successfully by Outridge and Stewart (1999) to characterise regional communities of modern Atlantic walrus as residents of one of three locations in the Canadian Arctic and to study walrus mobility within the region as a whole. Using ICP-MS, the authors found significant differences between $^{208}Pb/^{207}Pb$ ratios in walrus tooth cementum from sites with similar off-shore, but different terrestrial, geology. This indicated that terrestrial run-off was the major influence on the local marine signature (Outridge & Stewart 1999, 110). They tried, but rejected the use of Sr which, due to the homogeneity of the Sr isotope ratios in the marine environment, provided no resolvable geographical variation amongst marine mammals (Outridge & Stewart 1999, 111). The study was well constrained with extensive ecological and osteological considerations,

recording of age, sex and body size and the standardisation of the analytical samples (lower right canine). It is an excellent example of what can be achieved in a well integrated, inter-disciplinary project where ICP-MS proved sufficiently precise to be able to resolve isotope differences between samples.

Even fewer studies of archaeological remains have attempted to combine the two isotope systems of Pb and Sr to investigate ancient human mobility and residence patterns, although Price *et al.* (2001, 601) have recently indicated their intention to obtain Pb isotope data to complement the Sr isotope ratios of Neolithic Linearbandkeramik farmers in Central Europe. The studies by Montgomery *et al.* (2000) which is discussed further in Chapter Six, and of Åberg *et al.* (1998) are, therefore, the only notable examples to date. The paper by Åberg *et al.* (1998) compared Sr and Pb isotope ratios from five mediaeval individuals, each from a different location in Norway, with modern tooth correlates. The work arose from extensive prior environmental work and is based on sound background experience but does not address the fundamental difference between modern and archaeological material. Moreover, analysing one human sample from each site is insufficient to characterise either the range of local isotope variation or the population as a whole. In contrast to most animals, individual human behaviour is, perhaps, defined by its tendency to be idiosyncratic, atypical and culturally motivated and that of one person cannot necessarily be extended to an entire population.

The authors conclude that there is a clear difference between modern and archaeological Sr and Pb isotope ratios but neglect to consider that this may simply result from the archaeological samples being buried for several centuries, even though one tooth produced an unusually high (48ppm) Pb concentration. They assume, incorrectly, that diagenesis occurs only by slow leaching of skeletal material and that Pb and Sr behave in an identical manner. Leaching is irrelevant for isotope analysis, which is independent of elemental concentration. However, diagenetic incorporation of elements may of course introduce Pb or Sr of a different isotope composition into the skeletal tissue. No soil analyses were carried out from any of the five burial sites, no sample preparation or selection procedures described to attempt to counter post-mortem contamination and there is no contextual, osteological or sample information presented. This makes it impossible to ascertain which were bone and which were tooth samples,

what tissue was prepared from each and how the skeletal data related to the burial soils. Although this study failed to make the best use of archaeological material it does illustrate the different and complementary information that may be obtained from combined Sr and Pb isotope analysis.

4.4 Pb isotope studies

Pb isotopes have been used primarily to track changes in pollution and exposure through space and time as opposed to the movement of people into different exposure zones. Accordingly, there are many published studies that characterise and then identify the contemporary sources of Pb in cases of Pb poisoning, particularly in children (e.g. Rabinowitz 1987; Yaffe *et al.* 1983), or assess the relative contributions different sources, such as paint or petrol, have made to human Pb burdens (Delves & Campbell 1993; Farmer *et al.* 1994; Keinonen 1992). Most notably, a large body of such work has been published on source tracing contemporary human Pb exposure by Brian Gulson and co-workers at Macquarie University, Sydney (e.g. Gulson 1996; Gulson & Gillings 1997; Gulson *et al.* 1994a; Gulson *et al.* 1995; Gulson *et al.* 1994b; Gulson & Wilson 1994). However, these workers have also exploited the principle of different Pb sources having characteristic signatures to identify migrants in a forensic context. Whereas archaeological applications are based on the consumption of locally-derived diets, this modern study utilised the different industrial Pb sources that exist in different countries and which residents are thus exposed to throughout their lives. It proved possible to clearly distinguish first generation immigrants from individuals born in Australia on the basis of the Pb isotope signature of their teeth (Gulson *et al.* 1997a).

Although much success has been achieved in the application of these techniques to elucidate Pb exposure in contemporary humans, interpreting the results from archaeological remains, where the possible exposure sources are long gone and no biographical details exist, can prove problematic. However, even if the exposure sources themselves can no longer be identified, different geographical groups and cultural communities are highly likely to have been exposed to a cocktail of different sources of Pb through natural processes and cultural practices. The resulting Pb isotope

signature can be used to both delineate the field of variation within a population and to then identify individuals that have different exposure histories. It thus becomes possible to discriminate between burials and between cemeteries.

Pb isotope studies that utilise archaeological remains effectively fall into two groups: those that use archaeological material as an archive to track prehistorical and historical pollution and those that use exposure to different natural and anthropogenic Pb sources to identify mobility or cultural differences. The first group tend to originate from an environmental or purely analytical perspective and, as with the study by Åberg *et al.* (1998) already mentioned, have a tendency not to address the nature or limitations of the resource (i.e. archaeological teeth and bone) they are utilising, and would benefit considerably from a fuller consideration of the archaeological context. The second frequently arise from a desire to answer a specific archaeological question and whilst rich in archaeological detail, risk misinterpretation of the data through a failure to understand its nature or limitations. Moreover, most studies, archaeological and analytical, analyse bone which is problematic especially when samples and sampling sites are not standardised; tooth enamel is far more homogeneous and resistant to diagenetic alteration.

Two studies that have attempted to track historical trends in marine Pb pollution using teeth from Alaskan sea otters (Smith *et al.* 1990) and Canadian walrus and beluga (Outridge *et al.* 1997) have a very different approach to the use of the archaeological resource. The study by Smith *et al.* analysed modern and "preindustrial" teeth excavated from a midden on the Aleutian Island of Amchitka. Extensive sample preparation procedures and laboratory protocols to minimise contamination were carried out and the analyses performed by TIMS. The ancient teeth had a Pb isotope signature consistent with that of the Aleutian arc geology where they were excavated, whereas the modern teeth were clearly differentiated and the authors concluded they were consistent with modern industrial Pb sources.

However, such results are also consistent with the ancient teeth having a Pb isotope signature derived from the burial context (although the midden itself was not analysed). Little consideration was given in the paper to diagenetic alteration other than the following comments: *"Teeth constitute a unique indicator of lead exposure because*

they accumulate lead over the life of the organism. In addition, they are resistant to contamination and post-mortem diagenetic alteration, relative to other tissues. This is because the inner dentine of buried teeth remains is isolated from the surrounding soil by a protective layer of enamel, which is very impervious to soil lead alteration (J.E. Ericson, personal communication).” (Smith *et al.* 1990, 1517). And in the conclusions they state: *“ The exchange of soil lead is not considered to have significantly altered the lead composition of the preindustrial teeth. This is based on analogies with analyses by Ericson et al. (1979) who reported minimal diagenetic alteration of tooth enamel of buried ancient Peruvian remains.”* (Smith *et al.* 1990, 1520). Given that the authors specifically remark twice on the impervious nature of enamel to post-mortem contamination, it is curious that they should then choose to analyse dentine instead. Dentine is considerably less resistant to diagenetic alteration (see Chapter Six) and is not isolated from the soil solution because the root apex remains open throughout life to allow passage of blood vessels and nerves to the pulp chamber. In an intact tooth, diagenetic alteration of dentine generally progresses via the pulp chamber towards the enamel. Despite the meticulous analytical protocols employed, the work suffers from an unfortunate choice of samples and a lack of understanding of the nature and history of archaeological skeletal material which makes it impossible to be certain whether the Pb isotope data results from *in vivo* or post-mortem accumulation.

The study by Outridge *et al.* (1997) used the less precise analytical method of ICP-MS to analyse historical Pb isotope trends in archaeological and modern walrus and beluga tooth cementum (when mature, neither mammal has enamel covering the tooth dentine). Although no attempt was made to analyse burial soils, the authors investigated both archaeological and modern tooth cementum by LA-ICP-MS and found that the ratio of Pb in the outer to inner cementum was very similar in both sets of teeth. They interpreted this as an indication that post-mortem Pb contamination had not penetrated into the inner cementum in the archaeological samples. Neither was there a significant difference between Pb concentration in both sets of teeth. The Pb isotope ratios of all the modern beluga from the sampling area showed no significant difference, indicating that there was no geographical variation. When plotted with the archaeological samples however, a decreasing trend with time in the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios became apparent. The authors concluded that this indicates historical change in Pb pollution

sources in the region and ICP-MS provided the necessary precision to resolve temporal changes.

A pioneering archaeological pilot study was published in 1986 by Molleson *et al.* (1986) applying Pb isotope analysis by TIMS to archaeological human remains from the Romano-British cemetery at Poundbury Camp, Dorchester. The authors propose this as the first study to submit archaeological skeletal material for Pb isotope analysis. The archaeological considerations were good with thoughtful selection of individuals, although it was perhaps unfortunate that trabecular rib bone samples were chosen and no sample decontamination procedures appear to have been carried out. Nonetheless, although Pb concentrations were uniformly high in all four individuals (174-264 μg/g), the isotope ratios enabled the authors to discriminate between the four, thus indicating that the *in vivo* Pb signature had not, or had not entirely, been obscured by post-mortem contamination. Results from this thesis (section 6.4) would suggest that this results from a combination of two factors: the burial of individuals who already had a large *in vivo* Pb burden in low-Pb, alkaline Cretaceous chalk.

The interpretation of the results was heavily biased towards Pb-ore sources; unsurprising perhaps, given that one of the authors (Gale) had amassed a considerable body of Pb isotope data from Bronze Age Mediterranean tin, copper and bronze and British ore-Pb sources. One individual, a child aged ~6yrs, had a signature that was very different from British Pb ore ratios but matched those of Pb-Ag ores from Laurion in Greece, and they thus concluded the child was a recent immigrant to England from Greece. The local Poundbury soils or underlying Cretaceous chalk bedrock were not analysed. Had they done so, the authors would have discovered a possible Pb-source much nearer to home. The child's Pb isotope ratio falls on a mixing line between the that of Cretaceous chalk bedrock (see discussion in section 6.6.2.2), which formed both the burial soil and the local dietary signature, and the nearest British Pb ore source from which the Pb coffins discovered on the site were probably made, in the Mendips. This highlights the problem that although a number of *possible* sources of Pb exposure may be identified, it is probable that others, unanalysed and undiscovered, may also exist. However, the child's bone-Pb concentration (196 μg/g) appears very high for a natural, rather than anthropogenic, *in vivo* Pb exposure, particularly as Pb is present only at very

low concentration in Cretaceous chalk and hard water sources are known to offer some protection against Pb-uptake (sections 2.3.4, 6.6.1.3 and 6.6.2.2). The susceptibility of young children to Pb poisoning and their ability to absorb far more through the gut than adults, may account for this high concentration. Juvenile bones are also less well mineralised and, especially as trabecular rib bones were analysed in this study, the seemingly exotic ratio may result from a mixture of diagenetic Pb incorporated from the burial chalk and a biogenic bone-Pb ratio of Mendips origin.

A further interesting observation was that, of the three adults analysed two were associated with the urban settlement and enclosed in nailed wooden coffins and had very similar Mendips ore-Pb isotope ratios. The third was associated with the rural settlement, was interred in a simple coffin, and had a different bone-Pb isotope ratio from both the Mendips and the chalk, which the authors could not reconcile with any known Pb-ore source. The conclusions of this thesis (see Figure 9.2) would suggest that such a signature (and that of the child) if coupled with enamel-Pb < 1ppm, would derive from a non-local, country rock source, rather than anthropogenic ore. However, the bone-Pb concentration (174 μg/g) was rather high for purely non-anthropogenic Pb-exposure. Analysis of the tooth enamel of all four individuals would have given a clearer picture of the place of origin and constrained childhood exposure and would have provided a good baseline against which to assess the bone-Pb results.

Two papers published by Ghazi (1994) and Ghazi *et al.* (1994) attempted to determine the source of the unusually high Pb concentrations found in the bones of 18^{th} – 19^{th} century Omaha Native Americans (Reinhard & Ghazi 1992) using ICP-MS rather than TIMS. Some children and adult males had extremely high bone-Pb concentrations that were unlikely to result from natural *in vivo* sources. The author's assertions that the soil-Pb concentration was too small to cause significant diagenesis and that if it had occurred, all bones would contain the same concentration are not, however, necessarily justified. Whether the soil-Pb was sufficient to cause significant diagenesis would also depend on how much Pb the bones contained prior to burial and its availability within the soil. Three soil samples were analysed for Pb concentration only and the analyses were of bulk soil rather than bioavailable cations, making Pb mobility and the diagenetic isotope signature difficult to assess. Furthermore, the susceptibility of

individual bones to diagenetic alteration is extremely variable both on the macroscopic and microscopic scale and can vary with age, mineralisation and type of bone.

However, all faunal remains from the same site had very low bone-Pb which is perhaps the author's best indication that diagenesis had not occurred to any significant degree. Isotope analysis of both the mobile soil-Pb and the faunal bones would have clarified the issue but perhaps posed analytical difficulties with this instrumental technique given the very low Pb concentration in these particular samples. Traces of a red Pb-Hg pigment were found on the human remains and removed prior to analysis and metallic Pb artefacts were excavated from the graves. Pb isotope analysis of these and the human skeletal remains indicated that it was the red pigment, applied as part of a post-mortem ritual and perhaps also used ante-mortem, that made the largest contribution to the Pb content of the bone. If the tooth enamel from the burials had been analysed it may have proved possible to discriminate between biogenic and diagenetic Pb sources and standardise exposure levels to obtain a valid comparison between adults and children.

Yoshinaga *et al.* (1998) published a study by ICP-MS tracking sources of Japanese Pb exposure in prehistoric (Jomon) and historic (Edo) remains and comparing them with contemporary bones and teeth. The paper is technique-orientated and as a result poorly constrained from an osteological and archaeological viewpoint. There was no standardisation of skeletal tissue: the authors used "long bone shafts" with their surface removed, from the prehistoric period; ribs with the trabecular bone removed but incomplete surface removal, from the historic period; ribs with the trabecular bone intact, from modern autopsies and exfoliated, deciduous incisors from modern children. All adults were of unknown or unquoted age and the 16 archaeological samples came from eight different sites from which no burial soils were analysed. They dismiss diagenetic alteration on the basis that their results agree with those of two previous studies which showed higher Pb concentrations in historic remains compared with prehistoric remains, and that *"It is unlikely that excess Pb found in the Edo bones had been caused by diagenesis in all of the 3 studies."* (Yoshinaga *et al.* 1998, 409). Whilst the results may reflect *in vivo* values, it is still the case that diagenesis has to be considered at every site individually and cannot be dismissed on the basis that other archaeological remains from other sites produce similar Pb concentrations; all or some

may be contaminated. Also, a comparison of Pb concentrations in individuals of different ages needs to use skeletal elements that do not have an age-dependent Pb accumulation (e.g. bone, circumpulpal dentine). The mechanism of Pb incorporation in the deciduous teeth of children is very different to that of both trabecular and cortical adult bone (see section 6.2.1) and the process of root resorption may artificially concentrate the amount of Pb in deciduous teeth (Whittaker & Stack 1984, 40). Choosing to analyse enamel would have reduced inter-tissue, formation period and age related differences and also reduced diagenetic susceptibility. Despite using ICP-MS which is considerably less precise than TIMS, a separation was obtained between the unburied (contemporary) and the buried (prehistoric and historic) remains, although at the 2σ level the majority of data points were within error of each other.

A comprehensive study by Carlson (1996) attempted to distinguish Fur Traders from Native Americans buried in a 19th century North American cemetery on the basis of their differing Pb exposure histories. Extensive anthropological and osteological information such as age, sex and racial characteristics was presented as well as burial context and grave goods. Burial soil was analysed for exchangeable Pb and the Pb isotope ratios of both local faunal samples (bison and elk) and contemporary Pb artefacts were measured. The paper included a sound and realistic discussion of the effects of diagenesis and despite the choice of abraded cortical bone samples in preference to enamel, the bone-Pb signatures were very different from the mobile soil-Pb, precluding significant post-mortem uptake. The individuals identified as Fur Traders were closely grouped and similar to the Pb and Cu artefacts. The wild faunal samples formed a second distinct group whilst the two Native Americans did not: one (an elderly adult male) falling within the range of wild faunal samples, the other (a young adult female) exhibiting a signature similar to the Fur Trader group. Interestingly, the Pb concentration in these two individuals was also very different, the young female having an exceedingly high bone-Pb (192ppm) concentration that was very unlikely to be obtained from natural geological sources *in vivo*. Her similarity to the anthropogenic Pb source was, therefore, not surprising and such a high *in vivo* exposure would have swamped any contribution from natural, geological Pb, although some post-mortem contribution from the soil cannot be entirely ruled out. The results suggest that exposure to an anthropogenic, cultural source would result in a higher

skeletal Pb concentration, whereas natural exposure, uncontaminated by artefacts or pollution, would produce a lower skeletal Pb concentration and that the latter would, of course, be more easily overwhelmed by post-mortem contamination. Such an interpretation would be confirmed by conclusions reached in this thesis (Chapter Nine and Figure 9.2).

A suite of papers published by Kowal *et al.* (Kowal *et al.* 1990; Kowal *et al.* 1991; Kowal *et al.* 1989) documented work carried out on the remains of British sailors from the Franklin Arctic Expedition of 1845-8. The authors noted that Pb concentrations in bone (69-223 μg/g) exhumed from the permafrost or surface finds on well-drained beach gravels, equals, and in some cases exceeds, those found in modern cases of high and toxic exposure (Keenleyside *et al.* 1996, 464; Kowal *et al.* 1991, 194; Kowal *et al.* 1989, 125). Inuit and animal bones from the site ranged from 1-14 μg/g (Kowal *et al.* 1989, 125) and raised the prospect of endemic Pb-poisoning amongst the crewmembers. In an attempt to trace the source of the high Pb concentrations, the authors analysed ice from the graves, local Inuit and caribou bone and hair, and bone from modern western Canadians along with solder from two food cans found at the site. The sailors' Pb isotope ratio matched that of the solder and was very different from all the Canadian samples. The authors concluded that solder-Pb alone was responsible for the high Pb exposure amongst the Franklin crewmembers and because both the hair and bone isotope signatures matched, the Pb in both must have been acquired during the expedition. Farrer (1993, 406) has made a strong critique of the work, however, pointing out several flaws in the construction of the investigation and the authors' interpretation of isotope data, which are relevant to most studies that aim to use and interpret Sr or Pb isotope data in archaeological contexts. They are:

1. The Franklin sailors should be compared with their British contemporaries to ascertain if both groups have the same Pb concentrations and isotope ratios. As Farrer (1993, 400) states: *"The only controls relevant to the Franklin study, namely adult British males, preferably sailors, living in the 1840s are lacking*." Pb was widely used in 19th century Britain and such high Pb concentrations may have been endemic.

2. Given the long residence time of Pb in bone, the isotope ratio and the high bone-Pb, concentrations measured are unlikely to derive from the relatively short-term exposure of the expedition (i.e. < 3 years). If they are not diagenetic in origin, which appears unlikely in this case, they must represent exposure prior to the expedition.
3. Pb absorption in the gut increases on a purely liquid diet, in the presence of alcohol and from soft water supplied through Pb pipes. Sailors who were already sick, on a liquid diet of snow or ice-derived soft water obtained through Pb pipes from the ships water tanks and also receiving "wine for the sick" may well have had a large increase in Pb ingestion before death but this may be isotopically indistinguishable from earlier exposure.
4. As with soil concentrations, the presence of Pb in solder does not mean that it is mobile and will inevitably contaminate the canned food. Pb is electrolytically inhibited both by the tin plate and the tin in the solder itself.
5. Isotope ratios are exclusive. Samples that have different isotope ratios cannot be from the same source, e.g. the Franklin remains and the local Canadian samples. However, it does not follow that samples with the same isotope ratio are, of necessity, from the same source e.g. the Franklin remains and the solder; other sources possessing identical isotope ratios, e.g. Pb pipes on the ships water tanks, may also exist.
6. The claim by Kowal *et al.* (1991, 201) that the Pb isotope ratio in the solder and the sailors remains *"is so different from most lead sources in the British Isles, it is quite possible that the lead used in the solder manufacture came from some other nation"* is puzzling, as these ratios plot squarely within the field of British ore-Pb from the Mendips. Such Pb isotope ratios have also been found in other studies of British human remains and Pb artefacts both in this current thesis and in previously published work (Molleson *et al.* 1986, 250).

Farrer (1993, 405) concludes *"Thus, the only conclusions which can be drawn at present would seem to be that it is unwise to postulate the coincidence with a specific lead source of lead from any bone sample."* However, it would be possible to discover what Pb isotope ratio and level of Pb exposure the Franklin crewmembers were exposed to prior to sailing with the expedition by analysing the enamel in their teeth which would retain a childhood signature of early 19th century exposure. Furthermore,

although this study was primarily concerned with identifying the source of the purported Pb poisoning of the Franklin crewmembers, it nevertheless inadvertently illustrates the effectiveness of Pb isotopes to differentiate between immigrants and the indigenous population. Although Farrer criticises the use of the Canadian samples as irrelevant, they highlight quite clearly that the Franklin sailors originated from some place other than the place they were buried.

4.5 Sr isotope studies

Several studies have been carried out using Sr isotope ratios to investigate modern animal mobility and migration away from the place of origin through natural geological Sr uptake (Chamberlain *et al.* 1997; Hobson 1999; Koch *et al.* 1995; van der Merwe *et al.* 1990). Modern human Sr ratio studies that have demonstrated the utility of Sr as a source-tracing tool have primarily arisen through clinical research or investigations of the effects of ^{90}Sr fall-out from atmospheric nuclear explosions. Sr isotope ratio analysis has also been extensively applied on hominid and animal fossils to identify both migration and different feeding strategies (Elliott *et al.* 1998; Horn *et al.* 1994; Koch *et al.* 1992; Sillen *et al.* 1995; Sillen *et al.* 1998).

The seminal paper published in 1985 by Ericson is widely credited with bringing the potential for Sr isotope ratio analysis in migration studies to the anthropological and archaeological community. In it, he outlined his biogeochemical model and presented data from two small preliminary studies: two individuals from a coastal Malibu site and one individual from 7.5km inland. Tooth (core enamel is not specified in his methods but he advocates choosing this tissue elsewhere in the paper) and bone samples were analysed. The paper outlined many of the pitfalls and potential archaeological applications of Sr isotope ratio analysis. However, his prediction that *"it is possible that mobility patterns can be discerned by measuring the isotopic values on a crystal-by-crystal basis following the growth patterns in teeth using an ion probe"* (Ericson 1985, 508) is still analytically unfeasible and, as enamel does not mineralise in

accordance with visible incremental structures (see section 3.4), may never be viable in that tissue.

This paper was closely followed into press by the widely quoted, elegant study of Nelson *et al.* (1986) which presented the first investigation of Sr diagenesis in archaeological bone. The authors utilised the characteristic Sr isotope ratio of marine mammals (~0.7092) compared to the considerably more radiogenic Sr isotope ratio of terrestrial mammals inhabiting the ancient rocks of Greenland (0.7373-0.7583). The well-established marine Sr isotope ratio provided the necessary control so they could be certain what the Sr isotope ratio of the archaeological seal bones was before they went into the ground. Despite the fact that mechanical and chemical sample pre-treatment procedures were carried out, their results show that archaeological marine mammal bone buried on land could no longer be distinguished isotopically from terrestrial feeders. Furthermore, Sr concentration differences, which clearly distinguished modern seals (~1000ppm) from modern reindeer (~180ppm), were not preserved amongst archaeological seals and reindeer (all contained ~900ppm).

A leaching experiment of the excavated seal bone led the authors to conclude that diagenesis had occurred mainly by *exchange* of diagenetic Sr with biogenic Sr, as opposed to incorporation solely by addition. Moreover, they reasoned, this diagenetic replacement of *in vivo* Sr must be almost complete to produce such radiogenic Sr isotope ratios in marine mammal bone. However, it must be borne in mind that Nelson *et al.* used non-cortical bone samples, which are the most susceptible tissue to diagenetic alteration and also that marine mammal bone is considerably less dense than terrestrial. Although this first illustration of Sr diagenesis in bone was subsequently criticised for these and other reasons (Sillen & Sealy 1995), it has been a continuing obstacle for all subsequent workers wanting to apply the technique to archaeological bone. Nonetheless, it illustrated the possibility of using Sr isotope ratios as a dietary indicator to discriminate between marine and terrestrial diets and Sealy *et al.* (1991) extended this to archaeological human and faunal bone using the solubility profiling technique in an attempt to remove diagenetic Sr.

Throughout the 1990s the majority of archaeological dietary and migration studies using Sr isotope ratios were carried out by two groups: one under Nikolaas J. van der

Merwe at the University of Cape Town, South Africa and the other in North America led by Douglas T. Price and James Burton based mainly at the University of Wisconsin-Madison. The latter group have published a series of papers using Sr isotope ratios to identify prehistoric mobility in the south-western U.S.A. and Mexico (Ezzo *et al.* 1997; Price *et al.* 1994b; Price *et al.* 2000); an investigation of migration in the Bell Beaker period in Bavaria (Grupe *et al.* 1997; Price *et al.* 1994a; Price *et al.* 1998; Schweissing & Grupe 2000); and most recently on the spread of Neolithic Linearbandkeramik farmers in Central Europe (Price *et al.* 2001). These workers have made available an abundance of comparative data together with extensive archaeological background information, and the holistic approach is exemplified in the Grasshopper Pueblo study of Ezzo *et al.* (1997).

Their sampling strategy is to analyse M1 core enamel and compact femoral bone from each individual to determine locals from non-locals. Burial soil analyses are either absent from their case studies (Price *et al.* 2001; Price *et al.* 1994a; Price *et al.* 2000), not identified as such (Ezzo *et al.* 1997; Price *et al.* 1994b), or not taken from every burial site that they took samples from (Grupe *et al.* 1997; Price *et al.* 1994b). Furthermore soil data presented appears to be that of bulk soil analysis rather than exchangeable or soluble cations and bulk soil or whole rock Sr isotope ratios are not always representative of the bioavailable Sr (Sillen *et al.* 1998), although this is entirely dependent upon the individual rock constituents and its homogeneity. However, the authors point out the problematic nature of soil analysis and accordingly recommend using small animal bones to directly characterise the local food chain Sr isotope ratio instead (Ezzo *et al.* 1997; Price *et al.* 2002; Price *et al.* 2000). This suggestion has considerable merit but rests on the assumption that humans consumed such animals. It may, therefore, not be sufficient on its own to characterise human isotope variation at a site if the inhabitants were either not consuming the analysed animals or were obtaining the major portion of their diet from elsewhere but is clearly an important additional parameter.

They used both mechanical and chemical sample pre-treatment methods (i.e. soaking overnight in 1N acetic acid which has been criticised for altering the carbonate hydroxyapatite crystal structure in archaeological specimens by Lee-Thorp & van der Merwe 1991), in order to remove diagenetic contamination. However, the vast majority

of bone samples still cluster tightly at each site and have elevated Sr concentrations (some exceed 1000ppm) compared to enamel from the same individual. The extremely large differences between some enamel and bone pairs (e.g. 119ppm enamel, 938ppm bone Price *et al.* 1994b, 322) are difficult to explain by anything other than post-mortem bone contamination especially as the authors believe Sr concentration to be indicative of trophic level (Price *et al.* 1994b, 316). Sr concentrations are relatively consistent in all skeletal tissues (enamel, dentine and bone) in modern humans and do not normally reach such concentrations even in areas of high-Sr geology (see section 2.3.3). Whilst the authors are correct to point out that a milk-based diet is Sr-poor, so M1 enamel would be expected to contain less Sr than bone, it would be useful to test this hypothesis by also analysing enamel from a later forming tooth such as M3 for comparison.

The authors maintain that their pre-treatment methods remove diagenetic Sr phases and reject the possibility that Sr may be primarily incorporated by exchange with *in vivo* Sr in the carbonate hydroxyapatite lattice on the basis that skeletal Sr isotope ratio is much less radiogenic than that of the bulk soil (Price *et al.* 1994b, 323). This is true, although in this study only one soil sample was analysed and then compared to skeletal material from two, geologically diverse, burial sites. However, Sillen *et al.* (1998, 2466) found that bioavailable soil-Sr *is* usually much less radiogenic than whole soil or rock at his study sites. Bulk soil analysis is *not* a reliable indicator of the mobile and hence, diagenetic, Sr isotope ratio. Schweissing & Grupe (2000, 103) nevertheless, concluded that all individuals at Viminatium, near Belgrade were immigrants because their Sr isotope ratios did not match that of the bulk soil.

The conundrum posed as to whether and to what degree samples have been contaminated by burial Sr is unlikely to be solved easily and it is possible to argue either case and prove neither. For example, the observation that high Sr concentrations are only seen in conjunction with a local Sr isotope ratio whereas all immigrants have a low to moderate Sr content (Ezzo *et al.* 1997, 455) may be equally explained by diagenesis rather than a "*high-Sr local diet"*. Similarly, the proposal that all the female immigrants migrated to the site within the last 7-10 years of their lives, irrespective of age at death (and this varies considerably) (Ezzo *et al.* 1997, 456), seems improbable. It begs the question that if every immigrant female died 7-10 years after arriving at the

settlement, why women with any sense didn't leave after five. Results in this thesis (Chapter Six) suggest that the most parsimonious explanation for the differences observed by Ezzo *et al.* (1997) between enamel and bone Sr isotope ratios (bone being intermediate between soil and enamel values) is that Sr from the burial environment accumulated in all bone samples post-mortem.

An estimate of 7-10 years for Sr turnover in cortical bone probably underestimates the true figure by about 10 years but it is acknowledged that it is extremely difficult to quantify (section 2.4). Most importantly however, it does not take into account the huge variability of bone turnover rates in children and young adults (section 2.4), i.e. it cannot be assumed to have been the same for someone who died at ~20 years of age and someone who died at ~50 years. Such vital tissue formation considerations would have aided interpretations of the age profile of suggested immigrants where the authors note that the most mobile age groups were those in their 20s and 30s (Ezzo *et al.* 1997, 456). As the immigrants were selected on tooth enamel values, it has to be remembered that the enamel bears no relationship to subsequent age at death; it is a snapshot of diet and environment whilst the crown was mineralising. In the case of M1 this is from around birth to ~4years of age and the individuals could have migrated at any age after this. Given the many variables that can affect bone turnover rates *in vivo*, using bone Sr isotope ratios to estimate the age of migration in contemporary populations where the place of origin was known would be problematic. The introduction of a further unknown variable of diagenetic contamination may well render the results too imprecise to be meaningful.

Price *et al.* (2000, 911) advocate bone analysis because *"Measurement of dental enamel provides a signal of place of birth and measurement of bone indicates the place of death"*. However, it could be argued that information about the place of death can be obtained far more easily, cheaply and reliably in the vast majority of cases just by recording the place of burial, particularly as adult cortical bone ratios represent the last ~20 years of life and not perimortem values. Identification of immigrants can, therefore, be carried out just as effectively on tooth enamel analysis alone. Furthermore, as has also been pointed out by Horn and Müller-Sohnius (1999, 268), bone Sr isotope ratios appear rather redundant as they are virtually indistinguishable from the soil, providing evidence for the mobile soil Sr isotope ratio instead of adding

to the process of identification of migrants. In a ground-breaking paper Bell *et al.* (2001) have used density separation techniques to sample bone on the microscopic scale according to its stage of mineralisation at the time of death. Using this method the author's extracted fractions representing the last ~18 years down to the final few days of an individual's lifetime. There is no doubt that this technique has many applications beyond the stable carbon isotope analyses used in this study, but doubts remain over the resistance of Sr to post-mortem alteration in all skeletal tissues that are less well mineralised than mature enamel (see conclusions 9.2).

Horn and Müller-Sohnius (1999) have levelled several criticisms concerning sample preparation, data handling and interpretation specifically at the Grupe *et al.* (1997) Bell Beaker study. They point out that bulk soils samples do not represent the bioavailable Sr, thus characterising neither the local nor the diagenetic Sr isotope ratio. They maintain that aqueous soil extracts must be carried out from each grave or, alternatively, the bone Sr isotope ratio used instead; their own analyses of soil leaches from the region produced extremely variable (0.705-0.7105) Sr isotope ratios (Horn & Müller-Sohnius 1999, 263). They also point out that skeletal remains from twelve different archaeological sites cannot be treated as the same sample set. Moreover, whilst they acknowledge that enamel is considerably more resistant to diagenetic change than bone, they state that there is a *"life-long (slow) diffusive exchange of dental Sr with saliva via the pellicula which mantles teeth"* (Horn & Müller-Sohnius 1999, 263) which precludes the assumption that M1 enamel Sr represents the first ~4 years of life. However, this exchange is considered to occur only in the very surface of enamel and as Grupe *et al.* physically abrade the enamel surface prior to analysis, it should not contribute to the Sr isotope ratio. Furthermore, they maintain that because Grupe *et al.* did not remove the organic fraction from either bone or enamel prior to analysis they failed to remove the Sr metabolised shortly before death, which is located within the collagen. There is, however, no collagen in enamel (Chapter Three). The very small organic fraction (~0.3% vol.) consists of residual, matrix proteins that were incompletely removed at the end of matrix formation and they take no active role in the acellular, mature tissue. Removing this tiny organic phase may, in practise, have little bearing on the resulting enamel Sr isotope ratio or identification of the individual as an immigrant as Horn *et al.* (1994) have themselves demonstrated. Grupe *et al.* have strongly defended their protocols and particularly their use of bone analyses and

decontaminating procedures (Grupe *et al.* 1999). Nevertheless, there is evidence in the geochemical and palaeontological literature for Sr bone diagenesis and the apparent inability of many such chemical decontamination techniques to remove soil-derived Sr from bone (see section 3.6.3.1).

Sr isotope ratios have been also employed by the Cape Town group as an addition to their primary focus of stable (N and C) isotope analysis and they demonstrate quite effectively how this suite of isotopes can provide useful complementary palaeodietary data. They rely extensively on the solubility profiling technique developed by Sillen (Sillen 1986; Sillen 1989) which is performed on all tissues. Burial soil analyses are not reported from any of the sites. Sealy *et al.* (1995) published a study using Sr, C and N isotope analysis to investigate the life histories of five adults (two prehistoric, three historic) individuals from four sites in South Africa. The osteological and anthropological background was extensive and samples were carefully selected: enamel, dentine, trabecular rib bone and cortical long bone. No attempt was made to separate primary and secondary dentine.

Duplicate bone analyses were performed to assess the degree of Sr isotope ratio variation that could be obtained from biological tissues of one individual. Such data is scarce and accordingly the possible spread of ratios is poorly understood. They estimated this to be 0.00032, which is considerably larger than the measurement precision by TIMS and they advise that small differences in Sr isotope ratio should be interpreted with caution (Sealy *et al.* 1995, 297). Clearly, if this represents the normal biological variation within one bone of one individual, that of a population as a whole may be considerably greater. Moreover, as they point out, performing such a study on archaeological material may additionally underestimate the *in vivo* differences because *"Residual contamination from strontium in the soil will reduce variability in* $^{87}Sr/^{86}Sr$ *within a skeleton so that any intra-skeletal differences are minimum estimates."* (Sealy *et al.* 1995, 296).

In a further study that combined Sr isotopes with C and N isotopes, Cox and Sealy (1997) investigated the dietary signatures from eight individuals believed to be slaves drowned offshore when the slaving brig, the Pacquet Real sank in 1818. Many individuals had tooth decorations characteristic of peoples from Northern Africa.

Unfortunately, Sr isotope ratios were obtained for only five individuals: bone analyses were obtained for two individuals; enamel analyses for a further two and the remaining individual aged ~12 years had enamel, dentine, cortical femur and trabecular rib analyses performed. Again, no attempt was made to characterise the mobile soil-Sr however, as the cemetery was originally on the beach but was now further inland, it would be very likely to have a marine-like signature. All samples were subjected to physical surface cleaning and solubility profiling to remove post-mortem contamination. The three enamel values were different, indicating that these three juveniles originated from different childhood environments. Unfortunately, the Sr data was too incomplete to allow generalised statements for most individuals although the one individual who had four measurements taken had very similar enamel, dentine and femoral shaft ratios with a significant change in the rib Sr isotope ratio. This result was also obtained in the modern immigrant BAB analysed in this study (Chapter 6). Trabecular bone is, of course, the tissue most susceptible to change *in vivo* and post-mortem but interestingly, this change was echoed in the C isotope ratios which indicated a move from more to less tropical climate.

A similar approach using Sr, C and O isotope ratios was applied to bone from the Tyrolean Iceman (Ötzi) to determine whether he spent his final years in the North or South Tyrol (Hoogewerff *et al.* 2001). The burial environment of glacial ice is clearly highly unusual for archaeological remains and little is known about diagenesis under these conditions. However, the authors note that the Sr concentration of the ice (0.01ppm) is three to four orders of magnitude less than normal human bone concentrations. It would have been interesting to know what the Sr isotope ratio of the ice was, along with the bone-Sr concentration of the Iceman, in order to assess its effect on the skeletal remains. However, uptake of Sr from the ice into the bone may well have been negligible during the few months he lay submerged in water prior to the onset of winter. In this case, Sr isotope ratios could not differentiate between the North and South Tyrol because they were geologically identical but it was possible to rule out an origin on surrounding limestone regions (Hoogewerff *et al.* 2001, 987). Nevertheless, it is a pity tooth enamel could not be analysed for this study to provide both a comparison with the bone ratios and in order to establish his childhood place of residence.

In a recent palaeontological study Sillen *et al.* (1998) emphasised the necessity of characterising the environment and pointed out that it had previously proved impossible (Sillen *et al.* 1995) to interpret the skeletal isotope data obtained from the Swartkrans hominid fossils (robust Australopithecines and early Homo) when this was not done. All skeletal samples, save one enamel sample, were of fossil bone. The authors applied the solubility profiling to remove diagenetic strontium which they maintain is effective at this particular site although may not be so in every burial context. Sr isotope ratios are very different in modern grassland and modern waterside fauna and these characteristic differences were still retained in the fossil specimens (Sillen *et al.* 1998, 2470). However, the authors stress that differences between the bone and soil Sr isotope ratios were *minimum* differences, as any remaining diagenetic Sr would move the bone Sr isotope ratio towards those of the burial environment.

Both soil leaches and bulk soils were analysed, along with their respective flora and fauna and the authors concluded that soil leaches were far more representative of the Sr isotope ratio available to the food-chain (Sillen *et al.* 1998, 2466). Bulk soil Sr isotope ratios were generally more radiogenic and considerably more variable (0.71876 - 0.90060) than the plants growing on them (0.72320 – 0.75561) and it was not always the radiogenic soils that produced the most radiogenic plant Sr isotope ratio. All the hominid fossils, bar one, closely matched those of the local veld (grassland) fauna pointing to this environment, as opposed to that of the riverbank, being the main source of food for both hominids and contemporary hippos, baboons, wildebeest and hyraxes. Enamel was analysed from the adult male robust Australopithecine whose bone Sr isotope ratio was much less radiogenic than the veld environment. The authors hypothesised that, if the individual had migrated into the area, the enamel Sr isotope ratio should be even less radiogenic (i.e. more different from the soil/plant Sr isotope ratio) than both the bone and the local food web because, unlike bone, enamel does not turnover after formation. This proved to be the case, leading them to suggest that this individual was an immigrant to the area from elsewhere. This is an entirely reasonable interpretation of the enamel data. However, their conclusion that the change in the bone Sr isotope ratio towards that of the burial environment is a result of *in vivo* bone turnover, i.e. the individual spent enough time at the new locale for this to be noticeable in the bone Sr isotope ratio, is not necessarily the only one possible. The difference could be a result of the different resistance of enamel and bone to diagenetic alteration,

i.e. the bone will alter more quickly than enamel; both tissues may have had the same *in vivo* Sr isotope ratios. Nevertheless, this study was the first to extensively characterise the environment and food-web of a burial population in order to interpret the skeletal isotope data and clearly shows the importance of obtaining valid soil analyses and faunal signatures. The region under scrutiny was, however, considerably more varied both in age and rock types than any region investigated in this thesis.

Although published concurrently, the study by Latkoczy *et al.* (1998) contrasts sharply with the aforementioned study of Sillen et al (1998), the emphasis being firmly placed on the instrumental application and optimisation of HR-ICP-MS to obtain high-precision Sr isotope ratios, rather than the archaeological context. The site is a 7000 BP Neolithic mass burial of 67 incomplete individuals at a fortified site in Asparn/Schletz, Austria. All bone fragments exhibit multiple, traumatic lesions and the site has been interpreted as a complete population killed in a single act of conflict that coincided with the abandonment of the settlement (Latkoczy *et al.* 1998, 561). The archaeological purpose of the study was to identify the burials as either foreign invaders or inhabitants of the site. Unfortunately, there is no burial soil data, no age or sex data and samples are described merely as "bone", and were ground in an agate ball mill, which may cause contamination in low concentration samples (Royse *et al.* 1998, 3). Formic acid was used to remove surface contaminants and the authors point out that all the samples exhibited *"apparently perfect macroscopic bone conservation"* (Latkoczy *et al.* 1998, 562) but were too incomplete to identify morphologically. However, good macromorphological bone preservation can result precisely *because* fossilising elements such as Sr have been incorporated (see section 3.6.2) and good macroscopic preservation does not indicate even good histological preservation (Bell 1990, 90). Results from this thesis confirm that macromorphological tooth preservation appears to provide no guide to the integrity of the biogenic Sr and Pb isotope signature (Chapter 9). It does not, therefore, indicate that *in vivo* Sr isotope ratio is preserved, particularly when the bone is reduced to unidentifiable fragments and samples are not standardised.

It is, therefore, not surprising that *"a striking similarity in strontium isotope ratio among the group of individuals"* (Latkoczy *et al.* 1998, 565) from the mass burial is obtained. These results contrast markedly with a small number of apparently unrelated "reference" samples from another site, on different geology, 100km distant, which

produced variable and more radiogenic Sr isotope ratios. The authors consider these findings *"support the assumption that most of the individuals from Asparn/Schletz belonged to a single population*" (Latkoczy *et al.* 1998, 565). This may well be true but may equally show that they belong to the same *burial* population. Such inter-cemetery differences may also result from differential post-mortem contamination and the bioavailable Sr isotope ratio at each site, neither of which the authors investigated. This study, therefore, whilst an extensive and analytically rigorous application of an instrumental method to archaeological material, neither addresses the constraints of the samples, uses the best tissue for the purpose nor attempts to characterise the burial environment or local signature. A later paper (Latkoczy *et al.* 2001) attempted to address diagenesis in a study of early Bronze Age burials from Austria. However, whole soil digestions were used, ground in an agate mortar and pestle, and a huge range of soil Sr isotope ratios obtained, i.e. ~0.704 - ~0.773; unfortunately no data table is provided so these are estimated from the graph. The bone Sr isotope ratios exhibited much less (but still considerable when compared to similar studies) variation, i.e. ~0.711 – 0.718. The authors concluded that the bone samples were not contaminated with Sr from the burial environment because they were considerably more homogeneous than the bulk soil Sr isotope ratios (Latkoczy *et al.* 2001, 809), the exact opposite of what may perhaps be concluded from such data. However, as Sillen *et al*. (1998, 2466) have shown, bulk soil samples on most lithologies *are* considerably more radiogenic and more variable than soil leaches and the bioavailable Sr. Bulk soil analysis is, therefore, rarely indicative of diagenetic Sr and cannot be used to assess post-mortem contamination except perhaps in the case of extremely homogeneous rock units such as Cretaceous chalk.

4.6 Conclusions

The studies discussed in this chapter highlight several points. Whilst the resolution provided by TIMS is necessary for studies that require an accurate and precise isotope ratio to provenance to source, ICP-MS may suffice for archaeological investigations

that only require the ability to distinguish between the indigenous and the immigrant. The magnitude of the difference will, however, vary from site to site and whilst ICP-MS may offer an initial, rapid screening of samples (although chemical separation may be unavoidable in order to remove the high Ca/P matrix) analysis by TIMS or MC-ICP-MS may be required. Furthermore, the obtainable analytical precision may be far better than the intra-individual variability making such resolution unnecessary. Apart from the assessment by Sealy *et al.* (1995) of the Sr isotope ratio variability in human bone there does not appear to be any similar attempts to investigate the homogeneity of Sr and Pb isotope ratios in human enamel.

Virtually all studies appear to show that little additional information about migration can currently be obtained from archaeological bone Sr isotope ratios, most data points cluster tightly around that of the local environment or burial soil, even when chemical or mechanical cleaning treatments are performed. Analysis of the bioavailable soil Sr and Pb isotope ratios is clearly not straightforward but is nevertheless, vital to assess and interpret such data. It is virtually impossible to determine whether bone signatures that are identical to soil leaches are, or are not, diagenetic in origin. The few studies that have attempted to control this unknown (by analysing marine bone buried in a terrestrial context and *vice versa*) have failed to retrieve the expected *in vivo* signature. Clearly, it would be harder to argue the case for the integrity of the *in vivo* signature than diagenetic contamination in such cases. Furthermore, the many intrinsic and extrinsic variables that affect bone formation and subsequent turnover make interpretations on timing of migration problematic particularly between individuals of different ages. Tooth formation and timing is relatively immune to many environmental stresses and therefore has many advantages over bone analysis.

It is heartening to observe that, although admittedly few, the Pb isotope studies of archaeological human bone appear to show that isotope equilibriation with the soil has not occurred completely at most sites. Isotope ratios that are quite different from each other and the local soils have been obtained even in bone samples containing what would be considered a high physiological Pb burden; in fact, they may retain their biogenic integrity precisely because they were high in Pb, and thus not swamped by diagenetic Pb. This apparent survival of *in vivo* signatures in bone, which should be even better preserved in enamel, is encouraging for the future use of Pb isotopes in

archaeological studies. The ease with which *in vivo* skeletal signatures will be lost will depend predominantly on the bioavailability of soil-Pb and the *in vivo* Pb concentration. For example, ratios resulting from a high-Pb exposure are more likely to survive in soil with low bioavailable Pb, whilst a very low *in vivo* Pb exposure will be completely swamped or at least severely altered by mobile soil-Pb. This may occur even under conditions where Pb is present at low concentration and relatively immobile (see the Monkton study in Chapter Six). Similar considerations may apply to Sr.

In some contexts, however, Pb may not be particularly diagnostic of geological place of origin if most individuals were exposed to anthropogenic Pb artefacts that may have spread some considerable distance from source and produce an homogeneous, culturally mediated signature. Pb may, however, provide discrimination in marine environments when Sr analysis will, in turn, produce a homogeneous Sr isotope ratio signature. Combining both isotope systems gives much greater depth of information than using one alone and a thorough consideration of all the osteological and archaeological contexts and data should facilitate interpretations of the isotope data.