Use of Pb and Sr Isotopes in Human Teeth as an Indicator of Pacific Islander Population Dynamics

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Degree of
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Statement of Originality

The work contained in this thesis is the result of the sole and original endeavours of the author, Jovanka Jarić, except where noted otherwise. Sections of this thesis will be submitted for publication, in the papers given in the List of Publications.

Jovanka Jarić
University of Western Sydney
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List of Publications/Conference Presentations

Papers and presentations originating from the work submitted in this thesis are listed below:


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Use of Pb and Sr Isotopes in Human Teeth as an Indicator of Pacific Islander Population Dynamics

Keywords: Lead, strontium, isotopes, dental enamel, TIMS, MC-LAM-ICPMS, GFAAS, ASV.

Abstract: The study involved the investigation of ancient dental enamel derived from former inhabitants of Pacific Islands: a population whose movements were necessarily more restricted than their mainland counterparts. Lead and strontium isotope analysis of human teeth were undertaken using TIMS and MC-LAM-ICPMS. Exposure information was obtained from elemental concentrations of lead and strontium using LAM-ICPMS, GFAAS and ASV.

Isotopic measurements of lead within the dental enamel of these individuals suggest that the dominant source of biogenic lead exposure in these and other pre-metallurgical societies derived from the local water supply. It is shown that despite their limited mobility, the islanders retained a level of lead within their dental enamel at approximately 0.65µg/g. The data from these ancient populations are compared with measurements made on ‘moderns’ based at Broken Hill, NSW, as well as from other UK-based post-Iron Age populations. The results of this study indicate that the concentration of ancient lead within crystalline dental enamel in both ancient and modern populations can in certain circumstances be approximately the same, even when the degree of lead exposure is very high. This study proposes reasons for the discrepancies between these results and those obtained in previous studies, as well as discusses the implications of these analytical results for future studies in lead exposure in human populations.

Strontium isotope measurements showed that they are not useful indicators of either provenance or diet for populations on islands such as those of the Pacific region, which are composed of basalt. The natural variation in $^{87}\text{Sr}/^{86}\text{Sr}$ in bedrock samples is at least as great as the inter-island variability that would be used to distinguish between the various inputs, and thus constitute a signal.

In total 27 ancient human teeth were studied, 16 from a burial place on Tongatapu, Kingdom of Tonga and secondly, 11 from individuals whose dentition was left scattered around a hearth with the Sohano Rockshelter near Buka, PNG. In the first case it can be shown that although the majority of individuals were likely to have been born on the
islands of Tonga, some of the burials are those of individuals whose isotopic ‘signature’ is that of the Solomons, providing the first direct evidence of long-distance travel between islands of the ancient Near and Remote Oceania. In the second case it is shown that the overwhelming number of the teeth came from individuals who, in childhood, shared the same water source and were thus members of a single village-based population, whilst the remaining teeth were, once more consistent with a source somewhere within New Britain and the Solomons.
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Chapter 1

Provenance Analysis

1.1 Introduction

This thesis seeks to develop a method of using lead (Pb) isotope analysis to determine the point of origin of human remains recovered from archaeological deposits. As such, the program of research may be classified under the title of ‘provenance analysis’ and therefore falls within a rather ‘unfashionable branch of archaeological science’ (Wilson and Pollard, 2001). In view of the controversy, that has sometimes surrounded science-based provenance analyses within archaeology (see Budd et al., 1998) it is worthwhile beginning the current study by defining its scope through a brief preview of the present study and a review of provenance studies in general.

It is the assertion of this thesis that properly conducted provenance analysis can constitute a valuable item in the armoury of techniques available to archaeologists in their interpretations of the past. Despite this, it is also undoubtedly the case that in the past many provenance analysis programs have been poorly conducted and as a result, the activity is one of the least understood and appreciated aspects of science-based archaeological enquiry. It is the contention of this opening chapter that responsibility for much of the disenchantment with provenance studies within archaeology lies with the individual scientists and with the conceptual frameworks (both analytical and archaeological) that they employ. The work presented in this thesis seeks to develop a means by which Pb isotope analysis may be used, in future, for the study of population dynamics within ancient human populations in general and in particular to study the movement of ancient populations within the Pacific Islands. As well as producing what it
is hoped will prove to be a useful tool for archaeologists, it is the wish of the author that the work developed here will contribute to the rehabilitation of provenance studies within archaeology in general.

The idea of employing analytical techniques to determine the origins of ancient artefacts is not new. Indeed, in their published review of provenance analyses within archaeology, Pollard and Wilson (2001) point out that the idea has been current in archaeology for at least a century and a half. Although large-scale analytical chemistry programs for sourcing artefacts were envisaged prior to World War II, the lack of appropriate instrumentation restricted the scope of these studies. Provenance, in the sense of determining the source of manufacture of an artefact, really came into its own in the period after 1960. Unprecedented progress in analytical chemistry techniques in this period provided fresh impetus to the dream of being able to trace the source of an artefact back to its origins and thus a means to model ancient trading networks. Improvements in instrumentation (and particularly sample size requirements) went hand in hand with a ‘revolution’ within archaeological thought that saw the application of hard-nosed analytical science as a means to divest the discipline of both its antiquarian origins and its subjectivity.

Provenance analysis was an integral part of this generalised science-based movement within mainstream archaeology and as a result, a number of spectacularly large-scale programs of analysis were embarked upon (for example, the so called Stuttgart or SAM analyses of European Bronze Age metals and the petrological studies of the United Kingdom Neolithic stone axes (Cummins, 1974). Compositional analysis seemed to offer archaeology the promise of a revolution in the study of artefacts comparable to that provided by contemporaneous improvements in $\delta^{13}$C dating techniques. It is clear from the tomes of analytical results compiled at this time, that the scientists and archaeologists involved in these projects believed their analytical results had removed the need to study objects in terms of either their form or contextual information. For instance, any attempt to cross correlate the results of chemical analyses of Neolithic stone axes with real artefacts contained in museums would now be a truly monumental task. It should of course have been obvious from the outset that such programs were doomed to failure. However, the underlying geochemical implications of what was attempted in these programs seem to have escaped the notice of all concerned. From the 1960s period
onwards, based on the premise that the material analysed must contain information of geographical significance relating the object to its point of origin, an ever-increasing array of artefacts and materials were subjected to chemical analyses. As new analytical techniques developed, they were re-applied in successive waves to the materials of the past, with mixed results. Since the new techniques worked at higher instrumental precisions and on different suites of elements than their predecessors, the databases of measurements were rarely compatible thus generating more problems. Furthermore, inter-laboratory comparisons of the results obtained from early instrumental techniques such as Optical Emission Spectroscopy (OES) were later shown to be far less precise than originally thought (Jones, 1986). As with the application of $\delta^{14}C$ dating, the development of provenance study with archaeology has been marked by a series of crises that have undermined confidence in the results of past programs. Unfortunately, in contrast to radiocarbon, it has not been possible to rehabilitate the results of these past provenance programs through calibration.

All too often, the expensive datasets compiled through provenance studies cannot be used for the purposes envisaged therefore destined to be annexed in the appendix or archive of a project report. For mainstream archaeologists the results of the compendia of analyses are completely overwhelming and of little apparent utility. An already confused situation is not helped by the scientists themselves, who seem willing to engage in laborious disputes regarding the validity of the results of previously presented programs of analyses. These critiques of provenance analyses are often counterproductive, focusing on secondary issues, such as the ways in which data have been presented, rather than the capabilities of the method or the precision of the technique (Budd et al., 1995a, b; Gale and Stos-Gale, 1995). In the end, little of any substance has been achieved through these debates, other than reiterating the consensus on the subject. It is true however, that many of the compiled databases of analyses (and in particular Pb isotope analysis) have been too carelessly compiled to be of any relevance within archaeology. If the database were to be ‘cleaned up’, the results of many studies may be interpretable in ways that the authors never imagined. However, whilst the data remains tied to simplistic geochemical and outmoded archaeological models of ancient society, it contributes little to our knowledge of the past.
Chapter 1-Provenance Analysis

It is unnecessary to catalogue all of the analytical problems that have beset provenance studies within archaeology and are found scattered through the volumes of the major ‘Archaeometry’ literature, however they typically include:

- Inter-elemental incompatibilities in the precisions of results obtained using different analytical techniques (Jones, 1986);

- Variability in the precision of early results when re-measured within the same laboratory (Stos-Gale et al., 1996), and

- Inter-laboratory discrepancies in measurements undertaken on the same artefacts (Stos-Gale, Maliotis and Gale, 1998).

As a result of the rapid technological improvements that have taken place since the 1960s, ‘debates’ over the comparative merits of various techniques for analysing artefacts have subsided. Nevertheless, the relative peace that has broken out over analytical procedures does not alter the fact that if provenance analysis is to be successful, serious issues relating to the selection of material and the application of correct analytical protocols must be addressed prior to undertaking any measurements and certainly before drawing any archaeological conclusions.

Whilst it is fair to say that most scientists embarking on analytical provenance programs are now more aware of the problems associated with any measurements made on archaeological materials, there are still laboratories willing to compile new measurements and compare them with others contained within databases of dubious scientific veracity (cf. Spriggs, 1989). In view of the calamities that have beset so many previous attempts at provenance analysis, before embarking on another, it is necessary to make clear from the outset what a priori assumptions underlie any such work.

All provenance analysis is founded on a number of basic assumptions¹.

¹ This list constitutes what will hereinafter be termed the ‘provenance postulates’. A similar but not identical list of assumptions is to be found in Wilson and Pollard (2001).
(1) That some physico-chemical property of a material within the artefact can be defined as a unique characteristic of the point of origin;

(2) That the material identified as a ‘fingerprint’ either passes unaltered into the artefact material or its alteration can be modelled;

(3) That this characteristic material is measurable at sufficient accuracy and precision using current techniques;

(4) That the characteristic ‘fingerprint’ is not masked by other materials used in the artefact manufacture, or by physico-chemical processes relating to the use of the artefact in the past;

(5) That the chemistry of the characteristic material is not altered by long-term deposition in the buried environments of archaeological deposits, or else the alteration can be modelled;

(6) That the characteristic property has not been contaminated by handling and cleaning after excavation, and

(7) That the characteristic property of the material relates to, and can be interpreted within, a framework of human behaviour.

In addition to the above primary postulates of provenance studies, there is one further consideration, deriving from postulate number (1) that should always be taken into consideration when undertaking a program of provenance analysis: in practice, it is extremely difficult to ascribe provenance in a positive sense. Provided the source material has been sufficiently well defined, it is a relatively simple task to demonstrate a mismatch between source and test material. However, unless all possible sources are equally well defined and analytically isolatable from one another, it is only possible to ascribe provenance via a process of systematically eliminating the possible sources. Misuse of this truism has proven to be the undoing of many studies of archaeological material. In the early years of large-scale provenance studies, practitioners clearly hoped that all of the possible sources of the material studied would be chemically isolatable from one another,
thereby allowing the assignment of provenance in the positive sense. As the programs of analysis proceeded from the small-scale study of a limited number of sources and test material to full-blown pan-regional studies of all possible sources, the initially observable features, thought to be diagnostic of a particular source were found not to be unique.

This axiom of provenance studies obviously leads to another problem, that of insufficient funding. High precision multi elemental measurements undertaken on a statistically viable number of archaeological specimens remains an expensive undertaking and requires access to specialist equipment and geochemical expertise beyond the capabilities of most archaeological science practitioners. Whilst rapid semi quantitative identification of specimens need not necessarily be expensive, in many cases the inclusion of these imprecise measurements within a database of more precise analytical information serves only to corrupt the database as a whole. Although geologists, geochemists, mineralogists and petrologists routinely undertake large-scale high precision analyses of particular material within ore sources\(^2\), the results are not always directly applicable to archaeological studies, since:

- The measurements taken on geological material may not be of relevance to the particular archaeological study, even when the material is extracted from the same ore body. It is entirely likely that the source material used in many previous provenance studies is irrelevant to the study;

- Geochemical trace element analyses conducted on bulk rock carry no meaning in an archaeological context;

- Geochemical trace element and isotopic analyses conducted on individual mineral species and/or specimens do not provide any indicator of the trace elemental composition of any material extracted from the ore body in Antiquity. The composition of particular species is likely to vary through the ore body in unpredictable ways. Furthermore, particular elements or isotopes may be differentially partitioned between different mineral species that may or may not have been included into any material extracted in the past;
• Ore sources, on which sufficient numbers of analyses have been undertaken, are confined to those whose resources make them exploitable on the basis of present day economic considerations. It is clear from the traces of ancient mining activity found within the most marginal of ore deposits (O’Brien, 1995; Timberlake, 1994) that these considerations are not pertinent to Antiquity;

• Many sources of raw materials are not easily distinguishable chemically or petrographically, and

• Common fine-grained lithology’s like siltstone, shale, sandstone, marbles, etc have little to offer routine geochemistry or petrography. As a result, provenancing these materials require extensive fieldwork on the part of archaeological scientists coupled with extremely time consuming and extensively detailed geochemical investigations (Weisler and Kirch, 1996; Weisler, 1993a; Weisler and Woodhead, 1995; Woodhead and Weisler, 1997). Even with this preparatory work, success is by no means guaranteed. Although the unit costs of high-precision analytical measurements are still falling, the cost of such an endeavour is almost open-ended.

One often repeated regret expressed within archaeology is the failure of archaeological scientists to engage the participation of geochemists in the programs of provenance analysis (Woodhead and Weisler, 1997). Although the reasons for this are undoubtedly many and varied, they include the basic facts that:

• Although geo-scientists routinely undertake complete chemical characterisation of ore deposits for the purposes outlined above, it is much rarer for them to attempt to match secondary products to particular ore bodies;

• The expectations of geographical exactitude demanded within archaeology are often beyond the limits of the analytical procedures employed in the compilation of geological data;

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2 Ore in this sense is taken to refer to the source of any geologically-derived material exploited by humans and is not confined to metalliferous deposits.
• The time pressures placed on provenance analysis in terms of immediately drawing archaeologically relevant conclusions mean that many geochemists are unwilling to become involved in the projects, and

• Many archaeologists maintain that petrography or detailed geochemistry is unnecessary and that common lithology’s are simple to provenance on the basis of macroscopic identifications or on the basis of semi-quantitative trace element analyses.

In fact, where such collaborations have taken place, the results are amongst the more notable achievements of provenance studies (Williams and Jenkins, 1997; Renfrew and Dixon, 1976). What these successes indicate, is that when a provenance study is sufficiently well thought out in advance, the results can be spectacularly successful. In the case of obsidian analysis, it seems that archaeologists are capable of overcoming the complexities of the scientific method and making use of the results of chemical analyses within their mainstream archaeological studies (for example, Torrence, 1992). This suggests that the well-catalogued provenancing disasters of the past were specific to those studies, rather than systemic.

The instances of scientifically sound provenancing are actually comparatively rare and remain confined to materials that were transformed unaltered into artefacts. The most notable successes to date are those based on obsidian and amber, both of which are supercooled liquids.

Closer comparison of the methodologies applied within successful case studies and those that are ‘problematic’ shows that:

Successful instances of provenance analysis in archaeology have all proceeded from a known instance of geological/geographical variation within fingerprint material to a demonstration of the method’s viability through an archaeological case study, rather than the reverse.

In other words, the physico-chemical variation between the various possible sources used to ‘fingerprint’ artefacts was demonstrable prior to the method’s application within science-based archaeology. In contrast, where science-based archaeologists have
undertaken random sampling of artefacts or sources in the hope that the resultant
database of measurements will prove archaeologically useful (for example, Rohl and
Needham, 1998) the results have always proven to be intractable even when the most
sophisticated of multivariate statistical packages were employed to separate the various
fields.

Examples of success in provenancing other lithic materials have been considerably more
modest than those achieved on obsidian. Kempe and Harvey (1983) and Herz (1987)
have claimed success in compiling a database of oxygen, and carbon isotopes for
provenancing Classical Greek and Roman marbles. However, once more, the success of
this study is dependent on another form of a priori knowledge: the limited number of
possible sources of marble in the Classical period. There is no means by which such a
study could be extended to all possible marble found on all sites and in all periods in
Antiquity. Herein lays another of the empirically determined keys to success of any
program of provenance analysis:

The number of possible points of origin for the material to be analysed must be as small as possible
and the intra-source variability of the ‘fingerprint’ should be known prior to the commencement of
archaeological case studies.

A case in point may be seen in the successful discrimination between ambers of Baltic
and non-Baltic origin using Infrared Spectroscopy and δ¹³C Nuclear Magnetic Resonance
(Cunningham et al., 1983). The ability to establish a distinctive ‘fingerprint’ for various
sources of ambers is made possible by the limited number of localities at which amber
survives in the geochemical environment. The carefully delimited framework of these
investigations stands in contrast to the grandiose schemes of the provenance studies
undertaken in what Pollard and Heron (1996) termed the ‘golden age’ of archaeological
chemistry.

Successful provenance analyses of other lithic materials are not generally possible, as they
depend upon instances of material from a unique source, a condition encountered when
scientists isolated the individual rock outcrops used as the source of the famous bluestone
circle within the Stonehenge complex on Salisbury Plain (Howard, 1982). However, it
would be wrong to suggest that the successful application of analytical science to
questions such as this necessarily reduces the degree of uncertainty within archaeology. Interestingly, although the introduction of geological science to archaeology has led to agreement on one score, the investigation seems to have sparked its own controversy regarding the agency by which these stones arrived at their final destination. Some workers believing they were transported by hand, while others suggesting that they were glacially transported ‘erratics’ (Burl, 1999). This study raises another point that has often been missed in previous provenance studies:

As in the scientific study of thermodynamics, provenance analysis provides information regarding the start and end-point of an object. In itself, it tells us nothing about the kinetic pathway by which the object arrived at its final destination, or the time taken to get there.\(^1\)

If modest success can be claimed for provenancing artefacts made of naturally occurring materials, the wider application of provenance studies to objects where human agency has altered the chemistry of the raw materials is much more problematic. Although early large-scale provenance programs of the 1960s and 1970s attempted to provenance a whole range of inorganic materials, they focussed particularly on metals and ceramics. The end of the ‘age of innocence’ for large-scale provenance programs is spectacularly marked within literature when John Coles (1982), a long time believer in the value of such programs, finally and exasperatedly declared the whole exercise to have been a monumental waste of money! In retrospect, it is clear that archaeological scientists should have taken a longer look at the underlying assumptions regarding the production of metal artefacts and furthermore should have re-assessed the entire program of analysis in terms of other than provenance. Instead, and in part because of the effort that had gone into collating the 35000 analyses within the SAM program, a decision was taken to change the analytical technique to Pb isotope analysis and to carry on.

There is little point in reiterating the problems that have been encountered in the Pb isotope study of Mediterranean metalwork beyond the observation that in trying to source any metal artefact to an individual region or even mine (Gale and Stos-Gale, 1989) scientists are forced to make a number of basic assumptions regarding the human activities of production (e.g. recycling, and the composition of the various components of the smelt charge) for which there is not the slightest evidence. The methodology applied
to metal artefacts contrasts with that employed in ceramic provenance studies, where the one time hope of tracing individual clay sources has long since been abandoned in favour of chemical `characterisations’ based on particular ceramic forms (Neff, Bishop and Sayre, 1988, 1989). Interestingly, the attendant loss of geographical certainty has not diminished the usefulness of ceramic studies within archaeology. In fact, the move to `characterisation’ and away from `sourcing’ ceramics has opened up a whole series of archaeologically interesting questions regarding continuity and change of ceramic production within Antiquity. Although it may not be possible for science to answer these questions unequivocally, the resulting situation is a far healthier one than the blind and ultimately fruitless pursuit of raw material sources for which materials such as ceramics and metals are unsuitable.

It would be wrong to suggest that provenance analysis of metal and ceramics can never work. Once again, however, success depends on the research design and on the scale of the program envisaged. If the research is aimed at answering specific questions relating to, for instance, localised ceramic productions in prehistory, then the results have been successful and have been integrated into the archaeological picture of the period (Peacock, 1982). In the case of artefacts such as ceramics and metals, success in provenance analysis senso stricto depends upon identification of the presence of `fingerprint’ material within the test material that is unique to a particular source (postulate number 1).

One example of success in metal sourcing is in Lloyd Weeks’ Pb isotope study of Bronze Age metallurgical processing in the United Arab Emirates (Weeks, 1997), which reaffirms observations made by Niederschlag et al., (2003) of a marked shift in the Pb isotope `fingerprint’ occurring in all tin-bronzes in circulation in the Mediterranean World. Although the cause of this shift is not fully understood, it seems likely that it marks the presence of Pb contaminants within tin (Sn) ore. The geological age of these impurities indicates that they must derive from an ore source outside of Europe to the East.

These studies demonstrate that it is occasionally possible to use provenance metal within artefacts in a positive sense and that in these instances; science-based studies do furnish archaeologically useful information. They contrast starkly with those of the earlier

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3 This thermodynamic analogy should not be taken to imply that there is a 'natural, entropy-driven'
decades, where it was envisaged that analytical science would reveal some unforeseen large-scale ‘truth’ regarding material production in Antiquity, with disastrous results. These observations lead to another truism regarding provenance studies within archaeology:

That carefully applied, scientific study of material culture can provide corroborative evidence for mainstream archaeological studies. However, programs of scientific analysis have never been used successfully to set the archaeological agenda for studies of past peoples and cultures.

Despite the manifest of problems associated with conducting provenance studies on archaeological materials, in the above-mentioned review of science-based provenance analysis, Wilson and Pollard (2001) are notably optimistic and judge the results to have been generally successful. Whilst detailed review of this assertion lies beyond the scope of the present study, it should be noted that each of the provenance postulates (numbers 1-6) was determined only after the results of an analytical provenance program was called into question. It is unfortunate that the science-based archaeology literature contains many instances where at least one of the provenance postulates was violated. It is contended here that the grandiose claims made by early practitioners, coupled with the ‘boom-bust’ approach has played a major part in undermining confidence in provenance analyses within the so-called ‘processual’ archaeological circles, and provided ample ammunition to those archaeologists who would deny the utility of any science-based analytical programs within archaeology (for example, Thomas, 2000, 1991). In a period where science-based archaeology is forced to justify its utility in the face of what some assert is the real ‘revolution’ within archaeological thinking (see Trigger, 1989; Preucel, 1991; Shanks and Tilley, 1992), it is imperative that analytical scientists and archaeologists both recognise that:

1. Any new application of science to archaeology takes place only after all of the aspects of the provenance postulates have been thoroughly researched and validated, and

2. The results of any scientific program are only as valid as the archaeological theories of human behaviour to which they are attached.
The second point is a crucially important one, often overlooked within science-based archaeology. Although seldom stated, many archaeological science programs assume that the results of chemical analyses of archaeological material reflect only man’s extrasomatic means of adaptation and are therefore, in themselves, objective. As such, physico-chemical changes in characteristic ‘fingerprint’ materials within artefacts have been interpreted exclusively, in terms of:

- Adaptation or innovation in technology; or

- As the termini of long distance trade routes.

Both of these assumptions predate by some considerable time Lewis Binford’s statement of the limits of legitimate, science-based archaeological enquiry (Binford, 1989), and can be traced back to the culture-historical approaches that the ‘new archaeology’ was intended to replace. Framed in these terms, provenance studies provide little information regarding prehistory as they completely ignore questions of agency. Instead, artefacts are seen as compositional data and interpreted exclusively in terms of dehumanised ‘trading networks’. This view of material culture that sees objects as proxies for people has been questioned ever since Burgess and Shennan (1976) undertook their famous re-evaluation of the ‘Beaker Folk’. However, despite increasing evidence of the ideas that shape science-based archaeological endeavour reflective of present day ideologies imposed upon the archaeological evidence by archaeologists themselves (Hodder et al., 1995; Shanks and Tilley, 1992, 1989, 1987), it is remarkable how resilient these notions of the goals of science-based enquiry have proved to be. Recent articles have however suggested that analytical data retrieved from material remains could be interpreted in ways that lie outside of the culture-historical approaches (Pollard, 2001).

Mark Pollard’s article is important inasmuch as it finally signals recognition amongst archaeological scientists of the need to change the way in which the results of chemical analyses are interpreted within archaeology. By limiting the scope of interpretation of analytical studies to goals framed purely in terms of provenance or technological information, archaeological science is finding itself increasingly marginalised within a movement of mainstream archaeology that increasingly rejects the precepts of diffusionism and evolutionary theory that underlie such interpretations. It is fair to say
that Pollard’s ideas are controversial and has already met resistance from those who have compiled the databases of measurements (Tite, 1991). What Tite fails to recognise is that there was nothing intrinsically ‘scientific’ about the socio-economic framework within which the results of provenance programs were previously interpreted. In a world in which interpretations of radiocarbon dates are continually revisited, it seems strange that the interpretations of other forms of scientific analyses are in some way sacrosanct.

1.2 Background to Present Study

Provided that the program of provenance analysis embarked upon meets all of the requirements of the provenance postulates enumerated previously, then there is no \textit{a priori} reason to expect that the disasters of the past need necessarily be revisited. The current study is based on the development of a new analytical protocol for application within archaeological science. One based upon the innovative use of Pb isotope analysis for the study of ancient population dynamics within the Pacific. The study is the first to directly differentiate human individuals whose remains entered the burial environment on an island different from that on which they were born. As such, it is hoped that the Pb isotope analysis technique developed here will prove to be a useful one within Pacific Island archaeology and indeed within archaeology as a whole. It is emphasised that the current study does not claim that this technique will answer global questions as to the overall direction of settlement of the Pacific Islands, or others such as ‘who were the Lapita People?’ Answers to these kinds of questions would require sampling on a monumental scale as well as access to the skeletal tissues of the individual ‘founders’ on each of the islands of the Pacific. Patrick Kirch (1986) points out that the earliest Lapita sites themselves have not yet positively been identified, let alone the individual humans with which these sites were connected. In such circumstances, any global scientific isotope based equivalent of the Lapita Homeland Project would be foolhardy and exactly the form of expensive exercise that characterised the early forms of science-based archaeological enquiries described earlier in this chapter.

It is likely that for the foreseeable future questions on the global level of archaeological investigation will continue to hinge on the relative merits of particular suites of radiocarbon dates. However, it is envisaged that the Pb isotope method could prove to be a powerful tool for investigations at the level of the individual site or island group.
Within archaeology such as that of the Pacific Islands, where so much of the discussion currently depends upon stylistic variation between ceramic types, the technique opens a range of new possibilities for investigating the contacts through time between inhabitants of the site and other island groupings. To give just one example, in the case of the famous Roymata Burial (Garanger, 1972), the technique would have identified the island of origin of the king himself as well as the forty-seven individuals ceremonially buried alongside him.

If the method is deemed to be a useful one for Pacific archaeology, the potential exists for the isotopic investigation of dental enamel to become commonplace. The technique is currently relatively expensive requiring the use of Thermal Ionization Mass Spectrometry (TIMS) to achieve the analytical precisions needed to be able to distinguish between the geologies of the various islands of the Pacific. However, there is every indication that the costs of future analytical programs are about to decline significantly. The new generations of multi-collector Inductively Coupled Plasma Mass Spectrometers (MC-ICPMS), particularly those using Laser-Ablation, are already heralding a new era of relatively cheap analyses at precisions comparable to, or indeed better than those using TIMS and requiring little or no sample preparation.

The remainder of this chapter is given over to a description of the conceptual framework for this enquiry into the ancient migration of Pacific Islanders. It is important to outline how the problems that have beset so many other provenance studies within archaeology can be avoided here. The study contrasts with the majority of developmental studies of new methods within archaeological science, while the majority of the thesis is given over to understanding why the analytical method works, prior to its application to a number of archaeological case studies.

The distinction is an important one. Too often in the past, the desire to publicise archaeologically meaningful results has led scientists and archaeologists to draw conclusions either from incompletely defined datasets, or using immature analytical protocols. In the current study, various procedures have been undertaken in order to check the validity of the ‘provenance postulates’ as they relate to dental enamel. As with all analytical endeavours, the procedures employed are not exhaustive and were necessarily constrained by factors such as the analytical precisions of the currently
available instrumentation. Nevertheless, within these limitations, it is confidently asserted that the provenance conclusions drawn from the data are scientifically valid ones. As will be shown later, the importance of these developmental studies may stretch beyond the confines of the present study. In particular, the observations regarding diagenetic turnover of trace elements in skeletal hard tissue, are of some importance within other aspects of science-based archaeological endeavour and forensic science.

As pointed out earlier, the fact that the remains of any individual were recovered from an island different from that on which they were born does not, of itself, tell us anything about how the individual reached their final resting place or indeed whether they were transported there post-mortem? Whilst there are good reasons to assume that the particular fingerprint on which the analyses have been conducted is biogenically derived and therefore geographically significant, it should be recognised from the outset, that the data presented has been interpreted. At some time in the future, the same data may be reinterpreted in another way, one that is not yet possible to envision.

1.3 Provenance Analysis within Pacific Archaeology

The fact that at some period in prehistory stable populations were established on almost every habitable island on Earth must rank as one of humanity’s most remarkable achievements. The question of how this was achieved, using only the celestial bodies for navigation has intrigued western scholars ever since the island communities of the Pacific were ‘discovered’ some 200 years ago (Irwin, 1992). To many early scholars, the idea that these ancient communities’ sustained inter island contacts with their homelands after new islands had been settled was inconceivable (e.g. Sharp, 1963). In fact, it was not until 1986 that the plausibility of return journeys between islands was finally demonstrated to all those who still held to the notion of ‘accidental diasporas’ (Gladwin, 1970). That our ideas on the settlement of the Pacific Islands are now radically different from those of the early speculations of explorers and missionaries is due in no small part to the establishment of the inaugural academic chair dedicated to the archaeology of the Pacific in the mid 1950s. In retrospect, it is remarkable how rapidly the archaeology of the Pacific Islands changed following this single event. Within the space of twenty years following Professor Jack Golson’s appointment, he and the students that followed him, have entirely transformed our knowledge of Pacific prehistory. As noted by Kirch (1997),
these must indeed have been ‘heady days’. The forty-five years that have now passed since Golson’s appointment have seen the studies of Pacific prehistory develop into one of the most vital within archaeology with new discoveries made yearly.

It is interesting to note how much of our present-day knowledge of Pacific prehistory is dependent upon science-based analysis of material remains. Of course the timing of Golson’s academic appointment undoubtedly has played a role in this. The early students of Pacific prehistory were undoubtedly influenced by the scientific direction taken by the ‘New Archaeology’ expounded by scholars such as David Clarke in the UK and Lewis Binford in the USA, however this is only part of the explanation. In fact, without analytical science, Pacific archaeology would be extremely difficult. The material culture of the Island communities was based almost entirely on organic materials that are not preserved in the oxygenated conditions found in most local geochemical environments. One shudders to think, for instance, what chronology would have been applied to Gifford and Shutler’s initial discovery of ‘Lapita’ ceramics in 1954 (Gifford and Shutler, 1956), but for discovery of the radiocarbon dating technique by Willard Libby. Pacific archaeology is foremost amongst those that have benefited from the introduction of analytical science into the discipline and provenance analysis which is at the forefront of the methodologies employed. Mention has already been made of obsidian analysis as one of the successes of provenance studies in general. In Pacific archaeology, the successful sourcing of obsidian has become central to our entire understanding of inter island interactions within Near Oceania (for example, Gosden, 1991). However, obsidian analysis is not the only scientific technique to have become commonplace within Pacific archaeology. In addition to the ubiquitous radiocarbon dates and the more traditional archaeological activities such as petrological classification of ceramic types, any site report is now likely to contain detailed discussion of science-based studies of flora and fauna and more recently still, mitochondrial Deoxyribonucleic Acid (mtDNA) analysis of the excavated remains.

There is one further scientific technique, which, although far older in origins than the computer aided instrumental techniques, is still commonly employed for the study of Pacific Island migration, that of comparative linguistics. The technique, which involves the recognition of genetic similarities between island languages, is a last survival of the comparative sciences of the late 19th century and, as such, maintains its link to biological
evolutionism (Goodenough, 1997; Kirch, 2002). To those unfamiliar with the methodologies employed, comparative linguists can appear arcane. Unsurprisingly, therefore, the results of linguistic based studies are viewed with increasing scepticism by many present day archaeologists (Irwin, 1992). Nevertheless, the technique retains some important and influential supporters amongst present day archaeologists (see Kirch, 1997). A detailed critique of comparative linguistics is quite beyond the abilities of the current author and the forms of comparative linguistics employed within Pacific Island archaeology seem a world away from the essentialist theories of cultural evolutionism expounded by scholars such as F. Max Muller. Despite the criticisms levelled against their methods, the successes claimed by the comparative linguists are impressive and include:

- The distinction between ‘intrusive’ Austronesian and old Papuan language groupings within the islands of Melanesia;

- The recognition of Austronesian linguistic/cultural links between island communities overriding the old simplistic, threefold, racially based division of the Pacific island communities into Melanesian, Micronesian and Polynesian, and

- The construction of a considerable lexicon of words of a proto-Oceanic language thought to have been spoken by early migrants to Polynesia.

Frustratingly, other than through the radiocarbon dating of archaeological contexts containing ‘exotic’ imported commodity items such as obsidian, it has not been possible to scientifically corroborate the nature and directions of continued contacts between islands indicated by comparative linguists. Ever since the early application of radiocarbon dating to the initial study of the original Lapita assemblage on the Koné Peninsula of New Caledonia, the technique has been the only reliable dating method used in Pacific archaeology. Unfortunately, the application of radiocarbon dating in the Pacific continues to be problematic. The realisation that the dates provided by radiocarbon dating were not, of themselves, absolute calendar dates caused difficulties within Pacific archaeology similar to those encountered elsewhere. However, in the study of Pacific prehistory the problems of calibration were exacerbated by the reliance placed upon
radiocarbon dates, the shortage of datable charcoal remains and the consequent need to date other materials, particularly shell.

In principle, the relatively short lifetimes of crustaceans make them well suited to radiocarbon determinations. However, unbeknownst to the early practitioners, the shell of marine fauna is subject to ‘the marine dilution effect’ and therefore requires correction if it is to be used for absolute age determinations. Although, in theory, the necessary correction factors can be determined, in practice, any crustacean derived dates are considerably less precise than equivalent charcoal determinations and the veracity of many individual shell derived measurements is the subject of considerable debate amongst archaeologists.

By 1989, the accumulated radiocarbon database contained so many single low precision dates from Lapita sites rendering it almost unusable. In a paper whose implications stretch far beyond the archaeology of Pacific Islands, Matthew Spriggs undertook a chronometric cleansing of the radiocarbon database relating to Lapita. Although Spriggs’ conclusions regarding the dating of the ‘Lapita cultural complex’ have not yet been universally accepted, the paper has heralded a new era of scrutiny of any dates proposed for inclusion in the database. Because of Spriggs’ work, Pacific based archaeologists are now amongst the world’s most sophisticated clients of radiocarbon dating laboratories. It is clear from the precisions of the hygienically cleansed database of calendar dates (Spriggs, 1990), that although radiocarbon provides a means of dating the rapid spread of Lapita pottery across the Pacific (Kirch, 1997) the technique is incapable of determining the degree of sustained inter island contacts after initial settlement had taken place.

Recently, archaeologists placed great expectations on mtDNA sequencing to answer the questions of Pacific island migration (Merriwether et al., 1999; Matisoo-Smith et al., 1999; Hill and Serjeantson, 1989). Initially at least, this technique seemed to offer archaeologists the opportunity to trace the lineages of human individuals in a manner similar to forensic science applications. Unfortunately, archaeological scientists are once more working at a disadvantage compared to their colleagues in mainstream molecular biology since archaeological material recovered after long-term deposition in buried environments is affected by diagenetic alteration. If mtDNA survives long-term burial at all, it does so greatly reduced in length (a few hundred base pairs) and therefore requires
amplification using polymerase chain reaction (PCR) techniques before it can be statistically analysed. The risk of contamination of samples is consequently very high and particularly high degrees of specialist handling and preparation are required if the results are not to lead researchers to fallacious conclusions.

Although not yet widely discussed in archaeological literature, other issues may limit the productive crossover of techniques used in molecular biology into Pacific Island archaeology. Success in distinguishing genetic change across the Pacific Islands depends on the rate of mutation of mtDNA within the island communities. Articles appearing in both the press and scholarly literature suggest that mtDNA, which is matrilineal in origin, offers less opportunities for detailed discrimination between small population groups than had previously been thought (Sykes et al., 1995). To date, success is confined to the identification of an intergenic 9-base pair deletion identified in a sub-group of haplogroup B, a widespread East Asian clad of lineages\(^4\), said to be specific to Southeast Asians, but absent from the populations in island Melanesia that speak Austronesian (Hagelberg, 1997; Merriwether et al., 1999; Torroni et al., 1994). This conclusion is said to undermine theories that the initial settlement of Polynesia was undertaken by Melanesians (cf. Terrell, 1986). Therefore, as it stands, mtDNA studies have not yet elucidated very much that archaeologists had not already determined using other techniques. Leaving aside the fact that the results of the studies of haplotype mapping (Chiano and Clayton, 1998) and those of the initial mtDNA studies (Lum et al., 1994) currently contradict each other, there is every indication that in their enthusiasm to embrace this expanding branch of science, the genetic researchers, are violating some of the provenance guidelines outlined earlier. In the absence of a specific mutation marking the date of entry of Asiatic genes into the Polynesian population, DNA analysis alone cannot tell us when in prehistory the mixing event occurred. It is possible to postulate any number of historical scenarios for encounters between Oceanic populations and Asian women that would account for the presence of the base pair deletion observed, none of which can be proven (cf. Cavalli-Sforza, Minch and Mountain, 1992; Cavalli-Sforza et al., 1988; Kirch, 1997).

Of significant concern is the fact that biomolecular research is currently based upon comparisons of genetic mutations at the level of racially defined sub-groups of *homo sapien sapiens*. Many archaeologists seem unaware that discussions in ‘racial’ terms could take

\(^4\) A haplogroup, or clade, is a group of lineages that all descend from a particular mutation.
archaeology back down a path that many would not wish to retread. For instance, in trying to integrate the genetic and linguistic evidence for settlement of East Oceania, Kirch (1997) is forced to discuss the Diaspora in the same racially based terminology that he rejected earlier in the same work as “a highly artificial taxonomy that has ridden roughshod over the history of origins and relationships of these varied peoples and cultures”. Elsewhere in his exceptional synthesis of the Lapita cultural complex, Kirch makes careful use of the term ‘Oceanic’ for the first settlers of the Pacific, precisely to avoid the same racially based classification system. It is clear that the full ethical implications for genetic studies of past populations have still to be worked through by archaeologists. In the meantime, serious questions should continue to be raised about the genetic mapping and classification of humanity based on inter-racial characteristics. The potential risks of widespread mtDNA testing are exacerbated by the propensity of laboratories involved in genetic research to patent the genetic material that they isolate. It is hoped that researchers involved in the study of ancient bio-molecules will in the near future be able to move beyond discussions based on inter racial comparisons and instead begin to identify other more geographically specific markers. Until this time, and in view of the past (mis)uses of racial classification within archaeology and anthropology, the plans of First World scientists to produce a genetic map of the rest of the world’s population should be viewed with scepticism.

The above-mentioned analytical methods provide provisional answers to some long-standing questions regarding Pacific island migration. However, whilst all of these techniques have been used as indicators of Interarchipelago interactions, they have failed to provide direct evidence of these contacts. Evidence of inter island contacts still depends upon the stylistic classification of a range of exotic imported artefacts such as shell, adzes, ornaments and tools, or else relies upon ceramic typologies and comparative linguistics (Emory, 1968; Sinoto, 1983; Rolett, 1993; Ayres, 1983; Kirch, 1988; Aoyagi et al., 1993, 1991; Golson, 1971; Garanger, 1971).

1.4 The Lapita ‘Cultural Complex’ and Migration

Mention has already been made of Golson’s initial work on the distribution of Lapita pottery and its significance in establishing Lapita as an extensive cultural marker within Oceanic prehistory. By the end of the twentieth century, our knowledge of the ceramic
tradition named Lapita had been extended and developed into a sophisticated classificatory system stretching from Papua New Guinea out across Polynesia as far as Samoa (see Figure 1.0). However, it was Roger Green (1976) who first made the link between Lapita ceramics and the earliest phases of settlement of Oceania. Out of his pioneering study on the Reef Santa Cruz islands, Lapita was transformed from a ‘style’ and into an intrusive ‘cultural complex’ whose populations were involved in a range of unprecedented practices and whose innovations were not confined to ceramics alone.

![Map of the Pacific Islands](image)

**Figure 1.0.** Map of the Pacific Islands. Source: Kirch, 2002.

Although in more recent times, the clear distinction between Lapita ‘culture’ and that of island Near Oceania has been questioned (Gosden, 1991), excavations of Lapita sites throughout the Pacific continue to produce astonishing results, both in terms of the volume of ceramics recovered and the apparent speed at which the ‘cultural complex’ spread across the Pacific (Spriggs, 1990). Unfortunately, the very characteristic that makes the spread of Lapita such a remarkable cultural phenomenon (its speed of transmission) prevents Lapita ceramics from being used as a marker for continued inter island contacts after the initial settlement. One way around this problem is through the increasingly fine-grained subdivisions of pottery classifications based upon analysis of vessel forms, decorative styles and tempering materials (Summerhayes, 2000; Glover, 1968; Groves, 1960). Another possibility is to use elemental analysis of the ceramics as the basis of another science-based classification. The pioneering study of this type is that
of Shepard (1971) who used thin sections of pottery sherds as the basis for a classification of the geological origins of the inclusions noting in particular whether the inclusions were naturally present or had been added by the potter. Dye (1987) suggested that the sources of the sand used as temper within the Lapita ceramics, might have been used to determine the direction of movement of either ceramic vessels or raw materials between island communities. However, the same author concluded that the number of islands on which the requisite clay deposits can be located is vast and the results of any analyses undertaken are likely to be equivocal as to the source. He concluded that Lapita ceramics could have been produced entirely from raw materials found locally. Whilst this is, in itself, a useful conclusion, it does not greatly help archaeologists to elucidate the degrees of post settlement inter island contacts.

1.5 Background to the Current Study

There are a small number of other studies in Pacific archaeology which as well as being of considerable importance in their own right, provide the basis for the study undertaken here. As mentioned, potentially the most fruitful means of determining the degrees of inter island contact in Antiquity is through the study of intrusive ‘exotic’ materials and the identification of their sources, that is, provenance studies. In principle, study of the movement of these commodities is a far better measure of the movement of peoples than the stylistic similarities of artefacts; the latter may not indicate the long distance movement of people but may instead reflect the movement of ideas (Weisler, 1998). Although archaeological studies of such intrusive materials have generally focussed on obsidian, other classes of material such as shells and chert are also conducive to such analyses. However, whilst work on these materials are proving invaluable as a means of defining prehistoric exchange networks in Melanesia, they are of little help in deciphering the archaeology of Polynesia, since these exotic intrusive materials have only a limited distribution, or else they are entirely absent from the archaeological record. Even the ceramics indicative of the Lapita ‘cultural complex’ are far less abundant in Remote Oceania than they are in the Western regions of the Pacific. Under such circumstances, documenting distributions and inter island trade *via* petrographic analysis of pottery sherds or other materials is difficult and the results are said to be of only limited use to archaeologists (Dickinson, 1993; Dye, 1987). In an effort to overcome this problem, some researchers have turned to fine-grained basalt artefacts used for adzes and other
tools, as a means of documenting Polynesian island networks (Weisler, 1998, 1993a, c; Weisler and Kirch, 1996; Weisler, Kirch and Endicott, 1994). Fine-grained basalt has a limited natural occurrence but is distributed widely and in greater abundance than any other material class recovered. In contrast to other material culture, proof of inter island interactions and trade using artefacts made of igneous rock can be a very simple procedure. Volcanic artefacts found on non-volcanic coral atolls provide instant confirmation of inter island communication (Best, 1988). The addition of X-Ray Fluorescence analysis to the study of basalt artefacts has led to some degree greater understanding into Polynesian interactions (Best et al., 1992; Walter, 1990; Weisler, 1994). However, even using this analytical technique the degree of discrimination between the various sources of rocks and artefacts are imperfect. In order to overcome this problem, Weisler and Woodhead (1995) pushed the study of basaltic adzes one-step further and investigated the use of radiogenic isotope variations in basaltic artefacts and source rocks as a means of determining artefact provenance.

A considerable database exists for Pb, neodymium (Ne) and strontium (Sr) isotopes for most islands of Oceania. Of these, the three radiogenic Pb isotopes vary the most geologically and are therefore the most useful for provenance determinations. Each island possesses a unique Pb isotopic composition therefore allowing the evaluation of prehistoric interaction between islands over relatively short distances. Using these measurements Weisler and Woodhead (1995) were able to demonstrate that Pb isotope analyses of island material could be successfully used as an accurate discriminator of artefact source.

The most direct measure of migration across the Pacific would be one based upon study of human remains. Swindler and Weisler (2000) have suggested that the diversity in skeletal morphology observed in Pacific Island communities today, may reflect migration patterns in Antiquity. If this is the case, then a whole range of morphological measurements of dental tissues could be used to link island populations, particularly those on islands to which small numbers of people are thought to have moved first (founders effect) and which were subsequently affected by intermittent periods of genetic isolation (genetic drift) and later contact with other archipelagos. A number of archaeologists are currently studying skeletal hard tissue as a source of such data. Teeth, and in particular dental enamel, constitute a ubiquitous class of finds on Pacific Island sites, where the
aggressive geochemistry of burial environments has long since led to the destruction of more ephemeral items of material culture. Study of the morphology of dental remains has come to be of particular importance within the study of Micronesia (Swindler and Weisler, 2000; Matsuno, 1997) and evidence drawn from these studies has been used in models of population expansion into the region (Athens, 1990a, b; Intoh, 1997; Weisler, 1999a, b).

The discovery that the island groupings are isotopically distinguishable from one another is a significant one for analytical studies in Pacific archaeology and in particular to the current study. Provided suitable diagenetically unaltered material can be isolated, the Pb isotope ‘signature’ of skeletal hard tissue recovered from Oceanic archaeological sites must (in the absence of contaminants derived from activities such as extractive metallurgy) be of identifiable biogenic origin. The final questions and the ones that this study seeks to address are:

- The degree to which the biogenic integrity of dental remains is retained after long-term burial, and

- Whether the provenancing of skeletal tissue is a viable one within Pacific archaeology.

As shown in the chapters that follow, there is good reason to expect that such information is retained within the dental enamel, a class of material that is one of the most durable and commonly found on archaeological sites within the Pacific region even after the other fractions of the same teeth have disappeared.

The study presented here was developed from similar Pb isotope studies conducted within environmental science on modern populations and in particular the pioneering work of Professor Brian Gulson. Concerns over the toxic effects of escalating levels of Pb have led to innumerable studies into methods of reducing the environmental Pb burden on the present day human population. The concentration of blood Pb carried through the human body is regularly measured as a means of monitoring short-term in vivo exposures of a subject to the element (Kaplan, Peresie and Jeffcoat, 1980; Lansdown et al., 1974; P’An, 1981; Ryu, Ziegler and Foman, 1978). However, the residence time of Pb in blood is too short to make use of such measurements as a determinant of long-term Pb exposure. In theory, concentration measurements of Pb in bone could be used as an
indicator of exposure over a longer-term than equivalent measurements made on blood. However, in practice, the variable structure of bone tissues makes accurate determinations impossible (Wittmers et al., 1988). In contrast, teeth have a much better defined structure and have already proved to be a much more reliable indicator of long-term exposure (Rabinowitz et al., 1991; Strehlow, 1972; Brioso, 1992). Although total Pb concentration measurements can be used as a long-term indicator of high Pb exposure, a potentially much more useful means of controlling the Pb burden for any member of the modern population would be to identify the source of the pollution. This is impossible using concentration measurement alone.

Gulson and others have achieved considerable success in identifying the sources of the long-term Pb burden in modern populations through the analysis of radiogenic Pb isotopes retained within the inorganic fraction of teeth (Gulson, 1996; Ferguson, 1986; Woolley, 1984). Since the ‘signature’ obtained relates directly to the source of the exposure, the method has proved to be a particularly powerful indicator of previous Pb exposure in children living in the mining community of Broken Hill, New South Wales and a means of lowering the overall Pb burden in populations at risk from high levels of exposure (Gulson and Wilson, 1994). This thesis seeks to determine what information, if any, can be recovered through the study of archaeologically derived teeth of ancient Pacific Islanders and whether the isotopic signature of the excavated remains is a useful indicator of the island of origin (provenance) of an individual.
Chapter 2

The Uses and Abuses of Bone Chemistry in Archaeological Science

2.1 Introduction

This chapter takes its title from a well-known article written by Hancock, Grynpas and Pritzker (1989) and published in the journal *Archaeometry*. In that article they reviewed what they perceived as serious flaws in the methodologies being employed by science-based archaeologists to extract archaeologically meaningful results from the trace element compositions of archaeological bones. In the wake of the publication of this paper, the pace of science-based archaeological research into skeletal hard tissues has not slackened. Indeed the reverse has occurred. The last 15 years has seen an unprecedented expansion in the analysis of skeletal tissues, the range of analytical techniques employed and the variety of archaeological conclusions that are inferred from the measurements. Since this thesis explores the possibility of deploying Pb isotope analysis to determine the provenance of humans in antiquity, it is necessary to briefly review the major developments in science-based archaeology in the period since the appearance of Hancock, Grynpas and Pritzker’s acerbic, but essentially correct, critique of trace element compositional analysis of archaeological bone.

This chapter outlines the problems associated with the study of any archaeological skeletal hard tissues and provides the rationale for the choice of dental enamel as the only material suitable for chemical analytical studies of human remains. It then briefly reviews dental histology and the elements of bone research relevant to the thesis.
2.2 Archaeological Studies

The pre-conditions of the successful deployment of Pb isotope analysis within science-based archaeology are that:

- Pb$^{2+}$ ions enter tooth enamel in measurable quantities at some time during the individual’s lifetime, and

- Once trapped within the hard-tissue structure, the Pb$^{2+}$ ions accumulated in vivo remain unaltered by Pb$^{2+}$ ions within the groundwater of the burial environment.

Given that the deleterious health effects of Pb on the human metabolism have been known for some considerable time, it is surprising how little research has been conducted in order to determine where the accumulated Pb burden resides within the hard tissue matrix once it has entered the human body. Although a considerable amount of research has been conducted into the behaviour of Pb$^{2+}$ ions in the geochemical environment (Siegel, 2001), archaeological environments are considerably more complex than those described in the geochemical literature, which can generally be modelled solely in terms of metal ion inorganic ligand interactions. Research conducted by geochemists is not yet readily transferable to science-based archaeological research. Despite the absence of any direct evidence that corroborates the hypothesis (see Chapters 3 and 4), it is generally accepted by scientists that Pb$^{2+}$ ions accumulated in vivo, reside within the inorganic fraction of the hard tissue, having undertaken a limited replacement of the Ca$^{2+}$ ions that constitute the principal metal ion component of skeletal hard tissue. The lack of research into questions of low temperature Pb$^{2+}$ ion replacement mechanisms and diagenetically induced changes in overall composition reflects the overriding concerns of environmental and environmental health scientists, for whom post mortem changes in the accumulated Pb burden within an individual subject are of little or no consequence.

However, since questions of diagenetic turnover place such great limitations on the application of analytical science within both archaeology and forensic science, if Pb isotope analysis is to become a generally applicable analytical technique for provenance analysis, then determining where the Pb$^{2+}$ ions reside within the skeletal tissue is an integral part of establishing whether the results of any future analytical programs will be valid. A first step towards this must therefore be to determine the legitimacy of the long held views regarding the replacement of Ca$^{2+}$ ions (Chapters 3 and 4) and the degree of
diagenetic turnover affecting skeletal hard tissue once it enters the burial environment (Chapter 3).

Research into the diagenetic turnover affecting skeletal tissues after long-term storage in burial environments now features heavily within the science-based archaeological literature, particularly since Hancock, Grynpas and Pritzker pointed out the naivety of some of the assumptions that underlay early ‘archaeometric’ studies of bone. Much of the research now being undertaken represents a response by modern archaeological scientists to this earlier work, which took insufficient account of a significant diagenetic component in the signal responses that they were measuring. Naively, archaeological scientists often proposed that interactions between skeletal hard tissue and the burial environment did not occur (Rink and Schwarz, 1995). Although this postulate was of considerable analytical convenience (allowing scientists to draw directly on both the methodologies and results of environmental science research), it is now known to be invalid. Indeed, later more carefully controlled studies, particularly of archaeological bone, have traced anomalously high Pb\(^{2+}\) ion burdens within many samples to changes taking place post deposition, thereby invalidating the archaeological conclusions drawn from earlier works.

Until such time as the burial environment can be adequately modelled, accounting for the diagenetic contributions to a measurement of archaeological interest is fraught with difficulty. Success in determining whether a signal derived from archaeological hard tissue is contaminated depends upon either:

- A complete knowledge of the mechanism of both the desired signal accumulation and the potential for its contamination, or

- Access to two dependent variables that can provide a check of the validity of the signal and thence to apply a correction factor to it.

The number of physico-chemical variables that must be accounted for in order to completely model all archaeological environments and conduct inter-site comparisons of data is so large that it renders the task of isolating the diagenetic contribution to any measured signal almost impossible. A more practical strategy seems to depend on
isolating material that can be independently established as unaffected by conditions prevailing in the burial environment (see Chapter 5).

Due to their ubiquity on archaeological sites, it would be preferable if analytical studies could be undertaken on archaeological bones, rather than on particular skeletal tissues. Analytical studies of archaeological bone samples have a long history. Unfortunately, many of these studies have revealed that the structure of bone is extremely complex and highly variable, even between members of the same species, comparable age-at-death, and gender and derived from the same archaeological site (Price, Schoeninger and Armelagos, 1985). Furthermore, results presented in Chapters 3 and 4 question the long held belief that Pb$^{2+}$ ions accumulate within bone by a mechanism that involves ion exchange, or solid state substitution of Ca$^{2+}$ ions within the Hydroxyapatite (HA) structure: adding further to the structural complexity that must be disentangled if the diagenesis of bone is ever to be successfully modelled. As shown in Chapter 3, identifying any portion of human bone tissues (either archaeological or modern) that are suitable for inorganic compositional analysis has been unsuccessful. It is therefore concluded that there is currently no means by which the quality of any analytical measurement made on archaeological bone can be assured.

2.3 Diagenetic Turnover in Ancient Bone

Diagenetic changes within biological hard tissue have been shown to occur by at least one of three possible processes; heavy metal uptake, dissolution and recrystallisation of the bone mineral fraction (Sillen, 1989). Water and the partial pressure of dissolved oxygen are also significant factors affecting both the rate and extent of diagenetic turnover: acting either as a means by which exogenous and endogenous material is transported (Hedges and Millard, 1995) and/or participating in any redox processes occurring within the buried material.

2.3.1 Metal Ion Uptake

To date, several forms of diagenetic change of relevance to the current study have been noted to occur within archaeological bone. Krueger (1991) noted that the ratio of Pb$^{2+}$ ion to Ca$^{2+}$ ion concentrations within archaeological bone increases in some archaeological environments: a phenomenon that he traced either to the uptake of
complex ions present within the ground water or to dissolution of either the inorganic or organic component of the bone.

Attempts to move beyond these general statements regarding metal-ion uptake in hard tissue samples took a giant leap forward when researchers (Rae and Ivanovich, 1987; Millard, 1993) began to examine the kinetic factors that influenced the rate of metal ion uptake within archaeological bone. In particular, Millard (1993), using solutions containing U\textsuperscript{2+} ions, was able to show that both synthetic HA and archaeological bone absorb U\textsuperscript{2+} ions following a pattern that is consistent with a mechanism based on ion exchange, supporting diffusion, recharge and flow mechanisms. However, whilst in principle this important study opens the possibility of modelling ion exchange in archaeological samples free of further complications such as the reaction kinetics, given the wide structural variability and the difficulties of determining any structural information from archaeological bone, one must wonder how widely applicable Millard’s results are? Other potentially more useful ions, such as Sr\textsuperscript{2+} or the other ions that are routinely measured in dietary studies such as Mg\textsuperscript{2+}, Zn\textsuperscript{2+} etc., are much smaller and more mobile in aqueous environments than U\textsuperscript{2+} ions, making it difficult to draw any general conclusions from the study.

2.3.2. Recrystallisation

Another well documented diagenetic change taking place in archaeological bone samples is that of recrystallisation. Over long-term burial, X-Ray Diffraction (XRD) powder patterns obtained from samples of archaeological bone reveal that the bones become more crystalline over time: even in the absence of significant changes in the chemical composition of the sample (Sillen, 1989). Nielsen-Marsh and Hedges (2000) have suggested that the composition of the aqueous solution surrounding the bone samples plays a rate determining role in its rate of recrystallisation. However, research into the process of recrystallisation is, like all diagenetic studies, hampered by the complexity of the bone’s structure, and our understanding has not really moved forward greatly since the same authors observed that bone crystallinity increases in environments within which it is also undergoing dissolution; probably as the result of simultaneous recrystallisation (Nielsen-Marsh and Hedges, 1997).
2.3.3. Dissolution

The burial environment is undoubtedly the determining factor in how well archaeological bone is preserved (Piepenbrink, 1989; Jans et al., 2002). Of the many possible factors that could determine whether bone survives or not, the pH of the soil has been said to be the most significant factor (Gordon and Buikstra, 1981). Other studies have confirmed these basic observations and led researchers to the conclusion that acidic, well drained (i.e. highly oxygenated) soils such as sand and/or gravel present environmental conditions in which bone is unlikely to survive (Henderson, 1987; Waldron, 1987), and conversely, that well preserved bone generally comes from either fully waterlogged environments or relatively dry sites, with static water levels (Nielsen-Marsh and Hedges, 2000a, b). Henderson and Waldron’s findings seem to also imply that both redox potential and micro-biologically mediated breakdown of bone could exert a determining influence on both the degree of diagenetic interaction between buried bone and the surrounding groundwater, and its preservation. Collins, Child and Turner-Walker (1995) have suggested that collagen breakdown is purely a question of chemical hydrolysis: breaking up the chains of collagen until they reached a size that causes them to be leached out completely. Further evidence that microbiology, rather than straightforward chemical dissolution, constitutes the rate determining step in the dissolution of bone is provided by Henderson’s observation that bones can survive long-term burial in environments when judged simply in terms of their pH and oxygen availability.

A growing awareness of the importance of microbial activity within archaeological deposits has in recent years given a new lease of life to some old questions regarding the preservation of bone. Studies have suggested that it is ion exchange with the surrounding soil and bacterial action that causes disintegration and the transformation of the organic components (Lee and Klinowski, 1995), ultimately controlling the dissolution rate and therefore the rate of crystallisation (Nielsen-Marsh and Hedges, 2000a, b). These works have helped rationalise the well known observation: that bones which have lost the greater part of their protein content have an extremely poor histology.

2.3.4. General Observations

Even this very brief summary of the science-based archaeological literature makes it clear that our current understanding of the physico-chemical factors controlling the preservation of archaeological bone remain rudimentary. As mentioned above, one
possible reason for the lack of progress is that science-based archaeology is one of the few scientific disciplines for which long-term burial is a significant factor in the acquisition of meaningful data. Archaeological scientists have tended to use a uni-
disciplinary approach: concentrating on a single observable phenomenon such as recrystallisation, rather than all three factors. However, more recent approaches offer some promise that a greater qualitative understanding of bone diagenesis may soon be reached. Studies, such as those undertaken by Hedges and co-workers, have demonstrated the inter-relatedness of the three factors (recrystallisation, ion exchange and bacterial action) affecting the survival of bone in the burial environment. They emphasise for instance, that it is the loss of collag nous material from the bone that precipitates a reorganisation of the bone’s microstructure and which in turn affects the porosity, the rate of dissolution and therefore its crystallinity (Hedges, Millard and Pike, 1995). Further work by this Oxford-based group and others (Nielsen-Marsh and Hedges, 2000a, b; Nelson et al., 1986; Sillen and Parkington, 1996; Lee and Klinowski, 1995) continues to lay emphasis on a holistic approach to the problem of diagenesis. However, unless some means of fully characterizing each sample can be found, it is difficult to determine how these studies will move beyond the qualitative stage and produce results that enable researchers to undertake analytical measurements of bone, confident that the measurement was unaffected by diagenesis.

Despite the difficulties that they undoubtedly still face, the work of the Oxford Group reflects a growing appreciation on the part of archaeological scientists that diagenetic alteration represents a major hurdle to the recovery of biogenic information from archaeological bone. As well as rendering this recovery process quite impossible to use, Nielsen-Marsh and Hedges (2000a, b) have suggested screening procedures to be necessary in order to identify, discard or clean the samples of their diagenetic material, without introducing further gross contamination. Of far more concern are the works of scientists such as Price, Manzanilla and Middleton (2000a) and Price et al., (1992) who continue to suggest, “diagenesis is generally not a significant problem”. In these articles, rigorous experimentation in order to test the extent of diagenetic turnover in the manner of Hedges and co-workers is replaced by blind faith that simple acid cleaning is effective in removing most contaminants from bone samples, and rigorous screening by a series of arcane tests introduced in order to justify the a priori assumptions.
Some researchers have suggested that diagenetic alterations are ‘advantageous’ to science-based archaeology, providing a means of independently assessing the degree of diagenetic alteration and of generating a correction factor. Some have even gone so far to suggest that concentration measurements of F⁻ and Si²⁺ ions (which are entirely absent from bone in vivo, but present after excavation), can be used to determine a rate constant for their accumulation, thus providing a means of dating archaeological bone (Johnson, 1997). Apart from the obvious difficulties that the accumulation rate of these ions will depend on the porosity of the bone matrix, which as we have seen are variable in quite unpredictable ways, the concentrations of both these elements within groundwater are not constant and themselves vary in a quite unpredictable manner dependent on a wide range of biological, chemical and physical factors (see also Hedges and Millard, 1995).

Other methods of correcting for diagenesis are to be found within the literature. However at best these are of questionable value, at worst they are simply untrue. In this category appear methodologies such as the differential selection of compact bone instead of trabecular; giving the former primacy based on perceptions that it is denser and thicker (Grupe, 1988) and optical methods based on the colour that the bone has attained (Edward and Benfer, 1993).

2.3.5. Applications

Bone is now measured in a more comprehensive manner and for such a variety of applications within archaeology that a specialist journal (International Journal of Osteoarchaeology) is now published dealing solely with this one material. An assortment of analytical techniques is now routinely employed to furnish palaeodietary information as well as carbon for radiocarbon dating. In view of the difficulties in determining the degree to which a bone sample may have been chemically altered whilst in the burial environment, great care is necessary to determine whether the results of these examinations are valid.

The fact that protein can survive long-term burial, even over geological time scales (Bada, 1985) has generated considerable literature seeking to make use of proteinaceous material for archaeological scientific purposes (Hedges and Wallace, 1980; Weiner and Bar-Yosef, 1990). Foremost amongst these applications are:
• Dating techniques that seek to determine either the absolute age of the individual or its age at death (Hedges and Law, 1989);

• Dietary reconstruction using stable isotope analysis (DeNiro, 1985), and

• The extraction of mtDNA samples as a means of determining genetic relationships (Hedges and Wallace, 1980).

All works seeking to extract ancient biomolecules from archaeological bone depend on the constituent proteins having survived in an unadulterated form after deposition or deliberate burial, through to extraction and measurement. Most of the research groups involved in the collection of such material remain confident about the validity of the archaeological conclusions. However, some have faced considerable difficulties in accounting for possible diagenetically induced contamination of their samples; for some techniques, the difficulties have proved insurmountable (Child, Gillard and Pollard, 1993). Studies by this Cardiff (UK)-based group have suggested that microbiologically induced racemisation of some proteins (D:L ratio of aspartic acid) begins almost immediately after skeletal tissues enter the burial environment, and occurs at an unpredictable rate. If this conclusion is indicative of other diagenetic changes taking place in dental enamel, then it is a deeply disturbing one for the future of all science-based archaeological investigations based on skeletal tissues, including the present study. Fortunately, the currently available evidence (including that presented in Chapter 3), suggests that diagenetically induced racemisation is an isolated phenomenon: affecting only a limited number of readily extractable amino acids within dental enamel. Nevertheless this study does confirm the importance of constant vigilance and continued research work in order to ensure that any measurements relate solely to information accumulated in vivo. As the works of Thuesen and Engberg (1990) and White and Hannus (1983) have shown, both the proteinaceous material and the inorganic fraction of bone have an a priori propensity to be contaminated by interaction with the ground and adsorption onto HA. The work of archaeological scientists should therefore always be based on the question ‘Why has this material not interacted with the groundwater?’, rather than simply assuming that it has not, and seeking to justify this assumption later.
More traditional archaeological concerns such as provenance and paleo-dietary studies have been undertaken via analytical measurements made on the mineral fraction of archaeological bone. Initially these programs were based on trace element concentrations and all were later shown to have taken insufficient account of:

- The natural variation in the concentrations of the elements in the burial environments;

- Variations in concentration within a single bone or between individuals from the same site, and

- The possibility that the observed variation in trace element concentrations were the product of diagenetic changes in the structure of the bone rather than relating to any aspect of the subject’s in vivo activities (Hancock, Grynpas and Pritzker, 1989).

A number of early studies looked closely at Sr\(^{2+}\) ion concentrations, particularly following suggestions that the concentrations of this element in bone increase slightly with age (Tanaka et al., 1981). Other studies suggested that the relative concentrations of Sr\(^{2+}\), Na\(^{+}\) and Zn\(^{2+}\) ions decreased in childhood, increased during adolescence, remaining generally stable between the ages of 20 and 50, and then showed a slight increase in individuals over 50 years of age (Lambert et al., 1979). Ultimately, all attempts to extract archaeologically meaningful information from trace element measurements made on archaeological bone floundered after it was shown that trace element concentrations between individuals within a single population, typically varies by as much as 20% to 35% (Price, Schoeninger and Armelagos, 1985; Schoeninger, 1979). The same authors have postulated that age, gender and individual metabolism are possible reasons for such high variations. Whatever the truth of this, the fact that the variation is so high, renders inter-site comparisons meaningless (see Chapter 1).

The demise of trace element studies conducted on archaeologically derived bones coincided with rapid advances in the analytical precisions of instruments for measuring isotopic concentrations: particularly mass spectrometry. Of particular interest to archaeological scientists was the observation made by geologists that the isotope ratio of
\(^{87}\text{Sr}/^{86}\text{Sr}\) varied as a function of geological location and local groundwater. This prompted suggestions that measurements of this ratio within skeletal hard tissues could yield both paleobiological and paleoenvironmental data (e.g. van der Merwe, 1982; Price, Grupe and Schroter, 1994). Price et al., (2000) took these ideas one stage further when they postulated that due to preferential turnover rates in different hard tissues \textit{in vivo}, Sr isotope ratios in human bone reflected the source of a diet at around the time of death; whereas, due to their isolation from the metabolism, Sr isotope ratios within tooth enamel reflected an individual’s diet at the time of birth. Price et al. also suggested that the difference between the Sr isotope ratios within enamel and bone ratios in the same individual indicated differences in local geologies and signified that the individual had changed location during their lifetime. The one possibility that they systematically ignored is that the Sr isotope ratios found within the various tissues could be reflective of nothing more than the isotopic ‘signature’ of the locality where the bones entered the burial environment. Chapter 5 presents the results of an investigation undertaken as part of this thesis in order to verify Price’s hypotheses regarding both provenance analysis and diagenetic turnover.

2.3.6. Applications of Archaeological Teeth
Dental tissues have a number of intrinsic advantages over bone tissues for archaeological studies. Tooth enamel in particular, is denser, more crystalline and has been shown to be both structurally and isotopically stable for long periods (Sponheimer and Lee-Thorp, 1999). It is therefore likely to be far more resistant to diagenetic interactions and hence more likely to preserve biogenically derived information than any other skeletal hard tissue. Furthermore unlike in bone, dentine and cementum tissues (see section 2.4), there is no significant morphosis in enamel crystallinity as a function of time.

2.4 Dental Histology
The work described in the following chapters is based upon the premise that, in contrast to other elements of skeletal hard tissue, dental enamel, once formed is acellular. The following section summarises dental histology and thus provides a rationale for this postulate.
Deciduous tooth formation begins within 14 to 19 weeks of fertilisation in the developing foetus. Enamel mineralisation is completed soon after birth. Once enamel has formed it is not remodelled so its Pb\(^{2+}\) ion content is indicative of *in utero* exposure (Gulson, 1996). However, dentine is known to accumulate Pb\(^{2+}\) ions from the blood supply during early childhood (Shapiro, Needleman and Tuncay, 1972) and measurements made on this material is considered to be representative of post-natal exposure (Gulson and Wilson, 1994). Most of the permanent dentition begin forming within 3 to 4 months of birth and continues until the individual reaches approximately 12 to 16 years of age. As with deciduous teeth, permanent enamel is thought to preserve an isotopic record of any Pb\(^{2+}\) ions accumulated at this time. In contrast, dentine continues to accumulate Pb *via* the bloodstream and thus isotopic measurement of modern dentine in adults represents a time averaged signature of Pb\(^{2+}\) ion exposure prior to either tooth loss or death (Gulson, 1996).

Teeth develop as a consequence of interactions between the oral epithelium and underlying mesenchymal tissue. Initially 20 primary tooth germs develop; an additional 32 form the permanent dentition, developing through the fundamental Bud, Cap, and Bell stages (see Figure 2.0).
Figure 2.0. Developmental stages of tooth growth. Modified from www.crse.dent.umich.edu.

During the Bud stage, patches of epithelial cells grow into the underlying tissues to form the dental lamina (the patches of cells referred to as tooth buds). Usually 10 tooth buds develop upon dental lamina formation for the primary dentition. The Cap stage, (also known as proliferation, reproduction or multiplication) consists of growth in the cells combined with the tooth bud taking a hollowed cap like shape, where the epithelium of the cap gives rise to the enamel. The area under the cap is called the dental papilla, which gives rise to the dentine, cementum, and the pulp. The Bell stage is the last period of growth, (also referred to as histodifferentiation) and is characterised by the acquisition of tissue characteristics by cell groups. It is at this stage that the ameloblast cells form the enamel, odontoblast cells form the dentine and cementoblast cells form the
cementum. The ameloblasts and odontoblasts line up on a boundary line called the dentinoenamel junction (DEJ); the whole process referred to as morphodifferentiation. Upon completion of morphodifferentiation, cells along the DEJ deposit the matrix: a process known as apposition. Following apposition the matrix hardens through calcification (deposition of Ca\(^{2+}\) ions or other mineral salts). The tooth crown then receives layers of enamel, which form in a downward direction, beginning at the top of the crown and extending over the sides of the cementoenamel junction (CEJ). Once the crown of the tooth has formed, the root begins to develop eruption; eventually followed by the movement of the tooth into its correct position in the oral cavity. This whole process takes approximately 3 years for the permanent dentition. The developed tooth consists of 3 tissues: enamel, dentine and cementum (see Figure 2.1 below).

![Figure 2.1](https://www.adam.com)

**Figure 2.1.** Cross-section of a human tooth. Modified from www.adam.com.

**2.4.1. Formation of Enamel**

Enamel is composed of rods that extend from their site of origin at the DEJ. Each rod is formed by 4 ameloblasts. The head and tail of the rod are approximately 5µm and 1µm wide, respectively. Each rod is approximately 9µm long, the same size as a red
blood cell. Enamel is unique because it consists of mineralised epithelial tissue, whereas bone, dentine and cementum are mineralised connective tissues.

During the development of enamel, the ameloblast cells that form the enamel tissue as a mineralised secretory product influence the histology. The secretory ends are referred to as Tomes’ process. The products formed by each ameloblast are termed enamel rods or enamel prisms; the shapes of the rods determined by the Tomes’ process. In absence of the more elastic dentine, the enamel rods would remain unsupported thereby becoming more susceptible to fractures along the rod borders.

The keyhole shaped rods run all the way from the DEJ within 20µm to 40µm of the outer surface. This outermost section is prismless due to a change in shape of the ameloblasts as they end their secretory phase and begin their resorptive phase. This morphological phase involves the elimination of Tomes’ process resulting in the enamel losing both its rod and prism like pattern producing hexagonal (c-axis perpendicular to the enamel surface) inorganic crystals (see Figure 2.2).

As enamel matures, it loses both organic material and water, resulting in a product primarily composed of 97wt.% inorganic mineral phase referred to as HA, approximately 3% water and less than 1% organic matrix.
Figure 2.2. Transmission Electron Microscopy (TEM) of human tooth enamel. Longitudinally sectioned HA crystals (magnification x 125 000).

2.4.2. Formation of Dentine
Dentine formation begins shortly before enamel formation. Odontoblasts first lay down predentine, with the remainder of the dentine building up as a series of conical layers. Growth continues until the crown has been formed, leaving a space in the middle of the tooth for the pulp chamber. Mineralisation occurs simultaneously along collagen fibrils, following predentine formation. Crystallites are seeded in tiny vesicles, referred to as matrix vesicles, whereby the crystallites grow out radially, rupturing the vesicle walls. Mineralised dentine is spherical, with the crystallites fanning out in all directions from the centre and is referred to as calcospherites (Schmidt and Keil, 1971). As the calcospherites grow, they meet others, limiting their spread, therefore on completion of the mineralisation process a complex of radially crystalline intersecting hyperboloid bodies appear (Hillson, 1996).
The dentinal tubules extend from the pulp cavity to the DEJ, with some tubules passing beyond the DEJ and extending into the neighbouring enamel. Near the pulp chamber the dentine tubules are approximately 4μm in diameter and extend linearly towards the coronal extremity of the tooth. Dentine remains biologically and chemically active, (i.e. formation continues throughout life), this being in direct contrast to mature enamel, which consists almost entirely of crystalline calcium phosphate, contains no cells and exhibits no metabolic activity.

Dentine is composed of approximately 20wt.% organic material and is therefore much less mineralised than enamel (see Table 2.0, below). For an extended record refer to Table 1a.1 in Appendix Ia. The mineral phase in dentine is composed of ‘apatitic’ calcium phosphate (ACP); the crystals of which are much smaller than in enamel. The specific in vivo functions of many of the organic components in the calcified tissues are unknown. However, collagen, which makes up approximately 90wt.% of the organic material in dentine, provides tensile strength and acts as a heterogeneous nucleating agent for HA crystals (Neumans and Neuman, 1958).

<table>
<thead>
<tr>
<th></th>
<th>Mature Enamel wt.%</th>
<th>Dentine wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic</strong></td>
<td>≥ 96</td>
<td>72</td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td>&lt; 0.2 to &gt; 0.6</td>
<td>20 (18 collagen)</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td>3.9</td>
<td>8</td>
</tr>
<tr>
<td><strong>Major Organic Component</strong></td>
<td>Insoluble Protein</td>
<td>Collagen</td>
</tr>
<tr>
<td><strong>Inorganic Component</strong></td>
<td>ACP</td>
<td>ACP</td>
</tr>
<tr>
<td><strong>ρ (g/cm³)</strong></td>
<td>2.9 - 3.0</td>
<td>2.0 - 2.3</td>
</tr>
</tbody>
</table>

Table 2.0. Major components and features of mature tooth enamel and dentine. Source: Brudevold and Soremark (1967), Williams and Elliot (1989).

The remaining 10wt.% organic material within teeth comprises a series of polymers containing protein and carbohydrates, referred to as non-collagenous proteins, lipids and other organic molecules. The organic components within bone and dentine have been reviewed by Linde (1985).
The chemistry of cementum is similar to bone. Since, a priori, cementum has not been considered a source of material suitable for Pb isotope studies; its structure is not discussed.

2.4.3. The Organic Matrix of Enamel
The average organic content of mature human enamel lies in the range of 0.05wt.% to 0.10wt.% Its composition is known only vaguely and said to consist of approximately equal amounts of proteins and lipids, together with trace amounts of citrate, lactate and carbohydrate. The composition of the organic matrix is classified in terms of abundance. The abundant proteins comprise more than 90wt.% of the total organic fraction and consist of the hydrophobic proteins, proline-, histidine-, leucine- and glutamine-rich amelogenins; together with the acidic enamelines (rich in serine), glycine, aspartic acid and glutamic acid (Termine et al., 1980), (refer to Table 1a.2 in Appendix Ia). Amelogenins and enamelin proteins play major roles in the structural organisation and mineralisation of developing enamel. Some researchers have suggested that the relatively abundant hydrophobic amelogenins control the size, morphology and orientation of the mineral crystallites (Fincham and Moradian-Oldak, 1995) whereas the acidic enamelines are thought to be nucleators and regulators of enamel crystal growth (Termine et al., 1980; Traub, Joaikin and Weiner, 1985; Slavkin et al., 1988; Deutsch, 1989).

The enamelines comprise typically 10wt.% of the proteins, the remainder consisting of amelogenins. During maturation, most of the amelogenins are lost. Therefore the relative abundance of enamelines increases with time during maturation (Fincham, Belcourt and Termine, 1982). The amelogenins are hydrophobic, with molecular weights (MW) ranging between 7kDa to 26kDa (Fincham and Simmer, 1997). Higher MW amelogenins predominate during the early phases of enamel development.

In contrast, the outer enamel contains less protein than the inner regions, is more soluble and consists of glycine rich components of low MW, together with low MW peptides and amino acids.

2.4.4. The Organic Matrix of Dentine
The organic matrix in dentine is primarily composed of Type I collagen (Gay and Miller, 1978), the remainder consisting of a complex series of acidic glycoproteins,
phosphoproteins, serum proteins, lipids and small proteoglycans (Williams and Elliot, 1989). The role of lipids in the mineralisation process is currently unknown and has long been a topic of discussion particularly after histochemical investigations showed that phospholipids occur at the mineralisation sites. For a comprehensive review see Wuthier (1984).

The non-collagenous proteins are made up of proteoglycans, phosphoproteins, carboxyglutamic acid containing proteins (Gla-proteins), osteonectin, lipids, and small amounts (approximately 0.9wt.%) of citrate, and lesser amounts of lactate.

2.5 Rationale for the Current Study

As noted above, enamel mineralisation occurs during a relatively short period early in a vertebrate’s life, whereas bone is continually redeposited and remodelled in vivo. If the diet of an individual changes during its lifetime (or is variable among individual members of the same population), it should be obvious from measurements conducted on dental enamel: dependent on the isotope being analysed. Of course, these differences would be partially erased and averaged by in vivo remodelling, as they are in bone. However measurements of $\delta^{13}C$ made by Koch, Tuross and Fogel (1997) provided reason for optimism in this regard. They observed that although $\delta^{13}C$ indicated far greater degrees of diagenetic alteration in bone and dentine than had previously been reported, the ratio within dental enamel was paradigmatically different from all other tissues: suggesting that it had been biologically isolated from the metabolism in vivo and remained secure over long-term burial. This observation is confirmed by measurements presented in Chapters 5, 6 and 7 of the current work.

Since some pre industrial societies were, in principle, free of anthropogenic Pb$^{2+}$ ion pollution, any measurable accumulated Pb$^{2+}$ ion burden must have derived from a biogenic source. Thus, Pb isotope analysis of tooth enamel could provide paleo-environmental information and a reliable ‘baseline’ for present day environmental Pb$^{2+}$ ion exposure studies (Gulson, Jameson and Gillings, 1997). Although there are some difficulties with such a proposition, particularly regarding the selection of suitable samples, Chapter 4 revisits this possibility and rationalises some of the anomalies currently within the literature.
Brian Gulson demonstrated the potential of employing Pb isotope analysis as a means of reconstructing anthropogenic Pb\textsuperscript{2+} ion exposure histories of modern populations (Gulson and Wilson, 1994; Gulson \textit{et al.}, 1994). In principle, this method could be adapted for the study of the source of biogenically derived Pb\textsuperscript{2+} ions amongst archaeological populations, and in appropriate circumstances used to identify individual migrants among archaeological burial populations. This proposition is tested in the remaining chapters of this thesis.

2.6 Conclusion

This brief critical survey of the archaeological science literature confirms that some of the science-based archaeological research appearing in the literature remains critically flawed: particularly that undertaken on archaeological bone. However, in the years since Hancock, Grynpas and Pritzker first sounded the alarm bells regarding hard tissue analyses, a number of changes in research strategies have occurred that justify a general feeling of optimism in the future of this research field. Foremost amongst these, are the controlled investigations of diagenetic alteration in the archaeological environment and the consequent care taken by many groups to regulate their results in order to avoid reaching archaeological conclusions that are later invalidated by other investigations.

Unfortunately, much confusion still exists within archaeological science literature regarding the status of quantitative analytical measurements taken on archaeological bone. Most research has moved beyond the stage of simplistic trace element measurements, and instead focuses on isotopes. However, a number of works of the same form criticised by Hancock, Grynpas and Pritzker (1989) continue to be published within the literature.

Although isotope based research on archaeological bone removes one of the inherent difficulties regarding analytical studies (that of inter-subject chemical variability between individuals found on the same site), it does not, by itself, guarantee the biogenic integrity of the measurements made. Rather, in the face of what sometimes seems to be an overwhelming desire on the part of some archaeological scientists to extract some form of information from this most abundant of all archaeological materials, there is now sufficient evidence to suggest that all archaeological bone is recovered in a diagenetically
altered condition, thus rendering the results of most forms of chemical analysis meaningless.

In contrast, there is an extensive literature indicating that, with the exception of limited amino acid racemisation, the degree of diagenetic alteration of dental enamel in archaeological deposits is within the limits of analytical error, over the time spans encountered on most archaeological sites. The remaining sections of this work present the results of investigations undertaken to test this postulate.
Chapter 3

The Organic Chemistry of Lead in Teeth

3.1. Introduction

This chapter details the results of both elemental and isotopic measurements undertaken in order to determine which, if any, skeletal tissues recovered from archaeological deposits retain trace elements accumulated in vivo. As noted in Chapter 2, there have been a number of previous studies examining concentration and isotopic ratios of Pb and Sr in both archaeological and modern tissues in order to reconstruct individuals’ dietary and anthropogenic exposure histories. If Pb isotope analysis of archaeological hard tissue is to be used to complement traditional archaeological life history reconstructions and infer patterns of migration, then it is necessary to evaluate the structural integrity of the biogenically derived material under investigation rather than simply assuming it.

It has long been suggested that Pb$^{2+}$ ions replace Ca$^{2+}$ ions within the crystalline lattice structure of HA, which is the principal inorganic component of skeletal hard tissues (Neumans and Neuman, 1958). This observation seems to be substantiated empirically by a number of studies in which CaHA and PbHA has been synthesised by solid state reactions at high temperature and pressure. However, the results of these syntheses, which suggest that a complete solid solution series exists between Ca$^{2+}$ and Pb$^{2+}$ end-member HA, appear anomalous when compared with both the occurrences of Pb$^{2+}$ ions within the human body tissues and in the mineralogical world. The investigations presented in this chapter seek to establish where the trace amounts of Pb$^{2+}$ ions reside within the structure of skeletal hard tissues, in order to establish how they are incorporated into the skeletal remains and whether the in vivo distribution is maintained over long-term burial. The results call into question the extent of solid solubility of Pb$^{2+}$
ions in CaHA formed at low temperature and thus many of the long held assumptions regarding the use of skeletal hard tissue analyses within archaeology.

3.2. Experimental

Lead concentrations across distinct sections of the tooth were achieved with Laser Ablation Inductively Coupled Mass Spectrometry Microprobe (LAM-ICPMS), total elemental concentrations were determined using Anodic Stripping Voltammetry (ASV), while Pb isotope ratios were determined using Thermal Ionisation Mass Spectrometry (TIMS). The concentration data were cross correlated using Graphite Furnace Atomic Absorption Spectrometry (GFAAS) while isotope ratios were verified with Multiple Collector (MC)-LAM-ICPMS (see Table Ib.1a-d, Appendix Ib for results).

3.2.1. Sample History

All modern teeth were obtained from various dental surgeries and derive from individual residents of Australia, some of whom are known to be first generation migrants. Archaeological teeth and bone studies were undertaken on samples obtained from excavations of historical sites within Australia, some of whom were also said to be first generation migrants to the country. Privacy considerations prevent us from collecting or publishing personal details of either present day individuals, or the ancestors of individuals who may still be living. Total anonymity as to the sources of samples was maintained throughout the collection process and any references to such material in this thesis are made via their laboratory number only. The results of these measurements were then compared to identical measurements made on seven ancient Pacific Islander teeth. Full sample descriptions of the Islander teeth are listed in Table Ib.2, Appendix Ib.

3.2.2. Analytical Methodology

TIMS has been used to assess Pb isotope ratios due to the high precision of the isotope ratios including the less abundant (approximately, 1.4%) $^{206}$Pb isotope. LAM-ICPMS is used for the in situ analysis of trace elements in solid samples determining many elements in the periodic table. Coupled with improvements in instrumental precisions (particularly the development of the multiple collector magnetic sector), MC-LAM-ICPMS is now a powerful technique capable of measuring isotopic ratios of many
trace elements to detection limits between (0.01 and 0.10μg/g) with high spatial
resolutions (approximately, 50μm) (Norman et al., 1998).

The MC-LAM-ICPMS system combines a laser ablation micro sampler, an argon (Ar)
plasma ionisation source, and a multiple collector magnetic sector mass spectrometer.
Solid particles are physically ablated off the surface of the sample by laser beam, the
particles are carried in a stream of inert gas into an Ar plasma ionisation source where
they are ionised prior to measurement in a multi collector magnetic sector mass
spectrometer, an instrument specifically designed for high precision in situ analysis of
isotope ratios.

Recent years have seen a succession of rapid improvements in ICPMS as an analytical
technique within geochemistry. One of the most significant advances has been the
development of laser ablation as a means of sample ionisation, allowing rapid and precise
in situ determination of trace element abundances, without the need for wet chemical
extraction, thus removing one source of error and sample contamination.

Within science-based archaeology, LAM-ICPMS provides a means by which irreplaceable
archaeological materials can be analysed with minimal sample preparation or destruction
and a number of researchers have now published works detailing the advantages of LAM
over other available techniques. A number of theses publications are of significance to
the current investigation, as they relate either to the study of skeletal hard tissue (Evans et
al., 1994, 1995) or specifically to dental enamel (Prohaska et al., 2002; Montgomery et al.,
1999). And whilst difficulties relating to the relative abundance of ‘primordial’, $^{204}$Pb,
prevent quantitative measurements of radiogenic Pb isotope ratios, the technique does,
for the first time, allow researchers to make spatially resolved trace element concentration
measurements of Pb$^{2+}$ ions within skeletal material. Here the technique has been
employed to plot the distribution of Pb$^{2+}$ ions in cross sections of a number of individual
teeth and bones, in order to determine where the ions reside in the greatest
concentrations.

ASV was undertaken as a means of measuring the level of organometallic interaction in
human teeth. ASV is one of the most sensitive, convenient, and cost effective analytical
methods for detection and quantitation of metal contaminants in varying environments,
e.g. blood (Karpiuk et al., 1995), rivers (da Silva and Masini, 2000), biological materials
(Adeloju, Bond and Briggs, 1984) and drinking water (Savely, Emery and Connor, 2000).
Another advantage is that several metals (approximately 20 amalgam-forming metals, for
example \(\text{Pb}^{2+}, \text{Cu}^{2+} \text{and Cd}^{2+}\)) can be analysed simultaneously. ASV has also been shown
to be highly suitable for measuring organic compounds (including cardiac and anticancer
drugs, vitamins and pesticides) that exhibit surface active properties.

ASV involves the formation, adsorptive accumulation, and reduction of a surface active
complex of the metal. Metal ions in solution are reduced to metallic form and
concentrated as mercury (Hg) amalgam in an Hg film electrode. The solution is stirred to
carry as much of the analyte metal(s) to the electrode as possible for concentration into
the amalgam. After reducing and accumulating the analyte for some period of time, the
potential on the electrode is increased to reoxidise the analyte and generate a current
signal. Quantitation is achieved via the method of standard additions.

3.2.2.1. Thermal Ionisation Mass Spectrometry (TIMS)
TIMS analysis was conducted at the Continental Evolution Research Group (CERG),
Faculty of Sciences, School of Earth and Environmental Sciences, University of Adelaide
South Australia. A Finnigan MAT 262 mass spectrometer, equipped with seven movable
faraday collectors and a 13-sample turret with both manual and automated running
capabilities, was employed.

Gulson and Wilson (1994) have developed a methodology for conducting TIMS analyses
on specific dental tissues. With minor variations (Montgomery et al., 1999), this method
has been adopted as a standard procedure. Since its adoption greatly facilitates inter-
laboratory comparison of the results of these other studies the procedure was adopted
here. Teeth were sectioned into transverse slices using a diamond impregnated stainless
steel cutting disk, followed by a decontamination procedure using water, \(\text{H}_2\text{O}_2\) and acid
washing. Additional sections were prepared consisting mainly of enamel: incisal section is
isolated from the cervical section. The cervical section is then stripped of the pulpal canal
and secondary (circumpulpal) dentine leaving coronal dentine for analysis. Comparisons
of the Pb content in these tissues have been used successfully to study:

- The *in utero*, early childhood Pb exposure as well as the additional Pb\(^{2+}\) ion from
  endogenous sources to coronal dentine (Gulson, 1996; Gulson and Gillings, 1997;
Gulson, Jameson and Gillings, 1997);

- The Pb isotope ratios in adult permanent enamel in order to identify the sources of anthropogenic Pb$^{2+}$ ion exposure in modern populations, and

- Identify the country of origin of adult migrants to Australia, based on the characterisation of tetra-ethyl Pb fuel additives (Gulson, Jameson and Gillings, 1997).

All samples were cleaned ultrasonically in Millipore Alpha-Q H$_2$O for 5 minutes to remove dust, rinsed twice, dried down in high purity acetone and then weighed into pre cleaned (Savillex) PFA Teflon beakers. All samples were acid washed for 7 minutes in 1.5M Teflon distilled HCl to remove surface contamination. Elemental concentrations were obtained using the isotope dilution method involving measured quantities of solid samples dissolved in 16M quartz distilled nitric acid (HNO$_3$) followed by the addition of a measured amount of ‘spike’ highly enriched in one isotope, $^{208}$Pb or $^{84}$Sr. Separation was performed by conventional anion exchange column chemistry (Kempton, 1995).

### 3.2.2.1.1 Lead Analysis

The analytical precision and accuracy of Pb isotope determinations is limited by the need to correct for mass fractionation effects encountered during TIMS. This is overcome by spiking a second sample aliquot with a solution, artificially enriched in two Pb isotopes (Double Spike Technique). This method, detailed in Woodhead, Volker and McCulloch (1995), considerably improves the analytical precision and accuracy of conventional Pb isotope analyses by at least a factor of three, and is strongly recommended for studies of this type where extremely accurate and precise Pb isotope data are required. The analytical precision of measurements using this method has been determined as: ±0.003 (2σ) for $^{206}$Pb/$^{204}$Pb and $^{207}$Pb/$^{204}$Pb and ± 0.01 (2σ) for $^{208}$Pb/$^{204}$Pb.

Lead isotopes are more easily ionised than their lighter counterpart, Sr. Similarly, Pb does not have an isotope ratio that is invariant in nature; hence this fractionation needs to be corrected using a standard. Lead measurements were made using an Ion Counter and standardisation was performed using standard SRM981. Blanks were analysed for Pb. The mean blank was 75pg well within the expected range (51 - 189pg; $n = 10$). All of the
Pb sample data were normalised to reference standards using the accepted values of Kempton (1995) (see Table 3.0).

<table>
<thead>
<tr>
<th></th>
<th>(^{206}\text{Pb}/^{204}\text{Pb})</th>
<th>(^{207}\text{Pb}/^{204}\text{Pb})</th>
<th>(^{208}\text{Pb}/^{204}\text{Pb})</th>
</tr>
</thead>
</table>

**Table 3.0.** Lead isotope standards SRM981 achieved by Kempton (1995).

Experimental errors were estimated to be ±0.0330 (2σ) for the \(^{208}\text{Pb}/^{204}\text{Pb}\) ratios, ±0.0139 (2σ) for the \(^{207}\text{Pb}/^{204}\text{Pb}\) ratio and ±0.0169 (2σ) for ratio \(^{206}\text{Pb}/^{204}\text{Pb}\). Individual outgassed rhenium filaments were used to load samples. The silica gel, phosphoric acid method adopted by Gulson (1986) was employed since it provided adequate precision on extremely small sample sizes. An extended discussion on Pb isotope results is presented in Chapters 6 and 7.

### 3.2.2.2. Laser Ablation Inductively Coupled Plasma Mass Spectrometry Microprobe (LAM-ICPMS)

Mass spectrometry techniques are the only methods capable of measuring Pb\(^{2+}\) ion concentrations at the levels contained within dental enamel. Other surface analytical techniques such as Particle Induced Xray Emission (PIXE) spectroscopy are not sufficiently sensitive, even when used in wavelength dispersive mode.

LAM-ICPMS analyses were performed at the Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC), Macquarie University, Sydney, Australia. The LAM-ICPMS uses a Hewlett Packard HP4500 and Agilent 7500 ICPMS attached to a UV laser ablation microprobe. A Continuum Surelite I-20 Q-switched Nd:YAG laser was employed. The laser operated at a fundamental infrared (IR) wavelength of 1064nm. Two frequency doubling crystals provide second and fourth harmonics in the visible (VIS, 532nm) and ultraviolet (UV, 266nm) wavebands, respectively.

Analyses were carried out in time resolved mode with a laser repetition rate of 4Hz (more rapid pulse rates, for example, 20Hz produce strongly fractionated signals) and energy of 1mJ per pulse with ablation craters of approximately 20\(\mu\)m in diameter. Data accumulation was obtained from individual tissue sections. The LAM is fitted with a
Prior to analysis, all hard tissues were pre-cleaned with a Teflon fibre brush to remove adhered soil. Each sample was then ultrasonically washed for 5 minutes in Barnstead NANOpure Milli-Q H$_2$O (<1µg/g total heavy metal content) and then with analytical grade acetone (Fluka) (≤2µg/g Pb). The cleaned samples were set in epoxy resin blocks (Araldite LC191 and Hardener HY956; Meury Enterprise) and cut into halves using an Accutom Diamond saw (Struers) with Millipore Alpha H$_2$O. The two samples accordingly obtained were stored in acid leached Teflon screw cap vials for analysis. In order to reduce cross contamination, the samples were not polished.

Calibration was achieved by (1) an external standard (NIST612 glass) for relative element sensitivities and, (2) an internal standard, Ca$^{2+}$ ion as a correction for the ablation yield. Mount background values were obtained by ablation of the epoxy resin prior to each analysis. Detection limits based on these operating conditions were 0.01 to 0.1µg/g, with precision less than 1% at the µg/g level: errors ($2\sigma$) are less than 0.9% for $^{208}$Pb/$^{204}$Pb ratios, and 0.5% for $^{207}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb ratios.

3.2.2.3. Multiple Collector Laser Ablation Inductively Coupled Plasma Mass Spectrometry Microprobe (MC-LAM-ICPMS)

Sample preparation was achieved by methods detailed in section 3.2.2.2.

A multiple collector magnetic sector LAM-ICPMS for in situ analysis of isotopic ratios was used. A Nu Plasma, designed and manufactured by Nu Instruments of Wrexham (UK) with a 266nm UV laser microprobe, was used. Masses 202, 203, 204, 205, 206, 207, 208 were measured simultaneously in Faraday collectors and all measurements were made in static mode. Thallium (NBS997) was used to correct for mass fractionation using an exponential correction and a value of $^{205}$Tl/$^{203}$Tl = 2.3875 (Belshaw et al., 1998). The analytical precision ranges between ±0.02% and 0.03% ($2\sigma$).
3.2.2.4. Anodic Stripping Voltammetry (ASV)

All experiments were performed with a MacLab potentiostat (ADInstruments Pty Ltd, Castle Hill, NSW, Australia) connected to a two channel MacLab/2e interface and a Macintosh LC 475 computer. MacLab Echem software (version 1.5.2) was used to record the voltammetric measurements. A 1mm diameter glassy carbon (EE040) (Cypress Systems, Inc., Lawrence, Kansas, USA) working electrode was employed, insulated with polyetheretherketone. A miniature reference electrode with an internal silver/silver chloride (Ag/AgCl) reference electrode (EE008) and internal filling solution of 3M KCl, saturated with AgCl was used, whilst a platinum (Pt) wire operated as the auxiliary electrode. Homogeneity of all solutions was maintained using a magnetic stirrer.

All acids, ammonia (NH$_3$) solution, and reagents used were analytical grade (Sigma). Adjustments to pH were made with 1M NH$_3$. Stock solutions of 1g/dm$^3$ of lead chloride (PbCl$_2$) (Ajax Chemicals) were prepared by dissolving appropriate amounts of PbCl$_2$ in 0.1M hydrochloric acid (HCl). All stock solutions were stored in pre cleaned polyethylene bottles and refrigerated. Standards were prepared daily by appropriate dilution of the stock solution with Milli-Q water. All glassware (Borosilicate), Teflon, and polyethylene bottles were soaked in 2M HNO$_3$ for at least 7 days, washed 3 times with Milli-Q water, soaked in Milli-Q water, and finally soaked in 0.1M HCl until ready for use.

All tooth samples were caries free. Tooth samples were sliced into thin sections (~20µm) using a diamond bladed dental saw. Enamel was carefully removed using Teflon coated tweezers, weighed and stored in pre cleaned Teflon screw cap vials for further analysis. Dissolution of samples were performed by the wet digestion method described by Adeloju (1989), using HNO$_3$ (65wt.%). Aliquots (10cm$^3$) of dissolved enamel were decanted into a 125cm$^3$ Erlenmeyer flask, a pre cleaned glass funnel was inserted into the flask mouth and the contents then heated on a hot plate at approximately 563K until nitrogen dioxide (NO$_2$) fumes are observed. After cooling for 5 minutes between each application of heat, the digestion was repeated with two more additions of 10cm$^3$ HNO$_3$. Following the final addition of HNO$_3$ heating was continued until no more NO$_2$ gas evolution was observed. The flask was cooled for another 5 minutes after which time the funnel was rinsed into the flask using Milli-Q water. The contents of the flask were transferred to calibrated volumetric flask and made up to 30cm$^3$ via the addition of Milli-
Q water. The contents of each flask were then divided into 2 samples: one of which was subject to high pressure Hg vapour UV radiation for 3 hours. The remaining sample underwent no further pre treatment.

The working electrode was polished with 0.05µm aluminium (Al) slurry before each analysis. Deposition of the Hg film was performed at the beginning of each day using 50x 10⁻³cm³ of 1µg/dm³ Hg²⁺(aq) solution and an appropriate amount of pH buffer was pipetted into the voltammetric cell in order to obtain the appropriate pH (between 5 and 6). In situ reduction of the Hg film onto the carbon (C) electrode was achieved by applying a constant potential (-1000mV) for 600s. The parameters for voltammetric determinations of Pb²⁺ ions were: deposition potential, -1000mV versus Ag/AgCl (3M KCl); deposition time, 60s (stirred); rest period, 10s; SW pulse scan rate, 8V/s; pulse height, 50mV. Voltammetric peaks for Pb²⁺ appeared at -440mV. Concentrations of Pb²⁺ ions were measured using standard addition techniques. Lead blank levels were also determined by the standard additions method; (0.080 ± 0.001)µg/dm³. All measurements had a relative standard deviation of ≤5%.

3.2.2.5 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
GFAAS were performed using a Varian SpectrAA-800 flame atomic absorption spectrometer with a Zeeman background corrector, a Model 600 graphite furnace, an AS-70 Autosampler and a Model 3600 data station. The operating wavelength set at 217.0nm. Standard solutions were prepared by dissolution of apatite compounds in 0.1M ethylenediaminetetraacetic acid (EDTA) making up solutions of varying concentrations up to 10mg/g for Pb. Argon was used as the inert gas. All containers were cleaned using with detergent and treated with HCl and rinsed with NANOpure Milli-Q H₂O. All samples were analysed in triplicate and a precision less than and equal to 4% was achieved.

3.3. Results and Discussion
The LAM-ICPMS concentration results presented here are only semi quantitative, due to the unavailability of a suitable Pb bearing HA standard that is matrix matched to tooth enamel. In contrast to previous studies (Montgomery et al., 1999), where the data were
collected as Time Resolved Analyses (TRA), the concentration profiles were compiled from individual point data measured across tooth cross-sections.

Figures 3.0 and 3.1 (Table Ib.3 Appendix Ib) show typical Pb$^{2+}$ ion concentration profiles obtained through LAM-ICPMS analysis of the samples in this study. The concentration profile data not shown in these figures are tabulated and profiled in Table Ib.4 and Figure Ib.1a-b (Appendix Ib), respectively.

They are also similar to the profiles obtained by Montgomery et al., (1999) and bear out the observations by Zaichick, Ovchjarenko and Zaichick (1999) that Pb$^{2+}$ ions are non-uniformly distributed across the tooth, and those of Cleymaet et al., (1991), who observed significant decreases of Pb$^{2+}$ ionic concentration with etch depth.

![Figure 3.0](image-url)  
**Figure 3.0.** LAM-ICPMS of Pb$^{2+}$ ion concentrations across the longitudinal section of a modern Broken Hill human tooth.
Lead ion concentrations are significantly higher in the outer, non prismatic enamel sections and the dentine layers of the teeth, than in the crystalline enamel layers (typically by at least two times greater). Comparison of these results with others in the literature, highlights one of the inherent difficulties in conducting hard tissue analyses on whole teeth: that in the absence of a detailed knowledge of the mechanism of Pb$^{2+}$ ion interactions in the oral environment, it is extremely difficult to interpret the results of whole tooth analyses because they have effectively been conducted on three entirely different materials: cementine, dentine and enamel. Mackie, Elliot and Young (1977), Steenhout and Pourtois (1981) and Bercovitz and Laufer (1990), for instance, all reported that Pb$^{2+}$ ion concentrations vary as a function of position within the oral environment; with anterior teeth containing the highest concentrations. Purchase and Fergusson (1986), Pinchin, Newham and Thompson (1978), Proud (1976) and Lockeret (1975) suggested that differences between Pb$^{2+}$ ion concentrations were particularly marked between pre molars and canines; both of which contain significantly lower concentrations than incisors. In an attempt to rationalise this empirically determined rule, Stack (1983) suggested that the concentration of Pb$^{2+}$ ions varied as a function of the proportion of circumpulpal dentine in the various types of teeth. However, this observation runs contrary to the observation made by De la Burde and Shapiro (1975) that the Pb$^{2+}$ ion
concentrations in circumpulpal dentine do not seem to be related in any simple manner to tooth type. Similar levels of confusion surround the effects of carious teeth on measured Pb$^{2+}$ ion concentrations (cf. Brudevold et al., 1977; Davies and Anderson, 1987 with results obtained by Buttnar, 1969; Proud, 1976; Moses, 1976; Devise and Ritchey, 1974; Gil et al., 1994 and Zaichick and Ovcharenko, 1996). It is clear from the results of these studies, that inter-laboratory comparisons of results are only possible between measurements, made in situ on directly comparable fractions of the dental tissue. Table 3.1 presents the results of concentration measurements determined by ASV of dentine made on both canine and premolar teeth from modern, historic and prehistoric individuals together with similar data collected from trabecular bones from the same individuals (see Table Ib.1a Appendix Ib for cross correlation using GFAAS).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dentine</th>
<th>Bone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Canine</td>
<td>Premolar</td>
</tr>
<tr>
<td><strong>Modern</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M27</td>
<td>n.a</td>
<td>0.367 ± 0.071</td>
</tr>
<tr>
<td>M28</td>
<td>0.312 ± 0.061</td>
<td>n.a</td>
</tr>
<tr>
<td>M31</td>
<td>0.421 ± 0.041</td>
<td>0.461 ± 0.023</td>
</tr>
<tr>
<td>M38</td>
<td>0.513 ± 0.060</td>
<td>0.446 ± 0.022</td>
</tr>
<tr>
<td><strong>Historic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA1</td>
<td>0.293 ± 0.053</td>
<td>0.511 ± 0.040</td>
</tr>
<tr>
<td>HA2</td>
<td>0.421 ± 0.082</td>
<td>0.413 ± 0.041</td>
</tr>
<tr>
<td><strong>Prehistoric</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AT2</td>
<td>0.317 ± 0.061</td>
<td>0.323 ± 0.056</td>
</tr>
<tr>
<td>AB12</td>
<td>n.a</td>
<td>0.451 ± 0.032</td>
</tr>
<tr>
<td>AB27</td>
<td>0.450 ± 0.038</td>
<td>0.344 ± 0.097</td>
</tr>
</tbody>
</table>

Table 3.1. Comparison of modern, historic and prehistoric teeth and bones measured using the ASV method. (n.a denotes sample not available). All measurements are in µg/g.

These data confirm that the concentrations of Pb$^{2+}$ ions within both dentine and bone vary dramatically, even within the same individual. It seems that contrary to the above mentioned studies, there seems to be no correlation between tooth type and Pb$^{2+}$ ion concentrations within individual tissue types.

Furthermore, in the cases of the archaeologically derived individuals, the Pb isotope ratio
measurements of both dentine and enamel consistently match the local isotopic signature at the point of burial (see Table 3.2), whilst that obtained from the modern individuals (both of whom are more than 40 years old), matches that of the tetra-ethyl Pb additive that was formerly added to Australian petrol (Table 3.3). From these results and those of the literature (Waldron, 1983; Pike and Richards, 2002), it seems to be extremely difficult to interpret the trace elemental concentration data obtained from archaeological dentine and bone in terms of anything other than the local geology at the point of deposition. Without details as to the life history of the subjects, it is difficult to use isotope data alone to infer the rate of turnover, the residence time of Pb$^{2+}$ ions within the individual \textit{in vivo}, or the individual constituent components of the isotope signature, all of which are masked by that of petrol.

In contrast to the data for dentine and bone, Pb$^{2+}$ ion concentrations within individual dental enamel samples from the same subject, vary within experimental error limits of the individual measurements, indicating that tooth type was not a determining factor in the measured concentration. Nevertheless, in the interest of consistency and in order not to introduce extra variables into the experiments on archaeological teeth, it was decided to conduct all measurements on caries free, premolar teeth. Similarly, in modern samples, teeth with glasionomer filler particles and composite fillings were also rejected; even though the contributions of Pb$^{2+}$ ion contamination from filling materials to the overall measured concentration have been shown to be insignificant (Øilo, 1992).
<table>
<thead>
<tr>
<th>Island</th>
<th>Sample</th>
<th>Enamel</th>
<th>Dentine</th>
<th>Bone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ID</td>
<td>208Pb/204Pb</td>
<td>207Pb/204Pb</td>
<td>206Pb/204Pb</td>
</tr>
<tr>
<td>Tongatapu</td>
<td>AT2</td>
<td>37.9704</td>
<td>15.5511</td>
<td>18.4780</td>
</tr>
<tr>
<td></td>
<td>AT3</td>
<td>37.9919</td>
<td>15.4670</td>
<td>18.4572</td>
</tr>
<tr>
<td></td>
<td>AT5</td>
<td>37.9616</td>
<td>15.5796</td>
<td>18.3706</td>
</tr>
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<td></td>
<td>38.0909</td>
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<td></td>
<td></td>
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<td>38.4260</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>38.4013</td>
</tr>
</tbody>
</table>

Table 3.2. Pb isotope of enamel, dentine and bone samples of archaeologically derived human skeletal remains. The Pb isotope ‘signature’ of all archaeologically derived dentine and bone samples are consistent to that of the local groundwater at the point of burial. Local groundwater Pb isotope ratios are highlighted in grey. TIMS errors (2σ, n = 5): 208Pb/204Pb (±0.01); 207Pb/204Pb and 206Pb/204Pb (±0.003). See Table 3.0b Appendix Ib for cross-correlation using MC-LAM-ICPMS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Enamel</th>
<th>Dentine</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>208Pb/204Pb</td>
<td>207Pb/204Pb</td>
</tr>
<tr>
<td>M41</td>
<td>36.2478</td>
<td>15.4234</td>
</tr>
<tr>
<td>M38</td>
<td>36.1022</td>
<td>15.4006</td>
</tr>
<tr>
<td>M37</td>
<td>36.0415</td>
<td>15.4272</td>
</tr>
<tr>
<td>M36</td>
<td>36.2823</td>
<td>15.5001</td>
</tr>
</tbody>
</table>

Table 3.3. Pb isotopes of enamel and dentine samples of modern Broken Hill residents. The local Broken Hill orebody 206Pb/204Pb ratio is approximately 16.00 while gasoline is 16.56 (Gulson, 1996). Errors (2σ, n = 5): 208Pb/204Pb (±0.01); 207Pb/204Pb and 206Pb/204Pb (±0.003). See Table 3.0c Appendix Ib for cross-correlation using MC-LAM-ICPMS.
The study presented here suggests that only core enamel is suitable for measurements of biogenically derived Pb$^{2+}$ ions. This is unfortunate, since higher, (and thus more easily measurable), concentrations of the element are present in other hard tissues. In particular, non-prismatic, surface enamel is considered to be a potential source of information regarding pre-eruptive Pb exposure in modern humans (Brudevold et al., 1977). However, in common with other enquiries (Montgomery et al., 1999), in the current study the non-prismatic layer was removed prior to measurement being conducted on the core, prismatic enamel. The Pb$^{2+}$ ion concentration in the surface enamel layers is known to increase with age. Although the additional Pb$^{2+}$ ions might derive from the core enamel; in which case its incorporation within the measurement would be justifiable and would greatly facilitate sample preparation, it is also possible that it may represent post-eruptive uptake of Pb$^{2+}$ ions by the enamel surface derived from the oral environment (Cleymaet et al., 1991). Although Montgomery (1999) has shown that post-eruptive chemisorption of Pb$^{2+}$ ions from within saliva does not occur to any measurable extent, the risk of introducing diagenetically derived Pb$^{2+}$ ions into the measurements made on core enamel was considered too great for this material to be included.

### 3.3.1. Metal Ion Replacement

The data presented in Table Ib.4 (Appendix Ib), show that Pb$^{2+}$ ion concentration in the core enamel fraction of teeth to be beyond the limit of detection of all but mass spectrometric techniques. This observation, which is consistent with measurements presented by Budd et al., (2000), runs contrary to the suggestion that Pb$^{2+}$ ions replace Ca$^{2+}$ ions within the inorganic hydroxyapatite fraction of skeletal hard tissues. The core enamel fraction of teeth contains the highest proportion of CaHA of any tissue in the human body and yet, at the same time, the lowest concentrations of Pb$^{2+}$ ions. Table Ib.6 shows typical total Pb$^{2+}$ ion concentrations leached from dentine and enamel samples measured by ASV. The data demonstrates that the concentrations of Pb$^{2+}$ ions released are consistently higher within samples that were pre-treated using UV radiation, due to the breaking of organometallic bonds, prior to ASV measurement being undertaken (see Figure 3.2 and 3.3). The differences between pre-treated and non-pre-treated samples are particularly marked in dentine samples, which contain between 2 and 8 times greater concentrations than those of enamel (Figure 3.4). Nevertheless, it illustrates that even in dental enamel, which has a relatively low organic content, Pb$^{2+}$
ions in skeletal tissues are not locked into the inorganic lattice-like structure of CaHA but at least a significant proportion (and perhaps all) is bound to the proteinaceous organic components of the enamel.

![Graph](image)

**Figure 3.2.** Comparison of total Pb\(^{2+}\) ion concentrations of Dentine and UV-Treated Dentine samples determined with ASV. Archaeological teeth (2 to 27); modern teeth (36 to 41).

![Graph](image)

**Figure 3.3.** Total Pb\(^{2+}\) ion concentrations of Enamel and UV-Treated Enamel samples determined with ASV. Archaeological teeth (2 to 27); modern teeth (36 to 41).
Chapter 3-The Organic Chemistry of Lead in Teeth

Figure 3.4. Total Pb$^{2+}$ ion concentrations of archaeologically derived and modern human teeth. Comparison between Non-UV/UV Enamel and Non-UV/UV Dentine samples determined with ASV. Errors are within data columns where not shown. Archaeological teeth (2 to 27); modern teeth (36 to 41).

Given the location of the city of Broken Hill next to one of the world’s largest Pb-Ag-Zn deposits, it is unsurprising to see that modern teeth from subjects living in this location have dentine Pb$^{2+}$ ion concentrations far higher than those found within ancient Pacific Island populations. The Pb$^{2+}$ ion concentrations within dentine ranged from 5.71µg/g to 35.05µg/g (Figure 3.5); the higher values were obtained from this modern industrialised conurbation. The upper limit found in the current study is comparable to that found in other studies conducted on children whose Pb exposure was said to be dangerously high (Delves et al., 1982). Interestingly, although the data cannot be considered to be more than semi-quantitative, the Pb$^{2+}$ ion concentration within core dental enamel is consistently 0.65µg/g or less, regardless of either the age of the individual or the concentration of Pb$^{2+}$ ions within the subject’s dentine.
In order to complete the separation of any organometallic Pb$^{2+}$ ions, it was necessary to use UV irradiation (Bargagli, 1998) since it leads to a photooxidation of the metal binding ligands, resulting in the complexes ‘demetalating’ (Buchler, 1978) and liberating the metal ions into solution.

It was suggested as early as 1951 by MacDonald and co-workers, that Pb$^{2+}$ ions may in the first instance, be absorbed onto the surface of apatite crystallites. Nanci, Slavkin and Smith, (1987) and Yanagisawa (1989) proposed that enamelines are tightly bound to the apatitic crystal surface forming envelopes around the individual crystals while amelogenins are located in the intercrystalline spaces (see Figure 3.6). This proposal was corroborated by Fincham and Simmer, (1997) who further proposed that amelogenins form around the developing crystallites as nanospheres, preventing lateral (a-b-face) crystal growth and crystal to crystal fusions.

Figure 3.5. Total Pb$^{2+}$ ion concentrations of Enamel and Dentine archaeological and modern tooth samples determined using ASV. Errors are within data columns where not shown. Archaeological teeth (2 to 27); modern teeth (36 to 41).

---

1 Quasi-spherical, supramolecular structure of the order of 18-20nm in diameter and composed of approximately 100 amelogenin monomers (Moradian-Oldak et al., 1995)
Figure 3.6. Cartoon illustration of possible amelogenins (circles) and enamelins (triangles) with Pb\(^{2+}\) ions attached (solid circles). Redrawn from Sasaki, Takagi and Yanagisawa, (1997); Pb\(^{2+}\) ions added as possible site of adsorption. The amelogenins and enamelins surround the whole crystal.

There are approximately 2% H\(_2\)O in enamel and 10% in dentine. Water exists in at least three forms within dental enamel:

1. Loosely bound water removable at 373K; a greater concentration occurring in the inner than the outer enamel possibly a direct correlation with the higher concentration of protein (1%) in the inner enamel;

2. Water removable between 373K and 1073K occupying sites usually taken up by phosphate and Ca ions, and

3. Water occupying hydroxyl sites removed at temperatures above 1173K.

Figure 3.7, shows that this higher energy radiation results in further significant increases in the amount of Pb\(^{2+}\) ions released into solution; indicating that, whether the Pb\(^{2+}\) ions are bound to proteins or to water within proteins, the bond energies of Pb\(^{2+}\) ion interactions with the organic component of skeletal tissues are high.
It is currently accepted that Pb$^{2+}$ ions are first absorbed from within the gastrointestinal tract or the lungs, after which time they enter the bloodstream, either as a free cation, or as a stable complex ion that may subsequently undergo reactions with other diffusible ligands within plasma (Clarkson, 1986). The high results presented in this section may be a consequence of such a mechanism; Pb$^{2+}$ ions entering the human body via absorption into the bloodstream. Although the reaction mechanisms by which this occurs have yet to be elucidated, laboratory based experiments have indicated some plausible pathways by which this process might be occurring in the human body and these are already proving to be useful, particularly in managing the toxicity of Pb$^{2+}$ ions, using suitably designed organic ligands to mitigate the adverse effects of this metal (Clarkson, 1986).

At the molecular level, extensive studies have been made on the interaction of many metal ions with proteins. In these studies, particular emphasis has been placed on the role of enzymes and the propensity for Pb$^{2+}$ ions to disrupt these reaction mechanisms (Jaffe et al., 2001). Several investigators have proposed that the toxicity of Pb$^{2+}$ ions is at least partly due to its ability to disturb the homeostasis of Ca$^{2+}$ ions within the body (Pounds, 1984; Bronner, 1992). Early work in nutrition demonstrated that physiologic regulators of Ca$^{2+}$ within the body’s metabolism could exert a similar influence over Pb$^{2+}$

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**Figure 3.7.** ASV determination of total Pb$^{2+}$ ion concentrations of UV-Treated Enamel and UV-Treated Dentine of archaeological and modern tooth samples. Archaeological teeth (2 to 27); modern teeth (36 to 41).
ions (Mahaffey, Goyer and Haeman, 1973; Mahaffey, Six and Goyer, 1972). More recent studies have emphasised the role of intracellular-Ca\(^{2+}\) (Cai) as a secondary messenger within the human metabolism and this work has formed the basis of research directed towards identifying the molecular targets with which Pb\(^{2+}\) interacts. Habermann et al., (1983) have, for instance, shown that proteins such as calmodulin have a greater affinity for Pb\(^{2+}\) ions than for Ca\(^{2+}\) ions: a result seemingly confirmed by research indicating that Pb\(^{2+}\) ions are the most effective ‘blocker’ of voltage dependent Ca\(^{2+}\) channels at the cellular level (Nachshen, 1984). Simons and Pocock (1987) demonstrated that Pb\(^{2+}\) ions enter adrenal chromaffin cells through these Ca\(^{2+}\) channels and Schanne et al., (1989) have shown that a correlation exists between the presence of Pb\(^{2+}\) ions and increases in the concentrations of Cai in osteoblasts. However, whilst extensive research continues to demonstrate the affinity of Pb\(^{2+}\) ions for Ca\(^{2+}\) binding proteins and suggests that Pb\(^{2+}\) ions may disrupt the regulation of Cai or modulate the influx of Ca\(^{2+}\) ions from the extracellular medium, researchers are still some way from determining the actual effect of Pb\(^{2+}\) ions on the mobilisation of Cai in living cells.

### 3.4. Diagenesis

It has been emphasised at several junctures that the greatest difficulty in science-based archaeological studies of ancient bone and teeth is that of accounting for diagenetic turnover. The results obtained from UV-treated teeth, previously presented, confirm that even within archaeological teeth, Pb\(^{2+}\) ion concentrations within dentine can be as much as 200 times higher than in the core enamel layers of the same tooth and on a par with those obtained from members of the present day population of Broken Hill (NSW). Clearly, viewed simply in terms of time averaged in vivo Pb exposure, these results are anomalous. As mentioned above, Broken Hill is one of the largest Pb-Ag-Zn deposits in the world. At times in the history of the ‘Line of Lode’, mining practice involved open cast techniques, coupled with the practice of crushing and concentrating the Pb bearing ore onsite. This has left the city with problems of monumental proportions in terms of the Pb exposure of its population. Concerns for the well being of this community of Broken Hill have prompted a joint investment between the NSW Health Department and the NSW Environmental Protection Authority to reduce blood Pb levels in Broken Hill children to that observed in non contaminated areas elsewhere in Australia. Whilst it remains a remote possibility that something in the cultural practices of the pre-industrial
Island Melanesian and Polynesian populations of New Britain and Tongatapu led to their exposure to levels of \( \text{Pb}^{2+} \) ions similar to those of Broken Hill. However a more likely explanation is that the \( \text{Pb}^{2+} \) ion concentrations measured in these ancient teeth represent the time averaged \( \text{Pb}^{2+} \) ion burden accumulated \textit{post mortem} within the protein fractions of dentine.

The data presented in Table 3.3 which shows the Pb isotope signatures for the same samples supports the view that the \( \text{Pb}^{2+} \) ions in dentine are subject to complete diagenetic turnover even over, archaeologically speaking, comparatively short burial periods (<100 years). The Pb isotope ‘signature’ of all archaeologically derived dentine and bone samples measured in this study was consistently shown to be identical to that of the local groundwater at the point of burial: even in cases where the enamel layers were clearly different. Two possible explanations are postulated:

1. The individuals spent much of their lifetimes at or near the point of burial, or
2. The \( \text{Pb}^{2+} \) ions were accumulated \textit{post mortem} as the result of diagenetic alteration.

In an attempt to determine, which of these possibilities is correct, Pb isotope analysis was undertaken on drilled samples of bone from a 19\textsuperscript{th} century immigrant to Australia. In the hope of identifying a diffusion front for the replacement process (Millard, 1993) cores were sectioned and separate analyses undertaken on each sample. The data for the drilled cores are presented in Table 3.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dentine</th>
<th>Sample</th>
<th>Bone</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>( \text{Pb}^{208}/\text{Pb}^{204} )</td>
<td>( \text{Pb}^{207}/\text{Pb}^{204} )</td>
<td>( \text{Pb}^{206}/\text{Pb}^{204} )</td>
</tr>
<tr>
<td>( C1 )</td>
<td>36.3242</td>
<td>15.4134</td>
<td>16.7211</td>
</tr>
<tr>
<td>( C2 )</td>
<td>36.3646</td>
<td>15.4746</td>
<td>16.7125</td>
</tr>
<tr>
<td>( C3 )</td>
<td>36.2164</td>
<td>15.3293</td>
<td>16.7144</td>
</tr>
<tr>
<td>( C4 )</td>
<td>36.4033</td>
<td>15.4729</td>
<td>16.7229</td>
</tr>
<tr>
<td>( C5 )</td>
<td>36.1661</td>
<td>15.3597</td>
<td>16.7337</td>
</tr>
<tr>
<td>( C6 )</td>
<td>36.2870</td>
<td>15.4225</td>
<td>16.7106</td>
</tr>
<tr>
<td>( C7 )</td>
<td>36.4594</td>
<td>15.3082</td>
<td>16.7123</td>
</tr>
</tbody>
</table>

Table 3.4. Pb isotope analysis of human bone and dentine of a 19\textsuperscript{th} Century immigrant to Australia from Cornwall (UK) determined by TIMS. Australian \( \text{Pb}^{206}/\text{Pb}^{204} \) isotope ratio is approximately 16.71 whereas the \( \text{Pb}^{206}/\text{Pb}^{204} \) ratio for Cornwall is approximately 18.35. Errors (2\( \sigma \), \( n = 5 \)): \( \text{Pb}^{208}/\text{Pb}^{204} \) (±0.01); \( \text{Pb}^{207}/\text{Pb}^{204} \) and \( \text{Pb}^{206}/\text{Pb}^{204} \) (±0.003).
No isotopic residue of the subject's Cornish (UK) origin could be found in any of the layers of bone or dentine analysed. The study by Gulson and Gillings (1997) on modern migrant populations has indicated that \textit{in vivo} remodelling of dentine is $1 \pm 0.3\%$ per year while the estimated rate of exchange with residence time in bone relative to enamel/dentine is approximately $6\%$ per year. Since the half-life of Australian Pb in trabecular bone is 7 to 13 years (Nilsson \textit{et al.}, 1991; Christoffersson \textit{et al.}, 1986) and the individual is known to have lived in Australia for considerably less than 7 years, it can reasonably be concluded that the isotopic signature of his country of origin has been completely lost \textit{post mortem}, rather than \textit{in vivo}.

### 3.4.1. Background Lead Levels

The profiles shown in Figures 3.0 and 3.1, exhibit the same trends that have come to be expected of teeth recovered from both modern and ancient populations (Budd \textit{et al.}, 2000; Budd \textit{et al.}, 1998). However, the Pb$^{2+}$ ion concentrations in dental enamel of Pacific Island teeth are at least two times greater than in equivalent material recovered from Neolithic, north-western European populations (Budd \textit{et al.}, 2000). These measurements cast new light on the question of the 'natural' background level of Pb$^{2+}$ ions in the human body.

The consumption of minerals and burning of materials for energy production have all sharply increased the transfer of trace elements from inactive pools in the lithosphere to Pb$^{2+}$ 'reservoir' pools that are easily exchangeable between abiotic and biotic components of ecosystems. In recent times, the extent of human interference with biogeochemical cycles of trace elements has become so significant that scientists have sought to define what they have termed the anthroposphere (the portion of the biosphere that is affected by human activities) (Kabata-Pendias and Pendias, 1995). However, research into environmental Pb$^{2+}$ ion exposure limits have not, until recently, generated much research into what level of Pb$^{2+}$ ion exposure might constitute a 'natural' background limit for a population. In one sense this is surprising, as it is by no means clear whether the present exposure limits can be attained simply by reducing Pb$^{2+}$ ion output to the atmosphere. On the other hand, this lack of research reflects difficulties in obtaining sample material that is unaffected by anthropogenic Pb pollution. It is clear that the information required on background levels of biogenically derived Pb burden cannot be sought amongst present day populations.
The ubiquitous presence of Pb\(^{2+}\) ions within modern industrialised environments renders futile any search that scientists might undertake to find an individual whose life is not touched in some way by anthropogenic exposure to the element. However, as noted elsewhere, (Patterson et al., 1991; Budd et al., 2000), provided that the skeletal material is unaffected by diagenetic turnover, careful selection of archaeological material provides one means of accessing human remains that contains no anthropogenically derived Pb\(^{2+}\) ion component.

Initial studies on background Pb\(^{2+}\) ion exposure indicated that the average biogenic Pb\(^{2+}\) ion burden of ancient populations was 0.58\(\mu\)g/g (Hisanaga et al., 1988). At two times less than equivalent measurements made on modern populations, this result is roughly in line with the Arctic ice-core data showing that atmospheric Pb\(^{2+}\) ion levels have increased 200 fold since inception of extractive metallurgy in the Ancient World (Candelone et al., 1995). However, in a more recent study Budd et al., (2000) suggested that a value of (0.31 ± 0.04)\(\mu\)g/g represents a more realistic value for the background level of Pb\(^{2+}\) ions within the pre-metallurgical, European Neolithic period. This newly derived baseline value of Pb\(^{2+}\) ion exposure is at odds with the varve derived data and only just less than the Pb\(^{2+}\) ion levels determined using comparable methods within the human dental enamel of modern populations (Gulson and Gillings, 1997; Gulson, 1996; Gulson and Wilson, 1994). Using the results of their study, Budd et al., (2000) suggest that airborne emissions may not be the dominant pathway by which Pb\(^{2+}\) ions enter the human body: casting doubt on the utility of further general reductions in airborne Pb\(^{2+}\) ion exposure limits.

Of further concern, is the observation that the newly determined baseline concentration for biogenic Pb\(^{2+}\) ionic exposure is actually higher than the toxicologically determined threshold for the onset of Pb\(^{2+}\) induced health effects (Needleman, 1999): implying that the new environmental exposure thresholds 0.20\(\mu\)g/g may, in practice, be difficult to achieve. Clearly, the results of both studies cannot be correct.

The results presented in Table 3.5, rationalise the apparent discrepancy between the results of these two previous studies. Unfortunately, due to the inherent difficulties in modelling the behaviour patterns of long dead populations, neither group of researchers was able to pinpoint the source of the Pb\(^{2+}\) ion burden in their respective surveys.
The Pb$^{2+}$ ion concentrations found in dental enamel derived from Near Oceanic and Melanesian populations studies are consistently less than (0.65 ± 0.02)µg/g. However, in contrast to the mainland population studies mentioned earlier, in the case of Pacific Islanders it is possible to narrow down the factors contributing to the overall Pb$^{2+}$ ion burden of these island communities and thus determine the source of their Pb$^{2+}$ ion exposure. From the isotopic data presented in Table 3.2 we can be reasonably certain that the individuals were born and raised on the islands on which their bodies were found buried. Whilst we can never discount the possibility that as children these people undertook return lengthy journeys from islands with identical isotopic ‘signatures’ to those on which they are buried, such a scenario seems unlikely. A further possibility is that a significant proportion of the Pb$^{2+}$ ion burden found in the teeth was carried on the prevailing winds to near Oceanic islands from a mainland Asian source. Airborne Pb$^{2+}$ ion emissions are deposited near the source, although some particulate matter (less than 2µm in diameter) is transported over long distances and results in the contamination of remote sites such as arctic glaciers (Robinson, Mahaffey and Silbergeld, 1995) however it is assumed that Pb$^{3+}$ ion emissions from Asian based materials processing did not reach the islands in sufficient quantities to alter the Pb$^{2+}$ ion burden of these Oceanic communities. The probability of such airborne pollution carrying the same isotopic signature as the island geology on which the individuals were buried would likewise be

<table>
<thead>
<tr>
<th>Reference</th>
<th>Tooth Code</th>
<th>Pb Concentration (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulson and Gillings (1997)</td>
<td>517F (C)</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>517F (C-1)</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>517M (C-2)</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>H914CR</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>H915CR</td>
<td>0.18</td>
</tr>
<tr>
<td>Budd et al., (2000)</td>
<td>A$_{decid}$</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>A$_{decid}$</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>B$_{decid}$</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>B$_{perm}$</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>C$_{perm}$</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>D$_{decid}$</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>D$_{perm}$</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 3.5. Comparison of Pb$^{2+}$ ion concentrations in tooth samples: Budd et al., (2000) and Gulson and Gillings (1997).
infinitesimally small. Having eliminated the two possible extraneous sources of Pb\(^{2+}\) ion exposure, there are only two possible sources of Pb\(^{2+}\) burden for the individuals concerned, both of which are biogenic:

- The sea and its fauna, and
- Land based agricultural production and the local freshwater supply.

There are two possible sources of seaborne Pb\(^{2+}\) ion burden, which in the event that their contributions are significant, should be isotopically distinguishable. These are:

- Fish and other edible products of the island and its environs, and
- Pelagic fish.

Quite apart from the unlikelihood that pelagic fish were a dominant source of food for the islanders, there are scientific reasons to reject them as the source of Pb\(^{2+}\) ion burden for these ancient populations. Firstly, even allowing for the isotopic signature of the Pacific Ocean being heterogeneous, there seems to be no a priori reason to expect that the isotopic ‘signature’ of pelagic sea life would be isotopically indistinguishable from the islands that are the focus of the study. Furthermore, as noted by Patterson et al., (1991), the concentration of Pb\(^{2+}\) ions within mixed layer open ocean waters is insignificant when compared to that of ground waters and, after taking into account factors such as the biopurification of Pb\(^{2+}\) ions within fish, it can be stated with a degree of certainty that even if pelagic fish were a significant part of the island community’s diet, their contribution to the overall Pb\(^{2+}\) ion burden of the islanders was insignificant. The same considerations regarding biopurification pertain to the fish, shellfish and crustaceans caught off the islands’ coastlines.

It would seem from Table 3.2, that the overwhelming contribution to the Pb\(^{2+}\) ions trapped within the analysed dental enamel must have been derived from a land-based source. However, the convincing empirical evidence for biopurification of terrestrial foodstuffs furnished by Patterson et al., (1991) fails to provide a rationale for the much higher biogenic Pb\(^{2+}\) ion level observed in dental enamel of the Pacific islanders. The consistently high Pb\(^{2+}\) ion concentrations observed in the dental enamel of ancient island communities indicate that some means existed for Pb\(^{2+}\) ions to bypass the natural
purification processes and enter the bloodstream in the limited time taken for enamel to be laid down. It is suggested here that the single possible source for such a ‘high’ Pb\(^{2+}\) ion exposure for the inhabitants of these islands is the drinking water. In the case of small tropical islands this is rainwater and groundwater.

Groundwater tends to contain more dissolved material than stream water because of its more intimate and longer contact with organic material, soil and rock particles. Also it tends to be less well mixed than surface waters. Often there is a fairly direct relationship between the composition of a given groundwater and its host rock. However, this does not always hold true. Other factors include:

- Porosity and permeability of the host rock;
- Abundance and type of organic matter in the host rock, and
- Length of time since contact (of the groundwater) with the atmosphere.

Firstly for basalt/andesite the host rock is dominated by silicate and aluminosilicate minerals and these react with percolating water (saturated with CO\(_2\)). Some of the volcanic rocks also contain significant quantities of sulphides, e.g. PbS which have a different mode of reaction.

\[
PbS + 1.5O_2 + H_2O \leftrightarrow Pb^{2+} + SO_4^{2-} + 2H^+ \\
\downarrow [\text{If water is aerobic}] \\
Pb \text{ oxide/hydroxide derivatives}
\]

Similarly, the characteristics of groundwater in CO\(_3^{2-}\) host rocks is explained in terms of the following equilibria:

\[
XCO_3 + H_2CO_3 \leftrightarrow X_2+ 2HCO_3^- \\
\downarrow \\
H_2O + CO_2 \leftrightarrow H^+ + HCO_3^- 
\]

Thus the solubility of CO\(_3^{2-}\) is related to the concentration of CO\(_2\) in the water. Rainwater has a \(\rho \approx 10^{3.5}\) atm for CO\(_2\) whereas groundwater has considerably higher values (up to about 10\(^2\) atm). The solubility of CO\(_3^{2-}\) is controlled by the CO\(_2\)
concentration and whether or not the system is open ($\rho$ for CO$_2$ remains constant) or closed (no exchange of CO$_2$ with the gas phase). The solubility of CO$_3^{2-}$ is also influenced by the presence of other cations in the CO$_3^{2-}$ structure and the ionic strength and composition of the aqueous phase. The effect of ionic strength (increased solubility with increasing ionic strength) is well known. The influence of ions (for example, Pb$^{2+}$, Mg$^{2+}$) in the CO$_3^{2-}$ structure generally leads to increased solubility (Plummer and Mackenzie, 1974).

Solubility details for the various inorganic Pb(II)-anion combinations that are likely to be present and thus limit the mobility of the Pb$^{2+}$($aq$) ions in the island’s geochemical environment are presented in Table 3.6.

<table>
<thead>
<tr>
<th>Element / Compound</th>
<th>Solubility</th>
<th>Water</th>
<th>Organic solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble in glycerol, very slight in alcohol</td>
</tr>
<tr>
<td>Pb(CH$_3$COO)$_2$</td>
<td>221g/100mL at 50°C</td>
<td>Soluble in glycerol, very slight in alcohol</td>
<td></td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>0.99g/100mL at 20°C</td>
<td>Insoluble in alcohol</td>
<td></td>
</tr>
<tr>
<td>Pb(NO$_3$)$_2$</td>
<td>37.65-56.50g/100mL at 0°C</td>
<td>Soluble in alkali chlorides</td>
<td></td>
</tr>
<tr>
<td>Pb$_2$O$_4$</td>
<td>0.0010g/100mL at 20°C (Litharge)</td>
<td>1g in 2,500mL absolute alcohol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0023g/100mL at 23°C (Massicot)</td>
<td>1g in 75mL absolute methanol</td>
<td></td>
</tr>
<tr>
<td>PbSO$_4$</td>
<td>42.50mg/1. at 25°C</td>
<td>Insoluble in alcohol</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6. Solubility of Pb$^{2+}$ ions and Pb compounds (ATSDR, 1992). All normal carbonates and phosphates are insoluble except those of the Group 1 elements (H$^+$, Li$^+$, Na$^+$, K$^+$, etc.) and NH$_4^+$.

The amount of dissolved Pb$^{2+}$($aq$) ions in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground water systems, a significant fraction of Pb$^{2+}$($aq$) ions are
undissolved and occurs as precipitates (PbCO$_3$, Pb$_2$O, Pb(OH)$_2$, PbSO$_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter.

A study conducted by Budd et al., (2000) assessing the concentration of accumulated Pb$^{2+}$ ion burden using CO$_3^{2-}$ rich soils, confirmed that the availability of Pb$^{2+}$(aq) ions is controlled through the formation of complex ions and the precipitation of CO$_3^{2-}$ containing minerals such as cerrusite (PbCO$_3$). These results are also comparable to those found by Patterson et al., (1991), reproduced in Table 3.7, for the Arizona site but rejected by the authors as being contaminated with diagenetic Pb$^{2+}$ ions.

<table>
<thead>
<tr>
<th>Site</th>
<th>Bone</th>
<th>Tooth Enamel</th>
<th>Site</th>
<th>Bone</th>
<th>Tooth Enamel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malibu</td>
<td>0.056 ± 0.003</td>
<td>0.032 ± 0.002</td>
<td>0.170 ± 0.009</td>
<td>0.181 ± 0.009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.040 ± 0.002</td>
<td>0.036 ± 0.002</td>
<td>0.220 ± 0.011</td>
<td>0.078 ± 0.004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.054 ± 0.003</td>
<td>0.040 ± 0.002</td>
<td>0.230 ± 0.012</td>
<td>0.111 ± 0.006</td>
<td></td>
</tr>
<tr>
<td>Arizona</td>
<td>0.089 ± 0.004</td>
<td>0.077 ± 0.004</td>
<td>0.650 ± 0.033</td>
<td>0.143 ± 0.007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.044 ± 0.002</td>
<td>0.016 ± 0.001</td>
<td>0.160 ± 0.008</td>
<td>0.114 ± 0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.067 ± 0.003</td>
<td>0.030 ± 0.002</td>
<td>0.220 ± 0.011</td>
<td>0.203 ± 0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.047 ± 0.002</td>
<td>0.010 ± 0.001</td>
<td>0.150 ± 0.008</td>
<td>0.050 ± 0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.093 ± 0.005</td>
<td>0.090 ± 0.005</td>
<td>0.190 ± 0.010</td>
<td>0.070 ± 0.004</td>
<td></td>
</tr>
<tr>
<td>Malibu</td>
<td>0.063 ± 0.003</td>
<td>0.043 ± 0.002</td>
<td>0.470 ± 0.024</td>
<td>0.107 ± 0.005</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.7. Concentration of accumulated Pb$^{2+}$ ion concentration burden in tooth enamel and bone samples from CO$_3^{2-}$ rich burial soils (Patterson et al., 1991). All measurements are in µg/g.

In the light of the measurements presented here, and contrary to the results presented in previous studies, it would now seem that the anomalous results are not those pertaining to the measurements made on the Arizona site, but rather those derived from the excavations at Malibu, previously taken as typical of pre-metallurgical Pb$^{2+}$ ion exposure. It is impossible without detailed background information regarding the geology and water source at the Malibu site, to state with any degree of certainty what factors led to the extremely low values for accumulated Pb burden found in the human remains recovered from the site. However, if as is suggested by the anaerobic conditions
described, both the redox potential and the \( \text{CO}_3^{2-} \) ion activity within the archaeological deposit may have been low. Under such conditions the mobility of \( \text{Pb}^{2+} \text{(aq)} \) ions may not have been controlled by the presence of \( \text{CO}_3^{2-} \) containing species and could therefore have been at least an order of magnitude lower than that revealed in archaeological populations elsewhere.

Comparison of the data for dental enamel within the modern population of Broken Hill show a much larger range of \( \text{Pb}^{2+} \) ion concentrations than those found in previous studies. The individuals, all of who are life long citizens of Broken Hill, carry an enamel based dental record of \( \text{Pb}^{2+} \) ion burden of the same order of magnitude as those found in ancient Pacific Island communities. Unfortunately, privacy considerations preclude the possibility of cross correlating the data collated with factors such as age, gender or previous occupation. However it is clear from the results of the study, that it is possible for an individual living in one of the most Pb contaminated sites in the world to have a \( \text{Pb}^{2+} \) ion burden of the same magnitude as an inhabitant of the pre-industrialised world. Clearly the \( \text{Pb}^{2+} \) ion burden of any individual in the modern industrial world is not related in any simple way to the level of atmospheric \( \text{Pb}^{2+} \) ions to which they are exposed.

It may be deduced from the ubiquitous presence of \( \text{Pb}^{2+} \) ions in the environment that the inhabitants of the city are exposed to roughly the same levels of atmospheric \( \text{Pb}^{2+} \) ion exposure. However it is clear from the dentine measurements, that some inhabitants of Broken Hill receive an additional \( \text{Pb}^{2+} \) ion burden that is assimilated within the bloodstream in very high concentrations. In the atmosphere, Pb exists primarily in the form of \( \text{PbSO}_4 \) and \( \text{PbCO}_3 \) (EPA, 1986). It is possible to postulate that within modern societies in which the Pb level falling to earth as dust may pass into solution and thence enter the bloodstream in concentrations higher than ‘background’ levels. Day et al., (1979) measured the solubility (extractability) in HCl of Pb from street dust collected in two industrial cities. The authors assumed that the Pb compounds were primarily oxides and halides emitted from automobiles. Under environmental conditions, these compounds can be converted to carbonates and sulfates. A study by Barltrop and Meek (1975) examining the absorption in rats of 12 different Pb compounds following oral exposure found that the absorption of metallic Pb was lower than the absorption of Pb salts. Lead carbonate had the highest absorption, which, the authors suggest, may reflect
the greater solubility of this compound in gastric juice; the Pb\(^{2+}\) ions were relatively insoluble in water and saliva, but were 800 times more soluble in simulated gastric juice.

Therefore, in light of these findings, the results presented in this chapter confirm that the baseline Pb\(^{2+}\) ion burden of ancient human populations could be as high as \((0.65 \pm 0.02)\) \(\mu g/g\). This figure seems to represent the upper limit for biogenic Pb\(^{2+}\) ion burden in populations with no exposure to anthropogenic Pb\(^{2+}\) ions. However, in the absence of CO\(_3\)\(^{2-}\) containing complex ion species within the ground water, the background Pb\(^{2+}\) ion level for Pb exposure can be much lower. These results suggest that there is no single concentration for ‘natural’ biogenic Pb\(^{2+}\) ion exposure. The Pb\(^{2+}\) ion concentration within dental enamel does not represent a cumulative Pb\(^{2+}\) ion burden, but instead is indicative of the source of Pb\(^{2+}\) ions circulating within the body at the time that the enamel is laid down and ranges typically between 0.40 and 0.65\(\mu g/g\) (see Table Ib.6, Appendix Ib).

As mentioned earlier, toxicological research has indicated that the deleterious effects of Pb\(^{2+}\) ions on the human metabolism are visible at levels as low as 0.20\(\mu g/g\). However, the research undertaken here indicates that despite the desirability of achieving this level of Pb\(^{2+}\) ion exposure, for some communities this may not be achievable unless steps are also taken to reduce the Pb\(^{2+}\) ion content of the water supply below equilibrium levels.

3.5. Conclusion

The work presented in this chapter provides the first indications that Pb\(^{2+}\) ions trapped in micro trace quantities within dental enamel remain unaltered over long-term burial. On the other hand, it is suggested that both archaeological bone undergoes complete post-depositional turnover in the groundwater even over comparatively short periods of time (less than 100 years). The results of this pilot study into the possibilities of using dental enamel instead of bone for paleodietary and provenance studies are expanded upon in the remaining chapters of this work. However, from the outset, it is important to bear in mind that findings of Chapter 3 indicate that contra Price, Burton and Bentley (2002), Price, Manzanilla and Middleton, (2000) and Muller et al., (2002), the Sr and Pb isotope signatures of archaeological bone and dentine do not necessarily relate in any way to in vivo activities of the subject, but instead are determined by the groundwater
geochemistry at the point of burial. It is suggested that the absence of an isotopic concentration gradient across a bone does not prove that diagenetic interaction has not taken place. Diagenetic turnover of Pb\(^{2+}\)(aq) ions do not appear to occur by the same ion exchange mechanism as U\(^{2+}\)(aq) ions (Millard, 1993). Instead it appears that Pb\(^{2+}\) ions introduced into the bone from the groundwater are subsequently diffused throughout the organic matrix of the bone, removing any trace of the isotopic interface used as ‘proof’ of diagenetic turnover. Studies of ancient skeletal material have the potential to unlock many aspects of prehistoric human subsistence. However, the study of skeletal material should be approached in a manner that treats the results obtained as a priori contaminated and sets out to provide evidence that they are not, rather than the converse. Unless this is done, then the potential of this material as a research tool will be unfulfilled, and science-based archaeological research will lurch towards another crisis when it is pointed out that the postulates, upon which the archaeological conclusions rest, are overturned.

The results presented show that the importance of Pb\(^{2+}\) ion measurements on archaeological material stretches beyond science-based archaeological concerns regarding the migration patterns of ancient populations. High levels of Pb\(^{2+}\) ions in body tissue have been shown to be fatal. Many scholars in the field of health studies are now convinced that even low levels of Pb exposure can cause subacute poisoning, congenital abnormalities, learning and behavioural problems and even death. The study undertaken here strongly suggests that most human Pb\(^{2+}\) ion uptake occurs via the respiratory and gastrointestinal tract. It is assumed that (on average) about 40% of inhaled Pb\(^{2+}\) ions are absorbed from the lungs (Patterson, 1980) and then entering the circulatory system. In adults approximately 10% of ingested Pb\(^{2+}\) ions are absorbed in the gastrointestinal tract, whereas in children this percentage may reach as high as 50%. Approximately 90% of ingested Pb\(^{2+}\) ions are eliminated unabsorbed through faeces (Kehoe, 1961), whereas approximately 76% of absorbed Pb\(^{2+}\) ions are primarily excreted in urine; excretion through gastrointestinal secretions makeup approximately 16%, and hair, nails and sweat less than 8% (Rabinowitz et al., 1973). The results presented suggest that the single most important factor limiting Pb\(^{2+}\) ion absorption into the bloodstream is the solubility of Pb\(^{2+}\) ions in the fluid in which it enters the body.
4.1 Introduction

It was Hatchett in 1799 who first demonstrated that teeth, like shells and bones, were composed of lime in combination with both $\text{PO}_4^{3-}$ ions and minor quantities of $\text{CaCO}_3$ (Elliott, 1964). For many years after Hatchett’s work, it was assumed that enamel, dentine and bone consisted chiefly of $\text{Ca}_9(\text{PO}_4)_5$ in an admixture with small amounts of $\text{CaCO}_3$. According to Elliot it was Bassett in 1917 who first suggested that hydroxyapatite (HA) was precipitated during the formation of enamel, dentine and bone. This hypothesis was soon verified by the first X-Ray Diffraction (XRD) study of bone, which confirmed that the crystalline inorganic fraction of hard biological tissues and the mineral species apatite were isostructural materials (Gross, 1926; de Jong, 1926). Since 1942, it has generally been accepted that the inorganic phase of enamel, dentine and bone consists essentially of a basic calcium phosphate with an apatite structure. Despite the general consensus regarding the structure of apatite, disagreements have continued to surface in the literature particularly regarding the presence of impurities, isomorphous substituted changes, the pre- and co-existence of other calcium phosphates and the inconsistencies between the stoichiometries of biogenic and mineralogical apatites. Other structurally similar Ca-apatite structures have been studied. Fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$) was independently described more than 60 years ago by Naray-Szabo (1930) and Mehmel (1930) and the first accurate structural studies of chlorapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{Cl})_2$) were reported in the early 1970s by Mackie et al., (1972). The International Mineralogical Association (IMA) currently recognizes 18 naturally occurring mineral species (see Table 1c.1, Appendix 1c) as members of the apatite group $A\text{}_3(X\text{O}_4)_3(Z)$ where $A = \text{Ba, Ca, Cs}$,
K, La, Na, Pb and Sr while \( X = \text{As, P, Si and V with partial replacement of } \text{PO}_4 \) with \( \text{CO}_3 \) and \( Z = \text{F, Cl and OH} \) (see Figure 4.0 for an example of mineral HA).

![Figure 4.0. Mineral HA. 15x micro photo, field of view 5mm. Perry Petalite prospect, Peru, Oxford Co., Maine, USA. Source: Dick Dionne collection (www.mindat.org).](image)

The mineral fraction of dental enamel is neither chemically well defined nor isolatable as single crystals. As a result, its structure must be determined approximately by XRD using powder methods, or otherwise inferred from other spectroscopic methods and/or analogies made using inorganic HA synthesised in laboratories. Synthetic HA has customarily been taken as a proxy for human Tooth Enamel (TE) and other biological apatites. This inferred structural similarity between HA and TE is still based on the similarity of the XRD patterns first observed by Gross (1926) and de Jong (1926). Whilst for many purposes this is a perfectly adequate model, particularly since the instrumental improvements in X-Ray Powder Diffraction techniques now allow the collection of structural data that formerly depended on single-crystal XRD, these synthetic studies provide no information regarding metal ion impurities, X-Ray amorphous inorganic solid phases, or ions that are bonded to any organic molecules that may be present within biological HA. It is, for instance, impossible to infer the position of \( \text{Pb}^{2+} \) ions within HA using XRD measurements on biological hard tissues, since \( \text{Pb}^{2+} \) ions are present in concentrations too low to determine their position within the structure. Therefore, researchers have based their inferences regarding \( \text{Pb}^{2+} \) ion substitution within the HA structure on measurements made on synthetic HA (Kim et al., 1997; Suzuki, Ishigaki and Miyake, 1984). However, as pointed out in the following sections, this use of synthetic mineral phases as a proxy for biological systems fails to resolve a number of anomalies.
This chapter re-examines the syntheses of Pb substituted HA and questions how closely they replicate the behaviour of biological HA in the light of the significant observation made in Chapter 3, that the majority of Pb$^{2+}$ ions in dentine and bone are tied to the organic matrix.

4.2 Studies of Synthetic Hydroxyapatite

Numerous studies of HA and TE crystals using high resolution electron microscopy have confirmed the structural similarity of HA and enamel crystals (Ichijo, Yamashita and Akahori, 1984; Kanaya et al., 1984; Ichijo and Yamashita, 1983). It is therefore generally accepted that human TE and other biological apatites are a Ca-deficient, carbonated, HA, containing 2-5wt.% CO$_3^{2-}$ ions (Young, 1975; Elliott, 1973; LeGeros, 1981), and that the small discrepancies from the idealised structure of pure HA, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, account for any observed differences in stoichiometry, composition, crystallinity and other physical and mechanical properties. However, the Ca$^{2+}$ ion deficiency and the crystallographic departures from the ideal have been the subject of some controversy and have led some researchers to question the validity of this model for biological tissues (Young, 1974; Simpson, 1972).

The general stoichiometry of biological apatites is (Ca,$\mathcal{A}$)$_{10}$(PO$_4$)$_6$(CO$_3$)$_x$(OH,F,Cl,Z)$_2$ where $\mathcal{A}$ represents minor (Mg$^{2+}$, Na$^+$ and K$^+$) and trace (Sr$^{2+}$, Pb$^{2+}$ and Ba$^{2+}$) elements, $X$ represents HPO$_4^{2-}$, sulfates and borates and Z represents (OH$^-$, F$^-$ and Cl$^-$). The substitution of other elements for Ca$^{2+}$ and PO$_4^{3-}$ ions is a relatively minor occurrence in most naturally occurring HA mineral samples.

Mineralogical HA has hexagonal symmetry (space group $P6_3/m$, unit cell dimensions $a = 9.432\,\text{Å}$, $c = 6.881\,\text{Å}$ (Kay, Young and Posner, 1964) (see Table 1c.2, Appendix 1c for atomic coordinates). The crystal structure of this mineral can be modelled purely in terms of Ca$^{2+}$, PO$_4^{3-}$ and OH$^-$ groups. However, measurements of the unit cell dimensions of biological apatite have shown that although the $c$-axis of dental enamel is not significantly different from that of inorganic mineral samples, the $a$-axis in dental enamel is approximately 0.02Å longer (LeGeros et al., 1977; LeGeros, 1974) and the Ca/P molar ratio is approximately 1.64 compared to pure end-member mineralogical HA, which has a Ca/P ratio of 1.67.
The HA structure consists of phosphate tetrahedra that form two non-equivalent cationic sites, \((\text{Ca}_4\text{I})\text{Ca}_6\text{II}(\text{PO}_4)_6\text{OH}_2\)). The ten \(\text{Ca}^{2+}\) ions are shared between two crystallographically different symmetry sites. Calcium(I) atoms comprising four \(\text{Ca}^{2+}\) ions, \(4(f)\), are located in columns along the three fold axes at 1/3, 2/3, 0 and 2/3, 1/3, 0 positions, situated approximately halfway along the \(\varepsilon\)-axis of the unit cell. The Ca(I) atoms are bonded equidistantly to six oxygen atoms (forming a twisted prism) and to three additional oxygen atoms positioned at a longer distance. The Ca(I) atoms are therefore bonded to nine oxygen atoms attached to six different phosphate tetrahedra: linking the Ca(I) columns with channels passing through the structure in the \(\zeta\) direction. The remaining six \(\text{Ca}^{2+}\) ions referred to as Ca(II) are positioned in the centre of these two channels and are located in a position of sixfold \(6(\delta)\) symmetry, with two triangles of Ca(II) ions on the mirror planes at \(\zeta = 1/4\) and \(3/4\), rotated at \(60^\circ\) about the \(\epsilon\)-axis. Since the Ca(II) atoms are situated around the hexagonal screw axis they have an irregular seven fold coordination with six oxygen atoms from five phosphate groups. The oxygen atom from the hydroxyl group occupies the seventh site (Kay, Young and Posner, 1964) (see Figure 4.1).
Figure 4.1. HA structure. The O(IV) atom is positioned at \( z = 0.2008 \) Å above and below the Ca(II) triangle. The PO\(_4\) groups are shown as tetrahedra. Source: (Kim et al., 2000).

The crystal structure determination of HA by Kay, Young and Posner, (1964) demonstrated that the oxygen atoms of the OH groups occupy disordered positions approximately 0.3 Å either above or below the triangles formed by the Ca(II) atoms, producing a mirror plane and an hexagonal symmetry. It has been proposed that, in truth, HA is monoclinic pseudo-hexagonal with a space group \( P2_1/b \), having cell parameters \( a = 9.421 \) Å, \( b = 2a, c = 6.881 \) Å, \( \gamma = 120^\circ \), with OH\(^-\) ions stacked in a head to tail manner along the \( c \)-axis in columns, that are ‘anti-parallel’ (Elliot, Mackie and Young, 1973). It was concluded that the observed degree of disorder of the OH\(^-\) groups resulted from the presence of impurities within the structure and that consequently these dislocations can alter the OH\(^-\) ion direction within columns and establish the hexagonal symmetry noted in earlier studies.

Based on studies of synthetic apatite, the structure of HA has been said to be capable of incorporating a variety of cationic and ionic substituents (LeGeros and LeGeros, 1984).
Only three elements are said to be capable of complete solid-state substitution of Ca\(^{2+}\) ions: Pb\(^{2+}\), Sr\(^{2+}\) and Cd\(^{2+}\) ions (hereafter HA is referred to \(\alpha\)HA where \(\alpha\) is the cationic substituent). The \(\alpha\) and \(\epsilon\)-axis of SrCaHA and CdCaHA is said to vary linearly with composition, thereby satisfying Vegard’s Law (Bigi et al., 1986). Although a complete solid-state substitution series for PbCaHA is said to exist, it is also noted to deviate from Vegard’s Law (Andres-Verges et al., 1983; Verbeeck et al., 1981). The lack of Pb\(^{2+}\) ion substitution in dental enamel or indeed the naturally occurring CaHA mineral phase contrasts with these studies of synthetically produced HA and is clearly anomalous. It suggests the need for a study of the phase relationships of the Pb\(^{2+}\) solid solution series at ambient temperatures. This following study seeks to establish the limits of solid solution in dental enamel and elucidate why the complete solid solution series does not exist in nature or within the oral environment.

4.3 Experimental Method

As a means of understanding the incorporation of Pb\(^{2+}\) ions into HA and its deviation from Vegard’s Law, CaHA, PbHA and a series of PbCaHA were synthesised at different temperatures, characterised using XRD methods and the crystal structures determined by Least-Squares Refinement.

Hydroxyapatite can be synthesised by various methods (see Table 1c.3, Appendix 1c). All solution based precipitation procedures within the literature begin by adding phosphate containing solutions drop-wise to a stirred Ca\(^{2+}\) ion solution in order to control the rate of hydrolysis and thus the formation of \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\) (Akao, Aoki and Kato, 1981).

4.3.1 Synthesis and Identification of the PbHA-CaHA Solid Solution Series

\(\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2\) precipitates were prepared using a range of solutions with Pb\(^{2+}\) to Ca\(^{2+}\) ratios varying from 0 to 10 using the following equation:

\[
(10-\lambda)\text{Ca(CH}_3\text{COO})_2 + \lambda\text{Pb(CH}_3\text{COO})_2 + 8\text{NaOH + 6Na}_2\text{HPO}_4 + \text{H}_2\text{O} \rightarrow \\
\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2 + 20\text{Na(CH}_3\text{COO}) + 6\text{OH}^- + 6\text{H}^+ + \text{H}_2\text{O}
\]

Solutions were made up from \(\text{Ca(CH}_3\text{COO})_2\), \(\text{Pb(CH}_3\text{COO})_2\), \(\text{Na}_2\text{HPO}_4\) and NaOH mixed in various proportions in separate 1m\(^3\) volumetric flasks. The solutions were then
boiled to aid dissolution. The acetate solutions were added to a 3-necked round bottom flask (0.5dm³ capacity). The Na₂HPO₄ solution was added into a quick-fit dropping funnel closed by a hollow ground glass stopper. Hydroxyapatite species were produced by direct precipitation through the drop-wise addition of Na₂HPO₄ and NaOH solution to the constantly stirred acetate solution. The apparatus was de-oxygenated prior to the addition using nitrogen gas. A positive pressure of N₂(g) was maintained throughout the addition procedure by slowly bubbling the gas through the liquor throughout the whole procedure in order to prevent the formation of carbonate apatite species. The pH was maintained at 9.5 ± 0.5 by a pH-stat meter using 0.1M NaOH. All reagents were AnalR grade. The precipitate was refluxed for 18 hours to improve the homogeneity and crystallinity of the product, and allowed to slowly cool while still under a nitrogen atmosphere. The precipitate was vacuum filtered using a glass sinter and washed with Milli-Q water until the wash solutions reached pH7. The filtrate was then vacuum oven dried at 383 ± 1K to remove adsorbed water (Mayer, Wahnon and Cohen, 1979) and then calcined at various temperatures ranging from 573-1173K for several hours.

4.4 Characterisation Methods

Structural determinations were made using XRD methods. Lead and Sr isotope ratios within the solid phases were determined using TIMS (results were corroborated with MC-LAM-ICPMS). The elemental concentrations of the supernatant solutions were determined with ASV (results confirmed with GFAAS); phosphorus ion concentrations were determined using Inductively Coupled Plasma Spectroscopy (ICPS) (see Table Ic.4 in Appendix Ic for the correlation data). Sample preparations and the equipment employed for all elemental concentration determinations, except GFAAS (for Ca²⁺ ion determination) and ICPS are outlined in Chapters 3 and 4.

4.4.1 Powder X-Ray Diffraction (XRD)

All samples were ground in a pre-cleaned agate mortar and analysed using a Phillips PW1825-20 Powder Xray Diffractometer (40kV and 30mA with a Cu target) using monochromatic CuKα X-Ray radiation (1.5406Å). Data was collected in 0.02° steps; the 2θ diffraction range was 5° to 85° at a scanning speed of 15s per step. Samples were ground into a fine powder and the powder diffractometer calibrated after three sample
runs using Si NIST 640 standard. Results were analysed using TRACES processing package (Diffraction Technology Pty Ltd).

Lattice constants were calculated from the determined positions of more than fourteen of the most intense reflections via least squares refinement of cell dimensions by Cohen’s Method using the LAPOD software (Langford, 1971).

4.4.2 Graphite Furnace Atomic Absorption Spectrometry (GFAAS)
GFAAS were performed using a Varian SpectrAA-800 flame absorption/emission spectrometer with a Zeeman background corrector. Standard solutions were prepared by dissolution of apatite compounds in 0.1M ethylenediaminetetraacetic acid (EDTA) making up solutions of varying concentrations up to 10mg/g for Ca$^{2+}$ ions. The GFAAS was configured for the analyses of Ca$^{2+}$ ions using 422.7nm wavelength and an Argon atmosphere. The configurations for Pb$^{2+}$ ion analyses were those detailed in Chapter 3. All samples were analysed in triplicate except where stated otherwise.

4.4.3 Inductively Coupled Plasma Spectroscopy (ICPS)
Phosphorus analyses were performed using a Perkin-Elmer Optima 3000 Emission Spectrometer. A nitrous oxide acetylene system was used at 177.5nm wavelength. Standard solutions were prepared as described in section 4.4.2. All analyses were in triplicate.

4.4.4 Equilibrium Constant and $\Delta G^\circ$ determinations
The calcined solids formed using the methods outlined in 4.3.1, were identified using XRD methods. Excess HAP was then returned to the reserved mother liquor and the mixture was constantly stirred and maintained at 298K in a water bath and allowed to reach equilibrium (approximately 6 weeks). After 8 weeks the pH of the solutions was measured using a Radiometer pHM93 instrument fitted with a PHC2401 combination electrode and filtered using GF/F fibreglass filter paper. Concentrations of the filtrate (Ca and Pb) were measured using a Perking Elmer 3030 AAS.

From these results, total ionic species concentrations at equilibrium were calculated using the COMICS program (Perrin and Sayce, 1965) giving free concentrations of Ca$^{2+}$(aq), Pb$^{2+}$(aq) and $\text{H}_2\text{PO}_4^-$ (aq). Stability constant data were taken from the compilations of
Smith and Martell (1976). The activities of the constituent ions were calculated using the relationship,

\[ a_i = m_i \gamma \]

where \( m_i \) = molal concentration and \( \gamma \) = activity coefficient. Activity coefficients were calculated for ionic strength \( I \) using the relationship,

\[ I = 0.5 \sum c_i \zeta_i^2 \]

where \( c_i \) = concentration and \( \zeta_i \) = charge, coupled with the Debye-Huckel equation,

\[ \log \gamma = -A \zeta^2 \left( \frac{I^{0.5}}{1 + I^{0.5}} - 0.3I \right) \]

where \( A \) is a constant dependent on the temperature and dielectric constant of the solvent, having a value of 0.509 for water at 298K. The Standard Gibbs free energy of a reaction can be calculated using the relationship,

\[ \Delta G^o_{\text{reaction}} = -2.303RT \log K \]

where \( K \) = the equilibrium constant for the reaction, \( T \) = temperature and \( R \) = universal gas constant (8.314 Jmol\(^{-1}\)K\(^{-1}\))

\[ \Delta G^o_{\text{reaction}} = \Delta G^o_{(\text{products})} - \Delta G^o_{(\text{reactants})} \]

4.5 Results and Discussion

4.5.1 Characterisation Using GFAAS and ICPS

Table 4.0 shows the results of GFAAS and ICPS measurements of Ca:Pb:P made on the precipitates recovered from the various experiments calcined at 1073 ± 1K. These data confirm that to within experimental error, the solid phases formed were consistent with a PbCaHA stoichiometry of the same proportions as that of the initial acetate solutions.
Table 4.0. GFAAS determinations (Pb$^{2+}$ and Ca$^{2+}$), ICPS determinations (P), lattice parameters and unit cell volume for the whole compositional range of PbCaHA. * denotes a two phase compound.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>wt.%</th>
<th>Lattice Constants</th>
<th>Cell Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$_0$(PO$_4$)$_6$(OH)$_2$</td>
<td>n/a</td>
<td>79.99 6.78 9.863 7.392 0.749</td>
<td>622.67 0.008</td>
</tr>
<tr>
<td>Pb$_0$Ca$_3$(PO$_4$)$_6$(OH)$_2$</td>
<td>2.45</td>
<td>75.98 7.99 9.834 7.378 0.750</td>
<td>617.96 0.008</td>
</tr>
<tr>
<td>Pb$_7$Ca$_2$(PO$_4$)$_6$(OH)$_2$</td>
<td>12.41</td>
<td>72.98 9.12 9.732 7.297 0.750</td>
<td>609.83 0.007</td>
</tr>
<tr>
<td>Pb$_0$Ca$_4$(PO$_4$)$_6$(OH)$_2$</td>
<td>15.44</td>
<td>62.41 11.02 9.681 7.208 0.745</td>
<td>592.53 0.006</td>
</tr>
<tr>
<td>Pb$_0$Ca$_6$(PO$_4$)$_6$(OH)$_2$</td>
<td>20.09</td>
<td>46.11 13.58 9.632 7.151 0.742</td>
<td>578.15 0.008</td>
</tr>
<tr>
<td>Pb$_0$Ca$_7$(PO$_4$)$_6$(OH)$_2$</td>
<td>25.65</td>
<td>34.23 14.42 9.563 7.081 0.741</td>
<td>563.44 0.006</td>
</tr>
<tr>
<td>Pb$_0$Ca$_9$(PO$_4$)$_6$(OH)$_2$</td>
<td>30.91</td>
<td>14.52 16.24 9.523 6.931 0.728</td>
<td>554.21 0.006</td>
</tr>
<tr>
<td>Pb$<em>0$Ca$</em>{11}$(PO$_4$)$_6$(OH)$_2$</td>
<td>*</td>
<td>*</td>
<td>9.515 6.925 0.728</td>
</tr>
<tr>
<td>Pb$<em>0$Ca$</em>{17}$(PO$_4$)$_6$(OH)$_2$</td>
<td>34.33</td>
<td>7.85 17.19 9.471 6.933 0.732</td>
<td>545.22 0.004</td>
</tr>
<tr>
<td>Pb$<em>0$Ca$</em>{18}$(PO$_4$)$_6$(OH)$_2$</td>
<td>36.12</td>
<td>5.69 17.64 9.464 6.920 0.731</td>
<td>543.52 0.006</td>
</tr>
<tr>
<td>Pb$<em>0$Ca$</em>{19}$(PO$_4$)$_6$(OH)$_2$</td>
<td>37.91</td>
<td>4.21 17.89 9.453 6.893 0.729</td>
<td>538.43 0.003</td>
</tr>
<tr>
<td>Pb$<em>0$Ca$</em>{25}$(PO$_4$)$_6$(OH)$_2$</td>
<td>39.58</td>
<td>2.19 18.01 9.444 6.885 0.729</td>
<td>532.59 0.005</td>
</tr>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>42.12</td>
<td>n/a 19.84 9.419 6.882 0.731</td>
<td>528.68 0.004</td>
</tr>
</tbody>
</table>

4.5.2 Characterisation of Pure PbHA and CaHA using XRD

The powder diffraction patterns of calcined PbHA and CaHA have cell lattice parameters, $a = 9.863 \pm 0.008\text{Å}$ and $c = 7.392 \pm 0.008\text{Å}$ and $a = 9.419 \pm 0.004\text{Å}$ and $c = 6.882 \pm 0.004\text{Å}$, respectively. These values are in close agreement with those reported elsewhere within the literature (see Table 4.1). Since few of the reported methods of synthesis agree about the temperature and pressure of the calcining step, it is possible that minor differences in the lattice parameters reflect differential thermal expansion of the HA at high temperatures (see Figure 4.2, which shows how the lattice constants vary with the temperature of the calcining step).
<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaHA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.423</td>
<td>6.884</td>
<td>Lagergren and Carlstrom (1957)</td>
</tr>
<tr>
<td>PbHA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.890</td>
<td>7.280</td>
<td>Bhatnagar (1971)</td>
</tr>
</tbody>
</table>

**Table 4.1.** A review of the varying lattice parameters for CaHA and PbHA.
Figure 4.2. Lattice constants vary with the calcining temperature.

4.5.3 Syntheses of PbHA-CaHA Solid Solution Series
Nasaraju et al., (1972) reported that the lattice parameters of PbCaHA produced at 1073K vary linearly with the composition. This observation is confirmed in the current study (see Figure 4.3). Since according to Vegard’s Law, the unit cell parameters in a complete
solid solution series should, in theory, change linearly with composition, plots such as that produced in Figure 4.3 confirm the existence of a complete solid solution series between CaHA and PbHA in samples calcined at temperatures greater than 973K.

![Figure 4.3](image-url)  
**Figure 4.3.** Solid solution series of PbCaHA calcined at 1073K. Errors are within data points.

More recently, it has been suggested that a solid solution series calcined at 623K (Andres-Verges et al., 1983) and 373K (Bigi et al., 1991) deviates from Vegard’s Law (see Figure 4.4). However, despite what appears to be *prima facia* evidence indicating a phase change, the authors continued to interpret the change of gradient in terms of a complete solid solution series, suggesting that the discontinuity is indicative of preferential substitution of Pb$^{2+}$ ions at the sixfold Ca(II) position.
Figure 4.4. Solid solution series of PbCaHA at 623K (Andres-Verges et al., 1983) and 373K (Kim et al., 2000).

Figure 4.5 shows the lattice parameter data versus wt.% Pb in the current study for syntheses calcined at 573K. As can be seen there is a change in slope at approximately 40wt.% Pb. In similar syntheses within literature, Andres-Verges et al., (1983) reported a discontinuity at 30wt.% Pb, Bigi et al., (1991) and Kim (2000) at 50wt.% Pb, Verbeeck et al., (1981) between 20wt.% Pb and 30wt.% Pb and lastly Hadrich, Lautie and Mhiri, (2001) between 40wt.% Pb and 70wt.% Pb. Although all of these authors continued to use these curves as confirmation that a solid solution series exists, the evidence that the change of slope relates to a Pb$^{2+}$ preference for the sixfold position at Ca(II) sites is, at best, equivocal.
Figure 4.5. Lattice parameter data versus wt.% Pb obtained in the current study for syntheses calcined at 573 ± 1K. Errors are within data points.

The similarity of outer electron configurations of Ca$^{2+}$ and Pb$^{2+}$ ions, ionic radii (0.99 Å and 1.20 Å respectively), coupled with the X-Ray data confirming that CaHA and PbHa are isostructural, suggests that a solid solution series can exist between these endmembers. Inegbenebor, Thomas and Williams (1989) have claimed that a similar complete solid solution series exists between other members of the apatite group with the same space group, chlorapatite (Ca$_{10}$(PO$_4$)$_4$(Cl)$_2$) and pyromorphite (Pb$_{10}$(PO$_4$)$_6$(Cl)$_2$). However, in the case of HA, although Figure 4.3 indicates that such a sequence does exist at high temperature, it is suggested that at lower temperatures this solid solution series breaks down (see Figure 4.5). At low temperatures, deviations from Vegard’s Law become increasingly large (see Figure 4.6). Clearly, these results are anomalous and cannot be explained simply in terms of preferential solid substitution.

Figure 4.7 illustrates lattice parameter, $a$, versus wt.% Pb for syntheses calcined at 473K. The systematic increase in the lattice constants and consequent increase in the unit cell volume is plotted in Figure 4.8. Whilst the overall lattice parameter, $a$, for the complete series is linearly correlated where $y = 9.4314 \pm 0.0043x$ and the coefficient of linear
regression, $r$, is 0.9863, the lattice parameter, $c$, and volume, $V$, deviate from Vegard’s Law (Figures 4.8 (a) and (b)).

\[ \text{Figure 4.6. Lattice constant, } a, \text{ of the } \text{Ca}_{10-x}\text{Pb}_x\text{PO}_4\text{(OH)}_2 \text{ series calcined at } 473 \pm 1\text{K against wt.}\% \text{ Pb.} \]
Figure 4.7. The $\text{Ca}_{10-x}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$ series calcined at 473 ± 1K, where (a) Plot of lattice constant, $c$, versus wt.% Pb. The dashed line Pb denotes two phases at 15wt.% Pb. (b) Plot of unit cell volume ($\text{Å}^3$) against wt.% Pb. All standard deviations are within the symbols.

Although deviations from Vegard’s Law have also been reported at higher temperatures (Bigi et al., 1989; Nasaraju, Singh and Rao, 1972), the discrepancies are minor and in
general, provided that the calcining step is carried out at a temperature greater than 900K a complete solid solution series can be synthesized. According to the literature, both CaHA and PbHA break down at temperatures above 900K to produce thermally unstable species. At temperatures above 1073K, HA decomposes to produce oxyhydroxyapatite (OHA) (Chai and Ben-Nissan, 1994) and PbHA has been reported to be thermally stable to only 973K, breaking down into X-Ray amorphous compounds at temperatures between 973K and 1173K, due to the elimination of PO$_4$ (Sugiyama et al., 1999).
Figure 4.8. Lattice constant, $c$ (Å) versus wt.%Pb of synthetic PbCaHA at varying temperatures (310K to 623K) as per literature, (a) 623K: Andres-Vergas et al., (1983); (b) 373K: Bigi et al., (1991); (c) 373K: Kim et al., (2000); (d) 310K: Rao (1976).
The XRD patterns for PbCaHA produced by other workers at 473 ± 1K are reproduced in Figures 4.9 to 4.11. The compounds formed between 30-100wt.% Pb (Figures 4.10 and 4.11) were isostructural with pure end-member PbHA (Figure 4.11). In the entire range 0-100wt.% Pb, the relative intensities of the reflections did not change; however, the overall intensities and degrees of crystallinity were found to vary in direct proportion to the total concentration of Pb²⁺ ions present, in agreement with similar observations made elsewhere (Andres-Verges, 1983; LeGeros et al., 1980). The overall composition of the precipitates approximates to that of Ca₉₇₆₇Pb₃(PO₄)₅OHH₂, indicating that the Ca²⁺ ions were also present in the powder. Admixtures of end-member CaHA together and PbHA are easily distinguishable using XRD powder diffraction methods. Particularly distinctive are the reflections [211, 002, 112 and 300] (see Figure 4.12). However, it is impossible to determine on the basis of powder diffraction data for the coprecipitated phases whether the Ca²⁺ ions were incorporated into the PbHA structure or were present as an X-ray amorphous or cryptocrystalline compound of the same stoichiometry.
**Figure 4.9.** Powder XRD profiles of $Ca_{10-x}Pb_x(PO_4)_6(OH)_2$ calcined at 473K where $x$ is 0 to 0.7.
Figure 4.10. Powder XRD patterns of Ca$_{10-x}$Pb$_x$(PO$_4$)$_2$(OH)$_2$ calcined at 473K where $x$ is 1.0 to 4.5.
Figure 4.11. Powder XRD patterns of Ca_{10-x}Pb_x(PO_4)_6(OH)_2 calcined at 473K where x is 6 to 10.
Figure 4.12. X-ray powder patterns of: (a) Pure CaHA; (b) A 1:1 ratio mix of CaHA:PbHA where the arrows denote Ca peaks within the predominantly PbHA pattern and (c) Pure PbHA.
In the compositional range where 0.5<x<1, XRD powder patterns showed the presence of both broad and double peaks, indicating a miscibility gap between CaHA and PbHA, confirming that at low temperatures the complete solid solution series for CaPbHA does not exist. In an effort to determine whether the mixture of crystalline apatites was metastable or the result of incomplete recrystallisation, the calcining step was increased from 5 hours to a period of 2 weeks and mixtures formed initially at 473K were calcined a second time at 1073K. No further recrystallisation was observed, leading to the conclusion that once formed, the lattice energy of any mixture cannot be overcome.

There is a considerable history of studies indicating that a miscibility gap exists in the solid solution series of the apatite group. Lagergren and Carlstrom (1957) failed to produce a complete solid solution series of SrCaHA from aqueous solutions at 873K. Instead, their experiments produced mixtures of two apatic components and an apatite group component surrounded by other adsorbed inorganic compounds. However, these results were summarily dismissed by Collin (1959) who reasoned that: "... the pure CaHA and SrHA particles were in contact at only a relatively few points and diffusion occurred only across these few boundaries..." rendering the formation of a solid solution series, kinetically impossible. Driessens (1979) attempted to explain his analogous observations in terms of maxima in the $\Delta G_i$ of apatites within the miscibility gap. However, these results were also dismissed by Heijliger, Driessens and Verbeeck (1979) who postulated that the existence of miscibility gaps in PbCaHA compounds stemmed from an inability to properly synthesise the material. Whilst this last possibility must be accepted, it is noted that successful syntheses are highly temperature dependent and that in the experiments conducted in the current study, formation of the complete solid solution series depends on performing the initial calcining step at above circa 1073K.

The behaviour of the series CaHA-PbHA can be rationalised in terms of the thermodynamic data based upon the following equation at 298.2K:

$$Pb_5(PO_4)_3(OH)(\delta) + 5Ca^{2+}(aq) \rightarrow 5Pb^{2+}(aq) + Ca_5(PO_4)_3(OH)(\delta)$$

From the thermodynamic data obtained from the equilibration experiments, the Log $K_p$ values for CaHA and PbHA are -31 and -76.8, respectively. $\Delta G^\circ_{reaction}$ is thus 137.4kJmol$^{-1}$ and log K is equal to 2.14. It can be seen from the magnitude of the equilibrium
constant that for CaHA to form, the \(a(\text{Ca}^{2+})\) compared to \(a(\text{Pb}^{2+})\) has to be 8 times greater, suggesting that in a solution containing both anions, PbHA is more likely to form. Furthermore, it is corroborated by experiments conducted in this study, which also indicates that crystals of \(\text{Ca}_x\text{Pb}_{1-x}\text{HA}\) are confined to compositions of \(0<x<0.1\). Assuming that for compositions where the solid solution series is continuous therefore behaving ideally, it can be seen from the magnitude of the equilibrium constant that Pb can theoretically be incorporated into CaHA. However, due to the relatively low levels of available \(\text{Pb}^{2+}\) ions compared to \(\text{Ca}^{2+}\), only small amounts will dope into the lattice, limited by the poor low temperature miscibility of Pb in CaHA.

A similar observation in the \(\text{PbWO}_4\)-CaWO₄ solution series was noted by Chang (1967) and Hsu (1981) where the series was only continuous above 998K and that below this temperature there is a miscibility gap. Chang (1967) reported that this gap existed below 973K only between 2 and 98 mol\% Pb. The size of the miscibility gap observed in the CaHA-PbHA series is considerably smaller that that of the tungstate minerals, probably due to the greater solubility of phosphate ions compared with tungstate. From the thermodynamic data at 298.2K based on the equation,

\[
PbWO_4(s) + \text{Ca}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{CaWO}_4(s)
\]

\(\Delta G_\text{reaction}^0\) is 19.4 kJmol\(^{-1}\) and \(\log K = -3.39\). For scheelite to form at ambient conditions in preference to stolzite, the \(a(\text{Ca}^{2+})\) compared with that of \(a(\text{Pb}^{2+})\) has to be 2500 bigger.

In terms of oxidised zone geochemistry a complete solid solution compositional range is possible between CaHA and PbHA. However, this is a highly unlikely occurrence in view of the limit of activities in groundwater and competition from other cations that limits the formation of these minerals. In ground waters associated with oxidising deposits that contain Pb, a 10:1 \([a(\text{Ca}^{2+}):a(\text{Pb}^{2+})]\) ratio with sufficient phosphate activities is required to form plumbian CaHA under ambient conditions. In view of the relative solubilities of the two minerals in the geochemical environment, this would not seem unreasonable. However, since the concentration ratio of these cations in the geochemical environment is rarely less that 10:1 the proportions of Pb incorporated within CaHA would be extremely small (c.f. Chapter 2). Where the ratio is not large enough to meet the thermodynamic and kinetic requirements for the precipitation of
CaHA, then PbHA will form instead. However, as noted below, the formation of PbHA is further limited by the presence of Cl(aq) ions.

Suzuki, Ishigaki and Miyake (1984) have shown that the stability of HA solid solutions increased in the presence of other anions such as Cl. Furthermore, these workers also noted that CaHA, and thus the solid solution series, break down at pH 4.0, below which the solid-state products were an admixture of CaHA and PbHA. However, at pH 4.0, the solid solution could be stabilised if HCl was used to control the pH of the reaction mixture rather than HNO₃. As noted earlier, it has been suggested that a complete solid solution series exists between end member Ca₁₀(PO₄)₆(OH)₂ and Pb₁₀(PO₄)₆(OH)₂ at temperatures as low as 373K. As shown by Suzuki, Ishigaki and Miyake (1984) the presence of even small amounts of Cl ions in the reaction solutions increases the relative stability of the CaHA structure allowing its precipitation even at below pH 3.0. This observation can be rationalised using the thermodynamic data collected in this study. According to the equation:

\[
Pb₁₀(PO₄)₆(OH)₂(s) + 2H⁺(aq) + 2Cl⁻(aq) \rightarrow Pb₁₀(PO₄)₆(\text{Cl})_2(\text{s}) + 2H₂O(l)
\]

with a \( \Delta G^\text{reaction} \) of 26.3 kJmol⁻¹ and a \( \log K \) of 4.6, in geochemical environments of even mild salinity levels \( (10^4 \text{ mol.dm}^{-3}) \), the stability field for PbHA is completely obliterated by that of pyromorphite.

There is widespread acceptance that HA is not the initial solid-state product formed in precipitation reactions of the form outlined here. Ben-Nissan, Chai and Evans (1995) have shown that the crystallisation of CaHA passes through a number of poorly characterised transient, metastable solid phases prior to the formation of HA during calcination (cf. Table 4.2). At a pH greater than 7, the initial phase formed from supersaturated CaHPO₄ solutions is an unstable X-Ray amorphous calcium phosphate (ACP). This solid is rapidly converted into octacalcium phosphate (OCP) with a Ca/P ratio of 1.33, followed by its transformation into HA with a Ca/P ratio of 1.67. However, solutions with lower degrees of supersaturation are said to produce HA with extremely fine crystals without an X-Ray amorphous precursor (Moreno and Vaughese, 1981). Some workers have suggested that ACP plays a role as a transient phase or template in biomineralisation. However, as noted by Mathew and Takagi (2001) the
evidence that ACP is an integral component in hard tissues is currently equivocal. With an increase in acidity of CaHPO$_4$ solutions under ambient conditions the mineral phase dicalcium phosphate dihydrate (DCPD, or brushite) is precipitated (Nancollas, 1984).

Biological apatites are not known to form β-tricalcium phosphate (β-TCP). Nevertheless, the mineral whitlockite has been noted in many biological mineralisation processes and has a similar structure to β-TCP (Calvo and Gopal, 1975).

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>Mineral</th>
<th>Empirical Formulas</th>
<th>Ca/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicalcium phosphate dihydrate</td>
<td>DCPD</td>
<td>Brushtite</td>
<td>CaHPO$_4$2H$_2$O</td>
</tr>
<tr>
<td>Dicalcium phosphate</td>
<td>DCP</td>
<td>Monetite</td>
<td>CaHPO$_4$2H$_2$O</td>
</tr>
<tr>
<td>Octacalcium phosphate</td>
<td>OCP</td>
<td></td>
<td>Ca$_{10}$(PO$_4$)$_6$5H$_2$O</td>
</tr>
<tr>
<td>β-Tricalcium phosphate</td>
<td>β-TCP</td>
<td>Whitlockite</td>
<td>β-Ca$_3$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>CaHA</td>
<td></td>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
</tr>
<tr>
<td>Tetracalcium phosphate monoxide</td>
<td>TCPM</td>
<td></td>
<td>Ca$_4$(PO$_4$)$_3$O</td>
</tr>
<tr>
<td>Defect apatites</td>
<td></td>
<td></td>
<td>Ca$_{10+x}$(HPO$_4$)$<em>x$(PO$<em>4$)$</em>{6-x}$(OH)$</em>{2-x}$</td>
</tr>
</tbody>
</table>

Table 4.2. Calcium phosphate phases. Source: Ben-Nissan, Chai and Evans (1995).

Nancollas (1982) and LeGeros (1981) showed that stabilities of the various CaHPO$_4$ phases precipitated from solution involves a complex interplay of kinetic and thermodynamic factors, with various cations and anions capable of catalysing nucleation and growth processes without necessarily being incorporated into the crystal lattice structure of the metastable CaHPO$_4$ phases formed. The formation of these metastable minerals complicates the Ca$^{2+}$-PO$_4^{3-}$-H$_2$O system still further. From the empirical evidence it is clear that the activation energies for many of the transitions to more thermodynamically stable species are high. Where the recrystallisation processes are interrupted a state of metastable equilibrium may persist for some considerable time. In the absence of an effective catalyst such as those available in biomineralisation processes, at normal laboratory temperatures and pressures the recrystallisation rate is effectively terminated prior to the formation of crystalline HA.

It is evident from the results presented here that in addition to the thermodynamic factors discussed above, the crystalline mineral species formed after calcining depends on
the relative rates of nucleation of CaHA and PbHA and that solutions containing the latter species do not recrystallise to Pb containing CaHA at temperatures below 1073K.

CalciumHA and PbHA are both insoluble basic salts and at high temperatures both become unstable and decompose into various poorly characterised phases. Pure end-member CaHA breaks down into a number of phases at 1273K including α-TCP, β-TCP, β-CPP (β-calcium pyrophosphate) with Ca/P ratios between 1.33 and 1.50 to CaO and stoichiometric HA; Ca/P ratios between 1.50 and 1.67 (Ben-Nissan, Chai and Evans, 1995). As mentioned earlier, CaHA begins to dehydroxylate at temperatures above 1073K, decomposing to OHA, $\text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_{2}\cdot 2\cdot \text{H}_2\text{O}$, where $[]$ is a vacancy on the hydroxyl site; decomposition of OH$^-$ ions causes CaHA to decompose into a series of other poorly characterised CaHPO$_4$ species (see Table 4.3). The decrepitation of HA does not occur instantly but rather happens slowly over a wide temperature range. It is reported to depend on the partial H$_2$O pressure during heating (Liao et al., 1999). It was also noted that OHA absorbs water rapidly after cooling, forming a transient non stoichiometric compound, $\text{Ca}_{10}^{(\text{PO}_4)_{6}^{2-}}(\text{OH})_{2}\cdot 2\cdot \text{H}_2\text{O}$. The formation of this high temperature transitional phase seems to be an essential precursor to HA and it is therefore postulated that OHA plays a decisive role in the incorporation of Pb$^{2+}$ ions into the Ca based HA mineral when the solid is cooled to low temperature (Liao et al., 1999).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>298-473</td>
<td>Loss of adsorbed H$_2$O</td>
</tr>
<tr>
<td>523-823</td>
<td>2HPO$_4$$^{2-} \rightarrow$ P$_2$O$_4$$^{3-} + $ H$_2$O</td>
</tr>
<tr>
<td>823-973</td>
<td>P$_2$O$_4$$^{3-} + 2\text{OH}^- \rightarrow 2\text{PO}_4$$^{3-} + $ H$_2$O</td>
</tr>
<tr>
<td>973-1123</td>
<td>2\text{OH}^- \rightarrow \text{O}^{2-} + $ H$_2$O$^\uparrow$</td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}(\text{OH})</em>{2}\cdot 2\cdot \text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}(\text{OH})</em>{2} \rightarrow \text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}(\text{OH})</em>{1.5}\cdot \text{O}_{0.5}} + $ H$_2$O</td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}(\text{OH})</em>{2} \rightarrow \text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}(\text{OH})</em>{0.5}\cdot \text{O}_{0.75}}$</td>
</tr>
<tr>
<td>1373-1473</td>
<td>$\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}} \rightarrow 2\beta\cdot\text{Ca}</em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}} + $ Ca$_4$P$_2$O$_9$</td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}(\text{OH})</em>{2} \rightarrow 3\beta\cdot\text{Ca}_{10}^{(\text{PO}<em>4)</em>{6}^{2-}} + $ CaO + H$_2$O</td>
</tr>
<tr>
<td>1398</td>
<td>$\beta\cdot\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}} \rightarrow \alpha\cdot\text{Ca}</em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}$</td>
</tr>
<tr>
<td>1573</td>
<td>$\text{Ca}<em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}(\text{OH})</em>{2} \rightarrow 2\alpha\cdot\text{Ca}_{10}^{(\text{PO}<em>4)</em>{6}^{2-}} + $ Ca$_4$P$_2$O$_9 + $ H$_2$O</td>
</tr>
<tr>
<td>1673</td>
<td>2Ca$_3$(PO$<em>4$)$<em>2 + $ Ca$</em>{10}^{(\text{PO}<em>4)</em>{6}^{2-}}(\text{OH})</em>{2} \rightarrow 4$Ca$_4$P$_2$O$_9 + $ P$_2$O$_5 + $ H$_2$O</td>
</tr>
<tr>
<td>1843</td>
<td>Liquid Phases</td>
</tr>
<tr>
<td>1973</td>
<td>CaO</td>
</tr>
</tbody>
</table>

Table 4.3. Thermal decomposition reactions of stoichiometric apatites. Source: Ben-Nissan, Chai and Evans (1995).
4.6 Conclusion

The results produced here confirm that a miscibility gap exists in the Ca-PbHA solid solution series at low temperature (Bigi et al., 1991, 1989; Verbeeck, 1981; Narasaratju, 1972). It is clear that the degree of solid-state substitution of Ca$^{2+}$ ions into the PbHA lattice depends on two factors: the temperature of the calcining step and the relative proportions of Ca$^{2+}$(aq) and Pb$^{2+}$(aq) ions in the reaction mixture. The width of the miscibility gap changes with temperature of the calcination step and disappears when the precipitate is sintered at temperatures above 1073K. Below this temperature the relatively high rate of crystallisation of PbHA precludes the possibility of Pb substitution into CaHA phase. The precipitation of any crystalline CaHA phase would seem to depend upon Ca$^{2+}$(aq) ions predominating in the initial reaction mixture. Unless the reaction mixture was calcined at above 1073K, when the solid solution series was complete, no instance of Pb substitution into the CaHA lattice was ever observed in the experiments completed here. This indicates that at lower temperatures, the lattice energy of PbHA is too high to permit diffusion and incorporation of Ca atoms into the structure. It is clear from plots of lattice parameter versus composition of the reaction mixtures that some degree of solid-state substitution of Ca into PbHA does occur at temperatures lower than 973K. However, and in contrast to previous studies, it is unclear from the experiments whether complete incorporation of Ca is achieved, or whether the precipitates consisted of a mixture of crystalline PbHA together with an X-ray amorphous or cryptocrystalline Calcium(II) salt.

It is evident from the results presented here that the identity of any solid-state product formed after calcination depends largely on the relative rates of formation of the mineral species formed and that in the case of Ca(II) phosphate species the rate of recrystallisation to the thermodynamically stable CaHA is slow, resulting in the long term persistence of metastable phases of indeterminate structure and stoichiometry.

The existence of the miscibility gap observed in the Ca-PbHA solid solution series helps to rationalise some observations regarding the occurrences of these phases in the natural and biochemical environments. Firstly, at ambient temperatures, it seems that the degree of solid-state substitution of Pb into crystalline CaHA such as dental enamel is markedly small since PbHA is more likely to form (c.f. Chapter 3). Secondly, as shown above, in
the presence of even small amounts of halide ions, such as Cl(aq), pyromorphite is formed preferentially to PbHA at temperatures as low as 373K, which may explain why PbHA has never been observed as a naturally occurring mineral species. It is suggested that the long standing debate as to whether the PbCaHA system forms a complete solid solution series, can be rationalised in terms of variations in parameters such as pH, temperature and pressure employed during syntheses and that the final products are those determined largely by kinetic, rather than thermodynamic factors (Brown and Fulmer, 1991).
Chapter 5

Isotopic Analysis of Modern and Ancient Human Teeth by TIMS and MC-LAM-ICPMS

5.1 Introduction

Of all the classes of material found in archaeological deposits, skeletal hard tissues offer archaeologists the most direct access to evidence of past human activity. Unlike other materials, interpretation of chemical analyses of bone and teeth, relate directly to the life histories of individuals rather than collective societal groupings. They are therefore free of many of the criticisms regarding cross cultural generalisations that are often levelled at other aspects of science-based archaeological research (e.g. Thomas, 1991). Most hard tissues grow incrementally throughout the life of an organism, adding new layers of mineralised, calcified material on a daily, seasonal and annual basis, the composition of which reflects both ambient environmental chemistry and physiological condition (Hillson, 1996). Measurements made on skeletal tissues in general and teeth in particular have been shown to reflect the environmental or dietary exposure of both modern humans and animals to various trace elements (Blanusa, Ivcic and Simeon, 1990). Comparative analysis of trace element data from whole, acid digested teeth are however, problematic. As noted by Gulson and Gillings (1997), measurements of trace elemental data derived from skeletal tissues do not provide useful environmental information regarding life histories, since variations in elemental concentrations in different parts of a tooth are averaged into a single figure, thereby losing their environmental significance. Furthermore, any period of atypical environmental chemistry or physiology complicates the integrated picture of lifetime exposure presented throughout any analysis of whole teeth. Using isotopic analyses, which are measured as ratios and are therefore dimensionless, it is possible to avoid many of the structural complications encountered
when dealing with skeletal tissues. Provided that the isotopic signature survives intact over long-term burial, it should be possible to extract information relating to past Pb\textsuperscript{2+} ion exposure from any ancient skeletal tissues (Hillson, 1986). Unfortunately, the problems of diagenetic turnover have led us to reject archaeological bone as a source of such information (Chapter 3). In contrast, teeth are generally well preserved on archaeological sites and have been shown to survive leaching or contamination in buried environments (Montgomery et al., 1999).

The number of trace elements that are potential sources of environmental information regarding the life histories of modern individuals is large and the subject of a considerable literature. However, other than in exceptional circumstances (bog or glacially preserved and mummified remains) biological soft tissues do not survive long-term burial. As a result, ancient environmental information can only be obtained from elements trapped within hard tissues. Interest amongst scientists in palaeo-dietary reconstructions has focused on the isotopes of Sr and Ca (Burton, Price and Middleton 1999; Burton and Wright, 1995) and C (Tykot et al., 1996), and as a result of these investigations a considerable science-based archaeological literature now exists regarding the use of these isotopes. Unfortunately, most of the analyses to date were conducted on archaeological bone and therefore, as shown earlier, the integrity of the biogenic information contained within the material is open to question. More recently, however, a series of works by a group based at Bradford (UK) has suggested that biogenically derived Sr isotopes survive intact within dental enamel and can be used to provenance ancient individuals (Montgomery et al., 1999). In more recent papers, the same group has suggested that isotopes of oxygen (O) may also be used to furnish ancient provenance information, since like Pb\textsuperscript{2+}, its isotopic signature is also said to be overwhelmingly determined by the source of drinking water. Obviously, increasing the number of independent variables included in any study would add greatly to the precision of any provenance assignments. This chapter critically assesses the viability of Sr, Pb, O and C isotope analyses as a means of gathering provenance information from archaeologically recovered samples of dental enamel.

5.1.1 Lead Isotopes
The application of Pb isotopes in archaeology relies on interpretation of the radioactive decay series of two unstable isotopes of uranium (U), and one of thorium (Th), to three
isotopes of Pb. Provenance analysis relies on the systematics of radioactive decay and is based on the assumption that the isotopic composition of Pb is not changed by isotopic fractionation during natural low temperature processes such as biological activity and weathering.

Lead has twelve isotopes, four naturally occurring isotopes and 8 radioisotopes. The three naturally occurring isotopes are formed by the radioactive decay of $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ to $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$, whose relative abundances are approximately 24.1%, 22.1%, and 52.4%, respectively. Lead (204) is a non-radiogenic or primordial isotope, and its absolute abundance is thought to have been constant since the formation of Earth. Isotopic abundances are expressed as ratios either as $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ or as the 204-based ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, which have higher sensitivity for errors.

Lead isotope analysis offers two major advantages over other radioactive decay schemes. Firstly, the isotopes are produced by three entirely independent decay series. Secondly, Pb isotopes are stable and their relatively high mass number means that any error produced through fractionation in low temperature biological and geological environments is insignificant (Gulson and Wilson, 1994). Therefore, the assumption that Pb isotope ratios remain unaltered by natural weathering is almost certainly justified. In addition, Pb is a comparatively rare element compared with the light isotopes, whose natural abundances allow greater opportunity for the formation of ‘mixed’ isotopes from different sources (Gulson and Gillings, 1997). Lastly, isotope variations originating from heterogeneous source rocks, preferential weathering or particular rock phases, combine to produce isotopic reservoirs that are representative of the underlying local geology (Erel, Harlava and Blum, 1994).

Lead in the form of galena (PbS) is a major component in many cupriferous and all argentiferous ore deposits. Trace amounts of the element are also present within hard rock samples. The average crustal abundance of Pb$^{2+}$ is 14μg/g. The natural contribution to the Pb$^{2+}$ content and fluxes of various ecosystems overwhelmingly depends on the composition of the lithosphere, that is, the dominant geology, in any locality. The dispersion of trace elements in geochemical environments is governed by weathering and mass transport mechanisms. Therefore, trace element concentrations
including Pb$^{2+}$ ions in local host rock types determine the characteristics of neighbouring soils, sediments, plants, surface and groundwater’s.

In addition to the primary sulfides, Pb forms a number of highly insoluble secondary Pb(II) and occasional Pb(IV) alteration products in oxidised environments. The identity of the particular mineral phases formed depend upon the relative activities of the various anions stable in oxygenated environments, the redox potential, pH and occasionally the presence of other cations that may form mixed cation salts with Pb$^{2+}$ ions (see Chapter 4). The most common of the oxidised mineral species of Pb are anglesite (PbSO$_4$), cerussite (PbCO$_3$), hydrocerusite (Pb$_3$(CO$_3$)$_2$(OH)$_2$), pyromorphite (Pb$_5$(PO$_4$)$_3$Cl) and mimetite (Pb$_5$(AsO$_4$)$_3$Cl), occurrences of which are sometimes found in sufficient quantities to be of economic importance. Although, some twenty five other Pb minerals are known, these are not economically as important. Lead bearing ores are widely distributed across the world and commercial deposits are worked in over 50 countries.

Lead isotope ratios in Oceanic Island Basalts (OIBs) are generally, though not uniformly, higher than in Mid Ocean Ridge Basalts (MORBs). Nearly all oceanic basalts, including most MORBs, plot to the high $^{206}$Pb/$^{204}$Pb side of the Geochron, implying a net increase in $\mu$ (where $\mu = ^{238}$U/$^{204}$Pb) of the mantle. The study of these basalts has led to the development of mantle evolution models in which the depleted upper mantle can be envisaged as an open system periodically replenished by plumes carrying the previously incubated chemical signatures of ancient recycled oceanic crust to the uppermost mantle level (e.g. White, 1993). This would explain both the discrepancy between the present Th/U and U/Pb in depleted mantle and the corresponding time integrated ratios inferred from Pb isotope signatures (White, 1993). There are systematic differences in isotopic composition between MORB and OIB. There are at least two major reservoirs in the mantle. The conventional interpretation is that MORBs are derived from the uppermost mantle, which is the more Pb$^{2+}$ depleted of the reservoirs implicated in oceanic volcanism. Most of the geochemistry of the MORB source can be described in terms of depletion of incompatible elements due to partial melting and removal from the melt. Oceanic islands are thought to be surface manifestations of mantle plumes which rise from the deeper mantle.
5.1.2 Strontium Isotopes

Rubidium (Rb) $^{87}\text{Rb}$ decays by beta particle emission to $^{87}\text{Sr}$. Rubidium is a highly soluble element, incompatible in mafic and particularly ultramafic systems. Strontium is also relatively soluble but is less incompatible, however, is relatively compatible in silica rich igneous systems, partitioning preferentially into plagioclase. Strontium ratios have been used to interpret the genesis of igneous rock suites. During initial differentiation of the molten Earth, due to its tendency to substitute for potassium (K) in crystallising minerals such as micas and alkali feldspars, Rb would have been enriched in crustal material. Due to its ability to substitute for Ca$^{2+}$ ion species in more mafic minerals, the daughter isotope of $^{87}\text{Rb}$ (the Sr$^{2+}$ cation) is more uniformly distributed in both the mantle and crust. Both elements are lithophiles. However, Sr is more abundant in the mantle relative to its parent Rb. Over time crustal rocks will contain increasing amounts of radiogenic $^{87}\text{Sr}$ relative to mantle rocks. The production of radiogenic Sr is expressed as a ratio relative to a reference isotope $^{86}\text{Sr}$ using the following equation:

$$
^{87}\text{Sr}/^{86}\text{Sr} = (\frac{^{87}\text{Sr}}{^{86}\text{Sr}})_{\text{initial}} + (\frac{^{87}\text{Sr}}{^{86}\text{Sr}})_{\text{radiogenic}} \times (e^{\lambda t} - 1)
$$

(5.1)

By plotting $^{87}\text{Rb}/^{86}\text{Sr}$ verses $^{87}\text{Sr}/^{86}\text{Sr}$, equation 5.1 is expressed as a straight line, where the term $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{initial}}$ is the $y$-intercept corresponding to Basaltic Achondrite Best Initial (BABI) values for achondrite meteorites, which provide an estimate of the initial Sr isotope composition of the earth when it formed out of the solar nebula. The slope of this line is proportional to the amount of time the rock has remained in a closed system with respect to Rb and Sr. Provided that melting occurs under equilibrium conditions, primary magma should inherit the isotopic signature of the mantle source. Analyses of recently formed MORBs show ratios ranging from 0.704 to 0.707 with most around 0.705. In magma generated in the upper crust or contaminated by significant volumes of crustal material the ratio would be greater than 0.707. Some granite has ratios that are near those of basalt. This is taken to as an indication that particular granite is probably a differentiated product formed from mantle derived basalt. Other granite, however, have much higher ratios (as large as 0.730), signifying that they were derived from pre-existing crustal material. However, the majority of granite fall in the range 0.707 to 0.712, indicative of some degree of interaction between mantle derived magmas and crustal rocks in the formation processes. Overall, as a result of these formation processes, the mantle has a relatively uniform and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, whereas the continental crust has a
much more variable, and on average, higher ratio.

5.1.3 Oxygen and Carbon Isotopes

Oxygen isotope ratios are said to provide indicators of the origins of chemical and isotopic heterogeneity in the mantle sources of basaltic lavas. The value of $\delta^{18}O$ in apatite phases is regarded as less prone to post depositional isotopic exchange than O contained within carbonates. It is postulated, therefore, that the $\delta^{18}O$ in apatite minerals mirror the values of precipitating fluids in sedimentary, igneous or metamorphic processes and of body fluids in biological systems. The O isotope ratio in the body's fluid is said to be determined by the value of local drinking water, which in turn depends upon that found in rainfall. Oxygen-18 values found at any locality will therefore vary depending on the local climate, latitude, altitude and distance from the sea.

Since its isotopic composition is modified by processes occurring at relatively low temperatures in the hydrosphere and in fluid rich systems in the crust, $\delta^{18}O$ measurements are used as reliable tracers of subducted material. Interactions with the hydrosphere create large variations in the $^{18}O/^{16}O$ ratio found in the oceanic crust and associated sediments. In layered dike sequences, pillow basalts, and sediments at the top of the subducted crustal section, these interactions either lead to the crustal values becoming strongly $\delta^{18}O$ enriched by alteration and low temperature exchange (less than 573K), or else moderately $\delta^{18}O$ depleted by high temperature exchange with sea water in the gabbroic lower crust. These large variations in $\delta^{18}O$ within subducted material should generate measurable $\delta^{18}O$ variations in OIBs. Oxygen isotope measurements can, in principle (and in a relatively straightforward manner), be used to quantify crustal contributions to mantle sources. Since the concentration of O is similar in all rocks, O isotopes provide an indicator of crustal recycling.

Eiler et al., (1996) surveyed fifty seven ocean island basalts covering the significant mantle reservoirs previously documented using studies of radiogenic isotopes (e.g. EM1, EM2, HIMU, high and low $^3He/^4He$). They identified significant correlations between O and radiogenic isotope ratios. Their measurements showed that EM2 basalts are enriched in $\delta^{18}O$ relative to normal upper mantle, consistent with the presence of subducted

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* EM – Enriched Mantle; HIMU – High $\mu$
sediiments in their sources. Furthermore $^{87}\text{Sr}/^{86}\text{Sr}$ is positively correlated with $\delta^{18}\text{O}$ among all OIBs. Lastly, they showed that HIMU lavas and lavas with low $^3\text{He}/^4\text{He}$ ratios are often depleted in $\delta^{18}\text{O}$ relative to normal upper mantle. This is consistent with the presence of recycled lower oceanic crust within this material.

Although O isotope measurements are used as an indicator for elucidating the chemical evolution of the mantle sources of OIBs, questions still remain regarding their effectiveness as a sourcing method in archaeologically derived remains. Firstly our understanding of O isotope fractionation in the buried environment is rudimentary. The possibility of exchange of O between phosphate minerals and ground waters is said to be unlikely. However, this has never been proved. Furthermore, the isotopic ratio of water falling as rainwater will be affected by a number of climatic factors including:

1) Global fluctuations in $\delta^{18}\text{O}$ as water becomes trapped within ice sheets;
2) Re-homogenisation of snow/ice due to melting/refreezing;
3) Vertical air movement, and
4) Changes in atmospheric air circulation patterns will certainly affect the sources/paths of atmospheric moisture falling as rain.

However, none of these factors can be determined with any degree of certainty for past environments.

In principle, it might be possible to obtain a measurement of biogenic significance from measurements of the stable isotopes of C ($^{13}\text{C}/^{12}\text{C}$). Stable C isotope measurements have previously been used within science-based archaeology to derive palaeodietary information (Schutkowski et al., 1999). However, as with the O isotopes, the degree of interaction and exchange between organic compounds within the geochemical environment is completely unknown. Statements to the effect that C within samples of dental enamel (which also have low organic content) are unaffected by diagenetic turnover would be based on little more than faith. Indeed, as noted earlier, in the only known study of this problem, (Child, Gillard and Pollard, 1993) it was shown that the organic component of dental enamel was affected by microbiological activity soon after burial and that the changes occurring were unpredictable. Until such time as our knowledge of geochemical environments improves, there seems little hope of extracting
reliable biogenically derived information from ancient skeletal tissues (inorganic fraction) using measurements of the stable isotopes of O and C.

5.2 Analytical Methods

Strontium isotope ratios were determined using TIMS in fully automatic mode and corroborated using MC-LAM-ICPMS. Strontium concentrations were measured with LAM-ICPMS and verified using GFAAS (see Table 1.1, Appendix 1).

5.2.1 TIMS Sample Preparation

TIMS sample preparation is discussed in Chapter 3 while section 5.2.1.1 discusses Sr isotope analysis.

5.2.1.1 Strontium Analysis

Strontium samples were loaded onto an outgassed single tantalum (Ta) filament. Blanks were less than 350 μg, with reference standards throughout the course of analysis averaging values of $^{87}$Sr/$^{86}$Sr 0.710192 ± 0.000026 (2σ, n = 6) for the NBS987 standard. Strontium isotope ratios were normalised during run time to 0.1194 (Royse, Kempton and Darbyshire, 1998) and minimum uncertainties were calculated from external precisions of standard measurements at 12 μg/g. Sample data are reported relative to the accepted value of NBS987 of 0.710235. In view of the possibilities of sample contamination from laboratory preparations, blank runs were performed. The mean Sr blank was 162 μg (range 51 – 350 μg, n = 10), well within the expected range. Concentrations for enamel Sr$^{2+}$ ions were commonly between 70 – 420 μg/g in samples weighing 15 – 155mg. Consequently, the average blank contribution of $^{87}$Sr/$^{86}$Sr ratio was ±0.000116 (±0.012%), a relatively insignificant contribution, therefore corrections were not necessary.

5.2.2 LAM-ICPMS Sample Preparation

Sample preparation is examined in detail in Chapter 3 Section 3.2.2.2.

5.2.3 MC-LAM-ICPMS Sample Preparation

Sample preparation is discussed in detail in Chapter 3 Section 3.2.2.3.
5.2.4 GFAAS Sample Preparation

Sample preparation is discussed in detail in Chapter 3 Section 3.2.2.5.

5.3 Results and Discussion

The South Pacific is anomalous in terms of the Sr and Pb isotope ratios of its hot spot basalts, a thermally enhanced lithosphere and possibly a hotter mantle. Staudigel et al., (1991) studied the Sr and Pb isotope characteristics of twelve Cretaceous seamounts in the Marshall and Wake seamount groups (western Pacific Ocean) that originated in the South Pacific Isotopic and Thermal Anomaly (SOPITA). The range and values of isotope ratios of the Cretaceous seamount data coincide with SOPITA; the northern part is dominated by EM, Samoa, Tahiti and Marquesas and the southern part by HIMU, Cook/Austral and Foundation chains. These define two major mantle components suggesting that isotopically extreme lavas have been produced at SOPITA for at least 120Ma. Shallow bathymetry and weakened lithosphere beneath some of the seamounts studied suggests that at least some of the thermal effects prevailed during the Cretaceous as well. It was suggested that the lithosphere in the eastern and central SOPITA appears to have lost its original depleted mantle characteristics, probably due to enhanced plume/lithosphere interaction, and it is dominated by isotopic compositions derived from plume materials.

Studies by Spooner et al., (1977) of zeolite- to amphibolite-facies altered basalts on Cyprus, showed that \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios were increased relative to fresh basalts and gabbros. Similar results have been obtained on altered ocean basalts. High \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in altered mineral products can be leached away in dilute acid so that unaltered minerals yield the original magmatic Sr isotope ratios. Spooner et al., (1977) suggested that interchange of seawater Sr with ocean crust Sr occurs during hydrothermal circulation and may buffer Sr isotope composition of seawater:

\[
\begin{align*}
\frac{^{87}\text{Sr}}{^{86}\text{Sr}} & \\
\text{Fresh Ocean Crust Average} & = 0.703 \\
\text{Seawater Average} & = 0.709 \\
\text{Continental Rocks} & > 0.712
\end{align*}
\]
There is considerable variation in $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater with time that can be linked to varying plate activity. Altered oceanic crust which is subducted at Benioff Zones may modify the isotopic composition of island arc magmas from “normal” mantle values. The hydrous fluids driven off as the subducting slab heats up as it goes down subduction zones will be enriched in the heavier isotope of these elements. Therefore it is not surprising that island arc magmas differ in their isotopic ratios from other mantle derived igneous rocks. Spooner et al., (1977) also showed that O isotope ratio values in the Troodos Complex and other Mediterranean ophiolites were higher ($\delta^{18}\text{O} = \text{cira } 9$) than in fresh ‘mantle derived’ basalts ($\delta^{18}\text{O} = 6$) and were consistent with alteration by seawater at high temperatures of $\text{cira } 623\text{K}$. Interestingly, because O is the most abundant element in any rock, it is necessary to exchange almost all the O in the rock to significantly change the isotopic ratio. Therefore, large volumes of seawater must interact with ocean crust at spreading centres, implying that if O can be exchanged on this scale then many other elements can be changed also. For example, Heaton and Sheppard (1977) showed that the isotopic composition of hydrogen (H) in water in equilibrium with chlorite and amphibolite from altered dykes from Cyprus was indistinguishable from that of seawater.

Alternatively, along the Pacific spreading system, with the exception of Gorda and Juan de Fuca Ridges, there is good agreement between the positive and negative Sr and Pb distributions. Positive and negative values are generally well distributed on either side of a boundary located at 25°S (Eastern microplate) (see Figure 5.0), delineating two large-scale provinces. The southern province extends from the Australian Antarctic Discordance (AAD) up to 25°S including the north Chile ridge, whereas the northern province encompasses the East Pacific Rise (EPR) north of 25°S and the Galapagos spreading centre. The southern domain is defined assuming that the intervening unsampled portions of the EPR, Pacific Antarctic Ridge (PAR) and Southeast Indian Ridge (SEIR) exhibit coherent isotope signature. In the southern province, the main exceptions to the systematics occur principally along the PAR near 54°S, where the Hollister ridge is known to interact with the PAR, and along the south Chile ridge near 46°S, where the source of basalt is suspected to be contaminated by the nearby subduction zone and not due to seawater.
A large-scale division of the Pacific mantle exists; northern MORB on average have higher Sr and lower Pb isotopic ratios \((0.70257 \pm 0.00026 (2\sigma); 18.39 \pm 0.37 (2\sigma))\) than their southern counterpart \((0.70248 \pm 0.00022 (2\sigma); 18.51 \pm 0.48 (2\sigma))\) (Vlastelic \textit{et al.}, 1999). However in general the Pacific N-MORB has lower \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios and higher \(^{206}\text{Pb}/^{204}\text{Pb}\) than the mid-Atlantic N-MORB (White, Hofmann and Puchelt, 1987). Overall, Sr isotope ratios steeply increase in alkaline rocks \((0.7024 \text{ to } 0.7046)\) and Sr isotope ratios values for the Pacific as a whole give little meaning to discussions of ‘average Pacific basalts’.
The Sr isotope ratios plotted in Figure 5.1 are typical for the Pacific region and for pure, mantle derived, hydrothermal fluids (estimated at 0.7035; Albarede et al., 1981). Unlike the basalts of Cyprus, within Pacific basalts there is no sign of any seawater Sr interaction. From Figure 5.1, it is obvious that provenance analysis within the Pacific region on the basis of Sr isotope ratios is an extremely difficult enterprise. Most island groupings, other than Samoa, are tightly grouped around a single ratio, and whilst ‘outliers’ might be distinguishable from local inhabitants on individual islands, there is little hope of sourcing the island of origin for these individuals on the basis of Sr isotope measurements. Although Montgomery (2002) has used Sr isotopes for provenancing archaeologically
derived tooth samples from sites in Great Britain, success in this case was based upon the highly variable underlying geology of the British Isles. The Sr isotope ratios of the Pacific basalts do not vary sufficiently to allow provenance analysis within Oceania, other than in the negative sense of determining that an individual was not born on the island where they were buried.

5.3.1 Strontium Isotope Analysis of Ancient Pacific Island Tooth Enamel
Sr isotope measurements were made on the archaeological materials from the two case studies (see Chapters 6 and 7) in the hope that the isotopic ratio might provide a useful ‘characterisation’ of the subjects. Results of the tooth enamel analyses from the Island of Tongatapu (Polynesia) and Buka (Melanesia) are presented in Table 5.0. Strontium tooth enamel concentrations for Tongatapu (denoted AT#) range between 82.13 ± 2.46µg/g and 418.60 ± 25.12µg/g. They are therefore significantly lower than that of the bedrock samples of 128 to 737µg/g (Turner, 1997; Ewart et al., 1998; Loock et al., 1990). There is no linear correlation between Sr concentrations and \( \frac{\text{Sr}}{86}\text{Sr} \) ratios (as indicated by the Pearson correlation coefficient \( r = 0.050 \)), there is a very weak negative correlation. The \( p \)-value is equal to 0.906 and therefore a straight line model is not useful for describing the relationship between \( \text{Sr}^{2+} \) ion concentration and \( \frac{\text{Sr}}{86}\text{Sr} \) ratios. Regression accounts for only 0.20% of the variation in \( \text{Sr}^{2+} \) ion concentrations.

Strontium tooth enamel concentrations for the Island of Buka are also significantly lower than those of the local bedrock basalt, in some instances by as much as two orders of magnitude\((69.45 ± 1.74µg/g to 324.95 ± 13.00µg/g)\) (Woodhead unpublished data, 2002). These samples also show a weak negative correlation between \( \text{Sr}^{2+} \) ion concentration and \( \frac{\text{Sr}}{86}\text{Sr} \) ratio; \( r = -0.246, p = 0.465 \) and \( r' = 0.061 \) where regression accounts for 6.1% of the variation in \( \text{Sr}^{2+} \) ion concentrations. No significance can be attached to either of these correlations.

The \( \text{Sr}^{2+} \) ion concentrations and the isotope ratios in groundwater, soil, plants and animals, vary as a function of the local geology (Faure, 1986). Although \( \text{Sr}^{2+} \) ion concentrations in plant and animal tissue fluctuate with trophic position, due to the very small relative mass differences of the Sr isotopes (m = 84, 86, 87 and 88) the isotopic composition of Sr is not significantly fractionated either by biological processes or during Sr transport in any ecosystem (Graustein, 1989). As noted earlier, variations in the
Earth’s bulk composition affecting \(^{87}\text{Rb}/^{86}\text{Sr}\) ratios are sufficient to constitute measurable differences in \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios over the planet’s surface. For sedentary populations, the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio in hard tissues should therefore match the Sr isotopic composition of their local habitat.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr}) ((\mu g/g))</th>
<th>Sample</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr}) ((\mu g/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(AT)1</td>
<td>0.70338 ± 0.000026</td>
<td>(AB)1</td>
<td>0.70435 ± 0.000026</td>
</tr>
<tr>
<td>(AT)2</td>
<td>0.70344 ± 0.000026</td>
<td>(AB)2</td>
<td>0.70371 ± 0.000026</td>
</tr>
<tr>
<td>(AT)3</td>
<td>0.70311 ± 0.000026</td>
<td>(AB)4</td>
<td>0.70389 ± 0.000026</td>
</tr>
<tr>
<td>(AT)4</td>
<td>0.70365 ± 0.000026</td>
<td>(AB)5</td>
<td>0.70327 ± 0.000026</td>
</tr>
<tr>
<td>(AT)5</td>
<td>0.70352 ± 0.000026</td>
<td>(AB)6</td>
<td>0.70314 ± 0.000026</td>
</tr>
<tr>
<td>(AT)8</td>
<td>0.70354 ± 0.000026</td>
<td>(AB)7</td>
<td>0.70359 ± 0.000026</td>
</tr>
<tr>
<td>(AT)11</td>
<td>0.70358 ± 0.000026</td>
<td>(AB)8</td>
<td>0.70366 ± 0.000026</td>
</tr>
<tr>
<td>(AT)12</td>
<td>0.70347 ± 0.000026</td>
<td>(AB)12</td>
<td>0.70364 ± 0.000026</td>
</tr>
<tr>
<td>(AT)13</td>
<td>0.70361 ± 0.000026</td>
<td>(AB)17</td>
<td>0.70368 ± 0.000026</td>
</tr>
<tr>
<td>(AT)14</td>
<td>0.70353 ± 0.000026</td>
<td>(AB)26</td>
<td>0.70363 ± 0.000026</td>
</tr>
<tr>
<td>(AT)15</td>
<td>0.70357 ± 0.000026</td>
<td>(AB)27</td>
<td>0.70363 ± 0.000026</td>
</tr>
<tr>
<td>(AT)16</td>
<td>0.70437 ± 0.000026</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.0. \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratios and \(\text{Sr}^{2+}\) ion concentrations of Tongatapu (\(AT\)#) and Buka (\(AB\)#) tooth enamel samples. Isotope errors (2\(\sigma\), \(n = 6\)) ±0.000026 for \(^{87}\text{Sr}/^{86}\text{Sr}\).

The majority of tooth enamel \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratios from the Island of Tongatapu (Table 5.0; Figure 5.2a) fall between 0.70338 and 0.70365 while the mean \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio for tooth enamel samples is 0.70355, comparable with that of the mean for the local basalt bedrock samples and that of the local water supply (0.70381). Furthermore, the Sr isotope ratios, from all the individuals from Tongatapu, including the two most distant from the mean, are compatible with the underlying bedrock of the island. The significance of the ‘outliers’ is discussed in chapter 7.

The results obtained from Buka (see Table 5.0; Figure 5.2b) are remarkably similar. The majority of samples closely match the isotopic signature to the island in close proximity to where they were found, and in fact are more tightly grouped than the data obtained from Tongatapu.
Figure 5.2. Plot of Sr\textsuperscript{2+} ion concentration (µg/g) versus \(^{87}\text{Sr}/^{86}\text{Sr}\) of Pacific Island tooth enamel samples compared with local bedrock basalt (dashed ring: Woodhead unpublished data, (2002)); (a) Tonga Island, and (b) Buka Island, North Solomon Islands. Tooth enamel errors for \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios are ±0.000026 (2\(\sigma\); \(n = 6\)) (Errors are within symbols).
Comparison of the isotopic data presented in Figures 5.2a and 5.2b highlights the difficulties in discussing provenance on the basis of Sr isotope ratios. Although both islands are a few thousand kilometres apart, they are indistinguishable on the basis of Sr isotope measurements. Of the eleven Buka enamel samples (Figure 5.2b), eight are clustered within the local bedrock basalt isotopic field and a further one falls just outside of the range for this field. The remaining three samples are considered as outliers.

Although the samples from Buka show none of the variation in Sr\(^{2+}\) ion concentration seen within the Tongatapu samples, it is uncertain what significance if any, could be attached to this observation if the samples were not also tightly grouped in terms of their isotopic signature. The Sr\(^{2+}\) ion concentrations in the Tongatapu samples would seem to indicate that in childhood these individuals were involved in some practices that were different to those of other individuals. Previous studies have suggested that Sr\(^{2+}\) ion concentrations in calcified tissues can be used as an indicator of past diets (Toots and Voorhies, 1965; Sillen and Kavanaugh, 1982). According to these workers, high Sr\(^{2+}\) ion concentrations in hard tissues are a consequence of high Ca\(^{2+}\) diets. In archaeological terms it seems reasonable to infer that a high Sr\(^{2+}\) ion concentration is reflective of a diet rich in plant food sources such as nuts and seeds, whereas low Sr\(^{2+}\) ion concentrations may reflect a greater emphasis on meat intake or other food sources low in Ca\(^{2+}\) ions. However in the case of Tongatapu, where the concentrations of Sr\(^{2+}\) ions of four individuals are between two and four times higher than that in the local water supply (approx. 100\(\mu\)g/g), possibly due to local isolated variations in bedrock or soil concentrations or the more likely, that there is no correlation between samples and the environment.

It is suggested that possible geological variations in Sr\(^{2+}\) ion concentrations must be discounted first, before any palaeo-dietary information can be inferred. Unfortunately, in the absence of other information regarding the individual inhumations or their \textit{in vivo} practices, it is impossible to ascertain what might have caused these individuals to accumulate anomalously high levels of Sr\(^{2+}\).

Some researchers have suggested that local variations in Sr isotope signatures can be used to trace the migration patterns of animals \textit{via} measurements made on the various hard tissues formed at specific stages of its life cycle (Price, Grupe and Schroter, 1994; Price \textit{et
Ezzo, Johnson and Price (1997) have pushed this idea still further by suggesting that it is possible to provenance human migrants to a particular locality using Sr isotope data. Whatever the veracity of these conclusions, it is clear that within Oceania, any provenance determinations made on the basis of Sr isotope measurements is only possible in the negative sense of identifying individuals that were not born on a particular island. Furthermore, as shown in Figures 5.2a and 5.2b, considerable caution must be exercised before drawing even this conclusion. As a result of the natural variation in the isotopic signature of soil, any cut-off value introduced in order to distinguish migrants is necessarily regionally specific and somewhat arbitrary. A number of studies have reported considerable Sr isotopic variability within individual volcanic centres of the ocean islands (Duncan et al., 1986; Wright and White, 1987). It has been proposed by Woodhead and McCulloch (1989) that any large-scale Sr isotopic variations within the source need not be associated with shifts in the major and trace element chemistry of the eruptive products. Instead, the variations may be enforced by sources with distinctive melting histories. It was concluded that extreme isotopic variations can occur over relatively small scale lengths (approximately 10km), therefore placing severe constraints on any petrogenetic model that uses Sr isotopes. Paradoxically, Grupe et al., (1997) maintain that although geochemical differences in $^{87}$Sr/$^{86}$Sr ratios can be small, they are in fact highly significant in terms of provenance. They argue that since modern mass spectrometers have a measurement error of approximately ±0.00003 and ±0.00001, for Sr isotope ratios a difference of 0.001 (0.710 to 0.709) is the equivalence of 33.3 and 100 measurement units, and therefore constitutes a significant isotopic shift. What is notable is that the isotopic signatures of the majority of individuals found at both the Tongatapu and Buka sites are extremely tightly grouped around a value, which corresponds to the average isotopic ratio for the water supply. This result is suggestive of groups living in a single locality and drawing their predominant source of accumulated Sr$^{2+}$ ions from a single source. This intriguing coincidence is discussed in more detail in Chapters 6 and 7.

5.4 Conclusion

It is clear from the foregoing discussion that of all the possible isotopic systems suggested as potential sources of provenance or palaeo-dietary information, only Pb isotope analysis is suitable for use within Pacific Archaeology. Strontium isotope analysis, which has been
suggested as a source of both palaeo-dietary and provenance information elsewhere, is not suitable, at least as a stand-alone means of determining provenance. The natural variation in isotopic signatures between islands is insufficient to determine which island is the source of ‘outliers’ (see Chapter 1). Similar considerations pertain to the study of stable O and C isotopes in inorganic fractions. In the case of these elements the degrees of fractionation, natural variation in isotope signature and diagenetic interaction in buried environments have yet to be determined.
Chapter 6

Provenance Studies
Case Study I: Sohano Rock Shelter-Buka Island-North Solomons-PNG

6.1 Introduction
As noted in Chapter 1 the rationale for this application of Pb isotope analysis within Oceania is provided by the studies undertaken by Woodhead and Weisler (1997) and Weisler and Woodhead (1995) who in an attempt to elucidate the exchange systems of Eastern Polynesia where ‘typical’ trade items such as obsidian or ceramics may be absent, have focused their provenance based research on the Pb isotopes contained within the relatively abundant fine grained basalt adzes and other tools (Weisler, Kirch and Endicott, 1994). A significant number of islands of Oceania are constituted as fine grained basalt outcrops (islands). Early provenance studies were based on a simple procedure: the presence of basalt artifacts on non-volcanic coral atolls providing instant confirmation of inter-island communication (Best, 1988). In an attempt to extend the uses of basalt artifacts for provenance studies, some researchers have suggested that petrologic examination could be used as the basis of a method for distinguishing between individual island basalts (for example, Poulsen, 1987). However, Weisler (1993a, b, 1990) pointed out that within Oceania many island basalts are formed in geologically similar settings, rendering any attempt at provenance analysis on the basis of basalt petrology almost impossible. Weisler and Kirch (1996) demonstrated that the use of the non-destructive Energy-Dispersive X-ray Fluorescence (EDXRF) technique to Polynesian artefacts made from basalts is effective in discriminating large numbers of fine-grained basalt artefacts into geochemical groups, but its efficacy being somewhat enhanced when used with other techniques. In an attempt to overcome difficulties, Weisler and Woodhead (1995) proposed Pb isotope analysis as a means of greatly differentiating between basalt sources. Although the basaltic outcrops of the Pacific formed in geologically similar ways, they did
not erupt contemporaneously. Therefore, in principle, it is possible to employ isotopic analysis as a means of providing a geological date for the eruption that led to the island’s formation (Faure, 1986). Using the database of Pb isotope measurements for Oceanic island groupings, Weisler and Woodhead (1995), began a study of the movement of basalt adzes from their geologic sources to their eventual deposition within archaeological deposits. Their successful application of Pb isotopes within Pacific Archaeology was based on the fact that the parent/daughter isotopic ratios represented in the mantle source vary as a function of variations in basaltic rocks from the ocean basins. The studies conducted by Weisler and Woodhead on islands of Polynesia show that they have a sufficiently diverse range of isotopic compositions to form the basis of a tool for provenance analysis.

In isotopic terms, the island archipelagos are constituted as discrete blocks, whose isotopic signatures should, in theory, be distinguishable from one island to another. Unfortunately, this is not always the case. Overlap between source fields remains a problem with any isotope based provenancing method, and in this application, the parallel nature of the fractionation histories of most oceanic islands places a limit on the degree of discrimination between possible sources (Weisler and Woodhead, 1995). A further difficulty lies with the island Pb isotope database, compiled in order to determine the overall age of various island arcs. The number of individual measurements used to define each island is currently relatively small and heavily weighted in favour of islands with significant mineral resources. Therefore the picture that analyses provide of the overall isotopic variation of island groups is incomplete. Although it is possible to determine the movement of portable material culture at the inter-archipelago level, more precise determinations of provenance are, as yet, beyond the capabilities of the database. In spite of these difficulties, the studies of Weisler and Woodhead (1995) demonstrate that Pb isotope analysis can be a powerful addition to the science-based tools used to study the archaeology of remote Oceania. This chapter explores the possibility of extending the application of Pb isotope analysis to provenance studies within the Pacific region in general.

Despite the sometimes heated debates between archaeologists working in Pacific Archaeology, with very few exceptions all agree on one point: that the settled communities of the islands of Polynesia and parts of Micronesia were established via an
easterly movement of peoples through the region now known as Melanesia. This deduction, which was originally based on comparative linguistics, has been confirmed by every form of scientific analysis subsequently applied to the question of settlement. Despite the consensus regarding the direction of migration, archaeologists remain bitterly divided as to a whole range of features of the movement of peoples and in particular questions regarding the so-called ‘fast train’ model for Polynesian settlement, established through comparative linguistics (Allen, 1984). Although it is beyond question that the islanders of Polynesia speak languages grammatically classified as ‘Austronesian’, the significance of this fact is still the subject of scholarly debate. There is no agreement as to how this movement of peoples came about, when it occurred and what, if any, was the relationship between the languages now spoken throughout Polynesia and the movement of peoples that led to the human colonisation of the Pacific? Into these discussions of language theories, archaeologists such as Jack Golson added a final ingredient: that of Lapita pottery. For most archaeologists, Lapita is far more than a ceramic form found in abundant quantities on sites ranging in dates from c.3600-2500BP (Kirch and Hunt, 1988a, b) stretching from the Bismarck Archipelago through the Solomons and Vanuatu, to Fiji, Tonga, and Samoa in the Far East (Kirch and Hunt, 1988a). In the hands of ‘fast train’ theorists, Lapita has also been inextricably tied to initial settlement of Oceanic islands.

Behind the rhetoric of the sometimes highly charged academic debates that seem to hinge on seemingly highly technical points, there are serious issues regarding the boundaries of permitted enquiry within both archaeology and comparative linguistics, and the kinds of scientific inferences that can be drawn from material culture. These deliberations affect science-based archaeology worldwide. However, within a region such as the Pacific, which has no written histories, it is particularly important to ensure that correct conclusions are drawn from scientific analyses of material culture, since archaeology is the only means via which the peoples of the region can come to understand their ancient heritage. The following brief review of the archaeological literature regarding settlement provides the background to the provenance study undertaken on teeth found in the Sohano Rock Shelter near Buka, PNG.
6.1.1 Settlement in the Pacific

One point of commonality between the positions of the ‘fast-train’ and ‘slow-boat’ theorists is that both recognise the central importance of Near Oceania to the story of the dispersal of peoples across the Pacific. Since the advent of radiocarbon dating within archaeology and its subsequent calibration, sites within Papua New Guinea and particularly within the Bismarck Archipelago (encompassing New Britain, radiocarbon dates for human settlement. These include a cluster of four cave sites on New Ireland including one Matenkupkum, with an occupation layer said to date to approximately 35,000BP (Allen, 1994). In West New Britain, recent radiocarbon dating of 35,000BP at the site of Yombon has furnished the earliest known dates for the island interior and excavations conducted at the Pammak Rock Shelter have demonstrated that the island was occupied from at least 10,000BP (Pavlidis and Gosden, 1994; Fredericksen, Spriggs and Ambrose, 1993). Prior to the commencement of the Lapita Homeland Project, the earliest evidence for human settlement in Near Oceania was a date of 11,000BP from Misisil Cave on New Britain (Specht, Lilley and Normu, 1981). Since the mid 1980s, however, there has been a dramatic increase in the number of Pleistocene age sites discovered (Smith and Sharp, 1993). Carbon-14 dates obtained from excavations at the Kilu Rock Shelter of 28,000BP (Wickler and Spriggs, 1988) are said to prove that the Pleistocene inhabitants of Near Oceania were not confined to the large landmasses of New Guinea but had, even at this early date, spread at least as far as the North Solomons. The map of sites with occupation during the early to mid Holocene, now extends to Lolmo Cave in the Arawe Islands along the New Britain coast (6100 to 5250BP) and the Lebang Takoroi cave site on Nissan Island with a calibrated basal date of 5268 to 4564BP (Gosden et al., 1989).
Figure 6.0. Map of Melanesia (Source: Kirch, 2002).
Alongside the growing corpus of knowledge regarding the early settlement of Near Oceania, research has continued into the significant changes in settlement, trade and agricultural practices that are said to have taken place within Near Oceanic practices during the period up to 8000BP. After this date, in the mid Holocene, there is a gap (known as the ‘long pause’) in the archaeological record, the length of which, depending on one’s point of view, lasts between 2000 years (Irwin, 1998) to a matter of 500 or so years (Kirch and Weisler, 1994). After this gap in the cultural record, Near Oceania became the ‘homeland’ for the cultural phenomenon known as ‘Lapita’.

Sites dating to the period 8000-3500BP are clearly crucial to our understanding of the development of Lapita. As noted earlier, the disappearance of known settlement sites in the period after 8000BP has given rise to two quite separate theories of Lapita as a cultural phenomenon and quite different research strategies for its elucidation. Those who support a gradualist or indigenous model of Lapita continue to search for signs of cultural continuities within Near Oceania, whereas supporters of a model based on intrusive Austronesian speakers place higher emphasis on cultural discontinuity across the years of Lapita expansion to eastern Polynesia. Fortunately, unlike for the preceding 2000 years there are a steadily increasing number of sites, which have produced radiocarbon dates for the period just prior to the supposed expansion (Green, 1982).

The long recognised flaw in fast track theories of Lapita expansion is its failure to explain how, in the absence of exogenously derived population pressures, a relatively minor group of islands such as those of the Bismark Archipelago could have generated the population growth necessary to colonise the islands as far as islands of Remote Oceania in the space of some twenty five generations. In an effort to source the pre-Lapita traditions that he believes led back to Mainland Southeast Asia, Bellwood (1992, 1989, 1987, 1979) and Spriggs (1991, 1990, 1989) have attempted to trace the precursors to Lapita back through the chain of islands to the North of the Bismark Archipelago, to the islands of the Philippines and beyond into Mainland Asia. The most likely route proposed for the passage of Lapita peoples passes southward through the series of islands to the West of the Wallace Line. Spriggs has conducted a number of surveys and excavations of sites to the North of the Bismark Archipelago, hoping to produce a credible series of radiocarbon dated sites that will link Near Oceania to the ceramic based Neolithic cultures of the Philippines and Taiwan. However, whilst intrusive theory proponents such as Spriggs, can now point to a pre-Lapita ceramic based cultural
tradition of incised and stamp impressed pottery within ‘homelands’ on the Halmahera group of islands to the West of New Guinea, these ceramic finds do not, of themselves, settle questions regarding the mass movement of populations through the region. Instead they indicate that these pre-Lapita cultures were in contact with Mainland Asia. As noted by its detract radiocarbon dating and linguistic evolutionism. If either of these were to collapse, then serious doubt would be cast on the credibility of ‘fast-train’ theories.

The danger in approaching Lapita solely in terms of a ceramic tradition is that the phrase ‘Lapita people’ comes simply to see people-as-pots. In such a worldview, the presence of Lapita ceramics on an island signifies whether the ancient population of that place was settled by Lapita People. Therefore, even in the absence of further material evidence the existence of Lapita pottery carries with it the implication that these arrivals were necessarily accompanied by the rest of the material baggage of the Lapita ‘cultural complex’. The dangers of reductionism in such approaches is obvious. In the process of tracing a ceramic tradition, the cultural diversity of the Pacific Islands is reduced to that of a cultural complex consisting of certain settlement patterns, a distinctive subsistence tool set and (above all) pots. Having exposed the evidence of Lapita, archaeologists may feel justified to move on to the next island in their search for more ceramics and carbon to determine the spread of these migrants. In fairness to the researchers concerned, perhaps encouraged by the scrutiny of the sceptics (Kirch, 2002), show that the fast-train theory amply demonstrates that they are well aware of the reductionism charges that could be laid against them. Indeed many go to some lengths to describe Lapita both in terms of innovation and tradition. Furthermore the chronometric hygiene applied to the accumulated radiocarbon database was particularly important and has ensured that dates for Pacific island archaeology are amongst the best policed in the world.

Nevertheless, and despite the best efforts of the most ardent supporters of the intrusive Lapita Peoples, it would seem that unless science-based archaeologists can find a means to move from the study of material evidence as a proxy for humans to direct measurements made on skeletal tissues it may never be possible unequivocally to answer the kinds of questions that archaeologists are posing of the archaeological record. It is suggested that Pb isotope techniques developed as part of the present study, may prove useful in questions of ‘Lapita Peoples’, allowing the questions of dispersal to be approached using measurements made on people rather than ceramics, and may assist
archaeologists in deciding which of the diametrically opposed explanations of settlement is the correct one. The ‘fast train’ theories of Lapita dispersal imply very large numbers of peoples moving large distances through Island Melanesia and Near Oceania. It would seem unusual if these migrants had left no trace of their passage in the isotopic signatures on early Lapita sites. The remainder of this chapter presents the results of a pilot study undertaken in order to determine the limitations of Pb isotope analysis to questions of migration within the region labelled by others as the ‘Lapita Homeland’.

6.2 The Northern Solomons: Island of Buka

As mentioned above, recently produced evidence from pre-Lapita sites in both the Bismarcks and Solomons is shedding the first significant light on a range of issues regarding early settlement of the Pacific region. However, prior to the Lapita Homelands Project, such was the paucity of evidence that even this newly acquired information, highlights how little is known of the initial 30,000 years of human prehistory in the region.

The oceanic distance between New Ireland and Nissan via the Feni Islands involves open sea distances of 50 to 60km, and therefore represents a significant barrier to any biological and/or cultural dispersion. The Island of Buka is situated at the northern end of the Solomon Islands chain at latitude 5° 15’ 0S and longitude 154° 37’ 60E (see Figure 6.1). Despite its comparatively small size, the archaeology of the island provides a remarkable record of the human settlement of Near Oceania and indicates its importance in past exchange interactions. Investigation of prehistoric exchange mechanisms with Near Oceania suggests that human occupation on Buka began at least 28,000BP, implying that occupation of the Solomons may also have occurred at this time (Wickler, 1990). Due to their position, the Bismarcks are of crucial importance to any understanding of Oceanic prehistory, as they seem to be ‘stepping stones’ in the theory of Lapita dispersal, linking the Bismarcks to the remainder of the Solomons (Wickler, 2001).
Figure 6.1. Map of mainland Papua New Guinea and Buka Island (Source: www.riverbendnelligen.com).

6.2.1 Geology and Topography

The island of Buka comprises volcanic hills in the southwest, tectonically uplifted cliffs with raised coral reefs in the north and east and low lying mangrove swamps in the south and west. While most of the island’s coastline is bounded by a narrow fringing reef, the western coastline is surrounded by a barrier reef that connects a chain of small limestone islands.

Buka is mostly covered by elevated coral reef consisting of Plio-Pleistocene Sohano Limestone (edging out onto Sohano Island and the north coast of Bougainville), bordered by a limited calcareous sand littoral platform. In contrast, the island's basement volcanic rocks consist of interbedded volcanioclastic breccia (sandstone and siltstone with spilitic basalt-basaltic andesite predominating), constituting Late Eocene to Early Oligocene Atamo volcanics (Wickler, 2001).
6.2.2 Archaeological Material

As part of his 1967 pioneering studies in Pacific prehistory, Jim Specht undertook an excavation on Sohano Island, a small coral limestone island at the western end of the Buka Passage running between Buka and Bougainville Islands (Figure 6.1). Test excavations a year earlier by Ron Lambert of the Australian National University (ANU) unearthed several types of pottery (Lampert, 1966). It was these discoveries that led Specht from his contemporaneous excavations at Watom Island on the northern end of New Britain to Buka Island.

The Island of Sohano is approximately 1.10km long and 0.50km wide with a total land area of approximately 0.55km². The Rock Shelter site was first referred to as Sohano Hospital due to the existence of a hospital on the level ground in front of the shelter. Sohano was the administrative centre of what was the Bougainville District in 1967 and coded as site DAA covering an area of approximately 25,000m². Most of the finds were small pieces of pottery, shell, stone artefacts and a few fragments of human bones and teeth (pers. comm. Specht).

Site DAA extended 250m south from the base of the limestone cliff where the excavations were located and 100m west from the shoreline within grounds of the nearby hospital (see Figure 6.2) south of the island. Site DAA was divided into two trenches, referred to as DAA/I (inside the shelter) and DAA/II (outside the shelter). Site DAA/I¹ is divided into sediment sequences with five major groupings of layers and lenses:

Layer 1 — present day;
Layer 2 — well inside the shelter mouth (last 150 years);
Layer 5-6 — a complex of disturbed fireplaces, fire ash and limestone erosion detritus inside the shelter, extending to the back wall (last 1000 years);
Layer 7-12 — complex of fireplaces and ash lenses ending near the shelter mouth, the age uncertain, and
Layer 14 — the earliest occupation level at the site.

¹ There are no radiocarbon dates for DAA/I. The dates presented here are approximations as per Jim Specht (pers. comm.)
Site DAA/II
2, radiocarbon dated, has a very different stratigraphy:

Layer 1  recent sediments with road gravel;
Layer 2  ‘clean’ brown clay that seems to represent a phase of low use of the site, or perhaps its abandonment, dated at 1200BP;
Layer 3  two parts, one upper and one lower. Both consisted of clayey erosion sediments, with the lower unit being more sandy covering approximately 1000 years (inadequate dates to be precise), c.2200-1200BP. A large amount of shells and pottery were recovered from this layer;
Layer 5  two parts: beach sand with the upper part containing clayey sediment or a palaeosol. Dated to 2480 ± 140BP (ANU-272; uncalibrated) on charcoal and corroborated by other measurements obtained from a calcareous beach sand sample of 2851-2155 cal BP (2σ). Shells were quite common in this layer, whilst pottery scarce, and
Layer 6  the pre-occupation beach sand.

The teeth were located within various layers in the trenches. There was no organised deposit of bones and teeth due to its use as a casual shelter, with people lighting fires and scuffing the uppermost loose powdery sediment. As a result any structure within the upper deposits would have been disturbed. In contrast, the lower layers were clayey sediment and less susceptible to disturbances. The recovered teeth were unearthed amongst copious fire ash, charred bones and dispersed material representing limited portions of the anatomy; not suggestive of formal burials. Although it was first proposed that the burnt teeth and bones might have been a result of cremation or cannibalism, the latter suggestion was later abandoned (pers. comm. Specht).

The teeth were unique for the purposes of Pb isotope analysis, since they undoubtedly represented the remains of more than one individual and yet were found in a single archaeological context. From an archaeological viewpoint the study provided the opportunity to answer some of the questions regarding the origins of these individuals who died at a period almost contemporaneous with the proposed Lapita Diaspora.

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2 Although stipulated, that DAA/II has been radiocarbon dated, not all dates were provided by Specht.
Figure 6.2. Excavation plan for site DAA on Sohano Island (Source: Wickler, 2001).
Figure 6.3. Sohano Island: Location of archaeological site (Source: Wickler, 2001).
6.3 Experimental

Lead and Sr isotope ratios were ascertained with TIMS while elemental concentrations were determined using GFAAS. Results reported here are only those of TIMS and GFAAS, with verification achieved by MC-LAM-ICPMS and ASV (see Table Ie.1, Appendix Ie). Sample preparations and the equipment employed for these determinations are given in Chapter 3.

6.4 Results and Discussion

6.4.1 Lead Isotopes

Lead isotope ratios determined using TIMS from samples excavated from the Sohano Rock Shelter are plotted in Figure 6.4. Statistical assessment of Figure 6.4(a) shows a positive correlation between the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, where $r = 0.780$ and $p = 0.007$, while the coefficient of determination, $r^2 = 0.571$ accounts for 57.1% of the total variation due to the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios alone. This data contrasts sharply with U versus Th data presented in Figure 6.4(b), where any linear correlation is insignificant ($r = 0.012$, $p = 0.940$) while $r^2 = 0.1$ denotes a 1% contribution by the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio to the total variation.

Figure 6.5 illustrates the isotopic signatures of eleven tooth enamel samples, coupled with isotope source fields for Feni Island (Stacke and Hegner, 1998), New Britain (Woodhead and Johnson, 1993), and Bougainville (pers. comm. Woodhead). Regression analysis of the data presented in Figure 6.5(a) shows a positive linear correlation, $r = 0.756$ and $p = 0.007$ between $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, characteristic of daughter isotopes from a U parent. As with the data obtained from enamel samples, the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio accounts for 57.2% ($r^2 = 0.572$) of the total variation within the plot. Likewise the island geological data shows little correlation between the U and thorium (see Figure 6.5(b)), leading to the conclusion that U and Th must have originated from either different sources within the underlying basalt or else behave differently in the local hydrothermal fluids. The comparatively large spread of data within these plots is undoubtedly the result of partial mobilisation of both elements during hydrothermal alteration in this

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3 Thanks are expressed to Jon Woodhead for granting permission to include this data, which due to commercial interests, is shown as a ring rather than as individual points.
geologically complex region (Finlow-Bates and Stumpfl, 1981; Pascual et al., 1997; Valsami-Jones and Ragnarsdottir, 1997; Nesbitt et al., 1999).
Figure 6.4. Lead isotope ratios determined by TIMS for tooth enamel samples excavated from the Sohano Rock Shelter. Statistical analysis shows a linear correlation in (a) whilst (b) are quite scattered. Five out of the 11 samples are statistically identical while 2 others share the same source field. The remaining 6 belong to other fields within the Melanesian basin. Errors for the tooth enamel samples (2σ, n = 5): $^{206}\text{Pb}/^{204}\text{Pb}$ (±0.01), $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ (±0.003).
Figure 6.5. Isotope ratios obtained by TIMS for Melanesian Islands compared with tooth enamel samples of individuals from the Sohano Rock Shelter; (a) Plot of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios; (b) Plot of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. Ratios were acquired from the GEOROC database: Feni Island (Stracke and Hegner, 1998); New Britain Arc (Woodhead and Johnson, 1993); the rings denote isotope ratios for Bougainville (Woodhead unpublished data). Seven out of the 11 individuals studied match the local bedrock with the possibility of one other matching the local source pool also. Errors for the tooth enamel samples ($2\sigma$, $n = 5$): $^{208}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.01$); $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.003$).
The results of the isotopic analyses are surprising. Seven of the individuals possessed Pb isotope signatures consistent with that of the local bedrock. The Pb\(^{2+}\) ion concentrations contained within tooth enamel samples varied between 0.017 ± 0.004 μg/g and 0.265 ± 0.013 μg/g (see Table 6.0) and are significantly lower than the Pb\(^{2+}\) ion concentrations contained within the local basalt samples, 1.9 to 5.5 μg/g (Stracke and Hegner, 1998; Woodhead and Johnson, 1993). Furthermore, a high proportion of the samples were grouped around a single \(^{207}\)Pb/\(^{204}\)Pb isotopic signature of 15.542 ± 0.003 (see Figure 6.6) which is significantly different from the isotopic signature of the soil in which they were buried (measured from soil contained on the samples as 15.549 ± 0.003 (n = 6). The homogeneity of the isotope signature for the samples (which is significantly greater than that derived from modern populations) suggests that most of the individuals whose remains are found at the Sohano Rock Shelter received their childhood Pb burdens from a restricted number of sources. Whilst the results cannot be taken as conclusive proof, they certainly suggest that this signature derives from the individuals having accessed the same water source. This being the case, it also seems likely that the seven individuals were from a single locality/community, and passed the overwhelming proportion of their childhood in that place, receiving food from a very restricted agricultural source.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(^{208})Pb/(^{204})Pb</th>
<th>(^{207})Pb/(^{204})Pb</th>
<th>(^{206})Pb/(^{204})Pb</th>
<th>Enamel Pb (μg/g)</th>
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<td>15.5530</td>
<td>18.7121</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Table 6.0. Pb isotope ratios and Pb\(^{2+}\) ion concentrations for tooth enamel samples from the Sohano Rock Shelter. Pb isotope ratios were determined by TIMS while Pb\(^{2+}\) ion concentration data by GFAAS. Errors 2σ (n = 5): \(^{208}\)Pb/\(^{204}\)Pb (±0.01); \(^{207}\)Pb/\(^{204}\)Pb and \(^{206}\)Pb/\(^{204}\)Pb (±0.003), Pb concentration (±0.02).
A comparison of the tooth enamel Pb isotope ratios with the 4.55Ga Geochron (Figure 6.7), shows that the overwhelming majority of samples plot on the mid to high side of the $^{206}\text{Pb}/^{204}\text{Pb}$ Geochron, implying a net increase in the U/Pb ratio (µ) of the mantle. As seen in Figure 6.7a, two of the individuals plot on the low side, three plotting under the growth curve suggesting a source depleted in Th relative to U while the remaining six individuals plot on the Geochron. All the data, except for the single data point (AB1), an outlier which plotting the highest on the $^{206}\text{Pb}/^{204}\text{Pb}$ Geochron, is consistent with the isotopic signature of the local bedrock for Buka-Bougainville. Interestingly the results in Figure 6.7b plot significantly below the Geochron indicative of depletion in $^{207}\text{Pb}$ relative to $^{206}\text{Pb}$. 

Figure 6.6. Plot of Pb$^{2+}$ ion concentration (µg/g) versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratio for tooth enamel samples and soil samples from the Sohano Rock Shelter. All soil samples contained Pb$^{2+}$ ion concentrations between 4.8 and 5µg/g. Errors for GFAAS concentration data are ±0.02 (2σ, n = 5); and TIMS ratio data are ±0.003 (2σ, n = 5) for the $^{207}\text{Pb}/^{206}\text{Pb}$. 

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Figure 6.7. Pb isotope ratios of tooth enamel samples excavated from the Sohano Rock Shelter, (a) \(208\text{Pb}/204\text{Pb} \) versus \(206\text{Pb}/204\text{Pb} \) and (b) \(207\text{Pb}/204\text{Pb} \) versus \(206\text{Pb}/204\text{Pb} \). TIMS errors (2\(\sigma\), \(n = 5\)): \(208\text{Pb}/204\text{Pb} \) (±0.01); \(207\text{Pb}/204\text{Pb} \) and \(206\text{Pb}/204\text{Pb} \) (±0.003). Dashed line indicates 4.55Ga Geochron.
6.4.2 Strontium Isotopes

It was shown in Chapter 5 that in general, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope measurements are not useful indicators of either provenance or diet for populations on islands such as those of the Pacific region, which are composed of basalt. The natural variation in $^{87}\text{Sr}/^{86}\text{Sr}$ in bedrock samples is at least as great as the inter-island variability that would be used to distinguish between the various inputs, and thus constitute a signal. However, the data collected for the population buried at the Sohano Rock Shelter prove to be an unusual occurrence in this regard.

As expected there is little or no correlation between $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Pearson correlation coefficient, $r = 0.373$ and $p = 0.259$). This result is consistent with other studies which have shown that the Pb$^{2+}$ and Sr$^{2+}$ ion concentrations incorporated into skeletal hard tissues both in vivo or after burial, are independently variable (Montgomery, 2002). As with the Pb isotope results, a surprisingly high proportion of the samples plot at or near a single value ($0.70364 \pm 0.00003$). In addition to the one previously identified Pb isotopic ‘outlier’ an additional two samples showed some degree of variance from this mean value. However, once again, the results for Sr isotope analysis are remarkably consistent and strongly suggest that these people passed their childhood within a single community into which relatively few even near neighbours intermarried.
Figure 6.8. Plot of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios versus $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the local Melanesian source pool compared with tooth enamel samples of archaeologically derived individuals from the Sohano Rock Shelter. Ratios for the individual islands/island arcs were acquired from the GEOROC database: Feni Island (Stracke and Hegner, 1998); New Britain Arc (Woodhead and Johnson, 1993), the ring denotes isotope ratios for Bougainville (Woodhead unpublished data). Errors for tooth enamel samples: ±0.003 (2σ, n = 5) for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio; ±0.000026 (2σ, n = 6) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

Figure 6.8 shows the relationship between ancient individuals and the source of their Pb (and in this case Sr) isotope signatures is only visible in the isotopic data, which as they were measured as ratios are independent of concentration. Figure 6.9, which shows the same data plotted as concentrations, illustrates no correlations between source rocks and samples whatsoever. Despite the persistence of studies within the archaeological science literature using trace element concentrations as an indicator of diet and/or provenance (Schutkowski et al., 1999; Vuorinen et al., 1996; Ezso, 1994a, b; Rheingold, Hues and Cohen, 1983), these results suggest that no value can be placed on the conclusions of provenance or palaeo-dietary inferences drawn from measurements of Pb$^{5+}$ or Sr$^{2+}$ ion concentrations.
Figure 6.9. Plots of Sr\(^{2+}\) ion concentrations versus Pb\(^{2+}\) ion concentration. All concentrations were obtained using GFAAS. (a) Concentrations of archaeologically derived human tooth enamel samples. (b) Tooth enamel concentrations compared to two Melanesian island basalts; Feni Island (Stracke and Hegner, 1998) and New Britain Arc (Woodhead and Johnson, 1993). Due to the unavailability of elemental concentration data on the surrounding islands, only two islands have been used as comparisons. Errors (2\(\sigma\), \(n = 5\)): ±0.02 for Pb and ±2.5 for Sr.
6.4.3 Provenancing of ‘Outliers’

As noted in Chapter 1, it is extremely difficult to assign a provenance in the positive sense, with any degree of certainty. The islands of Near Oceania are geologically very active and the underlying bedrock geologies very complex. As a result many of the isotopic source fields that might be drawn for the various individual islands overlap each other. Other than in the above example, where the Pb isotopes have effectively a single value, it is difficult to envisage a situation whereby provenance can be determined at the level of an individual island.

As noted above there is one individual (AB1) whose Pb isotopic signature is at odds with that of the underlying bedrock. A further two individuals appear as outliers when consideration is taken of both the Sr and Pb isotope ratios. However, in view of the difficulties in accounting for all possible sources of isotopic variation in $^{87}$Sr/$^{86}$Sr little significance can be attached to this result. In view of the closeness of the match in Pb isotope ratios of these two to that of the rest of the measurements, they are considered likely to have been members of the same social group as the majority.

Of the remaining four teeth studied a further two (AB4 and AB5), although not as tightly grouped as those six from Buka-Bougainville, contained a Pb isotope signature corresponding to the New Britain Arc and the remaining two (AB2 and AB6) have signatures that correspond to islands within the Solomons. Unfortunately, the currently available database of isotope measurements for the Pacific is based on geological measurements made for the purposes of exploiting natural resources such as base and precious metals. Therefore whilst reasonably detailed data are available for the islands of the Bismark Archipelago and its environs, the equivalent data for the Solomons does not currently facilitate identification of individual islands within the group. Nevertheless it is clear from the results of the study that all of the individuals excavated by Specht at the Sohano Rock Shelter were inhabitants of ‘Near Oceania’ (Kirch, 2002), that is, individuals whose worldview stretched no further than the inter-visible archipelagos of the Bismark and Solomon chains.

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4 Even in the example studied here, whilst it is possible to state with a reasonable degree of certainty that the individuals were from a single social group, it cannot be stated where in Buka or Bougainville that location was.
Figure 6.10. Pb isotope ratios of individual Melanesian Island basalts compared with tooth enamel samples excavated from the Sohano Rock Shelter. Island basalt ratios were acquired from the GEOROC database: Feni Island (Stracke and Hegner, 1998); New Britain Arc (Woodhead and Johnson, 1993); Santa Cruz (White, 1993); New Zealand (Hart, 1985); Solomon Islands (Tejada et al., 1996); Samoa (Wright and White, 1987); the rings denote isotope ratios for Bougainville (Woodhead unpublished data). Errors for the tooth enamel samples (2σ, n = 5): $^{208}\text{Pb}/^{204}\text{Pb}$ (±0.01); $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ (±0.003).
6.5 Conclusion

From a scientific standpoint, the study conducted on the teeth from the Sohano Rock Shelter provides proof that Pb isotopic analysis of tooth enamel produces data that relates to the source of biogenic Pb$^{2+}$ accumulated in vivo, even after long-term burial.

In archaeological terms the isotope-based study of teeth from the Sohano Rock Shelter provides new pieces of archaeological information on the dental remains and the activities undertaken there. The individuals whose dentition accumulated within the shelter did not, as previously suggested, belong to captured individuals, but were for the most part drawn from a single population somewhere within Buka or perhaps Bougainville. The Pb and Sr isotope values for most of the teeth analysed have a single value: one that is different from the soil within the shelter. This unusual occurrence is not one that is found amongst modern populations. Even within modern industrial environments contaminated with tetra-ethyl Pb additives to petrol, a number of additional sources of Pb$^{2+}$ ions would be expected to show up as minor variations in measurements made on dental enamel (Gulson and Gillings, 1997). The fact that these ancient individuals have a single isotopic signature points to their exposure to a very restricted source of Pb: probably the water supply in conjunction with local agriculture.

It is certainly indicative of a sedentary population with children partaking in a relatively restricted set of practices taking place in one area. Interestingly, although the radiocarbon dates for the site are rather too old and imprecise and probably require re-evaluation, the occupation of the shelter is currently dated to a period well inside that of the Lapita dispersal. Despite this, the ‘outsiders’ to this highly restricted pool are consistent with origins in the Bismarks and the Solomons known to have been in contact since the Early Holocene (Kirch, 2002). For whatever reason, if the Lapita peoples were moving down into and through the Bismarks they are not found amongst the individuals unearthed at the Sohano Rock Shelter.
Chapter 7

Provenance Studies

Case Study II: Island of Tongatapu
Kingdom of Tonga

7.1 Introduction

Polynesia is the most cohesive and perhaps the most appropriate grouping of the three geo-cultural groups defined for Oceania (Thomas, 1989). The peoples classed as Polynesian inhabit islands within a triangle formed by Hawaii, Rapanui (Easter Island) and Aotearoa (New Zealand). The similarity of physical appearance and social customs across the region nominated as Polynesia, allow these peoples to be identified unambiguously with geographic locations somewhere within this triangle. However, as noted at several junctures within the current work, no single issue within Pacific Archaeology has inspired more debate and argument ‘ranging from the scholarly to the sublimely ludicrous’ than the problem of how these peoples came to be Polynesian (Kirch, 2002). Of seminal importance in any discussion of what constitutes Polynesian identity are questions of the degree of post-settlement contact that was maintained between island groupings. Despite suggestions that Polynesians were capable of maintaining post-settlement, inter-archipelago contacts, there has until now been no direct method of proving this. This study, which centres on a population buried on the island of Tongatapu shows for the first time that Polynesians were in continued contact with population groups outside of the island groupings on which they were buried.

Western interest into Polynesian origins began with the first European explorers and continued throughout the growth of anthropology as an academic discipline. Although professional academic investigations of issue date from the 1920s, these anthropology based studies took little or no account of archaeological evidence for settlement, relying
instead on the results provided by comparative linguistics. It is only with the advent of stratigraphic archaeology based research in the period post-WWII that researchers began seriously to consider the possibility that Polynesian culture had developed in situ within Polynesia, rather than being imported en masse, via migration waves from Mainland Asia. As noted earlier (Chapter 6), the advent of radiocarbon dating techniques within archaeology was of seminal importance within Pacific Archaeology, enabling researchers for the first time, to determine ‘absolute’ (calendar) dates for the settlement. The consensus view, formulated on the basis of distinctive ‘Lapita’ pottery forms, and radiocarbon dating evidence is that the earliest settlement sites currently known in Tonga, Fiji and Samoa, date from around 3200BP and followed a rapid Diaspora out of the Bismarck Archipelago that lasted no more than twenty-five generations. According to archaeologists who share this view, the dispersal of peoples of the ‘Lapita cultural complex’ was of critical importance to questions of Polynesian origins (Green, 1979). Thus, according to Kirch (1986), the “end” of Lapita (2450BP) is also the “beginning” of Polynesian culture. According to ‘fast-train’ theorists, Eastern Lapita was gradually transformed through a process of cultural change and adaptation to new island environments, thereby becoming something recognisably different, yet retaining many ancestral cultural patterns. For Kirch and the majority of Pacific Island archaeologists, ‘there was genetic, cultural and linguistic continuity between the Lapita pottery makers who first discovered and colonised the archipelagos of Oceania toward the end of the first millennium BC, and their descendants who would come to be known to the European world as Polynesians’ (Spriggs and Anderson, 1993).

Although the vast majority of archaeologists agree on the basic outline of the eastwards Lapita dispersal, there are disagreements regarding the rate of expansion, the degrees of contact that were maintained between newly settled island communities and homeland communities, and the point of origin of the ‘Lapita Peoples’ (Spriggs, 1990, 1989). One of these controversies centres on the so-called ‘long pause’ between the settlement of Fiji, Tonga and Samoa and those of the archipelagos of East Polynesia, the Cook Islands, Society Island, Marquesas Island and other groups (Kirch and Green, 1987). These arguments centre on the systematic reappraisals of the accumulated radiocarbon database conducted by Spriggs and Anderson (1993), who maintain that ‘there is nothing to demonstrate settlement in East Polynesia earlier than AD 300-600’. The opposing viewpoint is expressed by Kirch and Weisler (1994), who argue that the number of known early settlement sites on the Pacific Plate islands is currently too small to reach
definitive conclusions as to the extent of Eastern Polynesian settlement, and that many other sites may await discovery.

Although most archaeologists concur on the rate and direction of the Lapita expansion into Oceania, there are enigmatic occurrences of Polynesian populations within Melanesia, the significance of which cannot currently be determined by science-based means. The so-called ‘Polynesian Outliers’ have been variously considered as either remnant populations of the Lapita expansion or examples of populations that moved westward after most of the eastern Pacific Islands had been settled (Irwin, 1992). More recent studies have suggested somewhat more complex histories for these ‘outlier’ populations, including the possibility that the so-called ‘outliers’ represent examples of cultural replacement, rather than mass movement of populations. This possibility highlights the need to consider each island individually and the dangers inherent in any global grouping (Kirch, 1984; Davidson, 1992).

There is a vociferous minority of scholars who oppose any notion of a ‘Lapita Cultural Complex’ of the form outlined by Kirch. White (1992) and Terrell (1986) argue that Lapita is a ceramic tradition and nothing more. For Terrell, in particular, the linkages between ethnicity, language and culture that underpin the Lapita dispersal theories are a residue of culture-historical approaches to archaeology and have no place within modern archaeological theory. Rather than two phases of settlement by ethnic/linguistically distinct peoples, both White and Terrell believe that the Polynesian peoples evolved entirely from Melanesians and therefore Lapita is a transitory and entirely cultural phenomenon affecting a limited number of already settled islands.

As noted by Kirch (2001), questions of Lapita and the polarities represented by the stances taken by scholars such as Spriggs (1990) and Terrell (1986), stretch far beyond the rarefied atmosphere of academic debate, to questions of the place of western archaeology in determining questions of ethnic origins of ‘others’ within a post-colonial world (cf. Gosden, 1991). In support of the ‘Lapita Peoples’, processual archaeologists can muster an impressive array of evidence drawn from scientific techniques, ranging from paleoenvironmental studies (Steadman, 1989; Kirch and Ellison, 1994) to mtDNA (Hagelberg and Clegg, 1993; Hetzberg, Mickleson and Trent, 1991) and radiocarbon (Kirch and Hunt, 1988b; Hunt and Holsen, 1991; James et al., 1987).
As mentioned in Chapter 1, a number of science-based analytical programs have been undertaken on the material cultural remains of the Pacific in order to determine the scale and scope of trading systems within the Lapita homeland. By far the most successful of all provenance based studies on archaeological material have been the trace-element studies undertaken on obsidian. Proton-based emission spectroscopy has allowed archaeologists to plot the distributions of radiocarbon dating can provide an age for associated material, provide a date for the artefact’s entry into the archaeological deposit. Questions regarding the scale and distances covered by exchange systems within the Pacific region are fraught with difficulty. The extant material remains of exchange transactions (obsidian, chert, etc.) must represent only a fraction of the total range of transported, exchanged, or traded materials between Lapita communities. Furthermore, as pointed out earlier (Chapter 1), provenance analysis of artefacts, though useful, can only determine the end points of the journey taken by an artefact. It cannot be used to determine the pathway and the number of steps that were required in order for the artefact to reach its final resting place, or the time taken for it to get there. In the case of durable objects such as obsidian, the route taken from lava flow to final resting place may have taken a very long time to accomplish, and there is no proof that the populations at the point of deposition knew anything of its source. The problems relating to trade and exchange are compounded by the uneven distributions of artefacts across Oceania. Whilst distributions of materials such as obsidian, pottery and shell valuables constitute the principal ‘cultural markers’ for the Lapita dispersal, these materials are not found at the eastern limit of the Lapita cultural complex’ on the islands of Fiji and Tonga where ‘innovative’ tool types such as basalt adzes are found. In order to determine the extent of long-distance trade it would be preferable to work with material that can be proved to have moved from its origin to point of deposition on a more human time scale, such as human skeletal tissues. In principle, mtDNA studies of biological remains could be used in a way analogous to comparative linguistics, to elucidate the pathway by which peoples moved across the Pacific. However, if, as is suggested, the Lapita dispersal took place over a period of only twenty-five generations, there is little hope of elucidating ‘racial’ characteristics in other than the broadest of terms as Polynesian or Melanesian ‘stock’. This leaves environmental and radiocarbon dating as the techniques available for providing a fine-grained chronology for the movement of Lapita ceramics across the Pacific. Unfortunately there are limitations on the precision and accuracy of radiocarbon dating on archaeological sites. Although Spriggs’ (1990, 1989) chronometric hygiene
initiative has greatly improved the accumulated radiocarbon database, it seems unlikely that the problems of low precision measurements, reliance on shell date, etc., will be overcome in the near future. In fact, as scrutiny extends to the assumptions regarding the error limits quoted for radiocarbon dates within the Pacific, it is likely that more of the measurements within the accumulated database will have to be rejected, or else archaeologists will have to accept lower analytical precisions for their measurements. This will undoubtedly further unsettle some of the current chronometric distinctions between island settlements in the region.

The foregoing all too brief resume highlights some of the problems facing Pacific archaeologists as they attempt to interpret the cultures of Oceania. In the absence of direct analytical evidence, it is difficult to decide how archaeologists can differentiate between ‘cultural influences’ (cf. Terrell, 1986) and ‘cultural changes’ instigated by the relocation of peoples. Clearly, a science-based method of directly distinguishing migrants amongst ancient Pacific Islander communities could prove to be a valuable tool for answering questions regarding the movement of people across the islands of the Pacific. In particular it should be possible to settle a number of questions regarding the distances travelled by ancient islanders in their lifetimes.

7.2 Kingdom of Tonga

The Pb isotope pilot study presented here centres on the present day polity known as the Kingdom of Tonga. Tonga consists of 171 islands, spreading over 700km² of the South Pacific lying in western Polynesia (see Figure 7.0) between latitudes 15°S and 23°S and longitudes 173°W and 177°W. Only 45 of the 171 islands are inhabited. The Tongan islands lay NNE-SSW on the Tonga-Kermadec Ridge which extends over 1300km from New Zealand to Samoa and is west of the International Dateline. Tonga has a current population of approximately 100,000 with almost two thirds of its inhabitants living on the island of Tongatapu, the largest of the islands. The inhabited islands form four groups; the Tongatapu group (including the capital Nuku’alofa) the volcanic and coral islands of the Ha’apai group, the waterways of the Vava’u archipelago and lastly the remote volcanic Niuaus in the far north (see Figure Ie.1, Appendix I). Three types of islands can be found in two parallel chains situated on the Tonga Trench (Spennemann, 1990):
(1) Situated on the relatively shallow forearc platform, the islands Tongatapu, Ha’apai and Vava’u known as the Tongan Frontal Arc are an Eastern chain of islands consisting of coral reef limestone underlain by volcanic rocks;

(2) Sitting on the Tofoa Ridge and separated from the chain of coral limestone islands by a trough, is the western chain of active volcanoes, Tofua, Late, and Kao, and

(3) A chain of unstable islands (Fonuafo’ou and Metis Shoal) made up of volcanic ash and pumice is formed by a chain of active submarine volcanoes.

Along the forearc belt most of the islands are composed entirely of Quaternary limestone that is masked by tephra, with the islands of the Ha’apai Group in central Tonga also being exposed to Miocene volcanioclastic sandstone and mudstone (Cunningham and Anscombe, 1985).
Figure 7.0. Map of Tonga Islands, Western Polynesia (Source: Kirch, 2002).

7.2.1 Island of Tongatapu
The island of Tongatapu is an area of limestone raised reef shaped by the prevalent south-eastern swell and is situated approximately 2,000km northeast of Auckland, New Zealand (Taylor, 1978). Most of the island is less than 17m above sea level, though there are several small hills; the low northern coast is a reef platform, in places up to 200m in width while the western coast is a reef platform out from sandy beaches and rocky higher
land with the highest point (65m), between Fua’amotu and Nakolo (see Figure 7.1). The core of the island underlying the limestone reef is produced by Miocene volcanoclastics (Katz, 1976). There are numerous caves in the limestone reef, created by penetrating rainwater. Whilst the coastline is surrounded by coral reefs and overhanging cliffs (that surround most of the island), the central part is occupied by a shallow lagoon consisting of two sections connected with a small channel enclosed entirely by land, except for a channel at the northeast margin.

![Figure 7.1. Island of Tongatapu. Source: www.islands.com.](image)

7.2.1.1 Geology and Topography
Six soil series have been distinguished on the island of Tongatapu. Three are derived directly from andesitic tephras, one from redeposited tephra and two from marine deposits (coastal sand and lagoon deposits). The volcanic soil profiles are of varying depths, depending on the degree of erosion and weathering. The tephra layers increase in thickness from the east by approximately 1.5m to the west of the island where they reach
up to 5.5m, indicating that they were deposited against the prevailing winds from volcanic sources west of Tongatapu (Cowie, 1980).

7.3 The Archaeological Material
For the most part, studies of two-way inter-island interactions within Polynesia rely on projecting oral history back into prehistory. For example, the well known, historically recorded, interaction sphere of Fiji-Tonga-Samoa (Hjarno, 1980) is said to have had its genesis in prehistory (Davidson, 1978, 1977; Kirch, 1984). However, considering the amount of long-distance voyaging said to have taken place during prehistory (Irwin, 1992), frustratingly little or no material evidence of the two-way movement of commodities is attested within the archaeological record.

The tooth specimens analysed were recovered from a number of burial mounds from two (To-At-1 and To-At-2) major excavations in the grounds of Tonga College at ‘Atele on Tongatapu island, by Janet Davidson in 1964 (Davidson, 1969). The excavated burial sites fall into two groups:

- Small low mound corresponding with ‘commoners’ burial place (To-At-1), and
- A large mound probably a chief’s burial mound (To-At-2) (McKern, 1929).

Both the mounds were situated in plantation areas and despite evidence of ploughing in the adjacent field extending to the edges of To-At-1 and the edge of the ditch that surrounded To-At-2, according to Davidson neither had been disturbed. Davidson’s archaeological survey uncovered the remains of well over 100 individuals, with To-At-1 containing notably more immature individuals.

7.3.1 Specimens from Site To-At-1
Site To-At-1 is a small mound situated behind the water tower at Tonga College. A total of 27m² was excavated at this mound (see Figure 7.2). The site had been used intensively as a burial place, with the original layers later destroyed by a sequence of complicated series of inter-cutting burial pits in the central part of the mound. Excavations revealed a number of pits, a trench encircling the mound, two cooking sites and postholes of various eras. Five main layers were said to relate to four periods of occupation/use of the site.
(see Figure 7.3). The Stratigraphic profiles comprise uniform dark brown garden soil, interleaved with layers of subsoil (clay and white sand). The lowest portions of the profile consisted of a midden containing corals, shell and burnt coral oven stones, while the earliest burials on the site were confined to the uppermost layers. White sands were generally used as grave fill for the burials, with some burials almost completely full of sand, others having only a few centimetres and some had none at all. A dark stain was observed in the sand of some burials and was thought to be the result of the disintegration of black tapa cloth wrapping: a practice still followed in Tongan burials (Davidson, 1969).

Forty six individuals were unearthed from thirty eight separate interments at site To-At-1. Paleoanatomical studies revealed a large number of juvenile burials and are testimony to a high child mortality rate. Oral tradition relates that the site was used for burials prior to the mounds’ construction: a fact confirmed by excavation. However, unbeknownst to oral historians the sites use as a burial site was preceded by a period when it was used for cooking. Davidson (1969) suggests that the presence of imported volcanic cooking stones within this earliest cultural horizon and the presence of pits ‘resembling postholes’, attests to the early importance of the site.

Although samples of bone from the burial layers were submitted for radiocarbon dating, these contained insufficient amounts of extractable collagen for reliable dating. Nevertheless, the bone was reported to be no earlier than 1200BP (3σ; GaK-1203).
Figure 7.2. Plan of site To-At-1 showing area excavated. Source: Davidson, 1969.
Figure 7.3. Principal sections of site To-At-1. Source: Davidson, 1969.
7.3.2 Specimens from Site To-At-2

This site, which was first used as a house mound, encircled by a visible ditch is situated within plantation land approximately 500m west of the Hofoa Township. Two trenches were excavated:

- A long trench one metre in width with several sections (three on the north and south sides), and
- A second trench also one metre wide was set out at right angles to the first one, excavated only at the extremities, designated east and west (see Figure 7.4).

Initially the site was employed for residential use (evidenced by the presence of small scale house mounds and a general lack of midden material) and was later abandoned and used instead as a burial mound. Six main occupation layers were identified within the area of the mound itself with the various occupation layers merging towards the fringes of the mound.

The latest archaeological features of the site were burial pits, occasionally with undercut sides and covered with white sand. Several potsherds were found in the mound and in the trench extensions cut at either end of the main trench. Fragments of shell, a single adze, and non-human bone were unearthed in the fill of the ditches. In addition a number of plain and undecorated pottery sherds were found within the various archaeological horizons.

The burial pits were less disturbed than those found at site To-At-1 and the dark stains said to be indicative of black tapa cloth, was confined to a small number of adult burials. Collagen from bone samples was submitted for radiocarbon dating from two separate and distinct horizons. A left femur and right humerus provides a date of 770 ± 200BP\(^1\) (GaK-1204) while the left tibia and fibula furnished a date of 390 ± 110BP\(^1\) (GaK-1205).

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\(^1\) The low precision of the measurements is due to the small amounts of extractable collagen in the samples and renders the calibrated date ranges meaningless.
Figure 7.4. Plan of site To-At-2 revealing excavated areas. Stripped areas denote Test Pit A. Source: Davidson, 1969.
7.4 Experimental

Lead and Sr isotope ratios were determined using MC-LAM-ICPMS, ASV and TIMS. Elemental concentrations were determined with GFAAS. The results reported here are those of TIMS and GFAAS. The independently verified results obtained using MC-LAM-ICPMS, ASV are shown in Table If.1, Appendix If. The sample preparation techniques and the equipment employed for these determinations are outlined in Chapters 3 and 4.

7.5 Results and Discussion

7.5.1 Lead Isotopes

Tooth enamel samples from sites To-At-1 and To-At-2 were analysed and then compared with Pb isotope data available within the geochemical literature. By this means, it was possible to produce an isotopic template for determining the source of the individual’s ancient, in vivo, Pb exposure. As detailed in Chapter 3, it is suggested that this isotopic signature was overwhelmingly accumulated by ingestion and that, due to the geology of Tongatapu any variance from this signature provides prima facie evidence of an individual whose island of burial differs from that on which they were born.

The tooth enamel data from individuals inhumed on Tongatapu were then compared with the Pb isotopic data for the Cook Islands, Samoa, Hawaii, the Society Islands, Marquesas Island, Easter Island, Pitcairn Island, Gambier Island, Solomon Island, the New Britain Arc, Feni Island, Tonga Arc as well as the Island of Tongatapu itself. Although by no means exhaustively defined, these isotopic fields are defined using the best data currently available in the literature and represent the current geochemical isotope boundaries of the major island groupings within Oceania. If the precision and accuracy of provenance determinations are to be improved in the future, then it is certainly desirable to extend the number of host rock analyses in the database. However, for the purposes of the current study, which aims to determine the viability of the method, the current database is certainly adequate.

Lead isotope ratios for each island or archipelago fall into isotopically distinct ‘fields’ (Figure 7.6). There is some degree of overlap between adjacent fields, and as noted by Scaife et al., (1996) if teeth were found to have isotope signatures that fall in this region of
overlapping ‘isotopic space’, it would be impossible to distinguish which island groups were the point of birth. Fortunately, when viewed in all the three dimensions, the degree of overlap is slight (See Figure 7.6).

![Figure 7.5. Integrity of the Pb isotope measurements as provenance markers. Ratios for the individual islands/island arcs were obtained from the GEOROC database: Cook Islands (Hemond and Devey, 1994); Marquesas Island (Caroff et al., 1995; Desonie, Duncan and Natland, 1993; Kogiso et al., 1997); Solomon Islands (Tejada et al., 1996); Samoa (Wright and White, 1987; Hauri and Hart, 1997; Natland and Turner, 1985); Society Islands (Hemond, Devey and Chauvel, 1994; White and Duncan, 1996); New Britain Arc (Woodhead, Eggen and Johnson, 1998; Woodhead and Johnson, 1993); Hawaii (Rhodes, 1996; Lassiter et al., 2000); Tuamotu Island (Woodhead, 1996); Feni Island (Stracke and Hegner, 1998); Easter Island (Hanan and Schilling, 1989; Kingsley and Schilling, 1998); Gambier Islands (Dupuy, 1993); Tonga Islands (Turner, 1997; Ewart et al., 1998; Wendt et al., 1997; Loock et al., 1990; Gill, 1976).]
Figure 7.6. Three dimensional Pb isotope ratio plot of varying Pacific Islands. Note the disparity between Figure 7.5 and 7.6. The overlap becomes fairly small, allowing provenancing between tight fields.

Radiometric data obtained from the tooth enamel samples is shown in Table 7.0. A total of sixteen tooth enamel samples were analysed from sites To-At-1 and To-At-2.
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<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
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<td>AT13</td>
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<td>15.5849</td>
<td>18.3716</td>
</tr>
<tr>
<td>AT14</td>
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<td>15.6117</td>
<td>18.3662</td>
</tr>
<tr>
<td>AT15</td>
<td>38.0024</td>
<td>15.4786</td>
<td>18.5259</td>
</tr>
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<td>AT16</td>
<td>37.9729</td>
<td>15.4766</td>
<td>18.3231</td>
</tr>
</tbody>
</table>

Table 7.0. Lead isotope ratios for tooth enamel samples. Sample IDs between AT1 and AT7 belong to site To-At-1 while AT8 to AT16 correspond with site To-At-2. Errors (2σ, n = 5): $^{208}\text{Pb}/^{204}\text{Pb}$ (±0.01), $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ (±0.003).

The characterisation of isotope fingerprints for an archaeological individual is a process that is markedly different from that previously used to source a base-metal ore-deposit (Gale and Stos-Gale, 1982). The Pb isotope ‘fingerprint’ or ‘signature’ in dental enamel results from variations of concentrations and ratios affecting dietary inputs during a restricted period of childhood and should be considered as a single weighted mean value. It is expected that the isotopic signatures of an ancient population living in a small island community, would have a small range of values normally distributed about a mean that represents the predominant source of Pb burden, that is, the water supply. Additional inputs to the signature during childhood would be likely to shift the isotopic signature of the population, rather than spreading the data, (as occurs in Pb isotope analysis of ancient metalwork). Clearly, if the use of Pb isotope analysis of dental enamel is to be used as a provenance tool, a means must be devised of independently verifying the integrity of the measurements. Fortunately, unlike radiocarbon and Sr isotope analysis, Pb isotope ratios are not based on measurements of a single isotope. Instead, they are absolute values derived from three distinct decay series; two of which derive from a single element, U. An understanding of the geological significance of the data in terms of $^{206}\text{Pb}/^{238}\text{U}$,
$^{207}\text{Pb}/^{235}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ provides several means of checking the accuracy of the measurement without introducing \textit{a priori} assumptions regarding its conformability.

As expected, the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for the teeth are linearly correlated; Pearson correlation coefficient, $r = 0.715$ (see Figure 7.7). Since both of these radiogenic isotopes derive from a single elemental parent (U) and the islands of the Oceanic archipelagos were formed as the result of single isolated events in geological time, it is to be expected that the $p$-value or probability (in this case, 0.048) should show a straight line relationship for the uranogenic isotopes of Pb. As a means of determining the linear relationship, the coefficient of determination ($r^2 = 0.511$) was calculated and showed that the least squares line accounts for 51.10\% of the total variation in the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios. Similarly, statistical analyses of Pb isotopes for the varying islands also shows a strong linear relationship between $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ with all coefficients ranging between 51.92\% for the Tongan Arc to 99.68\% for Easter Island. However, there is a notable discrepancy between these results and those obtained for Samoa, Cook and the Marquesas Islands (which have coefficient of determinations, 11.87\%, 6.18\% and 20.42\%, respectively). This anomaly is attributed to either the relatively small size of the sample set for these islands or the collation of imprecise data ascribed from a multitude of authors. Although the $^{207}\text{Pb}/^{204}\text{Pb}$ data for these islands are linearly correlated coefficients are low (5.71\% for Samoa, 1.23\% for the Cook Islands and 0.15\% for the Marquesas).
Figure 7.7. Plot of Pb isotope ratios of tooth enamel samples from the Tonga College grounds and varying Pacific Island geologies, (a) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, (b) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ Tooth enamel errors (2σ, $n =$ 5): $^{208}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.01$), $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.003$).
The question of how to handle comparisons between archaeological and geological Pb isotope data has been the subject of intense debate (Sayre et al., 1992; Budd et al., 1996). Many multivariate statistical procedures have been proposed some of which have proved to be of dubious value whilst others are potentially useful, provided that the data conforms to a particular geological model. In the 1980s Differential Function Analysis (DFA) was a popular means of separating overlapping isotopic data, particularly amongst scientists based at Oxford (Gale and Stos-Gale, 1982). Whilst DFA remains a powerful method of quantitatively determining whether a sample is a member of a particular source group or not, its successful application depends upon all possible sources of variation being accounted for. Since archaeological scientists cannot revisit the past to ensure that this is the case, the method is not applicable within science-based archaeology. In an effort to separate the increasingly intractable Pb isotope data for the metalliferous ore deposits of the eastern Mediterranean, Sayre et al., (1992) suggested that the volume of isotope space occupied by individual ore source fields could be reduced using Linear Regression Analysis. Rather than including the precision on an individual measurement, the fields were reconstructed on the basis of 95% confidence limits. Whilst this approach might be viable if the sources of possible variation were geologically conformable and fully defined, once more, we cannot be sure that this is the case when dealing with the past. As has been pointed out by Baxter et al., (1999), the data points that characterise a Pb isotope ore field are far more likely to have a non-normal than normal distribution (being bi- or multi-modal) and thereby invalidating many of the statistical tests applied to the datasets. It seems that the problems associated with many aspects of provenance analysis in archaeology, stem from an almost overwhelming temptation to overstep the constraints set by the provenance postulates (see Chapter 1). Ultimately, as shown by Scaife et al., (1996) the best method of determining whether an archaeological sample is a member of a particular source group, is by visual examination of the 3D data plot. Using this method it is possible to determine whether an individual was born on the island group other than on which they were buried. However, it is much more difficult to say which island they were born on. Although isotope analysis on the Pacific islands has few of the mixing problems and complications that have dogged the use of Pb isotope analysis of metal artefacts (mixing, recycling, processing, contamination, etc), the isotopic map of Oceania is not complete, and therefore it is not yet possible to determine the provenance of individuals born outside of Tonga, in anything more than general directional terms.
Comparison of the isotopic data for the individuals buried on Tongatapu shows that all but four of the samples, outliers (AT6, AT7, AT9 and AT10), correspond to a volume of 3D isotopic space which also contains the basalt samples collected from the same island (Turner et al., 1997), consistent with these individuals having received their entire accumulated Pb burden entirely from the local geochemical environment of Tongatapu. No significant differences were found in the isotopic signatures of enamel discovered at the two sites. For the purposes of the discussion, these twelve samples are treated as a block corresponding with the island on which they were found. The four ‘outliers’ are discussed separately in section 7.5.2.

The mean of the isotopic ratios for these twelve samples are in good agreement with that of the local bedrock (see Figure 7.8). The mean of tooth enamel $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios are $37.9839 \pm 0.0100$ and $15.5414 \pm 0.0030$ respectively, compared with local bedrock samples procured from Turner et al., (1997); $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios $38.090$ and $15.540$, respectively. However, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio undergoes a visible shift in the mean of the tooth enamel ratios ($18.4229 \pm 0.0030$) compared with the local bedrock ratios ($18.515$). The significance of this shift is uncertain, as it is not yet based on a statistically viable number of samples and no comparable material was available from other islands in order to determine whether it is part of a generalised trend or a remnant of an activity that was culturally specific to Tongatapu.
Figure 7.8. Plot of Pb isotope ratios for 12 tooth enamel samples and local Tongan Island Arc bedrock ratios, (a) $^{208}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb, (b) $^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb. Outliers AT6, AT7, AT9 and AT10 not plotted here. Data for Tongan Islands was taken from (Turner, 1997; Ewart et al., 1998; Wendt et al., 1997; Loock et al., 1990; Gill, 1976). Tooth enamel errors ($2\sigma$, $n = 5$): $^{208}$Pb/$^{204}$Pb ($\pm 0.01$); $^{207}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb ($\pm 0.003$).
It can be seen from Table 7.1, that the Pb\(^{2+}\) ion concentration of tooth enamel ranges in concentrations from 0.026 ± 0.001µg/g to 0.351 ± 0.020µg/g. With a mean value of 0.135 ± 0.006µg/g, this concentration is approximately ten times less than the Pb content of the local bedrock samples, 1.32µg/g (Turner et al., 1997; Gill, 1976; Ewart et al., 1998; Wendt et al., 1997). Similarly, a comparison of Pb\(^{2+}\) ion concentration with \(^{208}\)Pb/\(^{204}\)Pb, \(^{207}\)Pb/\(^{204}\)Pb and \(^{206}\)Pb/\(^{204}\)Pb isotope ratios confirms that there is no correlation between Pb\(^{2+}\) ion concentration and isotope ratios (see Figure 7.8).

<table>
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<tr>
<td>ID</td>
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<tr>
<td>AT1</td>
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</tr>
<tr>
<td>AT2</td>
<td>0.045 ± 0.002</td>
</tr>
<tr>
<td>AT3</td>
<td>0.177 ± 0.007</td>
</tr>
<tr>
<td>AT4</td>
<td>0.105 ± 0.004</td>
</tr>
<tr>
<td>AT5</td>
<td>0.044 ± 0.002</td>
</tr>
<tr>
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</tr>
<tr>
<td>AT7</td>
<td>0.023 ± 0.001</td>
</tr>
<tr>
<td>AT8</td>
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</tr>
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<td>AT9</td>
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<tr>
<td>AT10</td>
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<td>AT12</td>
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<td>0.228 ± 0.009</td>
</tr>
<tr>
<td>AT15</td>
<td>0.047 ± 0.002</td>
</tr>
<tr>
<td>AT16</td>
<td>0.319 ± 0.013</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Tonga Islands</th>
<th>Pb Concentration</th>
</tr>
</thead>
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<tr>
<td>ID</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>VI</td>
<td>3.0</td>
</tr>
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<td>VII</td>
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**Table 7.1.** Tooth enamel Pb\(^{2+}\) ion concentration (µg/g) obtained by GFAAS for sites To-At-1 (AT1 to AT5) and To-At-2 (AT8 to AT16). Tonga Island Pb\(^{2+}\) ion concentrations were taken from: (I) Turner et al., (1997); (II) Gill, (1976); (III) Ewart et al., (1998); and (IV) Wendt et al., (1997). Tooth enamel errors (2σ; n = 5).
Figure 7.9. Plot of Pb isotope ratios for tooth enamel samples (green diamonds) and Tonga Island bedrock (purple circles) ratios. Lead ion concentration versus: (a) $^{206}\text{Pb}/^{204}\text{Pb}$, (b) $^{207}\text{Pb}/^{204}\text{Pb}$, and (c) $^{208}\text{Pb}/^{204}\text{Pb}$. Coefficient of determination, $r^2$ denoting the lack of correlation between Pb$^{2+}$ ion concentrations and Pb isotope ratios. Tooth enamel Pb isotope errors (2σ, $n = 5$): $^{206}\text{Pb}/^{204}\text{Pb} (±0.01); ^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb} (±0.003)$. 
7.5.2 Strontium Isotopes

Although measurements of Sr isotope ratios are not viable as a provenancing tool within Oceania, they have been included in the study as a comparative tool and crosscheck on the Pb isotope ratio measurements.

As anticipated, no correlation between Pb$^{2+}$ and Sr$^{2+}$ concentration of tooth enamel samples was found ($r = 0.095, \ r' = 0.009$) (Figure 7.10).

![Figure 7.10. Concentration (μg/g) plot of Pb$^{2+}$ ions versus Sr$^{2+}$ ions as determined by GFAAS. Errors: (2σ; n = 5).](image)

It has been suggested elsewhere (Budd *et al.*, 1998) that the predominant source of Sr$^{2+}$ ions in ancient populations is drinking water. Whilst this may be true for mainland populations, the lack of any significant correlation between Pb$^{2+}$ and Sr$^{2+}$ ion concentrations in the current study indicates that this is not the case for isolated island communities, where the overwhelming source of Sr$^{2+}$ ions is the marine environment, whereas that of Pb$^{2+}$ is primarily terrestrial. When the Sr isotope ratios of local Tongan Islands were plotted against tooth enamel samples from Tongatapu (Figure 7.11) the majority of samples form a fairly tight cluster around a single Sr isotope ratio of 0.70350 ± 0.00003 close to that of the seawater. However, the remaining two samples (AT3 and
AT16) show considerable variance from this mean. The reason for this variation, which bears no clear relation to composition of local bedrock, is unclear.

Figure 7.11. Plot of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ of tooth enamel samples and Tongan Island bedrock (Turner, 1997; Ewart et al., 1998; Wendt et al., 1997; Loock et al., 1990; Gill, 1976). Tooth enamel errors: $^{206}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.01: 2\sigma$; $n = 5$); $^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 0.000026: 2\sigma$, $n = 6$).

There is an exact correspondence between the Pb isotope signatures of dentine from site To-Ar-1 and that of the underlying geology (see Figure 7.12), indicating that in contrast to enamel, the dentine has probably reached post-depositional equilibrium with the burial environment. This result confirms, once again, that the Pb isotope signature accumulated in vivo in this dentine does not survive long term burial. The evidence accumulated throughout this study suggests that enamel Pb and Sr isotope ratios reflect values accumulated in vivo and that morphological changes in dental tissues within buried environments, including diagenetic turnover of metal ions do not affect the biogenic integrity of the isotope signatures.
Enamel samples from the four individuals denoted as outliers (AT6, AT7, AT9 and AT10) have Pb isotopic signatures that lie outside of the field determined for the local bedrock of Tongatapu. The two samples most at variance with the signature of the island bedrock (AT9 and AT10) belong to site To-At-2. The remaining two samples (AT6 and AT7) are derived from site To-At-1 (see Figure 7.13). Clearly these four individuals did not receive the biogenic Pb burden accumulated in their dental enamel from the island on which they were buried. They can therefore be considered as having moved to Tonga from ‘elsewhere’ during their lifetime, thus providing the first direct evidence for long-distance movement of archaeological populations in antiquity and for continued post-settlement contact between the islands of remote and near Oceania. It is clear from Figure 7.13, that four individuals have isotope signatures indicative of an entirely different dietary source to that of the remaining individuals. Unfortunately, there are insufficient details available regarding the individuals buried at sites To-At-1 and To-At-2, making it impossible to determine whether there is any correlation between the isotopic measurements and other classifications such as age or gender.
Figure 7.13. Plot of $^{208}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb of tooth enamel samples. Four (AT6, AT7, AT9 and AT10) samples are distinct outliers. Dashed line indicates 4.55Ga Geochron. Errors (2σ, n = 5): $^{208}$Pb/$^{204}$Pb (±0.01) and $^{206}$Pb/$^{204}$Pb (±0.003).

Interestingly, as depicted in Figure 7.13, AT6 plots above the growth curve, suggesting a source enriched in Th relative to U and in contrast to those of the vast majority of samples, which appear depleted in $^{208}$Pb relative to $^{206}$Pb. Furthermore all samples are significantly depleted in $^{207}$Pb (see Figure 7.14).
Figure 7.14. Plot of $^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb isotope ratios of tooth enamel samples. Samples AT6 and AT7 correspond with site To-At-1 while AT9 and AT10 to site To-At-2. Errors ($\sigma$, $n = 5$): $^{207}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb (±0.003). Dashed line indicates 4.55Ga Geochron.

One of the surprising aspects of the Pb isotope analysis is that the proportion of exotic individuals buried at To-At-1 and To-At-2 was so high (25%). One possible reason for this result might be that the soil and bedrock leaches affecting these individuals in vivo, produced far more variation and more radiogenic Pb isotope ratios than are normally associated with the geology of Tongatapu. If ratios such as these were encountered outside of Oceania then one might be led to conclude that these individuals had been affected by anthropogenic Pb exposure. The one possibility that can never be discounted in any provenance study is that the measured signal relates to some unknown past cultural practice involving early lifetime exposure to a Pb$^{2+}$ ion source of ‘foreign’ origin, rather than ‘natural’ exposure through the local water supply. However, the fact that exposure to an anthropogenic Pb source can be discounted in this case, and that the concentration of Pb$^{2+}$ ions is between 10 and 100 times lower in concentration than that found in the teeth, makes it far more likely that the isotopic signature is derived from underlying bedrock geology at the place of childhood residence. Even allowing for the fact that excavations at these two sites may have unintentionally skewed the results of the survey in favour of immigrants, the proportion of migrants indicates a far higher degree
of mobility between island groups within ancient Polynesia than is implied by most of the current models for the archaeology of the region.

7.5.3 Possible Origins

Attempting to identify the islands of origin of the individuals in the Tongatapu burials in a positive sense is not a simple operation. Due to the low Pb\(^{2+}\) ion concentrations within basaltic rocks, Pb isotope analysis is analytically more challenging than that of metalliferous ore deposits.

It is apparent from Figure 7.15 that the majority of tooth enamel samples match the ‘natural’ geological background signal for local Tongatapu without significant additional Pb\(^{2+}\) ion inputs from sources other than the local agriculture and water supply. In total, twelve of the tooth enamel samples match the local bedrock of Tongatapu Island, which is the result one would have expected if the individuals had passed their childhood years on the same island as they died (Figure 7.15). Two of the ‘outlier’ samples (AT9 and AT10) match the Pb isotope signature of islands within the Tongan Arc while the remaining two outliers (AT6 and AT7) possibly originated from somewhere within present day Solomon Islands. It is difficult to accurately identify the particular island within the Tongan Arc from which an individual originated. As suggested by Kaeppler (1978) the movement of marriage partners from Fiji and Samoa to Tonga could be feasible. It is entirely possible that fully accurate determinations of provenance will never be possible. Defining each island within the arc is likely to result in a series of overlapping isotope fields (see Figure 7.16). When account is taken of the analytical precision of the isotope measurements, determinations of provenance at the level of individual islands will become ambiguous. Nevertheless, in view of the range of isotopic variation exhibited by the islands within the Tongan Arc, or the Solomon Islands, it is highly desirable that the current database of basaltic measurements is increased.
Figure 7.15. Plot of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ for tooth enamel samples and representative islands of the Tongan Island Chain: Ata and Tofua (Turner et al., 1997); Niuafou’ou (Ewart et al., 1998); Tafahi (Wendt et al., 1997). Dashed line indicates 4.55 Ga Geochron. Tooth enamel errors (2σ, n = 5): $^{208}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.01$) and $^{206}\text{Pb}/^{204}\text{Pb}$ ($\pm 0.003$).
Chapter 7-Provenance Studies Case Study II: Island of Tongatapu, Kingdom of Tonga

Figure 7.16. Plot of $^{208}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb showing compositional ranges for a number of islands: Cook Islands (Hemond and Devey, 1994), Samoa (Wright and White, 1987; Hauri and Hart, 1997; Natland and Turner, 1985), Tonga Arc (Turner et al., 1997), Hawaii (Hofmann and Jochum, 1996; Rhodes, 1996) Easter Island (Hanan and Schilling, 1989; Kingsley and Schilling, 1977), Marquesas (Caroff et al., 1995; Desonic et al., 1993), Society Island (Hemond et al., 1994; Hauri and Hart, 1997), Tuamotu (Woodhead, 1996), Gambier (Dupuy et al., 1993), Solomon (Tejada et al., 1996; Tejada et al., 2002), New Britain Arc (Woodhead and Johnson, 1993; Woodhead, Eggin and Johnson, 1998), Feni (Stacke and Hegner, 1998), Fiji Island (Gill, 1984). Dashed line represents Pb isotope 4.55Ga Geochron.

7.6 Conclusion

The diverse geology and biotic variability on thousands of islands in the Pacific Ocean that has, since they were first ‘discovered’ by western explorers, set the stage for endless experiments in human adaptation as a means of understanding the evolution and transformation of these island societies. Despite the application of a wide assortment of scientific methods to the problems of the movement of peoples and ideas many questions still remain unanswered. Dissatisfaction with the equivocal results provided by studies of stylistic variation of ceramic typologies, particularly in a region where ceramic production is discontinuous, have led researchers to apply numerous science-based
strategies to answer questions of settlement and cultural contact between island groups. Although these methods have provided valuable information, elemental analyses of obsidian, pottery and basalt have proved useful in provenance studies. The results of the current study show that Pb isotope analysis can be a valuable addition to the scientific methods used within Pacific Archaeology and can be used with some confidence as a direct indicator of migration, at the level of the individual, within island communities. Although both Pb and Sr isotope analyses have been applied to the question of migration, only Pb isotopes have proved useful in resolving questions of provenance: providing direct evidence of long-distance post-settlement interaction between the Island of Tongatapu and islands somewhere within near Oceania.
Chapter 8
Conclusion

8.1 Diagenesis of Bone

Archaeological bone is recovered in a diagenetically altered condition, therefore rendering the results of most chemical analysis meaningless. Although isotope based research on archaeological bone removes one of the inherent difficulties regarding analytical studies (inter-subject chemical variability between individuals found on the same site), it does not, by itself, guarantee the biogenic integrity of the measurements made.

In contrast, there is extensive literature indicating that, with the exception of limited amino acid racemisation, the degree of diagenetic alteration of dental enamel in archaeological deposits is within the limits of analytical error, over the time spans encountered on most archaeological sites.

It has been shown that Pb\textsuperscript{2+} ions trapped in micro trace quantities within dental enamel remain unaltered over long-term burial and that both archaeological bone undergoes complete post-depositional turnover in the groundwater even over comparatively short periods of time (less than 100 years).

Results have confirmed that the Sr and Pb isotope signatures of archaeological bone and dentine do not necessarily relate in any way to \textit{in vivo} activities of the subject, but instead are determined by the groundwater geochemistry at the point of burial. It appears that Pb\textsuperscript{2+} ions introduced into the bone from the groundwater are diffused throughout the organic matrix of the bone, removing any trace of the isotopic interface used as ‘proof’ of diagenetic turnover.
The results presented show that the importance of Pb\(^{2+}\) ion measurements on archaeological material stretches beyond science-based archaeological concerns regarding the migration patterns of ancient populations. High levels of Pb\(^{2+}\) ions in body tissue have been shown to be fatal. The study undertaken here confirms that most human Pb\(^{2+}\) ion uptake occurs via the respiratory and gastrointestinal tract and that the single most important factor limiting Pb\(^{2+}\) ion absorption into the bloodstream is the solubility of Pb\(^{2+}\) ions in the fluid in which it enters the body.

8.2 Ca- and Pb-Hydroxyapatite Synthesis

It has been shown that a miscibility gap exists in the Ca-PbHA solid solution series at low temperature and that the degree of solid state substitution of Ca\(^{2+}\) ions into the PbHA lattice depends on two factors: the temperature of the calcining step and the relative proportions of Ca\(^{2+}\)(aq) and Pb\(^{2+}\)(aq) ions in the reaction mixture. Similarly, the size of the miscibility gap changes with respect to the temperature of the calcination step and disappears when the precipitate is sintered at temperatures above 1073K. However, below this temperature the relatively high rate of crystallisation of PbHA precludes the possibility of Pb substitution into CaHA phase. The precipitation of any crystalline CaHA phase would seem to depend upon Ca\(^{2+}\)(aq) ions predominating in the initial reaction mixture. Unless the reaction mixture was calcined at above 1073K, when the solid solution series was complete, no instance of Pb\(^{2+}\) ion substitution into the CaHA lattice was ever observed in the experiments completed here, indicating that at lower temperatures, the lattice energy of PbHA is too high to permit diffusion and incorporation of Ca atoms into the structure. It is clear from plots of lattice parameter versus composition of the reaction mixtures that some degree of solid-state substitution of Ca into PbHA does occur at temperatures lower than 973K. However, and in contrast to previous studies, it is unclear from the experiments whether complete incorporation of Ca is achieved, or whether the precipitates consisted of a mixture of crystalline PbHA together with an X-ray amorphous or cryptocrystalline Calcium(II) salt.

Furthermore, the identity of any solid state product formed after calcination depends largely on the relative rates of formation of the mineral species formed and that in the case of Ca(II) phosphate species the rate of recrystallisation to the thermodynamically
stable CaHA is slow, resulting in the long term persistence of metastable phases of indeterminate structure and stoichiometry.

The existence of the miscibility gap observed in the Ca-PbHA solid solution series helps to rationalise some observations regarding the occurrences of these phases in the natural and biochemical environments. Firstly, at ambient temperatures, it seems that the degree of solid-state substitution of Pb into crystalline CaHA such as dental enamel is markedly small. Secondly, as shown above, in the presence of even small amounts of halide ions, such as Cl(aq), pyromorphite is formed preferentially to PbHA at temperatures as low as 373K, which may explain why PbHA has never been observed as a naturally occurring mineral species. It is suggested that the long standing debate as to whether the PbCaHA system forms a complete solid solution series, can be rationalised in terms of variations in parameters such as pH, temperature and pressure employed during syntheses and that the final products are those determined largely by kinetic, rather than thermodynamic factors (Brown and Fulmer, 1991).

8.3 Isotope Studies

It has been confirmed by this study that of all the possible isotopic systems suggested as potential sources of provenance or palaeo-dietary information, only Pb isotope analysis is suitable for use within Pacific Archaeology. Strontium isotope analysis, which has been suggested as a source of both palaeo-dietary and provenance information elsewhere, is not suitable, at least as a stand-alone means of determining provenance. The natural variation in isotopic signatures between islands is insufficient to determine which island is the source of ‘outliers’. Similar considerations pertain to the study of stable O and C isotopes in inorganic fractions. In the case of these elements the degrees of fractionation, natural variation in isotope signature and diagenetic interaction in buried environments have yet to be determined.

8.3.1 Case Study I: Sohano Island, North Solomons

The study conducted on the teeth from the Sohano Rock Shelter provides proof that Pb isotopic analysis of tooth enamel produces data that relates to the source of biogenic Pb\(^{2+}\) accumulated in vivo, even after long-term burial.
The Sohano Rock Shelter study provides new archaeological information on the dental remains and the activities undertaken there. The individuals whose dentition accumulated within the shelter did not, as previously suggested, belong to captured individuals, but were for the most part drawn from a single population somewhere within Buka or perhaps Bougainville. The Pb and Sr isotope values for most of the teeth analysed have a single value: one that is different from the soil within the shelter. This unusual occurrence is not one that is found amongst modern populations. Even within modern industrial environments contaminated with tetra-ethyl Pb additives to petrol, a number of additional sources of Pb$^{2+}$ ions would be expected to show up as minor variations in measurements made on dental enamel (Gulson and Gillings, 1997). The fact that these ancient individuals have a single isotopic signature points to their exposure to a very restricted source of Pb: probably the water supply in conjunction with local agriculture. It is certainly indicative of a sedentary population with children partaking in a relatively restricted set of practices taking place in one area. Interestingly, although the radiocarbon dates for the site are rather too old and imprecise and probably require re-evaluation, the occupation of the shelter is currently dated to a period well inside that of the Lapita dispersal. Despite this, the ‘outsiders’ to this highly restricted pool are consistent with origins in the Bismarks and the Solomons known to have been in contact since the Early-Holocene (Kirch, 2002).

8.3.2 Case Study II: Tongatapu, Kingdom of Tonga
Comparison of the isotopic data for the individuals buried on Tongatapu show that all but four of the samples are consistent with individuals having received their entire accumulated Pb burden entirely from the local geochemical environment of Tongatapu. Similarly, there is no significant correlation between Pb and Sr concentration of tooth enamel samples; the lack of significant correlation indicating that the incorporation of these elements within dental enamel is not interdependent either in vivo or during burial, or indeed both.

Four individuals have Pb isotopic signatures that lie outside of the field determined for the local bedrock of Tongatapu, therefore not receiving their biogenic Pb burden from the island on which they were buried and can therefore be considered as having moved to Tonga from elsewhere during their lifetime thereby presenting unequivocal evidence for long-distance movement of archaeological populations in antiquity.
References


Encyclopaedic Handbook of Biomaterials and Bioengineering, Part B Applications, New York: Marcel Dekker Inc.


References


Foley, W.A. (1980). History of Migrations in Indonesia is seen by a Linguist, In J.J. Fox (Ed.), Indonesia: Australian Perspectives, Research School of Pacific Studies, Canberra, 1, 75-80.


Nature, 204, 1050-1052.

Hygienic Problems Relating to the Absorption of Lead: the Harben Lectures, Journal of 
Royal Institute of Public Health and Hygiene, 24, 177–203.

Kempe, D.R.C. and Harvey, A.P. (1983). The petrology of archaeological artefacts, 

Minerals, Methods of Data Correction and an Assessment of Data Quality at the NERC 
Isotope Geosciences Laboratory, NERC Isotope Geosciences Laboratory Series No. 78, 1-26.


Gomez Seamount Chain, Easter Microplate System: Pb Isotope Evidence, Journal of 
Geophysics Research, B103, 24159-24177.

Society, 95, 9-40.

Kirch, P.V. (1986). Island Societies: Archaeological Approaches to Evolution and Transformation, 
Cambridge: Cambridge University Press.


Strehlow, C.D. (1972). The Use of Deciduous Teeth as Indicators of Lead Exposure, Ph.D Dissertation, New York University, USA.


References


and Reconstruction: Approaches to Archaeology and Forensic Science, Manchester: Manchester University Press, 55-64.


Appendices
Appendix Ia

- Amino acid content of various protein fractions (Table Ia.1).

- Composition of mineralised dental tissues (Table Ia.2.).
<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>Mature Tuft Protein</th>
<th>Mature Total Protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspartate</td>
<td>79</td>
<td>96</td>
</tr>
<tr>
<td>Glutamate</td>
<td>136</td>
<td>130</td>
</tr>
<tr>
<td>Threonine</td>
<td>52</td>
<td>51</td>
</tr>
<tr>
<td>Serine</td>
<td>82</td>
<td>72</td>
</tr>
<tr>
<td>Hydroxyproline</td>
<td>&lt; 2</td>
<td>n/a</td>
</tr>
<tr>
<td>Proline</td>
<td>81</td>
<td>61</td>
</tr>
<tr>
<td>Alanine</td>
<td>69</td>
<td>79</td>
</tr>
<tr>
<td>Glycine</td>
<td>62</td>
<td>108</td>
</tr>
<tr>
<td>Valine</td>
<td>52</td>
<td>60</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>23</td>
<td>13</td>
</tr>
<tr>
<td>Leucine</td>
<td>111</td>
<td>96</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>51</td>
<td>17</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>49</td>
<td>37</td>
</tr>
<tr>
<td>Tryptophan*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxylysine</td>
<td>6</td>
<td>n/a</td>
</tr>
<tr>
<td>Lysine</td>
<td>40</td>
<td>53</td>
</tr>
<tr>
<td>Histidine</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>Arginine</td>
<td>36</td>
<td>49</td>
</tr>
<tr>
<td>Cystine</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Methionine</td>
<td>22</td>
<td>19</td>
</tr>
</tbody>
</table>

**Table Ia.1.** Amino acid content of various protein fractions separated from developing and mature enamel (expressed as residues per 1000 total residues). Source: Termine *et al.*, (1980). (*Not determined*).
<table>
<thead>
<tr>
<th></th>
<th>Developing Enamel</th>
<th>Mature Enamel</th>
<th>Dentine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight</td>
<td>Volume</td>
<td>Weight</td>
</tr>
<tr>
<td>Inorganic (%)</td>
<td>37</td>
<td>16</td>
<td>≥ 69</td>
</tr>
<tr>
<td>Organic (%)</td>
<td>19</td>
<td>20</td>
<td>&lt; 0.2 to &gt; 0.6</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.45</td>
<td></td>
<td>2.9 - 3.0</td>
</tr>
<tr>
<td>Calcium (%)</td>
<td>34 - 40</td>
<td></td>
<td>26 - 28</td>
</tr>
<tr>
<td>Phosphorus (%)</td>
<td>16 - 18</td>
<td></td>
<td>12.2 - 13.2</td>
</tr>
<tr>
<td>Ca/P ratio (weight)</td>
<td>1.92 - 2.17</td>
<td></td>
<td>2.1 - 2.2</td>
</tr>
<tr>
<td>Ca/P ratio (molar)</td>
<td>1.5 - 1.68</td>
<td></td>
<td>1.6 - 1.7</td>
</tr>
<tr>
<td>CO₂ present as carbonate (%)</td>
<td>1.95 - 3.66</td>
<td></td>
<td>3.0 - 3.5</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>0.25 - 0.90</td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Magnesium (%)</td>
<td>0.25 - 0.56</td>
<td></td>
<td>0.8 - 1.0</td>
</tr>
<tr>
<td>Fluorine (µg/g)</td>
<td>&lt; 25 to &gt; 5000</td>
<td>(surface)</td>
<td>50 - 10000</td>
</tr>
<tr>
<td>Iron (µg/g)</td>
<td>8 - 218</td>
<td></td>
<td>60 - 150</td>
</tr>
<tr>
<td>Zinc (µg/g)</td>
<td>152 - 227</td>
<td></td>
<td>200 - 700</td>
</tr>
<tr>
<td>Strontium (µg/g)</td>
<td>50 - 400</td>
<td></td>
<td>100 - 600</td>
</tr>
</tbody>
</table>

Table 1a.2. Composition of mineralised dental tissues. Source: Hillson (1996).
Appendix Ib

- GFAAS analysis of modern, historic and prehistoric teeth and bones (Table Ib.1a).
- MC-LAM-ICPMS of Pb isotopes of enamel, dentine and bone samples of archaeologically derived human skeletal remains (Table Ib.1b).
- MC-LAM-ICPMS of Pb isotopes of enamel and dentine samples of modern Broken Hill residents (Table Ib.1c).
- GFAAS determined total Pb$^{2+}$ ion concentration (µg/g), UV and non-UV treated enamel and dentine (Table Ib.1d).
- Ancient Pacific Islander teeth (Table Ib.2).
- LAM-ICPMS Pb$^{2+}$ ion concentrations for Figure 3.0 and 3.1 (Table Ib.3).
- LAM-ICPMS analysed tooth Pb concentrations (µg/g) of modern Broken Hill residents (Table Ib.4).
- LAM-ICPMS of Pb concentrations across the longitudinal section of modern Broken Hill human teeth: samples M21, M22 and M23 (Figure Ib.5a).
LAM-ICPMS of Pb concentrations across the longitudinal section of modern Broken Hill human teeth: samples M24, M26 and M29 (Figure Ib.5b).

ASV determined total Pb$^{2+}$ ion concentration (µg/g), UV and non-UV treated enamel and dentine (Table Ib.6).
<table>
<thead>
<tr>
<th>Sample</th>
<th>ID</th>
<th>Canine</th>
<th>Premolar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>M27</td>
<td>n.a</td>
<td>0.354 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>M28</td>
<td>0.401 ± 0.005</td>
<td>n.a</td>
</tr>
<tr>
<td></td>
<td>M31</td>
<td>0.416 ± 0.001</td>
<td>0.470 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>M38</td>
<td>0.489 ± 0.003</td>
<td>0.435 ± 0.005</td>
</tr>
<tr>
<td>Historic</td>
<td>HA1</td>
<td>0.286 ± 0.005</td>
<td>0.498 ± 0.007</td>
</tr>
<tr>
<td></td>
<td>HA2</td>
<td>0.452 ± 0.002</td>
<td>0.421 ± 0.007</td>
</tr>
<tr>
<td>Prehistoric</td>
<td>AT2</td>
<td>0.303 ± 0.007</td>
<td>0.338 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>AB12</td>
<td>n.a</td>
<td>0.476 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>AB27</td>
<td>0.423 ± 0.003</td>
<td>0.319 ± 0.008</td>
</tr>
</tbody>
</table>

Table Ib.1a. GFAAS analysis of Pb²⁺ ion concentrations of modern, historic and prehistoric teeth and bones. All measurements are in µg/g. (n.a denotes sample not available).
<table>
<thead>
<tr>
<th>Island</th>
<th>Sample</th>
<th>Enamel</th>
<th>Dentine</th>
<th>Bone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ID</td>
<td>$^{208}\text{Pb}/^{204}\text{Pb}$</td>
<td>$^{207}\text{Pb}/^{204}\text{Pb}$</td>
<td>$^{206}\text{Pb}/^{204}\text{Pb}$</td>
</tr>
<tr>
<td></td>
<td>AT2</td>
<td>37.9723±0.0089</td>
<td>15.5499±0.0033</td>
<td>18.4792±0.0050</td>
</tr>
<tr>
<td></td>
<td>AT3</td>
<td>37.9934±0.0084</td>
<td>15.4678±0.0036</td>
<td>18.4564±0.0049</td>
</tr>
<tr>
<td></td>
<td>AT5</td>
<td>37.9607±0.0092</td>
<td>15.5809±0.0035</td>
<td>18.3722±0.0047</td>
</tr>
<tr>
<td></td>
<td>AB12</td>
<td>38.4265±0.0095</td>
<td>15.5465±0.0035</td>
<td>18.6851±0.0046</td>
</tr>
<tr>
<td></td>
<td>AB17</td>
<td>38.4312±0.0095</td>
<td>15.5472±0.0034</td>
<td>18.6856±0.0044</td>
</tr>
<tr>
<td></td>
<td>AB26</td>
<td>38.4233±0.0088</td>
<td>15.5452±0.0036</td>
<td>18.6829±0.0048</td>
</tr>
<tr>
<td></td>
<td>AB27</td>
<td>38.4465±0.0096</td>
<td>15.5536±0.0036</td>
<td>18.7166±0.0051</td>
</tr>
</tbody>
</table>

Table Ib.b. MC-LAM-ICPMS of Pb-isotopes of enamel, dentine and bone samples of archaeologically derived human skeletal remains

<table>
<thead>
<tr>
<th>Sample</th>
<th>ID</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M41</td>
<td>36.2482±0.0087</td>
<td>15.4228±0.0035</td>
<td>16.5941±0.0045</td>
<td>36.3132±0.0091</td>
<td>15.4119±0.0035</td>
<td>16.6101±0.0043</td>
</tr>
<tr>
<td></td>
<td>M39</td>
<td>36.3472±0.0089</td>
<td>15.4682±0.0036</td>
<td>16.6109±0.0042</td>
<td>36.3734±0.0091</td>
<td>15.4488±0.0038</td>
<td>16.6126±0.0045</td>
</tr>
<tr>
<td></td>
<td>M38</td>
<td>36.1009±0.0090</td>
<td>15.3998±0.0034</td>
<td>16.4582±0.0041</td>
<td>36.1015±0.0090</td>
<td>15.3822±0.0034</td>
<td>16.4574±0.0044</td>
</tr>
<tr>
<td></td>
<td>M37</td>
<td>36.0408±0.0090</td>
<td>15.4267±0.0037</td>
<td>16.3835±0.0038</td>
<td>36.0278±0.0090</td>
<td>15.4264±0.0039</td>
<td>16.3869±0.0041</td>
</tr>
<tr>
<td></td>
<td>M36</td>
<td>36.2813±0.0091</td>
<td>15.5009±0.0036</td>
<td>16.5845±0.0045</td>
<td>36.3162±0.0091</td>
<td>15.5021±0.0036</td>
<td>16.5945±0.0045</td>
</tr>
</tbody>
</table>

Table Ib.c. MC-LAM-ICPMS of Pb-isotopes of enamel and dentine samples of modern Broken Hill residents. The local Broken Hill orebody $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is approximately 16.00 while gasoline is 16.56 (Gulson, 1996).
### Table Ib.Id

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Type</th>
<th>Enamel Pb</th>
<th>Enamel Pb (UV)</th>
<th>Dentine Pb</th>
<th>Dentine Pb (UV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT2</td>
<td></td>
<td>0.482 ± 0.096 (3)</td>
<td>0.468 ± 0.016 (6)</td>
<td>18.521 ± 0.556 (3)</td>
<td>35.084 ± 2.571 (3)</td>
</tr>
<tr>
<td>AT3</td>
<td></td>
<td>0.584 ± 0.175 (3)</td>
<td>0.623 ± 0.069 (3)</td>
<td>26.533 ± 0.687 (3)</td>
<td>31.658 ± 1.581 (3)</td>
</tr>
<tr>
<td>AT5</td>
<td></td>
<td>0.553 ± 0.111 (3)</td>
<td>0.526 ± 0.037 (3)</td>
<td>10.089 ± 0.384 (3)</td>
<td>28.105 ± 1.981 (7)</td>
</tr>
<tr>
<td>AB12</td>
<td></td>
<td>0.423 ± 0.252 (3)</td>
<td>0.358 ± 0.032 (3)</td>
<td>5.824 ± 0.214 (5)</td>
<td>19.569 ± 1.223 (3)</td>
</tr>
<tr>
<td>AB17</td>
<td></td>
<td>0.228 ± 0.084 (4)</td>
<td>0.157 ± 0.028 (5)</td>
<td>6.978 ± 0.331 (4)</td>
<td>45.685 ± 3.695 (5)</td>
</tr>
<tr>
<td>AB26</td>
<td></td>
<td>0.525 ± 0.210 (4)</td>
<td>0.529 ± 0.031 (5)</td>
<td>15.823 ± 0.520 (4)</td>
<td>19.721 ± 1.287 (3)</td>
</tr>
<tr>
<td>AB27</td>
<td></td>
<td>0.501 ± 0.268 (5)</td>
<td>0.362 ± 0.027 (4)</td>
<td>18.026 ± 0.618 (3)</td>
<td>24.453 ± 1.597 (3)</td>
</tr>
<tr>
<td>M41</td>
<td></td>
<td>0.668 ± 0.341 (3)</td>
<td>0.644 ± 0.049 (4)</td>
<td>34.628 ± 2.771 (4)</td>
<td>62.786 ± 1.764 (4)</td>
</tr>
<tr>
<td>M39</td>
<td></td>
<td>0.565 ± 0.371 (3)</td>
<td>0.416 ± 0.035 (4)</td>
<td>29.807 ± 2.067 (3)</td>
<td>68.205 ± 3.951 (4)</td>
</tr>
<tr>
<td>M38</td>
<td></td>
<td>0.624 ± 0.516 (3)</td>
<td>0.467 ± 0.047 (4)</td>
<td>23.389 ± 1.559 (3)</td>
<td>58.467 ± 3.998 (5)</td>
</tr>
<tr>
<td>M37</td>
<td></td>
<td>0.634 ± 0.498 (3)</td>
<td>0.520 ± 0.027 (5)</td>
<td>20.319 ± 3.105 (3)</td>
<td>42.068 ± 2.415 (5)</td>
</tr>
<tr>
<td>M36</td>
<td></td>
<td>0.749 ± 0.419 (3)</td>
<td>50.204 ± 0.246 (5)</td>
<td>34.578 ± 2.179 (5)</td>
<td>58.476 ± 4.541 (5)</td>
</tr>
</tbody>
</table>

**Table Ib.Id.** GFAAS determined total Pb$^{2+}$ ion concentration in μg/g, UV and non-UV treated enamel and dentine. Ancient Tongatapu (AT#), Buka (BT#) and modern Broken Hill (M#) samples have been analysed. Number of experimental runs (n) in parentheses.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Oceanic Island</th>
<th>Trench</th>
<th>Layer</th>
<th>Age</th>
<th>Tooth Type</th>
<th>Condition of Tooth</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT2</td>
<td>Tongatapu</td>
<td>To-At-1</td>
<td>-</td>
<td>1200 BP*</td>
<td>Canine</td>
<td></td>
</tr>
<tr>
<td>AT2p</td>
<td>Tongatapu</td>
<td>To-At-1</td>
<td>-</td>
<td>1200 BP*</td>
<td>Premolar</td>
<td></td>
</tr>
<tr>
<td>AT3</td>
<td>Tongatapu</td>
<td>To-At-1</td>
<td>-</td>
<td>390 to 770 BP*</td>
<td>Incisor</td>
<td>Root absent</td>
</tr>
<tr>
<td>AT5</td>
<td>Tongatapu</td>
<td>To-At-2</td>
<td>-</td>
<td>390 to 770 BP*</td>
<td>Molar</td>
<td></td>
</tr>
<tr>
<td>AB12</td>
<td>Buka</td>
<td>DAA/I</td>
<td>5</td>
<td></td>
<td>Canine</td>
<td></td>
</tr>
<tr>
<td>AB12p</td>
<td>Buka</td>
<td>DAA/I</td>
<td>5</td>
<td>1990 ± 1567 cal BP (2σ)#</td>
<td>Premolar</td>
<td>Root absent</td>
</tr>
<tr>
<td>AB17</td>
<td>Buka</td>
<td>DAA/I</td>
<td>5</td>
<td></td>
<td>Molar</td>
<td></td>
</tr>
<tr>
<td>AB26</td>
<td>Buka</td>
<td>DAA/II</td>
<td>13</td>
<td></td>
<td>Molar</td>
<td></td>
</tr>
<tr>
<td>AB27c</td>
<td>Buka</td>
<td>DAA/II</td>
<td>14</td>
<td>2851 ± 2155 cal BP (2σ)+</td>
<td>Canine</td>
<td></td>
</tr>
<tr>
<td>AB27p</td>
<td>Buka</td>
<td>DAA/II</td>
<td>14</td>
<td></td>
<td>Premolar</td>
<td></td>
</tr>
</tbody>
</table>

Table Ib.2. Ancient Pacific Islander teeth. Sample descriptions including origin, excavation layers, estimated age, tooth type and condition. To-At-1: The sectional profiles comprise a series of bands of dark brown topsoil-like material, interleaved with layers of subsoil; To-At-2: although there was no mound at this time, the burials were in pits, sometimes with undercut sides, and covered with white sand (Specht pers. comm). *Spenneman, (1989). # DAA/I/5, 5-6: 1884 ± 1706 cal BP (1σ) 1990 ± 1567 cal BP (2σ). + DAA/II/13, 14: 2750 ± 1706 cal BP (1σ), 2851 ± 2155 cal BP (2σ) (Specht pers. comm).
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Enamel 1</th>
<th>Enamel 2</th>
<th>Dentine 1</th>
<th>Dentine 2</th>
<th>Enamel 1</th>
<th>Enamel 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M25</td>
<td>0.21</td>
<td>0.25</td>
<td>0.24</td>
<td>0.28</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>AT2</td>
<td>0.20</td>
<td>0.17</td>
<td>0.12</td>
<td>0.14</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>-</td>
</tr>
</tbody>
</table>

Table Ib.3. LAM-ICPMS Pb^{2+} ion concentrations for Figure 3.0 and 3.1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Enamel 1</th>
<th>Enamel 2</th>
<th>Dentine 1</th>
<th>Dentine 2</th>
<th>Enamel 1</th>
<th>Enamel 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M21</td>
<td>0.35</td>
<td>0.33</td>
<td>0.33</td>
<td>0.15</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>M22</td>
<td>0.28</td>
<td>0.26</td>
<td>0.27</td>
<td>0.06</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>M23</td>
<td>0.24</td>
<td>0.26</td>
<td>0.25</td>
<td>0.27</td>
<td>0.19</td>
<td>0.17</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>M24</td>
<td>0.26</td>
<td>0.25</td>
<td>0.24</td>
<td>0.23</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>M26</td>
<td>0.28</td>
<td>0.31</td>
<td>0.25</td>
<td>0.18</td>
<td>0.19</td>
<td>0.24</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>M29</td>
<td>0.28</td>
<td>0.27</td>
<td>0.24</td>
<td>0.26</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>± (2σ)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table Ib.4. LAM-ICPMS analysed tooth Pb^{2+} ion concentrations (μg/g) of modern Broken Hill residents.
Figure 1b.5a. LAM-ICPMS of Pb$^{2+}$ ion concentrations across the longitudinal section of modern Broken Hill human teeth: samples M21, M22 and M23.
Figure 1b.5b. LAM-ICPMS of Pb$^{2+}$ ion concentrations across the longitudinal section of modern Broken Hill human teeth: samples M24, M26 and M29. There are distinctive high peaks within the enamel and dentine layers of human teeth.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Enamel</th>
<th>Dentine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Pb (UV)</td>
</tr>
<tr>
<td>AT2</td>
<td>0.522 ± 0.082 (3)</td>
<td>0.503 ± 0.038 (3)</td>
</tr>
<tr>
<td>AT3</td>
<td>0.595 ± 0.021 (3)</td>
<td>0.567 ± 0.098 (3)</td>
</tr>
<tr>
<td>AT5</td>
<td>0.554 ± 0.061 (7)</td>
<td>0.514 ± 0.121 (3)</td>
</tr>
<tr>
<td>AB12</td>
<td>0.423 ± 0.063 (4)</td>
<td>0.407 ± 0.062 (3)</td>
</tr>
<tr>
<td>AB17</td>
<td>0.227 ± 0.024 (7)</td>
<td>0.183 ± 0.042 (3)</td>
</tr>
<tr>
<td>AB26</td>
<td>0.532 ± 0.042 (5)</td>
<td>0.456 ± 0.026 (3)</td>
</tr>
<tr>
<td>AB27</td>
<td>0.491 ± 0.094 (3)</td>
<td>0.461 ± 0.084 (3)</td>
</tr>
<tr>
<td>M41</td>
<td>0.636 ± 0.097 (5)</td>
<td>0.550 ± 0.053 (4)</td>
</tr>
<tr>
<td>M39</td>
<td>0.594 ± 0.014 (3)</td>
<td>0.521 ± 0.018 (3)</td>
</tr>
<tr>
<td>M38</td>
<td>0.582 ± 0.026 (4)</td>
<td>0.547 ± 0.015 (3)</td>
</tr>
<tr>
<td>M37</td>
<td>0.602 ± 0.021 (4)</td>
<td>0.487 ± 0.020 (4)</td>
</tr>
<tr>
<td>M36</td>
<td>0.616 ± 0.051 (3)</td>
<td>0.599 ± 0.061 (4)</td>
</tr>
</tbody>
</table>

Table Ib.6. ASV determined total Pb²⁺ ion concentration in µg/g, UV and non-UV treated enamel and dentine. Ancient Tongatapu (AT#), Buka (BT#) and modern Broken Hill (M#) samples have been analysed. Number of experimental runs (n) in parentheses.
Appendix Ic

- Hydroxyapatite mineral species (Table Ic.1).
- Atomic coordinates for HA (Table Ic.2).
- GFAAS and ICP determinations of Pb, Ca and P concentrations, for the whole compositional range of PbCaHA (Table Ic.3).
# Hydroxyapatite Species

<table>
<thead>
<tr>
<th>Related Minerals (Strunz Grouping):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>7/B.39-10 Fluorapatite</td>
<td>( \text{Ca}_5 (\text{PO}_4)_3 \text{F} )</td>
</tr>
<tr>
<td>7/B.39-110 Belovite</td>
<td>( (\text{Sr,Ce,Na,Ca})_5 (\text{PO}_4)_3 \text{OH} )</td>
</tr>
<tr>
<td>7/B.39-115 Belovite-(La)</td>
<td>( (\text{Sr,La,Ce,Ca})_5 (\text{PO}_4)_3 (\text{F}_3 \text{OH}) )</td>
</tr>
<tr>
<td>7/B.39-120 Alforsite</td>
<td>( \text{Ba}_5 (\text{PO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-130 Morelandite</td>
<td>( (\text{Ba,Ca,Pb})_5 (\text{AsO}_4,\text{PO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-140 Hedyphane</td>
<td>( \text{Pb}_2 \text{Ca}_2 (\text{AsO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-155 Pyromorphite-Mimetite Series</td>
<td>( \text{Pb}_5 (\text{PO}_4,\text{AsO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-160 Mimetite</td>
<td>( \text{Pb}_5 (\text{AsO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-165 Clinomimetite</td>
<td>( \text{Pb}_5 (\text{AsO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-170 Vanadinite</td>
<td>( \text{Pb}_5 (\text{VO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-20 Chlorapatite</td>
<td>( \text{Ca}_5 (\text{PO}_4)_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-40 Carbonate-hydroxyapatite</td>
<td>( \text{Ca}_5 (\text{PO}_4,\text{CO}_3)_3 \text{OH} )</td>
</tr>
<tr>
<td>7/B.39-50 Carbonate-fluorapatite</td>
<td>( \text{Ca}_5 (\text{PO}_4,\text{CO}_3)_3 \text{F} )</td>
</tr>
<tr>
<td>7/B.39-60 Svbite</td>
<td>( \text{Ca}_5 (\text{AsO}_4)_3 (\text{F},\text{Cl},\text{OH}) )</td>
</tr>
<tr>
<td>7/B.39-70 Turneaureite</td>
<td>( \text{Ca}_5 [(\text{As,P})_4]_3 \text{Cl} )</td>
</tr>
<tr>
<td>7/B.39-80 Johnbaumite</td>
<td>( \text{Ca}_5 (\text{AsO}_4)_3 \text{OH} )</td>
</tr>
<tr>
<td>7/B.39-90 Fermorite</td>
<td>( (\text{Ca,Sr})_5 [(\text{P,As})_4]_3 (\text{F},\text{OH}) )</td>
</tr>
<tr>
<td>7/B.39-95 Fluorcaphtite</td>
<td>( (\text{Ca,Sr,Ce,Na})_5 (\text{PO}_4)_3 \text{F} )</td>
</tr>
</tbody>
</table>

**Table Ic.1.** Hydroxyapatite mineral species.
**Space Group**

*Atomic Coordinates*

P6$_3$/m (No.176).

O(1) in 6($h$): 0.3272, 0.4837, $\frac{1}{4}$, occ = 1
O(2) in 6($h$): 0.5899, 0.4666, $\frac{1}{4}$, occ = 1
O(3) in 12($j$): 0.3457, 0.2595, 0.0736, occ = 1
P in 6($h$): 0.3999, 0.3698, $\frac{1}{4}$, occ = 1
Ca(I) in 4($f$): $\Box$, $\Box$, 0.0010, occ = 1
Ca(II) in 6($h$): 0.2464, 0.9938, $\frac{1}{4}$, occ = 1
O$_{14}$ in 4($e$): 0.0, 0.0, 0.1930, occ = 1
H in 4($e$): 0.0, 0.0, 0.0617, occ = $\frac{1}{2}$

**Lattice**

Hexagonal, with lattice parameters:

\[ a_1 = a_2 = a_3 = 0.9432\,\text{Å} \]

\[ c = 0.6881\,\text{Å} \] and two formula units per cell.

---

**Table 1c.2.** Atomic coordinates for HA. Source: Kay, Young and Posner (1964). ‘occ’ refers to occupancy.
<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Ca</th>
<th>Pb</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(_{10})(PO(_4))(_6)(OH)(_2)</td>
<td>n/a</td>
<td>80.16 ± 3.21</td>
<td>6.59 ± 0.14</td>
</tr>
<tr>
<td>Pb(<em>{0.0})Ca(</em>{0.0})(PO(_4))(_6)(OH)(_2)</td>
<td>2.38 ± 0.05</td>
<td>76.09 ± 1.52</td>
<td>8.13 ± 0.25</td>
</tr>
<tr>
<td>Pb(<em>{0.0})Ca(</em>{3.0})(PO(_4))(_6)(OH)(_2)</td>
<td>13.10 ± 0.39</td>
<td>73.24 ± 0.73</td>
<td>9.04 ± 0.20</td>
</tr>
<tr>
<td>Pb(<em>{0.0})Ca(</em>{0.0})(PO(_4))(_6)(OH)(_2)</td>
<td>15.83 ± 0.63</td>
<td>61.95 ± 1.24</td>
<td>11.25 ± 0.24</td>
</tr>
<tr>
<td>Pb(<em>{0.3})Ca(</em>{3.3})(PO(_4))(_6)(OH)(_2)</td>
<td>20.26 ± 0.61</td>
<td>46.38 ± 0.92</td>
<td>13.61 ± 0.18</td>
</tr>
<tr>
<td>Pb(<em>{0.0})Ca(</em>{7.0})(PO(_4))(_6)(OH)(_2)</td>
<td>26.18 ± 0.52</td>
<td>34.57 ± 1.02</td>
<td>14.26 ± 0.21</td>
</tr>
<tr>
<td>Pb(<em>{0.3})Ca(</em>{8.5})(PO(_4))(_6)(OH)(_2)</td>
<td>31.21 ± 0.63</td>
<td>12.46 ± 0.31</td>
<td>16.24 ± 0.24</td>
</tr>
<tr>
<td>Pb(<em>{0.3})Ca(</em>{8.5})(PO(_4))(_6)(OH)(_2)</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Pb(<em>{0.0})Ca(</em>{9.0})(PO(_4))(_6)(OH)(_2)</td>
<td>34.59 ± 1.34</td>
<td>8.17 ± 0.16</td>
<td>17.29 ± 0.22</td>
</tr>
<tr>
<td>Pb(<em>{0.3})Ca(</em>{8.7})(PO(_4))(_6)(OH)(_2)</td>
<td>36.78 ± 1.12</td>
<td>5.98 ± 0.04</td>
<td>17.75 ± 0.43</td>
</tr>
<tr>
<td>Pb(<em>{0.3})Ca(</em>{9.3})(PO(_4))(_6)(OH)(_2)</td>
<td>38.14 ± 0.31</td>
<td>4.31 ± 0.01</td>
<td>17.98 ± 0.20</td>
</tr>
<tr>
<td>Pb(<em>{0.3})Ca(</em>{9.7})(PO(_4))(_6)(OH)(_2)</td>
<td>39.68 ± 0.41</td>
<td>2.31 ± 0.03</td>
<td>18.24 ± 0.25</td>
</tr>
<tr>
<td>Ca(_{10})(PO(_4))(_6)(OH)(_2)</td>
<td>43.56 ± 1.24</td>
<td>n/a</td>
<td>20.16 ± 0.18</td>
</tr>
</tbody>
</table>

Table Ic.3. GFAAS and ICP determinations of Pb, Ca and P concentrations, for the whole compositional range of PbCaHA. * denotes a two phase compound.
Appendix Id

- MC-LAM-ICPMS data of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and Sr$^{2+}$ ion concentrations of tooth enamel samples (Table Id.1).
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>Sr Concentration ($\mu$g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT1</td>
<td>0.70343 ± 0.00019</td>
<td>101.48 ± 4.07</td>
</tr>
<tr>
<td>AT2</td>
<td>0.70349 ± 0.00017</td>
<td>158.24 ± 2.71</td>
</tr>
<tr>
<td>AT3</td>
<td>0.70316 ± 0.00016</td>
<td>298.03 ± 6.89</td>
</tr>
<tr>
<td>AT4</td>
<td>0.70353 ± 0.00018</td>
<td>436.21 ± 19.78</td>
</tr>
<tr>
<td>AT5</td>
<td>0.70342 ± 0.00018</td>
<td>165.12 ± 5.89</td>
</tr>
<tr>
<td>AT8</td>
<td>0.70356 ± 0.00017</td>
<td>140.88 ± 6.71</td>
</tr>
<tr>
<td>AT11</td>
<td>0.70361 ± 0.00018</td>
<td>96.14 ± 5.14</td>
</tr>
<tr>
<td>AT12</td>
<td>0.70349 ± 0.00016</td>
<td>150.26 ± 3.77</td>
</tr>
<tr>
<td>AT13</td>
<td>0.70362 ± 0.00013</td>
<td>315.02 ± 24.58</td>
</tr>
<tr>
<td>AT14</td>
<td>0.70372 ± 0.00015</td>
<td>244.65 ± 9.18</td>
</tr>
<tr>
<td>AT15</td>
<td>0.70349 ± 0.00014</td>
<td>112.17 ± 2.09</td>
</tr>
<tr>
<td>AT16</td>
<td>0.70432 ± 0.00015</td>
<td>79.18 ± 2.31</td>
</tr>
<tr>
<td>AB1</td>
<td>0.70439 ± 0.00017</td>
<td>79.09 ± 2.15</td>
</tr>
<tr>
<td>AB2</td>
<td>0.70366 ± 0.00013</td>
<td>156.73 ± 5.49</td>
</tr>
<tr>
<td>AB4</td>
<td>0.70392 ± 0.00015</td>
<td>67.69 ± 1.29</td>
</tr>
<tr>
<td>AB5</td>
<td>0.70324 ± 0.00014</td>
<td>124.56 ± 2.56</td>
</tr>
<tr>
<td>AB6</td>
<td>0.70316 ± 0.00018</td>
<td>148.66 ± 3.05</td>
</tr>
<tr>
<td>AB7</td>
<td>0.70351 ± 0.00018</td>
<td>126.19 ± 3.89</td>
</tr>
<tr>
<td>AB8</td>
<td>0.70367 ± 0.00019</td>
<td>216.78 ± 9.76</td>
</tr>
<tr>
<td>AB12</td>
<td>0.70366 ± 0.00018</td>
<td>257.71 ± 13.63</td>
</tr>
<tr>
<td>AB17</td>
<td>0.70372 ± 0.00015</td>
<td>219.15 ± 11.22</td>
</tr>
<tr>
<td>AB26</td>
<td>0.70361 ± 0.00015</td>
<td>324.93 ± 9.97</td>
</tr>
<tr>
<td>AB27</td>
<td>0.70362 ± 0.00018</td>
<td>211.67 ± 8.10</td>
</tr>
</tbody>
</table>

Table Id.1. MC-LAM-ICPMS determined $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and GFAAS determination of Sr$^{2+}$ ion concentrations of Tongatapu (AT#) and Buka (AB#) tooth enamel samples.
Appendix Ie

- MC-LAM-ICPMS determined Pb isotope ratios of tooth enamel samples from the Sohano Rock Shelter (Table Ie.1).
<table>
<thead>
<tr>
<th>Sample Id</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
<th>Enamel Pb (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB1</td>
<td>18.9215 ± 0.0051</td>
<td>15.5274 ± 0.0036</td>
<td>38.4687 ± 0.0096</td>
<td>0.055 ± 0.002</td>
</tr>
<tr>
<td>AB2</td>
<td>18.4897 ± 0.0046</td>
<td>15.5242 ± 0.0033</td>
<td>38.2631 ± 0.0092</td>
<td>0.154 ± 0.003</td>
</tr>
<tr>
<td>AB4</td>
<td>18.7225 ± 0.0049</td>
<td>15.5243 ± 0.0031</td>
<td>38.3075 ± 0.0092</td>
<td>0.113 ± 0.001</td>
</tr>
<tr>
<td>AB5</td>
<td>18.7936 ± 0.0048</td>
<td>15.5409 ± 0.0033</td>
<td>38.3502 ± 0.0089</td>
<td>0.022 ± 0.002</td>
</tr>
<tr>
<td>AB6</td>
<td>18.4106 ± 0.0048</td>
<td>15.5411 ± 0.0034</td>
<td>38.1685 ± 0.0084</td>
<td>0.087 ± 0.003</td>
</tr>
<tr>
<td>AB7</td>
<td>18.6852 ± 0.0050</td>
<td>15.5432 ± 0.0033</td>
<td>38.4267 ± 0.0092</td>
<td>0.168 ± 0.006</td>
</tr>
<tr>
<td>AB8</td>
<td>18.6851 ± 0.0045</td>
<td>15.5407 ± 0.0031</td>
<td>38.4184 ± 0.0096</td>
<td>0.185 ± 0.002</td>
</tr>
<tr>
<td>AB12</td>
<td>18.6849 ± 0.0047</td>
<td>15.5435 ± 0.0037</td>
<td>38.4244 ± 0.0096</td>
<td>0.061 ± 0.005</td>
</tr>
<tr>
<td>AB17</td>
<td>18.6839 ± 0.0050</td>
<td>15.5426 ± 0.0031</td>
<td>38.4310 ± 0.0088</td>
<td>0.135 ± 0.006</td>
</tr>
<tr>
<td>AB26</td>
<td>18.6799 ± 0.0047</td>
<td>15.5419 ± 0.0033</td>
<td>38.4229 ± 0.0085</td>
<td>0.271 ± 0.002</td>
</tr>
<tr>
<td>AB27</td>
<td>18.7116 ± 0.0047</td>
<td>15.5533 ± 0.0034</td>
<td>38.4462 ± 0.0092</td>
<td>0.109 ± 0.003</td>
</tr>
</tbody>
</table>

Table Ie.1. MC-LAM-ICPMS determined Pb isotope ratios of Sohano Rock Shelter tooth samples and ASV determined Pb$^{2+}$ ion concentrations.
Appendix If

- Tongatapu tooth enamel samples. MC-LAM-ICPMS determination of Pb isotopes and ASV determination of Pb$^{2+}$ ion concentrations (Table If.1).

- Tongan archipelago with the four distinct island groups (Figure If.1).
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(^{208}\text{Pb} / ^{204}\text{Pb})</th>
<th>(^{207}\text{Pb} / ^{204}\text{Pb})</th>
<th>(^{206}\text{Pb} / ^{204}\text{Pb})</th>
<th>Enamel Pb (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT1</td>
<td>37.9716 ± 0.0095</td>
<td>15.5522 ± 0.0037</td>
<td>18.4965 ± 0.0039</td>
<td>0.032 ± 0.002</td>
</tr>
<tr>
<td>AT2</td>
<td>37.9709 ± 0.0095</td>
<td>15.5516 ± 0.0033</td>
<td>18.4787 ± 0.0044</td>
<td>0.052 ± 0.003</td>
</tr>
<tr>
<td>AT3</td>
<td>37.9915 ± 0.0091</td>
<td>15.4672 ± 0.0031</td>
<td>18.4569 ± 0.0046</td>
<td>0.179 ± 0.001</td>
</tr>
<tr>
<td>AT4</td>
<td>37.9916 ± 0.0084</td>
<td>15.4669 ± 0.0036</td>
<td>18.5137 ± 0.0044</td>
<td>0.101 ± 0.002</td>
</tr>
<tr>
<td>AT5</td>
<td>37.9623 ± 0.0087</td>
<td>15.5789 ± 0.0033</td>
<td>18.3748 ± 0.0048</td>
<td>0.051 ± 0.003</td>
</tr>
<tr>
<td>AT6</td>
<td>38.0132 ± 0.0091</td>
<td>15.4111 ± 0.0031</td>
<td>18.0126 ± 0.0049</td>
<td>0.118 ± 0.006</td>
</tr>
<tr>
<td>AT7</td>
<td>37.9251 ± 0.0095</td>
<td>15.3709 ± 0.0034</td>
<td>18.0365 ± 0.0049</td>
<td>0.185 ± 0.002</td>
</tr>
<tr>
<td>AT8</td>
<td>37.9612 ± 0.0095</td>
<td>15.5775 ± 0.0036</td>
<td>18.3705 ± 0.0050</td>
<td>0.061 ± 0.005</td>
</tr>
<tr>
<td>AT9</td>
<td>38.4872 ± 0.0096</td>
<td>15.6041 ± 0.0036</td>
<td>18.9108 ± 0.0051</td>
<td>0.135 ± 0.006</td>
</tr>
<tr>
<td>AT10</td>
<td>38.2666 ± 0.0092</td>
<td>15.5394 ± 0.0037</td>
<td>18.6152 ± 0.0047</td>
<td>0.271 ± 0.002</td>
</tr>
<tr>
<td>AT11</td>
<td>38.0099 ± 0.0080</td>
<td>15.6014 ± 0.0033</td>
<td>18.3369 ± 0.0050</td>
<td>0.336 ± 0.003</td>
</tr>
<tr>
<td>AT12</td>
<td>37.9884 ± 0.0091</td>
<td>15.5501 ± 0.0036</td>
<td>18.4612 ± 0.0046</td>
<td>0.085 ± 0.002</td>
</tr>
<tr>
<td>AT13</td>
<td>37.9941 ± 0.0084</td>
<td>15.5842 ± 0.0036</td>
<td>18.3712 ± 0.0044</td>
<td>0.144 ± 0.005</td>
</tr>
<tr>
<td>AT14</td>
<td>37.9892 ± 0.0076</td>
<td>15.6123 ± 0.0034</td>
<td>18.3658 ± 0.0048</td>
<td>0.235 ± 0.006</td>
</tr>
<tr>
<td>AT15</td>
<td>38.0028 ± 0.0091</td>
<td>15.479 ± 0.0036</td>
<td>18.5262 ± 0.0039</td>
<td>0.059 ± 0.002</td>
</tr>
<tr>
<td>AT16</td>
<td>37.9734 ± 0.0087</td>
<td>15.4754 ± 0.0031</td>
<td>18.3226 ± 0.0040</td>
<td>0.302 ± 0.003</td>
</tr>
</tbody>
</table>

**Table If.1.** Tongatapu tooth enamel samples. MC-LAM-ICPMS determined Pb isotope ratios and Pb\(^{210}\) ion concentrations evaluated by ASV.
Figure If.1. Tongan archipelago with the four distinct island groups. Source: Spennemann (1990).