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The source of Irish Chalcolithic and Bronze Age gold: a lead isotope and major element provenance study

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Abstract

Chalcolithic and Bronze Age Europe witnessed a marked growth in the deployment of exotic materials such as amber, jet and gold; a feature commonly linked to increases in social stratification. Of these, gold is poorly characterised in terms of provenance which is a significant obstacle if an understanding of the role this material played in prehistoric societies is to be achieved. A combined lead isotope and major element composition provenance study has therefore been performed on 67 Chalcolithic and Bronze Age Irish gold artefacts.

Methodologies that enable the lead isotope analysis of natural and artefact gold using both solution (external precision <250 parts per million) and laser ablation (external precision <1640 parts per million) multi-collector inductively-coupled plasma mass-spectrometry were developed. Analyses of 34 Irish gold deposits distinguished a series of gold bearing regions, with isotopic variation a function of source age (Early Caledonian, Late Caledonian and Variscan) and source composition (mantle, lower crustal, upper crustal). Based on lead isotope analysis alone, the majority of the Chalcolithic and Early Bronze Age artefacts are consistent with southern Irish Late Caledonian or younger mineralisation, with a smaller group too radiogenic to be of Irish origin. However no southern Irish gold source has the high silver (typically 9.5% to 14.5%), moderate copper (typically below detection to 0.79%) and moderate tin (typically below detection to 0.38%) concentrations recorded for these artefacts. Therefore a non-Irish origin for the majority of the gold is favoured.

Based on the current data, southern Britain is considered the most likely source region. Accordingly, the deployment of gold throughout Chalcolithic and Early Bronze Age Ireland is consistent with wider patterns of exotic material consumption, where distant sources were preferred even when local deposits were available. The control of exotic materials is one potential mechanism for individuals or groups to attain power, however there is little evidence for the control of gold procurement during the Chalcolithic or Early Bronze Age. Compositional data favours the exploitation of multiple alluvial deposits within one principle gold bearing region, alongside the absence of centralised fabrication centres. Conversely, preliminary data from Middle and Late Bronze Age gold artefacts suggests greater control over the metal supply due to a) the exploitation of a single, rich, deposit and/or b) the existence of centralised fabrication centres. This highlights a significant shift in the way gold was procured and/or deployed, and offers a new mechanism for the creation of the increasingly complex and stratified societies that began to form towards the end of the 2nd millennium BC.

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Finally, my gratitude goes to all my family, friends, and colleagues who could not be mentioned here, but offered priceless help and advice to me throughout the course of completing this thesis.

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

SIGNED: .... DATE: 20/03/2013

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Chapter 1: Introduction

Gold was first exploited in north-west Europe during the Chalcolithic (Taylor, 1980; Eogan, 1994), a time when agricultural subsistence dominated daily life and for which the archaeological record provides little evidence of social stratification (e.g. Harding, 2000; Kristiansen and Larsson, 2005). Increased production of gold artefacts during the Early Bronze Age was followed by major proliferations of goldworking industries during the Middle and Late Bronze Ages (Taylor, 1980; Eogan, 1994). Far greater quantities of gold were in circulation supplying industries that produced a diverse range of artefact forms, and the expansion of these industries mirrored wider social changes that were occurring at this time; by the onset of the 1st millennium BC there is evidence for increasingly complex and hierarchical societies alongside the emergence of elites (e.g. Harding, 2000; Kristiansen and Larsson, 2005).

Understanding how and why these new social structures formed is a central research aim in Bronze Age archaeology, and consequently recognising the changing patterns of procurement for key materials is highly desirable. The control of material resources, particularly metals, is frequently seen as a potential mechanism for acquiring power, and can play an important role in both the creation of elites and the development of complex societies (Mann, 1986; Earle, 1997). Furthermore, numerous societies consider materials such as gold, amber and jet as exotic for reasons including rarity, distinctive physical properties, and distant or esoteric origins (Harding, 2000; Chapman, 2008), whilst they are often associated with supernatural and cosmological forces (Saunders, 1998, 1999, 2003; Woodward, 2000, 2002; Sheridan and Shortland, 2003, 2004). Recognising the source locations of Chalcolithic and Bronze Age exotics is crucial for understanding the controls of their procurement, trade and exchange, and could help to explain the new social structures that formed during this period.

Significant quantities of Bronze Age gold have been discovered in Ireland, however acquisition of the raw material exploited by Irish goldworking industries is poorly understood. This is primarily due to the lack of archaeological evidence for gold extraction, both within Ireland and neighbouring regions of north-west Europe. As a result, scientific provenance studies are of critical importance if any understanding of gold procurement is to be achieved. Recent investigations studying the major element composition of Irish goldwork have highlighted the Mourne Mountains of Northern

Ireland as the most likely Irish source of Early Bronze Age gold (Warner et al., 2009, 2010a, 2010b), however doubts persist over the capability of these deposits to account for the quantity of gold consumed by Irish goldworking industries (Meighan, 2011). Consequently, after almost half a century of scientific research, no provenance study has been able to generate a consensus regarding which gold deposits were exploited for the manufacture of Irish Chalcolithic and Bronze Age goldwork.

The application of a new provenance technique that is independent from elemental characterisation is therefore required, and will allow critical evaluations of previous studies. Lead isotope analysis has frequently been employed in archaeological provenance studies (e.g. Cattin et al., 2009; Stos-Gale and Gale, 2009), yet it has never been applied to the study of Chalcolithic or Bronze Age gold. This thesis therefore presents a lead isotope provenance study of Irish Chalcolithic and Bronze Age gold artefacts, with the principle objective to further our understanding of gold exploitation during these early periods of metalworking.

Chapters 2 and 3 present the background information relevant to this study. Chapter 2 focuses on the archaeology by first detailing the chronological framework (Section 2.2.1). An overview of Bronze Age society and the evidence for increasing social complexity is then presented (Section 2.2.2), followed by a discussion on the role of exotic materials (Section 2.2.3). The goldwork is then introduced in Section 2.3. This consists of a discussion on the key artefact types referred to in this study (Section 2.3.1), and an overview of previous attempts to locate the source(s) of gold exploited during the Bronze Age (Section 2.3.2). This study will focus on Irish goldwork of the Chalcolithic and Early Bronze Age, therefore Section 2.3 will concentrate on artefacts from this region and chronological period. However goldwork from neighbouring areas of Europe will be considered when relevant, and assemblages dating to the Middle and Late Bronze Ages will also be briefly discussed. Finally, Section 2.4 introduces the principle objective of this study.

The ability to differentiate between different ore sources is critical to the success of archaeological provenance studies, with variations in the isotopic signatures of ore deposits relating to differences in source rock composition and source age (e.g. Marcoux et al., 2002; Tornos and Chiaradia, 2004). A geological understanding of the study region is therefore key, and due to a) the generally accepted opinion that an Irish gold source was exploited in the Bronze Age, and b) the current hypothesis regarding the Mourne Mountains of Co. Down, for this study is Ireland. Accordingly, Chapter 3 provides the necessary geological background. An overview of the geology of Ireland is first provided (Section 3.2), followed by a summary of the principle styles of gold mineralisation (Section 3.3) and an introduction to the gold deposits of Ireland (Section 3.4). The technique of lead isotope analysis is introduced in Section 3.5. This includes a discussion on the fundamentals of lead isotope systematics (3.5.1), an overview of published lead isotope investigations studying Irish mineral deposits (3.5.2) and the applicability of lead isotope analysis to archaeological provenance studies (3.5.3). Finally, the key aims of this project are detailed and briefly discussed in Section 3.6.

Chapter 4 presents the analytical techniques employed in this study. When this project commenced, no methodologies existed for the application of lead isotope analysis to studies of gold. Consequently both solution and laser ablation techniques have been devised, and are presented in Section 4.2 and Section 4.3 respectively. Artefact samples have also been analysed for their major element composition and mineral inclusion suite using an electron probe microanalyser and scanning electron microscope respectively. The methodologies employed for these techniques are present in Sections 4.4 and 4.5.

Lead isotope analysis has never been performed directly on Irish gold mineralisation, therefore it was important to characterise a comprehensive number of possible ore sources and investigate to what degree different gold bearing regions can be distinguished. Chapter 5 presents the analysis of 109 gold samples from 31 Irish gold deposits. Section 5.2 details the sampling strategy employed to collect these samples, and presents the locations of the sample sites. Section 5.3 discusses the sources of lead incorporated into Irish gold mineralisation, and the data are interpreted within the global two-stage lead evolution model of Stacey and Kramers (1975) and a model of Irish lead isotope evolution by Dixon et al. (1990) in Section 5.4. Section 5.5 then presents a more detailed discussion on the lead isotope signature of each of the key gold bearing regions of Ireland, allowing a full understanding of the lead isotope signature of Irish gold deposits to be achieved. This is followed by a synthesis on the formation of Irish gold deposits as inferred through lead isotope analysis (Section 5.6). One of the greatest criticisms of archaeological provenance studies is that unknown and unanalysed ore deposits can not be considered. By achieving an understanding of why ore deposits are characterised by certain isotopic signatures, such deposits can be included in discussions concerning ore source. Finally, with an understanding of the causes of the isotopic variation between Irish gold deposits achieved, the degree to which lead isotope analysis can characterise the gold deposits of Ireland is assessed (Section 5.7).

Chapter 6 presents the analysis of 52 samples from 50 Chalcolithic and Early Bronze Age Irish gold artefacts. All were donated for study by the National Museum of Ireland, Dublin. Due to the problems of artefact recycling and the possible exploitation of multiple sources, the focus of this project is on the earliest phase of goldworking. The isotopic composition of these artefacts should be at their least complex and best reflect the composition of the source deposits, whilst it is likely that the number of exploited sources would have been at its lowest. Characterising the earliest gold in circulation also aids investigations of chronologically later artefacts because recycling of pre-existing goldwork can be modelled. Analytical data (major element concentrations, lead isotope signatures and mineral inclusion suites) are presented in Section 6.2, followed by an assessment of isotopic and compositional heterogeneity (Section 6.3). Artefact associations and chronology (Section 6.4) and recycling/mixing (Section 6.5) are discussed, before the question of provenance is addressed (Section 6.6). In Section 6.6 the following three competing hypotheses are critically assessed: a principle source of Irish Bronze Age gold located within Ireland and identified through lead isotope analysis; a principle source of Irish Bronze Age gold located within Ireland but not analysed within this study; and a non-Irish principle source of Irish Bronze Age gold. The favoured hypothesis is presented, facilitating a discussion on the role of gold in Chalcolithic and Early Bronze Age societies (Section 6.7).

Critical to gaining a full understanding of gold exploitation throughout the Bronze Age is the need to recognise patterns of gold procurement, i.e. the number and location of gold sources and how this changed over time. Chapter 7 presents preliminary data from the analyses of Irish Middle Bronze Age and Late Bronze Age artefacts. The study of artefacts from these later periods is complicated due to the widespread practice of alloying copper with gold, the increased potential for mixing gold from multiple sources (to account for increases in the quantity of gold in circulation), and presumed higher rates of recycling. These factors, along with the small number of samples analysed, prevent detailed discussions on the gold sources exploited during later prehistory. Therefore after presenting the analytical data (Section 7.2), and discussing sample heterogeneity (Section 7.3), Section 7.4 assesses how a detailed lead isotope investigation into these alloyed artefacts could proceed. This includes preliminary attempts to correct the analysed isotopic signature for the input of copper derived lead, and a brief consideration on the sources of Irish gold in later prehistory. Section 7.5 draws all the data together to consider the potential of a full lead isotope provenance study of later prehistoric goldwork, before some broad conclusions are presented in Section 7.6.

Chapter 8 summarises the key conclusions that have been drawn throughout the course of this study; from the application of lead isotope analysis to studies of gold, through the ability of this technique to differentiate between different Irish gold deposits, to the identification of the gold sources exploited during the Chalcolithic and Bronze Age. The implications this has on the role that gold played in the increasingly complex societies is reaffirmed, before a discussion on how this study could be further developed in the future. All analytical data are presented in the appendices. Appendix A presents all analyses of alluvial and vein gold samples presented in Chapters 5 and 6, including grid references for sampling sites. Appendix B presents all artefact data discussed in Chapters 6 and 7, whilst Appendix C presents the corrected ratios of artefacts whose isotopic signature has been corrected for the input of lead derived from copper alloying.

Chapter 2: Goldworking and the Bronze Age

2.1 Synopsis

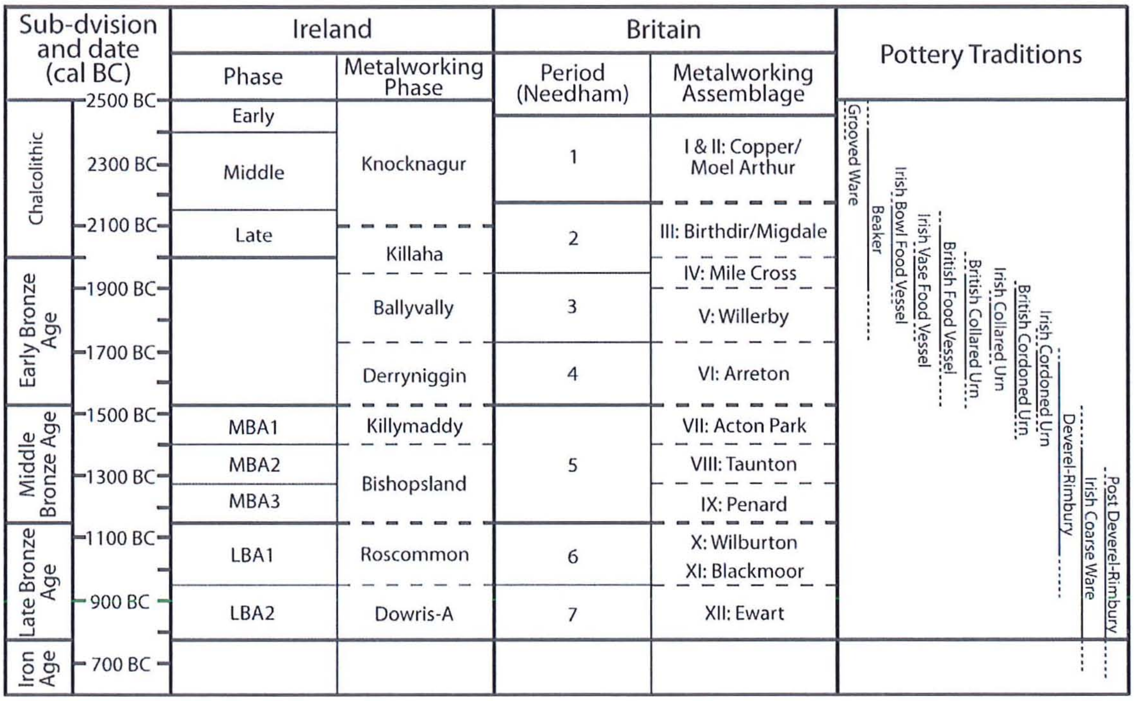
Chapter 2 provides the relevant archaeological background required for this study. Section 2.2 details the chronological framework (Section 2.2.1), before a brief overview of Chalcolithic and Bronze Age society (Section 2.2.2) and the role of exotics (Section 2.2.3) is provided. Section 2.3 introduces the goldwork, with a geographical focus on Ireland and Britain. A discussion on the key artefact forms referred to in this study is presented including an assessment on their typological origins (Section 2.3.1), before an overview of previous scientific studies that attempted to locate the source(s) of Bronze Age gold is provided (Section 2.3.2). Finally, Section 2.4 introduces the principle aim of this thesis: to perform a lead isotope provenance study on a collection of Irish Chalcolithic and Early Bronze Age gold artefacts.

2.2 Archaeological Setting

2.2.1 Chronology of the Irish and British Bronze Age

2.2.1.1 The Chalcolithic and Early Bronze Age

The appearance of Beaker pottery c.2500 BC marked the emergence of typical Chalcolithic material culture in Britain and Ireland. Along with the adoption of new technologies such as copper and gold working, pre-existing Neolithic traditions including the construction of ceremonial monuments continued (Needham, 1996, 2012a; Waddell, 1998; Parker Pearson, 2005; O'Brien, 2012). This is Period 1 in Needham's (1996) chronology of the British Bronze Age (Figure 2.1), a period where copper metallurgy was practised without the addition of tin (known as the Knocknagur Phase in Ireland, or metalwork assemblages MA-I and MA-II in Britain; Needham, 1996; Waddell, 1998). This Chalcolithic Period came to a close c.2200/2150 BC in Britain and by c.2000 BC in Ireland, where a new style of ceramics termed Food Vessels had emerged (Brindley, 2007; Needham 2012a; O'Brien 2012). Full Bronze working was now practised throughout the region; known as the Killaha Phase in Ireland and Needham's MA-III (Birthdir/Migdale) followed by MA-IV (Mile Cross) in Britain (Waddell, 1998; Needham et al., 2010a; 2010b). Lasting until c.1950 BC, this is Needham's Period 2 (Needham et al., 2010a; 2010b), and it witnessed the peak in use of both Beaker and Irish Food Vessels, the emergence of British Food Vessels followed by Urns, and the Irish gold lunulae tradition (Needham, 1996; 2012a).



Sub-dvision and date (cal BC)		Ireland: Phase	Ireland: Metalworking Phase	Britain: Period (Needham)	Britain: Metalworking Assemblage
Chalcolithic	2500 BC	Early	Knocknagur	1	I & II: Copper/ Moel Arthur
	2300 BC	Middle			
	2100 BC	Late	Killaha	2	III: Birthdir/Migdale
Early Bronze Age	1900 BC				IV: Mile Cross
			Ballyvally	3	V: Willerby
	1700 BC		Derryniggin	4	VI: Arreton
Middle Bronze Age	1500 BC	MBA1	Killymaddy	5	VII: Acton Park
	1300 BC	MBA2	Bishopsland		VIII: Taunton
		MBA3			IX: Penard
Late Bronze Age	1100 BC	LBA1	Roscommon	6	X: Wilburton XI: Blackmoor
	900 BC	LBA2	Dowris-A	7	XII: Ewart
Iron Age	700 BC				

Figure 2.1: Chronology of the Irish and British Bronze Age. Principal sources: Brindley (2007), Gerloff (2007), Needham (1996; 2012a), Needham et al. (2010a; 2010b), O'Brien (2012), Waddell (1998).

In continental Europe and Britain, Beaker pottery is associated with both domestic and burial contexts. The latter are typically single crouched inhumations (Needham, 1996; 2012a), which may also include distinctive grave goods (often termed the Beaker grave good package) such as copper knives, barbed and tanged arrowheads, stone wrist guards and v-shaped perforated buttons (Harrison, 1980). Conversely, in Ireland Beaker distribution is fragmentary and more typical of settlement contexts such as New Grange and Dalkey Island (Needham, 1996; Waddell, 1998). When found associated with burials they are usually in the distinctive Wedge Tombs, a tradition predominantly found in western Ireland that can contain both burnt and unburnt bones of multiple individuals (Waddell, 1998; O'Brien, 1999).

Irish Food Vessels (both bowl and vase type) are typically associated within funerary contexts, although examples have also been found at habitation sites (Waddell, 1998; Brindley, 2007). Whilst a small number were inserted into pre-existing monuments, most were associated with pit or cist burials which have a distributional bias complementary to the wedge tombs. Bowl Food Vessels have been discovered associated with unburnt single crouched inhumation burials similar to that of the British

Beaker burial tradition previously discussed. However in the case of the Vase Food Vessels, many are associated with cremation burials. Both burial traditions can contain grave goods; vase varieties tend to be associated with a secondary pot, whilst the bowl varieties can be associated with a range of objects such as bronze knives or polished stone axe heads (Waddell, 1998).

Needham's Period 3, c.1950 to 1750/1700 BC (Figure 2.1), witnessed the peak of British Food Vessels alongside the use of Collard and Cordoned Urns. There was a diversification of funerary practises in both Britain and Ireland, whilst the rich graves of Wessex I also belong to this period (Needham, 1996; Waddell, 1998; Brindley, 2007; Needham et al., 2010a; 2010b). Further developments in metalworking also occurred, with the Ballyvally Phase current in Ireland and MA-IV (Mile Cross) replaced by MA-V (Willerby) in Britain (Waddell, 1998; Needham et al., 2010a; 2010b).

The close of the EBA, c.1750/1700 to 1550/1500 BC, (Needham's Period 4; Figure 2.1) saw further changes in pottery, metalwork and burial practises (Needham, 1996; Needham et al., 2010a; 2010b; Waddell, 1998). Urn traditions dominated ceramics although there was still rare use of Beaker and Food Vessel pottery, and cremations were now the favoured burial rite (Needham, 1996; Brindley 2007; Needham et al., 2010a; 2010b). The Wessex 2 burial assemblages also date to this period, whilst metalwork of the Derryniggin Phase and MA-VI (Arreton) was in circulation in Ireland and Britain respectively.

2.2.1.2 The Middle Bronze Age

During the Middle Bronze Age (MBA) there is a marked increase in the visibility of settlement sites in the archaeological record of Britain, yet they remain uncommon throughout Ireland (Needham, 1996; Waddell, 1998). The MBA sequence of Britain is Needham's Period 5, c.1550/1500 to 1150/1100 BC (Figure 2.1), which correlates with the MA-VII (Acton Park), MA-VIII (Taunton) and MA-IX (Penard) metalwork assemblages of Britain (Needham, 1996; Gerloff, 2007; Needham et al., 2010a; 2010b). This period saw the peak of Deverel-Rimbury pottery traditions along with linked styles such as Trevisker ware (Needham, 1996; Needham et al., 2010a; 2010b).

Needham's Period 5 (Figure 2.1) corresponds with Ireland's MBA1, MBA2 and MBA3 (Waddell, 1998). Middle Bronze Age 1 and associated metalworking of the Killymaddy

Phase equates to the Acton Park assemblage in Britain and dates to c.1550/1500 to 1400 BC, MBA2 along with the Early Bishopsland Phase correlates with the Taunton metalwork of Britain and dates to c.1400 to 1300/1250 BC, whilst MBA3 and associated Late Bishopsland Phase equates to the Penard metalwork of Britain and dates to c.1300/1250 to 1150 BC (Waddell, 1998; Gerloff, 2007). These metalworking assemblages are characterised by an array of new bronze and gold forms such as spears, rapiers and torcs, whilst the Irish pottery record is dominated by a coarse flat-bottomed style (Waddell, 1998). In Ireland there was a decline in urn burials, and very little archaeological evidence for burial rites exists for the remainder of the Bronze Age (Waddell, 1998).

2.2.1.3 The Late Bronze Age

Ireland's Late Bronze Age (LBA) has been divided into two separate phases (Waddell, 1998). Late Bronze Age 1 is characterised by the Roscommon metalworking assemblage and dates to c.1150 to 950 BC (Gerloff, 2007, see Figure 2.1). This corresponds to the MA-X (Wilburton) and MA-XI (Blackmoor) metalwork assemblages of Britain and Needham's Period 6 (Needham, 1996; Gerloff, 2007), which saw the evolution of some pre-existing forms such as spearheads along with the introduction of others including swords (Waddell, 1998). In Britain, Post Deverel-Rimbury pottery dominated, whilst there was continued use of the coarse pottery in Ireland (Needham, 1996; Waddell, 1998).

Ireland's LBA2 and associated Dowris-A Phase metalworking corresponds with Needham's Period 7 and Britain's MA-XII (Ewart) metalwork assemblage (Needham, 1996; Gerloff, 2007). This phase dates to c.950 to 800/750 BC (Needham, 1996; Gerloff, 2007). It saw the peak in ornament and weaponry manufacture that had been building over the preceding centuries, with the production of numerous forms such as horns, buckets, cauldrons, razors, knives, swords, gorgets and dress fasteners (Waddell, 1998). Coarse pottery and Post Deverel-Rimbury pottery both continued to be used in Ireland and Britain respectively (Needham, 1996; Waddell, 1998). As the exploitation of iron commenced, the transition to the Iron Age began and metalwork evolved into the Irish Dowris-C and the British Llyn Fawr assemblages (Needham, 1996; Waddell, 1998; Gerloff, 2007).

2.2.2 The Chalcolithic and Bronze Age

2.2.2.1 Settlement

Due to the prominent role that agriculture played in daily life, settlements often occurred as part of extensive agricultural landscapes. Houses were incorporated into small hamlets or farmsteads with associated enclosures; typically all that remains today are pits, post holes and cooking places (Harding, 2000). Although there is an increase in the number of settlement sites in Ireland dating to the Chalcolithic relative to the preceding Late Neolithic, evidence still remains scarce. There is no defining settlement type or layout, buildings are insubstantial, and there is little evidence for enclosing or fortifying structures (Carlin and Brück 2012; O'Brien 2012). For example a domestic site at Graigueshoneen, Co. Waterford, consisted of stake holes defining a sub-oval structure, a hearth, and associated Beaker pottery (Johnston et al., 2008). Pit groupings may be the only surviving component of longer term occupation sites (Carlin and Brück 2012), and in Ireland these can contain a range of items such as pottery, animal bone, cereals and wild plant remains, flints, and other stone artefacts. Settlement evidence remains rare into the EBA, and again when visible they generally consist of oval or circular post built structures (Waddell, 1998), although two circular structures were accompanied by one of rectangular form at Omey Island, Co. Galway (O'Keeffe, 1993). Pit groups and occupation spreads, now also containing Food Vessels, date to this period too (McCormick, 1995; Carlin and Brück 2012). It is not until late in the EBA (in association with Cordoned Urns) that evidence for houses become more common (Carlin and Brück 2012), an example being the settlement site at Downpatrick, Co. Down (Pollock et al., 1964; Waddell, 1998),

As discussed by Harding (2000), different regions of Bronze Age Europe witnessed the development of different settlement types, such as hut platforms on the north-western moors or lake-side settlements in and around the Alps. Distributions could be dispersed, a trend more prevalent in north and north-west Europe, or agglomerated as seen across much of central southern and eastern Europe (Harding, 2000). However despite these variations, houses within each settlement tended to be similar in terms of shape, size and building materials; there is little evidence for social division or buildings specially equipped as seats of power (Harding, 2000). Settlement evidence therefore provides little evidence for complex social organisation during the Chalcolithic and Early Bronze Age.

As this period progressed, some areas saw a pattern of increasing settlement size and a trend towards more agglomerated layouts. There was also a tendency to add enclosing (potentially defensive) structures such as palisades and ditches; hillforts emerged late in the period (Harding, 2000). Some of the new settlement patterns that emerged across Europe could even start to be called proto-urban, and may have begun to achieve some degree of centrality (Harding, 2000). Although Irish settlement patterns could not yet be classed as the former, a shift to more complex settlement patterns did occur during the Middle and Late Bronze Ages. A growing diversity in settlement types included temporary occupation sites, lowland and wetland settlements, and hilltop enclosures (Waddell, 1998; Grogan, 1994; O'Sullivan, 2001).

Grogan (1994) discussed a four-tiered model of settlement organisation for North Munster during the later Bronze Age. Hillforts (for example Mooghaun) were interpreted as the highest status sites, with defended hilltop enclosures and enclosed lakeside settlements such as Knocknalappa fulfilling a more local function secondary to them. Small domestic enclosures, and on another level *fulachta fiadh* (burnt mounds associated with troughs for boiling water) were also found in the region. This model reflects a hierarchy of occupation sites, and is an indication of social organisation. Similar conclusions were reached in a study of MBA and LBA landscape and settlement on the upper Shannon estuary by O'Sullivan (2001). Hut sites such as the example at Carrigdirty Rock, domestic enclosures including those at Tervoe and Loughanleagh, and *fulachta fiadh* (for example those at Ballymacashel) were all located below a possible LBA hilltop enclosure at Carrigogunnel.

This shift in settlement pattern was not confined to Munster. Waddell (1998) identified a number of features characteristic of high status settlements including large size, the presence of banks, ditches, palisades or walls, evidence for metalwork or metalworking, the presence of exotic materials, high quantities of faunal remains, or location near to ritual sites, and identified settlements such as Haughey's Fort (Co. Armagh), Dún Aonghasa (Co. Galway) and Rathgall (Co. Wicklow) as possible high status sites topping an emerging settlement hierarchy.

It is however important to note that although the later Bronze Age witnessed the emergence of more substantial settlement sites, small scale habitation (such as Cullyhanna Lough, Co. Armagh; Hodges, 1958; Hillam, 1976) would have been more common. Indeed Grogan (1994) highlighted that no occupation sites representing the lower levels of society have been identified in the Mooghaun region to date. Despite this, the visibility of Irish settlement dating to the later Bronze Age is clearly higher than the preceding EBA, and although our understanding of Irish Bronze Age settlement patterns may change in light of a wealth of recent developer funded archaeology, current evidence suggests a significant increase in the variation between different sites as this period progressed. This may be indicative of a shift to more complex and centralised forms of social organisation, and can be linked to the emergence of elites in society.

2.2.2.2 Aggression

The emergence of fortified settlements throughout Europe, including the aforementioned Irish examples, may be indicators of increased levels of aggression as the Bronze Age advanced (Harding, 2000; Kristiansen and Larsson, 2005). Further evidence for this is seen in the new range of weaponry that was developed; weaponry specifically designed for killing humans rather than animals (Harding, 2000). The halberd, the sword and the spear, along with shields and armour were all developed, and wear patterns suggest many were used in acts of violence. However a significant proportion of armour and weaponry never saw such action and were apparently intended for parade or ritual; a considerable amount of which was deposited for ideological or symbolic reasons (Harding, 2000).

2.2.2.3 Death

Clear traditions are visible in the treatment of the dead during the Bronze Age (Harding, 2000). In general, the dead were either inhumed or cremated, buried in a flat grave or under a mound, and with varying degrees of grave goods. Different styles of burial, such as tumuli, cists or flat inhumations, were favoured in different regions of Europe at different times. In Chalcolithic and EBA Ireland, Beaker related burial traditions associated with wedge tombs or pre-existing burial monuments were complimented by Food Vessel associated traditions that employed pits, cists, flat cemeteries and cemetery mounds and demonstrated a shift to single crouched inhumation burials (Waddell, 1998).

Groups of rich graves have been identified, particularly from the EBA, including the Wessex group of southern England (Needham et al., 2010a) and Helmsdorf and

Leubingen of central Germany (Shennan, 1993; Harding, 2000). These have been interpreted as 'princely graves' demonstrating prestige display, and have been used as evidence for social stratification (Harding, 2000; Kristiansen and Larsson, 2005). The archaeological record demonstrates that differential burial practices did exist prior to the Bronze Age, for example the Linearbandkeramik adze burials and *Spondylus* burials from the European Neolithic (Shackleton and Elderfield, 1990; Bentley et al., 2012). Additionally when looking at the Bronze Age on a whole, rich graves are relatively uncommon and there is no clear overall trend of increasing complexity or differentiation in burial practices; in north-western Europe inhumation burials were replaced by a more mixed rite where cremations were common (Harding, 2000). Thus the degree of social stratification in graves is variable depending on area and period, and differences may reflect funerary traditions as well as the availability of materials and craft skills (Harding, 2000). Shennan (1993) relates rich graves to notions of prestige exchange, where societies located in the periphery of metal producing regions attempted to restrict or monopolise the control and exchange of such materials. It therefore appears that rather than the specific action of placing prestige items in burials, it was the ability to control such materials that was key.

2.2.2.4 Metallurgy

The introduction of metallurgy

The pattern of increasing complexity highlighted by settlement evidence is mirrored in the deployment of metals. The introduction and widespread adoption of metallurgy was one of the most significant developments of the Chalcolithic and Bronze Age. From its initial appearance when use was rare, to its increased deployment over the following centuries, it undoubtedly played an important role in the developing societies at this time.

Although native copper was first exploited in south-west Asia as early as the 11th-9th millenniums BC, the earliest copper smelting sites have been found in regions such as Serbia and Iran and date to the late 6th/early 5th millenniums BC (Roberts et al., 2009). Copper production reached central Europe by the late 5th millennium BC (Höppner et al., 2005), and Britain and Ireland by the mid-3rd millennium BC (Needham, 1996; Ottaway and Roberts, 2008). As previously discussed, the first use of metal in Britain and Ireland coincides with the appearance of Beaker pottery (Waddell, 1998; O'Brien, 2004; Parker Pearson, 2005; Fitzpatrick, 2009), therefore its widespread adoption by indigenous populations was apparently linked to contacts with Beaker using societies (Waddell, 1998; O'Brien, 1999, 2012).

Two opposing theories were originally developed regarding the spread of Beaker culture during the 3rd millennium BC: the ethnic hypothesis and the status hypothesis (Brodie, 1997, 2001). In the former, the Beaker assemblage was the product of a specific group of people who migrated across Europe, whilst in the latter it relates to the emergence of status hierarchies and ideologies of the individual in different cultures throughout the continent. Both models were seen as too simplistic by Brodie (1997, 2001), who presented an alternative theory that linked the spread of Beaker culture with the spread of metallurgy. The Beaker pottery style emerged in the lower/middle Rhine region c.2700 BC at a time when the Chalcolithic frontier divided the Neolithic communities of the north-west European lowlands. Both the north-westerly spread of metallurgy and the south-easterly spread of Beaker pottery were explained by marriage alliances that transferred people with the knowledge of each in opposing directions, indeed Brodie (2001) discussed ethnographic evidence that shows the frequency of marriage across social divides can increase when new cultural or economic environments arise. As the Chalcolithic frontier moved towards Britain and Ireland, similar mechanisms could have been in play. Long distance alliances bound through marriage would have resulted in the migration of people, thus introducing both the Beaker culture and metallurgy to Britain and Ireland.

Exploitation of gold had begun in the Balkans by the mid-5th millennium BC (Roberts et al., 2009), and reached Britain and Ireland around the same time as copper metallurgy (Needham, 1996). Although gold was not particularly uncommon in the Bronze Age, its use varied significantly both geographically and temporally reflecting changes in both fashion and availability (Harding, 2000). Examples include the abundance of late Neolithic/Chalcolithic gold in south-east Europe such as the Varna cemetery assemblages (Roberts et al., 2009), the goldwork of the EBA Wessex I grave series in Britain (Eogan, 1994; Needham, 1996), and the Irish goldworking assemblages of the later third, later second and early 1st millenniums BC (Taylor, 1980; Eogan, 1994).

The discovery of tin, and its subsequent alloying with copper, led to the creation of bronze. This new alloy was superior to copper in terms of its hardness, thus allowing the manufacture of more durable tools and weapons. The earliest tin-bronze is found in south-west Asia by the end of the 4th millennium BC (Roberts et al., 2009), and its widespread adoption occurred in Britain and Ireland towards the end of the 3rd millennium BC (Needham, 1996).

Both silver and lead metallurgy spread across Europe over a similar timescale (Ottaway and Roberts, 2008). Lead metallurgy was practiced as early as the 7th millennium BC in Anatolia, and reached Britain by the late 3rd to early 2nd millennium BC (Hunter and Davis, 1994). Silver artefacts have been discovered in the Balkans dating to the Chalcolithic (Harding, 2000), and a silver bound amber bead from Gussage Cow Down, Dorset, indicates this material had reached Britain by the EBA (Needham 2000b).

The deployment of metalwork

After the initial introduction of metallurgy, a restricted range of artefact types were manufactured. In Ireland this began with the production of copper axes, tanged knives and awls alongside rare items of gold in the Knocknagur Phase (c.2500 to 2100 BC). Technological developments, alongside the appearance of bronze, led to increased metal production and a more diverse range of objects including gold lunulae, a variety of axes, halberds and daggers, and the very first spearheads (Waddell, 1998). Towards the end of the EBA there was a marked decline in copper production in certain parts of Europe (Shennan, 1993). This resulted in attempts at controlling the production of copper and bronze through centralised production centres and the establishment of hill forts, whilst an increase in scrap metal hoards is testament to the practice of recycling old metalwork (Chapman, 2008). This decline also coincided with the appearance of settlement hierarchies and the emergence of a 'warrior ethos' (seen through the deployment of prestige weaponry), whilst there was an apparent shift to larger, centralised, copper smelting sites (Shennan, 1989, 1993). The emergence of settlement hierarchies in Ireland during the MBA coincides with the metalwork of the Bishopsland Phase, a time of increased production and a diverse range of bronze and gold objects (Waddell, 1998).

In the LBA there was a further expansion in metal production (Wells, 2008). This expansion is recorded in the metalwork of the Irish Dowris-A Phase, a culmination of the metallurgical developments from the preceding centuries (Waddell, 1998). Both the amount of metal in circulation and variety of objects under production peaked, with some of the most impressive items of bronze and gold dating to this period (Waddell, 1998). The apparent importance of prestige item display and the diversity of settlement types support the presence of an increasingly hierarchical society controlled by elites (Waddell, 1998). Waddell (1998) believed that EBA social relations were defined in terms of alliances and competition, with material goods playing an important role. Prestigious artefacts were seen as key factors in defining these social relations because some societies could only obtain certain materials through trade. Consequently, metalwork may have played an important role in the development of increasingly hierarchical societies.

Ore sources

The degree to which an ore source was controlled would have had important implications, with control of metal wealth often linked to social power (Earle, 1997). The increasing control of both metal production and deployment was cited as key when Earle (1997) discussed the emergence of Bronze Age chiefdoms in Denmark, and indeed this would have been the case in other regions that lacked direct access to ore deposits. It was postulated that with the introduction of metal into the prestige goods exchange system, control of the metal wealth could be gained by financing metalworkers. Prestige goods exchange was active during the Late Neolithic, however no centralised leadership emerged because these objects were manufactured from local materials using basic technologies that prevented easy control. Conversely in the EBA control of prestige items was easier. These objects were manufactured from metal of non-local origin that required specialist knowledge to transform. Similar ideas of acquiring wealth through control of the metal supply have been proposed when discussing apparent periods of prosperity in other areas of Europe, such as EBA central Germany when the rich burials of Helmsdorf and Leubingen were interned (Shennan, 1993).

Shennan (1993) also discussed how metal represented wealth to societies living local to the ore deposits; the metal is directly convertible into tools, weapons and ornaments, and is exchangeable with goods from areas that lack source access. Administering this metal wealth would grant some level of power. A restricted number of people controlling metal sources permits influence over patterns of deployment, whilst a lack of control creates greater freedom for materials to circulate. Harding (2000) argues for notions of territoriality during the Bronze Age. This would have included the control of local resources, and the input of labour and energy involved in mining would mean that control of such resources would not be surrendered lightly.

Significant research has investigated the sources of Chalcolithic and Bronze Age copper, with ore deposits and artefact assemblages characterised and linked through both elemental and isotopic analysis (e.g. Rohl and Needham, 1998; Northover et al., 2001; Niederschlag et al., 2003). Bronze Age copper mines have been identified throughout Europe including Ross Island, Ireland; Great Orme, Wales; the Mitterberg, Austria; and Rudna Glava, Serbia, and their changing patterns of influence over time have been recognised (Jovanović and Ottaway, 1976; Dutton and Fasham, 1994; Harding, 2000; O'Brien, 2004). The remains of mine adits and shafts, spoil dumps, mining tools and processing sites have all been located, providing important evidence of Chalcolithic and Bronze Age mining and mineral processing techniques.

Unlike copper, very little is known regarding the procurement and control of gold. It is likely that gold was extracted through placer mining techniques, and numerous locations have been proposed such as western Transylvania and the Wicklow Mountains of Ireland (Harding, 2000). Unfortunately direct archaeological evidence for placer mining is difficult to find due to its ephemeral nature. A discussion of attempts to source Bronze Age gold through scientific analysis follows in Section 2.3.2.

Similarly to gold, it is probable that tin was won from placer deposits. The visual appearance of tin minerals means that locating deposits containing tin would not have been straight forward; prior knowledge of its tendency to collect in placer deposits would have been required (Ottaway and Roberts, 2008). There are relatively few major tin deposits in Europe, with the key examples located in south-west England, Brittany, Iberia, and the Erzgebirge of central Europe (Penhallurick, 1997). Evidence for their exploitation during the Bronze Age is even rarer; Bronze Age axes have been discovered in tin workings at La Villeder, Brittany, and Bronze Age artefacts have been recovered from a number of tin grounds in Cornwall, south-east England (Penhallurick, 1986, 1997).

With the geographic restriction of ore sources throughout Europe, trade and exchange networks would have played an important role in society. During the Bronze Age these are believed to have been significant on both local and regional scales (Harding, 2000), and long distance trade was aided by developments in transport; wheels, pack animals and horses were all exploited at this time (Harding, 2000). There is also clear evidence for seafaring through the physical remains of boats (such as the Dover Boat; Clark, 2004) and the movement of material goods across seaways (for example the Langdon Bay hoard, Kent; Muckelroy, 1980).

Material trade may have occurred for a number of reasons. Raw materials, especially metals, were probably exchanged for economic and utilitarian needs; however the exchange of finished objects and exotic materials could have been necessitated by other factors (Harding, 2000); a theme expanded upon in section 2.2.3. The question of access to raw materials is also one of significance, as this would have a direct effect on the resulting supply chain. As Harding (2000) states, some materials such as clay and wood are available across most of Europe, whilst others such as metals are only found in certain locations. The latter would have been exchanged over greater distances.

Metals and society

The procurement of metal ore, it's processing into workable form, and the subsequent manufacturing of objects requires specialist knowledge and labour (Harding, 2000). Evidence from the settlement site of St. Veit-Klinglberg, central Austria, demonstrated the seasonal exploitation of copper from more than one source, whilst metalworking specialists lived off imported cereals and thus did not have to devote their time to subsistence agriculture (Shennan, 1989). It also suggests that initial phases of mining and smelting were carried out by small independent yet competing groups with no centralised control (Shennan, 1989, 1993). O'Brien (2004) explored the possibility that some of the mining practices employed at Ross Island during the EBA required experienced workers. When comparing to site based low-skill activities, the potential for an internal hierarchy was clear. However it was stressed that any leadership could have been tribal rather than individual and the mining activities may have been carried out seasonally by part time farmers, thus any social divisions created by specialisation may not have been in play year round. Nevertheless, when workers were employed in mining or metallurgy even if this was only at specific times of the year, they were unable to take part in a subsistence way of life. This would have created a skilled set of workers socially differentiated from others, who required the wider community to aid in the acquisition of materials necessary for daily life (Ottaway and Roberts, 2008). Clearly the new technological developments of the Bronze Age saw the economy diversify into new areas, creating new paths for specialisation and therefore social division.

Metal workers possessed skills that the general population did not have. In many societies the smith is intrinsically linked to the success of the community, and is a highly valued, sometimes feared, craftsman (Harding, 2000). Despite the wealth of metalwork from the Bronze Age, other traces of the metalworkers themselves are rare (Barber, 2003). It is difficult to ascribe tools solely to metalworking when they have many potential uses, and few metalworking sites have been identified to date relative to the quantity of finished articles that were in circulation (Barber, 2003). The presence of metalworking tools in burial contexts has led to the proposed identification of smiths in a number of burials throughout Europe (Harding, 2000; Fitzpatrick, 2011), suggesting that smiths were treated specially in death. However in Britain and Ireland there is an obvious lack of metalworker burials, with the Amesbury Archer (Wiltshire) and Kirkhaugh (Northumberland) being two possible examples (Fitzpatrick, 2011).

Childe (1930) believed smithing was a full time occupation, with smiths travelling between areas to practice their trade and the rest of society providing for them in return. It was also thought that metalworking skills were controlled and guarded by the smiths, therefore restricting the knowledge distribution and increasing the smith's importance. This view was based on the lack of evidence for permanent workshops, the agricultural focussed economy, the scarcity of raw materials in many areas, and the interpretation that hoards of broken or miscast objects were the stock of travelling smiths. Harding (2000) cited the incompatibility of this theory with ethnographical work by Rowlands (1971). Although smiths did travel on occasion, this was part of a wider settlement system controlled by a chief rather than a function of free trade. In other communities the smiths were permanent residents and metalworking was a part time or seasonal occupation. It was however noted that there are no ethnographic parallels for the deposition of hoards thus different system could have been in play during the Bronze Age (Harding, 2000).

2.2.2.5 Ritual

Ritual played an important role in Bronze Age life. Evidence exists for the use of natural features across Europe, with caves and wet places often being used for the deposition of objects, and rock outcrops being utilised for engravings (Waddell, 1998; Harding, 2000). Further ceremonial elements can be identified through the creation of significant places, for example the erection of standing stones, the creation and deposition of visually impressive bronzework that had no utilitarian purpose, and the playing of musical instruments (Harding, 2000).

The practice of depositing material in hoards, in particular large quantities of bronze, is an important aspect of the Bronze Age (Bradley, 1990). The condition of deposited objects varied from used to pristine, therefore it was not simply a case of discarding items that had reached the end of their lifespan (Bradley, 1990, Fontijn, 2008; Ottaway and Roberts, 2008). Many of these depositions were made in wet places, suggesting specific environments were often preferred, and there appears to be some underlying structure in the way hoards were deposited with certain objects or combinations favoured (Harding, 2000; Fontijn, 2008). Fontijn (2008) believed the practice of selective deposition acted to keep certain objects and their associated ideologies apart, whilst deliberately merging the biographies of the objects, the place of deposition, and the person carrying out the depositional act. Numerous other theories have been proposed including ritualistic offerings to enhance political power and simply the storage of metal stocks (Bradley, 1990, 2007; Fontijn, 2008).

Irrespective of the reason for deposition, and if they were placed individually, in hoards, or associated with burials, it represents vast quantities of wasted raw material and labour (Harding, 2000; Fontijn, 2008). The metals were never recycled, the metal stock in circulation became depleted, and more raw materials would be required (Ottaway and Roberts, 2008). Consequently the control of these depositional rituals may also have played a role in enhancing the power of individuals and creating elites (Waddell, 1998).

2.2.2.6 Society

The central and northern European Chalcolithic and Bronze Age, on a general scale, witnessed a shift from essentially Neolithic lifestyles to more complex societies characterised by the commodification of metal, division and specialisation of labour, and the intensification of goods exchange (Kristiansen and Larsson, 2005). By the end of the 3rd millennium BC a series of new technologies had been adopted across Europe, including metallurgy (copper, gold, tin, bronze), traction, and wool production (Kristiansen and Larsson, 2005), however many aspects of life remained similar to the preceding centuries; small farming and pastoral groups undertook large communal ventures building monuments (Harding, 2000). This was the case in Ireland where the construction of henges continued (O'Brien, 2012), and such projects undoubtedly required organisation, planning, and therefore control or leadership by specific individuals or groups (Harding, 2000).

The structure of these Chalcolithic societies was probably based around extended family units, with leaders achieving some form of ranking through participation in exchange networks, physical achievements or heroic deeds, whilst they most likely lived within an ancestrally centred cosmology (Needham, 2012). Based to the distribution of material culture (wedge tombs, Beaker pottery, copper metalwork), O'Brien (2012) argued that Chalcolithic Ireland had developed a regional character consisting of small segmentary communities. Society was therefore seen to be built on a tribal structure, each with a territorial identity. In line with the general patterns seen elsewhere in Europe, the Irish Chalcolithic was characterised by long distance exchange networks, craft specialisation, and the exploitation of gold and copper. However contrasts also existed; it lacked structured settlement patterns, the secondary products revolution, and the occupation of marginal environments.

There is evidence to suggest that some of the individuals buried with the Beaker grave good package in southern Britain were immigrants to the area (Fitzpatrick, 2011), therefore it seems viable that both Beaker culture and metalworking arrived from continental Europe and that two distinct cultures lived side by side during the Chalcolithic. There is however no evidence to suggest that this was a mass episode of immigration, especially in Ireland where Beaker contexts are seen to have a strong indigenous background (Waddell, 1998; O'Brien, 1999, 2012). Despite the adoption of Beaker associated innovations such as metallurgy, O'Brien (2012) believes the Beaker culture would have been accepted to varying degrees throughout the region.

Needham (2012) presented a model to explain how Beaker groups may have integrated with indigenous populations over the course of the Chalcolithic. Based on the distinct Beaker assemblage visible in the archaeological record today, the new arrivals continued with their own culture and belief system. It is also clear that the Beaker culture began to exploit pre-existing ceremonial traditions at some point after their arrival, thus at some point these two cultures began to coalesce. Reasons for this could range from the desire from indigenous societies for newly introduced technologies and materials such as copper and gold to the need for Beaker populations to live a peaceful co-existence in their new environment, and again marriage alliances would have been a mechanism for these two cultures to come together (Needham 2012).

In Ireland, the adoption of single burials in the Late Chalcolithic (post 2150 BC) is seen as the first evidence for 'overt social ranking' by O'Brien (2012, p.220), with British contacts seen as a possible stimulus. This tradition is a possible indicator for increasingly hierarchical and differentiated societies, with the increased deployment of metalwork allowing the embodiment and control of wealth (O'Brien, 2012). However this interpretation is not universally accepted. Carlin and Brück (2012) argued for widespread social continuity in Ireland from the Late Neolithic through to the Early Bronze Age, with only gradual transformations in social practice occurring between 2900 and 1700 BC. The form and character of settlement sites demonstrates little change, the appearance of Beaker (and Grooved Ware) ceramics outside funerary and ceremonial contexts suggests they were not restricted to specific social ranks, there was continued use of ceremonial monuments, and a diversity in funerary practices included the construction of wedge tombs which was interpreted as reinvention of earlier Neolithic burial traditions.

As the Bronze Age progressed and the use of large communal monuments fell out of fashion, there is further evidence for distinct shifts in society. There was an increasing trend in the display of wealth through material objects either as grave goods or through the deposition of hoards, and the MBA and LBA witnessed major proliferations in metalworking industries and the emergence of settlement hierarchies. By the end of the Bronze Age, the economic potential of many European Bronze Age cultures was realised (Kristiansen and Larsson, 2005), and powerful elites began to appear as more complex and stratified societies developed (Harding, 2000). How these elites acquired and maintained their status is an important question when trying to understand this social change, and is consequently a key aspect of Bronze Age archaeology.

Mann (1986) detailed four principle sources of power: control over economic, ideological, military and political resources. Economic power could be obtained via a) the exploitation of people in co-operation through labour, or b) the circulation and exchange of material goods for transformation and consumption. Mann (1986) also discussed the idea of 'power jumps', defined as inventions that could have been exploited to increase the power of certain individuals. One such example provided was the appearance of metallurgy, and it is clear that the exploitation of new materials or technologies such as gold or goldworking had the potential to provide individuals with power through the control of its procurement, transformation, deployment, trade and exchange. However the ability to control is not guaranteed, therefore an understanding of the location and number of sources for a particular material, and how this changed over time, is required.

2.2.3 Exotic Materials and the Bronze Age

2.2.3.1 Exotics and society

The significant role that artefacts, particularly metals, played in Bronze Age society is clear and numerous reasons can be behind systems of their exchange, ranging from simple human curiosity of foreign lands to creating indebtedness for competitive advantage (Needham, 2008). Rare materials, commonly termed exotics, were distributed unequally and may have reinforced social differences (Harding, 2000). However rarity does not have to be their defining characteristic, and exotic materials may gain their social significance through the long distances they travelled, the specialist knowledge required to procure them (Harding, 2000), or their physical properties/appearance and how these are perceived. Exotic materials were often preferred over local sources of equal quality, thereby emphasising the importance of distant origins and augmenting the reputation of the individuals or groups that had access to them (Helms, 1988; Chapman, 2008). Chapman (2008) explored the importance of the journeys these items took and how their meanings could be transformed as they were brought into different contexts. They could become commodities unconnected to persons, or gifts intrinsically linked to their producer; they could have acted as a measure of the worth of the person giving, the means to which value was created, or simply been the embodiment of value. Control of these exotics, whether through the control of procurement, exchange, or the skills of transforming the raw material into objects is therefore a potential source of high status and a mechanism for the creation of elites (Harding, 2000; Chapman, 2008).

The deployment of exotics is not a characteristic linked exclusively with Bronze Age society. As discussed by Chapman (2008), this practice was widespread in communities with apparently few inequalities; shells and lithics were exchanged over hundreds of kilometres and transformed into items of high social value as early as the Mesolithic. The tradition continued through the Neolithic, yet in these forager and early farming communities there was little variation in the stocks of exotic objects between different settlements. With the onset of the Chalcolithic and EBA there was a significant change in the way exotics such as gold, amber, faience and jet were deployed, with marked differences in scale between sites in the same region. This is perhaps best demonstrated by the cemetery at Varna, Bulgaria, that contained a wide range of artefacts and materials demonstrating high quality craftsmanship and exotic origin; some materials originated from as far away as central Asia (Chapman, 2008). Examples exist throughout Europe, such as the EBA burials of Wessex, southern England (Needham et al., 2010a), and Helmsdorf and Leubingen in central Germany (Shennan, 1993; Harding, 2000). The growing scale of exchange differentiation during the EBA resulted in an increasing elite dependence on the movement of exotics. Local identities could be expressed through a suite of exotic objects, while new personal identities were created such as specialist miners, smelters and craft-workers (Chapman, 2008).

Even though exotics can be found associated with individuals in grave contexts, this does not necessarily represent ownership. In discussing the precious cup tradition of the EBA, Needham (2006c) preferred the term ‘custodianship’, suggesting that objects were of communal, ritual, use and may have been deposited because they had reached the end of their lifespan or had a strong connection with their custodians. The role of these cups in communal rituals is consistent with the work of Woodward (2000, 2002) on EBA heirlooms and relics. Woodward highlighted the low numbers of amber beads found associated with the majority of burials suggesting that whole necklaces were rarely interned. Instead an interpretation of amber beads as heirlooms was preferred, with the beads carefully curated and re-used over time. The same was said for the jet varieties, and both materials display ‘magical’ physical properties; static electrical discharges are produced when rubbed with textile or fur. As a result, use in magical exploits or religious and supernatural ceremonies was proposed, and cosmologically driven exchange systems can be proposed (Needham, 2008). Needham (2006c) discussed the importance of these shamanistic equipments in communicating with gods and spirits, and consequently exotic materials were held in trust for the community and are only connected to individuals due to the specialised role they provided. These materials are not confined to grave contexts. Whilst gold was typically deposited in association with burials in the Wessex region of England, Irish goldwork, of which there was significantly more, was typically deposited as isolated finds or in association with other items of gold (Taylor, 1980; Eogan, 1994). Evidence for long term curation of Irish gold lunulae was presented by Cahill (2006), whilst communal roles have also been proposed (Eogan, 1994; Taylor 1994).

The supernatural significance of exotic materials was further developed by Sheridan and Shortland (2003, 2004) through their ideas of 'supernatural power dressing'. Jet and amber are known to have embodied magical powers in the eyes of numerous societies throughout the past, therefore they proposed that the embodiment of supernatural powers or talismanic forces within these materials would drive their appeal as prestige items.

Understanding the meaning of gold to prehistoric societies is a complex issue, and one that may never be fully appreciated. However some clues are available, namely the role gold played in other societies. The Americas has a long history of goldworking, and the metal held an important place within the world view of many indigenous groups. Amerindians recognised spirituality in various shiny objects including celestial bodies, fire, water, feathers and metals such as gold; they were charged with supernatural essence and cosmological power (Saunders, 1998, 1999, 2003). Saunders (1998) discussed the importance of light in these societies; bright light was associated with positive qualities and sacred or social values, whilst the absence of light was linked to negative attributes. These shiny materials, their procurement, and the embodied spiritual essence were all associated with the work of shamans, and formed their link to the spirit world. Light was associated with a realm inhabited by spirits, who could become visible to these shamans, priests or rulers (Saunders, 2003). Producing objects out of these materials converted the energy of light into material forms (Saunders, 1999). The objects became a store of supernatural or cosmological power that would have enhanced the powers of those who owned or controlled them (Saunders, 2003 citing Reichel-Dolmatoff, 1988; Helms, 1993), and they were seen as statements of social prestige due to a perceived association with purity, elite status and political power (Blanton et al., 1993). Amerindians therefore adorned themselves in objects of metals such as gold to symbolise their status and power through the perceived connections to the supernatural (Saunders, 2003 citing Reichel-Dolmatoff, 1981).

The association of light with the supernatural and cosmological was prevalent across the Americas, although the meaning of different shiny materials could vary between different societies due to availability, technological sophistication and local historical events (Saunders, 2003). Furthermore this association was not confined to the Americas, and parallels can be found across Africa, Asia, Europe and the Pacific over thousands of years (Saunders, 2003). Ethnographic evidence also links light and shininess with the spirit realm, ancestors and earthly forces (Saunders, 2003). The association between shiny materials such as gold and supernatural or cosmological powers has therefore been found in numerous societies across different geographical regions and periods of time. If the same connotations were present in the Bronze Age, then goldwork would fit in with the idea of supernatural power dressing proposed by Sheridan and Shortland (2003, 2004). Gold can be considered alongside amber and jet in a group of materials that embodied magical properties and supernatural forces, and that were used in ceremonies by specialists who controlled the knowledge of how these materials could be exploited.

Controlling materials with such connotations would clearly be an important aspect of exotic exchange. If sources were too common then controlling their exploitation would be difficult, an example being the Baltic amber trade. Although amber was found as an exotic material as far away as Mycenae, it was absent from the elite graves of southern Scandinavia because there were too many local sources for local control (Chapman, 2008). Understanding the procurement of exotic materials is therefore a fundamental aspect of their study if an understanding of their role and significance in society is to be achieved.

2.2.3.2 Sources of Irish and British Chalcolithic and Early Bronze Age Exotics

Jet

Regarding the exotics of the EBA such as jet, jet-like materials, amber, and faience, significant success in discerning their sources has been achieved. An overview of the research into the jet and jet-like artefacts of Scotland was provided by Sheridan (2002). Although jet (and amber) was in use in Scotland from the first half of the 4th millennium BC, there was a marked increase in the use of jet and jet-like materials towards the end of the 3rd millennium BC. During this period, Scotland appears to have been a focal point for its use; approximately two thirds of all the British and Irish jet spacer plate necklaces have been found in this region. Compositional studies (using XRF) by Sheridan (2002) demonstrated that the jet originated from Whitby, Yorkshire, rather than from more local sources, highlighting the importance of materials originating from distant sources.

Amber

The deployment of amber also increased significantly in the EBA (Beck and Shennan, 1991). The ultimate source of amber in Europe is considered to be southern Scandinavia, although it is unclear if this was the immediate source because it can also be found washed up on the eastern coast of England (Beck and Shennan, 1991; Needham, 2006a). The small number of finished amber artefacts discovered near the Baltic amber 'source' in eastern England, the large number of artefacts found in Britain and the lack of raw Baltic amber found in this region led Beck and Shennan (1991) to prefer a Baltic source. The authors also point out that the material would still be considered non-local in areas of inland Britain even if the immediate source was the east coast of England.

Faience

Faience is a glass like material produced by heating a quartz based paste, a flux, and a colourant (Sheridan and Shortland, 2003, 2004). It was used in the manufacture of beads and pendants across north-western Europe from the early 2nd millennium BC, with distribution centred on Britain and deposition primarily in burial contexts (Sheridan and Shortland, 2004; Sheridan, 2008). It is often associated with other exotic materials in the form of composite necklaces, for example the Exloo necklace, and its relative rarity and association with other exotic materials is seen as an indicator of the special status the material enjoyed (Sheridan and Shortland, 2004). Despite this association with other exotics materials, compositional studies (XRF and SEM) by Sheridan and Shortland (2004) reinforced the view that faience is a material created in Britain, the focus of its distribution, and was probably manufactured in more than one place. However as already highlighted, exoticness is not just derived from distance, and faience may also fit into this important range of mysterious materials due to the magical transformation of raw material into finished artefact by those with the access to the knowledge of manufacture (Sheridan and Shortland, 2004).

Gold

Significant concentrations of Chalcolithic and Bronze Age goldwork have been discovered in Ireland, and recent research has highlighted the Mourne Mountains as the most likely Irish source of gold during the EBA (Warner et al., 2009, 2010a, 2010b). A more detailed overview of studies concerning the provenance of Bronze Age gold follows in Section 2.3.2, however the present day low abundance of gold in the Mourne Mountains (Meighan 2011) means uncertainty over which sources were exploited remains. As a result, a true understanding of gold procurement is yet to be achieved. Furthermore, it is still unclear if and why gold can be considered an equivalent to contemporaneous exotic materials. Comparable to amber and jet, an exotic meaning may have been created due to distant geographic origins. Alternatively if widespread local sources were under exploitation, the intrinsic properties of gold (such as shininess) may instead have been key. An understanding of gold procurement would therefore enable an assessment of whether gold can justly be considered part of a Chalcolithic and Bronze Age network of exotic materials, and if so, why.

2.3 Bronze Age goldwork of Ireland and Britain

2.3.1 Overview of Bronze Age gold artefacts

2.3.1.1 Introduction

Goldworking reached north-western Europe in the mid 3rd millennium BC, and although some items (such as beads and coils) have been linked to pre-Beaker cultures in Iberia and France (Taylor, 1978; Eluère, 1982), its appearance in Britain and Ireland is typically associated with Beaker contexts. A number of noteworthy studies outline the various gold assemblages of the Bronze Age (Taylor, 1980; Eluère, 1982; Eogan, 1994), and it is clear that significant concentrations of goldwork were present in Ireland throughout this period. It is not the aim of this study to add to this list of publications, therefore the summary that follows focuses on the principle artefact forms of the Irish and British EBA that will be discussed in this study.

2.3.1.2 Primary Beaker goldwork

Principle artefact types

The earliest gold artefacts in Ireland and Britain have collectively been termed 'Primary Bell Beaker goldwork' by Eogan (1994). Technologically these objects were created using sheet gold techniques; ingots were hammered into shape then decoration applied using incision or repoussé (Eogan, 1994; Needham, 2000a). This tradition dates from the earliest Beaker contexts, c.2500-2200 cal BC (Needham, 1996). Discs and basket shaped ornaments are the most common artefact form, whilst beads, rivet caps, oval plaques, and other mounts or fittings were also produced (Eogan, 1994; Needham, 2000a).

Basket shaped ornaments

Basket shaped ornaments are longitudinally curled oval sheets of gold with a hook projecting from the middle of one side (Eogan, 1994). Examples found in Chalcolithic British Beaker burial contexts include: Boscombe Down West (Amesbury Archer), Wiltshire (2455-2300 cal BC 1σ; Fitzpatrick, 2011; Needham, 2012); Boscombe Down West (Archer's companion), Wiltshire (2460-2140 cal BC 2σ; Fitzpatrick, 2011); Radley Barrow Hills (barrow 4A), Oxfordshire (2470-2205 cal BC 1σ; Barclay and Halpin, 1999; Needham, 2012); and Chilbolton, Hampshire (2480-2345 cal BC and 2285-2030 cal BC 1σ; Russel, 1990; Kinnes, 1994; Needham, 2012). One pair has also been discovered in Ireland (Figure 2.2), although no details pertaining to its discovery have been recorded (Armstrong, 1933).

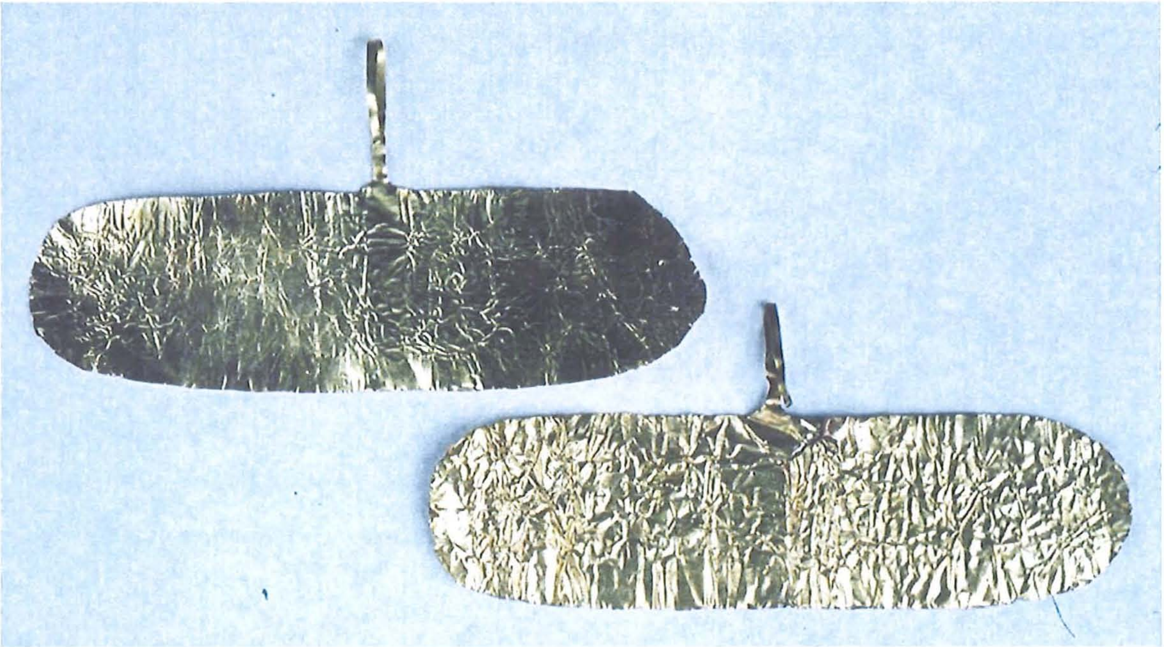


Figure 2.2: Pair of Irish basket ornaments (W73 and W74), find location unknown. Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

Eogan (1994) linked the basket ornaments with continental origins, whilst Taylor (1980) highlighted possible central European traits primarily due to their associations with Beaker artefacts. Gold basket shaped ornaments have been found in continental Europe: a fragment was discovered amongst Beaker Pottery at the site of Colledic, Brittany; whole examples were discovered in Poland at Wąsosz; and possible examples have been found elsewhere in Poland and the Ukraine (Taylor, 1994; O'Connor, 2004). These Polish and Ukrainian examples have been interpreted as being of Irish origin by local scholars based on the prevalence of EBA goldwork in Ireland, and indeed they date to post-2000 BC thus can not be prototypes of the British and Irish basket ornaments (O'Connor, 2004). Needham (2011) believed that if an external stimulus for these ornaments did exist, then the most likely candidates would be the coiled spatulate-ended ornaments from early Beaker contexts in central Europe. One gold ornament type may have been a chronological equivalent to the basket ornaments are the central European sub-rectangular sheets found in Beaker contexts in Bavaria, Bohemia and Moravia (O'Connor, 2004 citing Steffgen, 1997; Moucha, 1997; Stuchlík, 1997). Bronze basket ornaments have also been found in Britain, however they were not a stimulus for the gold versions because they were also chronologically later (Case, 1977; O'Connor, 2004).

The Benraw (formerly Deehommed or Dacomet; O'Connor, 2004) ornament is an atypical find from Co. Down, Northern Ireland (Figure 2.3), and no other parallels have been found in Britain or Ireland. Its form is similar to the basket ornaments although it was produced by folding a 'spoon' shaped sheet of gold (Armstrong, 1933). A possible association between this artefact and central European Únětice racquet headed pins (Taylor, 1980) is not indicative of a central European origin because the pins are chronologically later (O'Connor, 2004 citing David-Elbiali, 2000). Parallels drawn by Taylor (1980) to late Beaker earrings of identical construction found in Portugal highlights Iberia as the most likely source region for this artefact, and it is generally considered to be an import (Taylor, 1979).

There are no clear continental prototypes for the British and Irish type basket ornaments; the majority have been discovered in Britain and they are generally considered to be an insular ornament form (Fitzpatrick, 2011; Needham, 2011). Whilst Ireland has been seen as a potential source for the gold used to manufacture a number of these ornaments (Needham, 2011), a continental origin for at least some of the gold is still often assumed (Fitzpatrick, 2009; 2011). If the Benraw ornament is chronologically earlier, it could represent an Iberian prototype. It is worth noting that the Benraw ornament is significantly different compositionally from both the basket ornaments and the Iberian earrings (Hartmann, 1970, 1982; Taylor, 1999).

Figure 2.3: The Benraw ornament (1876:18). Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

Discs

Gold discs (for example Figure 2.4) first appear in Britain and Ireland as part of the primary Beaker goldwork (Eogan, 1994; Needham, 2000a), although a recent find at Tubney, Oxfordshire, indicates some were still in circulation a number of centuries later (Simmonds, 2012). The early forms are small (typically 30 mm to 50 mm in diameter), and those with direct Beaker associations usually have two central perforations (Eogan, 1994). Decoration can consist of cruciforms and bands of 'ladder' patterns, or concentric rings of repoussé dots (Eogan, 1994).

Case (1977) divided the EBA gold discs of Britain and Ireland into two groups based on decoration: type A discs have ladder patterned cruciforms motifs, whilst type B discs comprise of the remainder. It is the type A discs that fall into the primary Beaker phase. Examples such as the Mere and Farleigh Wick discs (Wiltshire) were found within Low-Carinated Beaker associated burial contexts suggesting an early Chalcolithic date (Needham, 2012). Those discovered in Ireland have rarely been found in burial contexts and the majority have no recorded details relating to their discovery (Armstrong, 1933): the small disc from Lough Gur was found in association with a Beaker occupation context (Cahill, 2006 citing Ó Ríordáin, 1953-4); the discs with a possible provenance of Corran, Co. Armagh, may have been recovered from a Beaker context (Case, 1977);

and the Ballyshannon discs were discovered with an inhumation burial (Case, 1977), although whether this was a Beaker or Food Vessel association is unclear.

Figure 2.4: Two gold discs from Rappa Castle, Co. Mayo (W267 and W271 respectively). Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

Clarke (1970) and Taylor (1980) highlighted similarities between the gold discs and the heads of some racquet-headed pins from the Únětice culture of central Europe. The discs were not seen as imports and instead formed part of the British Beaker assemblage; they were interpreted as imitations of the heads of these pins (Taylor, 1980). However the racquet-headed pins date to the classic Únětice with absolute ages of 2000-1800 BC, thus the latest chronology does not support an Únětice origin (O'Connor, 2004 citing David-Elbiali, 2000; Schwenzer, 2002). Gold discs have been recorded in Iberia, and are seen as responses to rather than stimuli for the Irish and British discs by Taylor (1980). Chalcolithic copper and gold examples have also been found in south-east Europe, Denmark and France (Eluère, 1982; Eogan, 1994; Gessner, 2005), and therefore offer potential prototypes for the Irish and British examples. Beaker V-perforated buttons were sometimes decorated with similar cruciform designs, for example jet versions found at Thwing and Rudstone, Yorkshire (Munro, 1902; Taylor, 1980). The origins of these buttons are believed to lie in the Globular Amphora and Corded Ware cultures of northern and northern central Europe (Herity and Eogan, 1977; Piggott, 1963). In fact cruciform designs are found throughout Europe on objects of amber, copper, shell, bone and clay from the Late Neolithic to Chalcolithic Coded

Ware culture (Gessner, 2005). There are clearly a number of possible continental influences for these discs and their decoration. Nonetheless, the concentration of finds in Ireland and Britain suggest an insular development is likely.

Plaques

Three gold oval plaques decorated with dotted and linear borders and sets of three transverse lines have a recorded find location of Belville, Co. Cavan (Figure 2.5). A fourth oval plaque of similar style, along with an undecorated gold band found in four pieces (a possible diadem), were found together at an unrecorded location also in Co. Cavan (Case, 1977; Eogan, 1994; also Figure 2.5). Together with the Co. Monaghan, Co. Roscommon and (possible) Co. Armagh discs, they help to form one of the main concentrations of Beaker goldwork in Ireland (Cahill, 2006). Case (1977) discussed typological links to the type A gold discs; decorations on the oval plaques are ladder-like in style, and akin to the discs they contain two central perforations. Although Taylor (1994) highlighted a possible association between the diadem and similar Iberian examples, the smaller oval plaques were seen to have affiliations to the basket earrings. Furthermore, compositional analysis supports a relationship with other Irish goldwork from this early period (Hartmann, 1970).

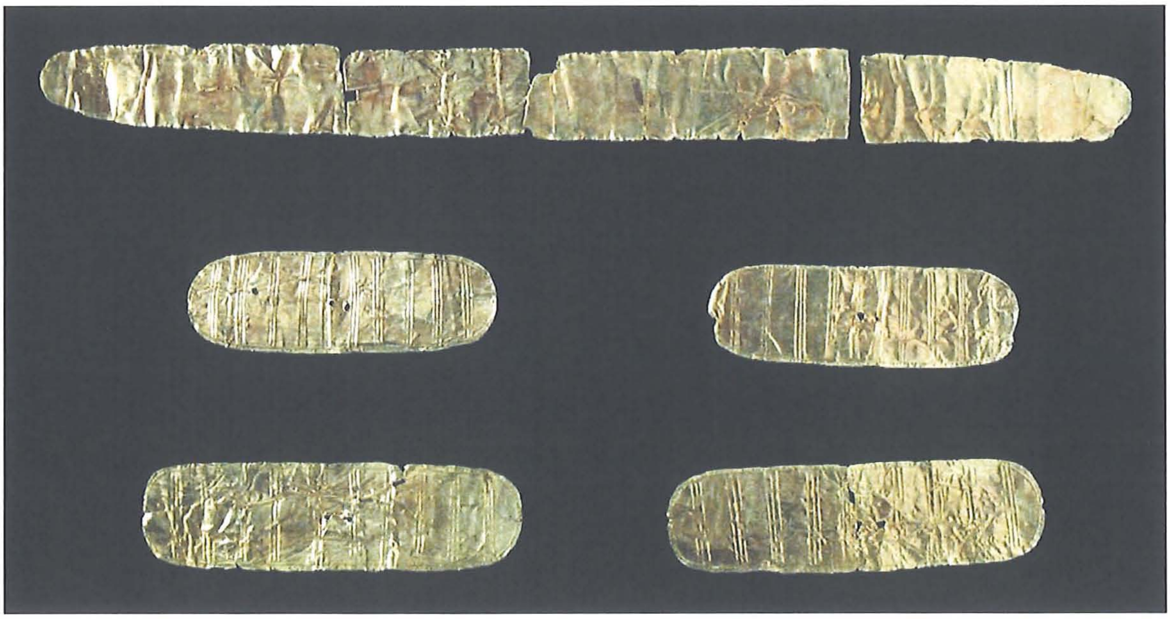


Figure 2.5: Co. Cavan oval plaques (Top W78 to W81, middle W75 and W71, bottom W76 and W72). Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

Rivet caps and beads

Rivet caps associated with stone wristguards have been found in Beaker burial contexts at Barnack (Cambridgeshire), Driffield (Yorkshire), and Culduthel Mains (Inverness-shire), whilst a gold bead from Chilbolton, Hampshire was also discovered associated with a Beaker inhumation (Eogan, 1994). Human bone from the Barnack and Chilbolton inhumations provided radiocarbon dates towards the end of the 3rd millennium BC (Needham, 1996), and all four burials have been placed between 2300 BC and 2100 BC in Needham's (2000a) suggested chronology of Bronze Age goldwork. Taylor (1994) highlighted stylistic similarities between the wristguards and an Iberian gold bracer from Aqua Branca, Portugal, whilst both the Barnack and Driffield burials also contain tanged knives suggesting links with central Europe.

2.3.1.3 Goldwork from insular Early Bronze Age traditions

Principle artefact types

Goldworking continued in Ireland and Britain after the initial Beaker phase of production. This period correlates with phases 2 to 4 of Needham's (1996) chronology of the Bronze Age, and dates from c.2200 BC to 1500 BC. Perhaps the most famous artefacts of this period are the crescent-shape sheet ornaments known as lunulae, whilst the production of gold discs continued. This period also witnessed the Scottish gold hilt band and Wessex linear traditions along with the emergence of the embossed goldwork tradition.

Lunulae

Detailed overviews of this artefact type have been provided by Taylor (1980) and Eogan (1994). Lunulae (e.g. Figure 2.6) were produced by hammering an ingot into a cresentic shape, with geometric decoration applied through incision, punching and hammering. When present, decoration is confined to one face, with the principle motifs being cross-hatching, parallel lines, zig-zags, triangles and lozenges (there are rare examples of undecorated lunulae). Designs are typically concentrated towards the terminals, while the edges of the lunulae are also stylised to produce patterned borders.

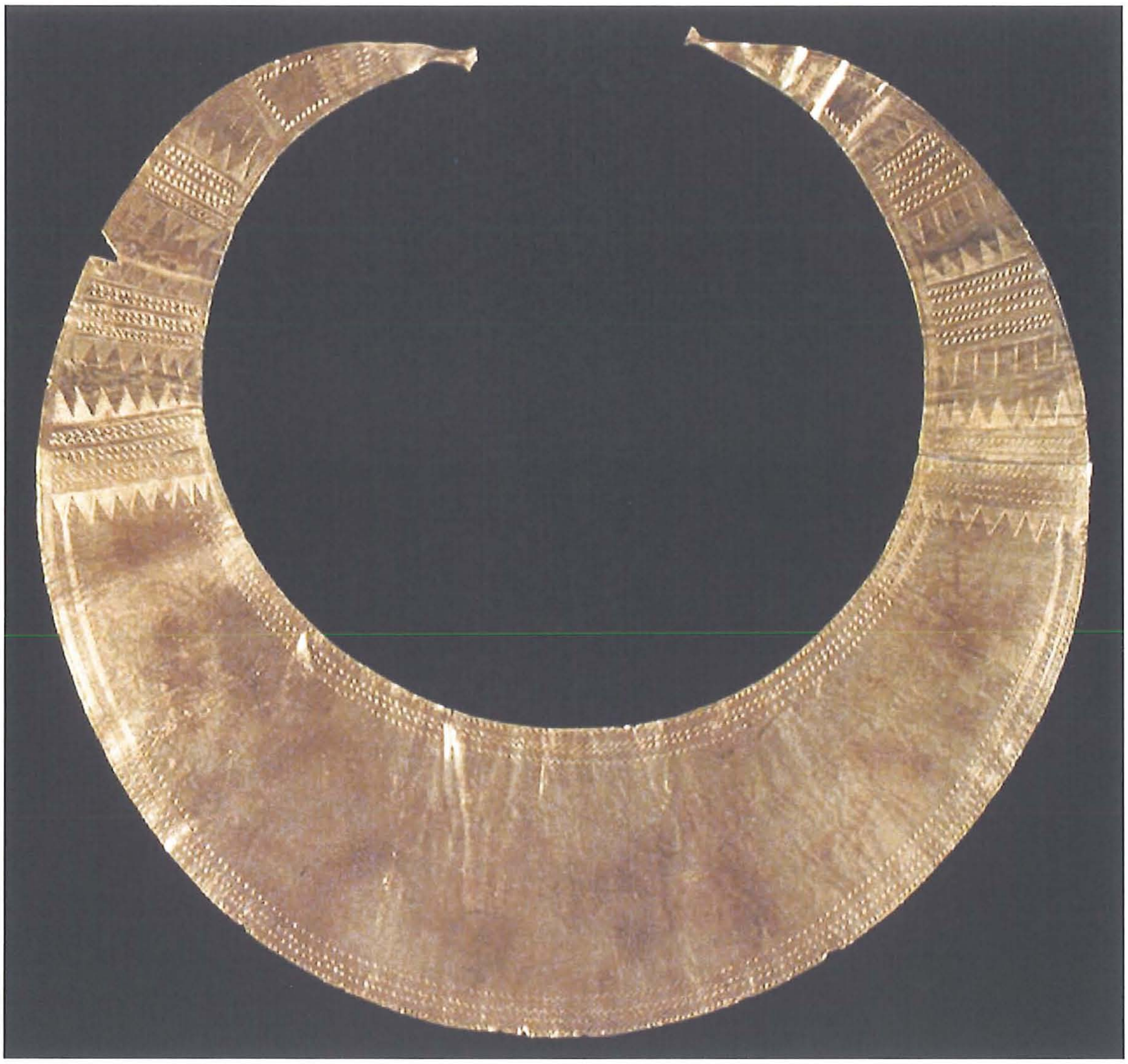


Figure 2.6: Banemore classical lunula R1756. Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

Eogan (1994) lists 115 examples of lunulae, and a further three have been discovered since publication: a whole lunula from Coggalbeg, Co. Roscommon (Kelly and Cahill, 2010); a fragment from Brampton, Cumbria; and fragments from Garlieston, Dumfries and Galloway (Pitts, 2011). Their distribution is heavily concentrated in Ireland (Figure 2.7).

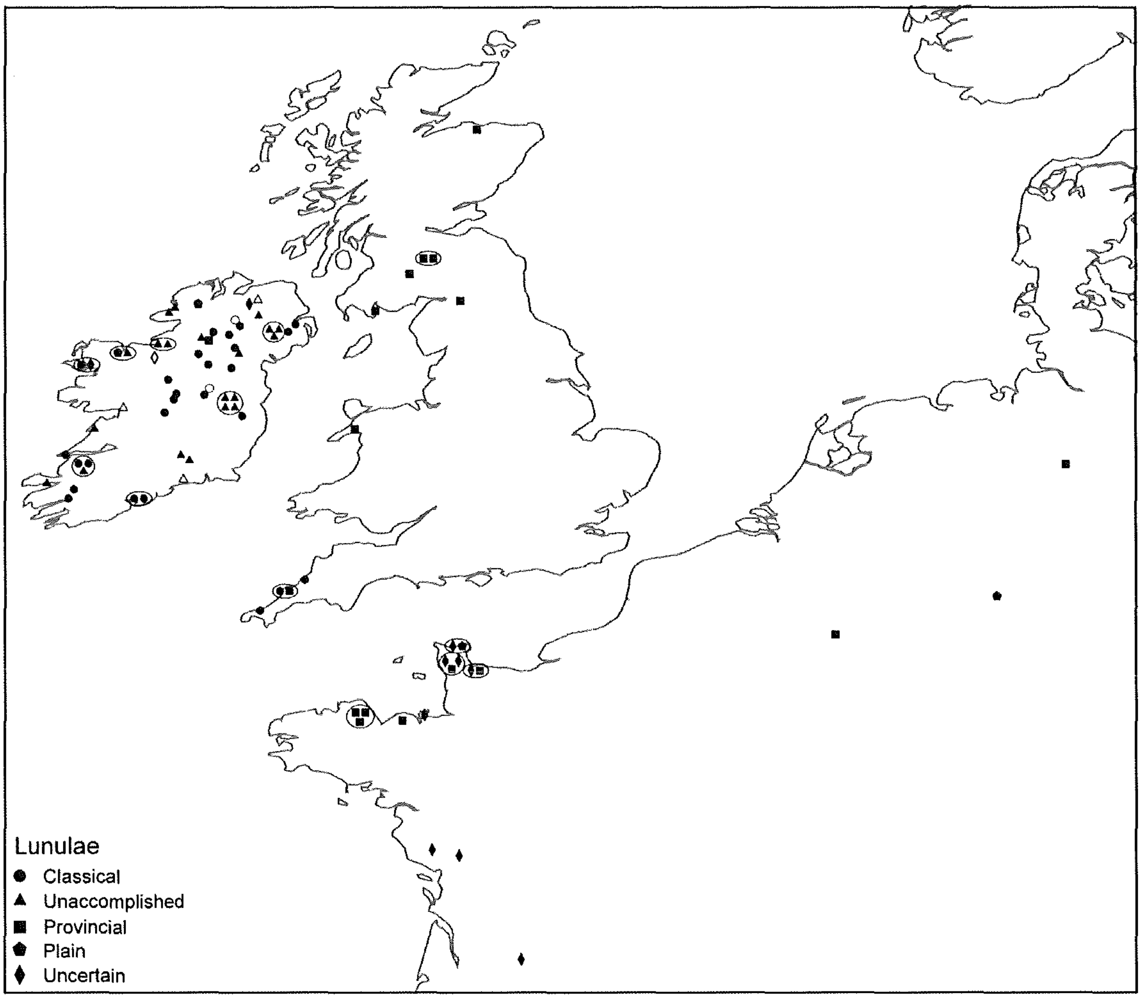


Figure 2.7: Distribution of EBA gold lunulae. Open symbols represent lunulae attributed to a county only, those enclosed by a black ellipse were found together. Details from Eogan (1994) with recent additions.

Out of the 115 lunulae listed, Eogan (1994) details 86 that have been discovered in Ireland (although only 47 have exact details of their find location). Including the recently discovered examples, that equates to c.74%. The remaining were typically found in western Britain and coastal north-west Europe: 15 in France (predominantly northern Brittany and Normandy), seven in Scotland (although two are considered as modern day imports), five in England, two in Germany, and one in both Wales and Belgium. Similar EBA crescentic gold collars have also been found in Portugal and Scandinavia (Taylor, 1980; Eogan, 1994), although their styles are more removed from the lunulae discussed here (Taylor, 1994). Taylor (1980) classified the lunulae into three key groups based on shape, ornamentation and distribution: the classical, unaccomplished and provincial. An overview of these types follows.

The classical lunulae (e.g. Figure 2.6 and Figure 2.8) are the most sophisticated in both the skill of manufacture and precision of decoration (which in most cases is symmetrical). They were beaten thinner and wider therefore producing the most surface area for the mass of gold used, and had both thinner and smaller terminals than the other types. An evolution from open to completely filled area design was proposed by Taylor (1980), mirroring a similar evolution in later indigenous Beaker groups. The vast majority of the classical lunulae have been discovered in Ireland, with the only definite non-Irish examples being three from Cornwall, England. Two possible examples are sometimes attributed to Scotland, however their provenances are questionable and it is probable that they were imported into the country in the recent past (Wallace, 1986; Eogan, 1994).

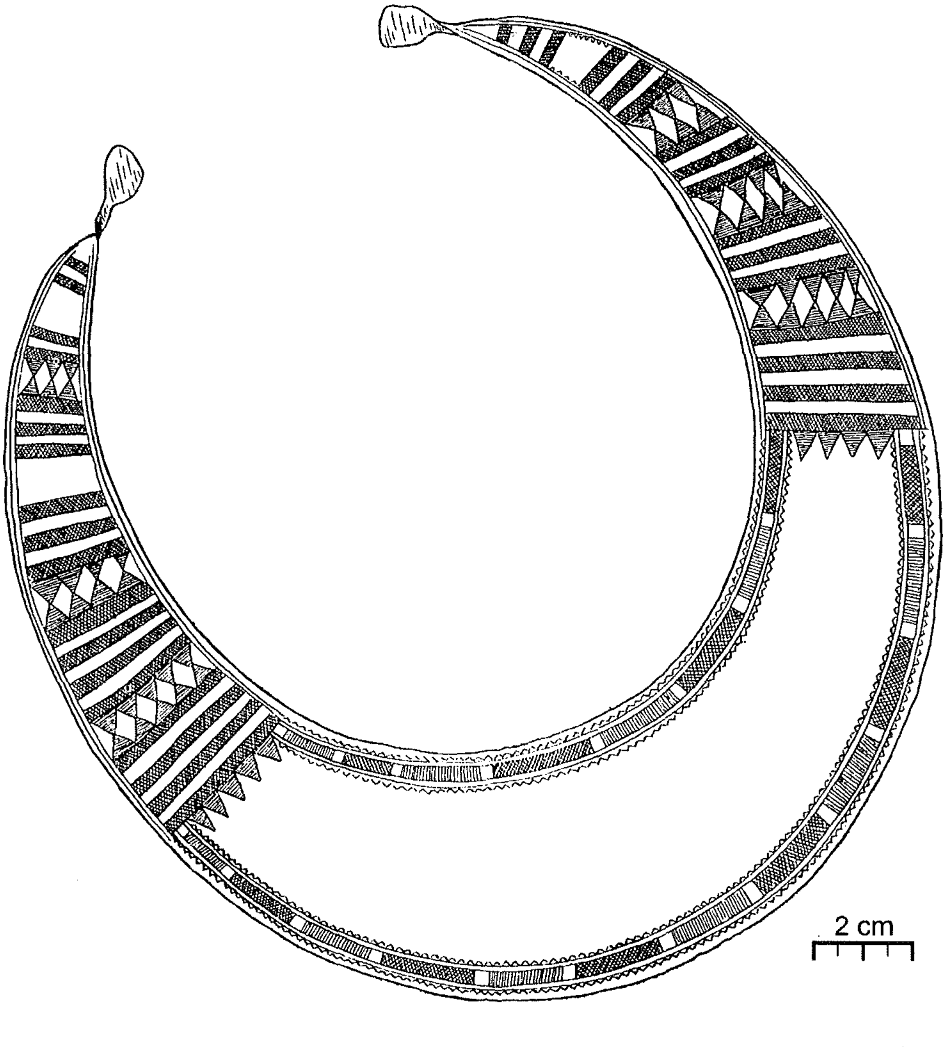


Figure 2.8: Mullingar (1884:7) classical lunula. From Armstrong (1933), plate IV no. 23.

The unaccomplished lunulae (e.g. Figure 2.9) are seen by Taylor (1980) as related yet inferior to the classical type. They are narrower, were manufactured using less gold, and their decoration is of a poorer standard; mistakes are visible in the geometric designs with over-run lines and frequent asymmetry. The gold was not beaten as thin as the classical forms, resulting in increased rigidity that would cause the lunulae to stand away from the neck more. Taylor therefore recognised the existence of craftsmen that lacked both the skill of the 'classical smiths', and their ability to obtain greater quantities of the raw material.

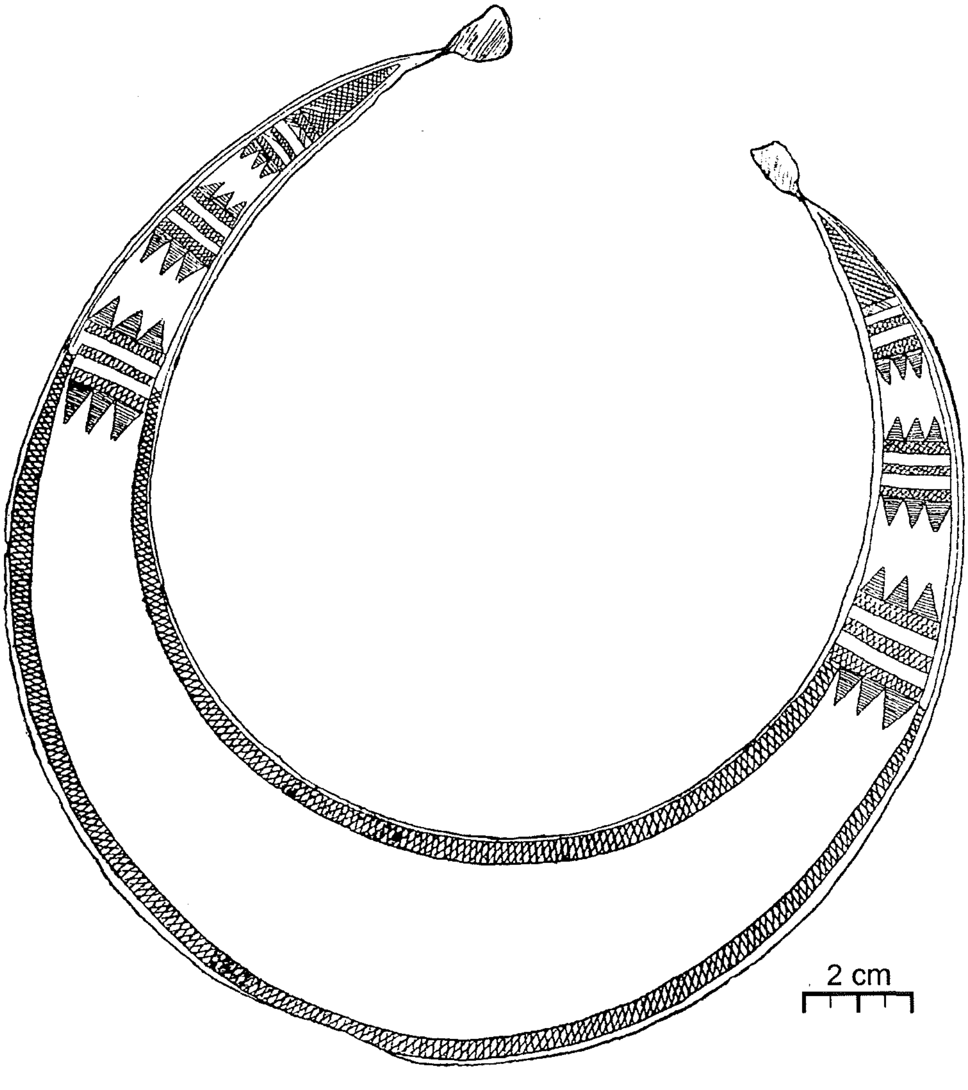


Figure 2.9: Unaccomplished lunula W6, find location unknown. From Armstrong (1933) plate II no. 8.

Evidence for experimentation was also presented in terms of the motifs applied and their positioning; longitudinal decoration was attempted which is unparalleled on the classical lunulae. The Ballinagroun lunula (NMI accession 1998:74) is of particular significance because unaccomplished decoration has been applied that overprints a more skilled classical design. The size and shape of the lunula is also considered typical of a classical form (Taylor, 1980). This indicates some degree of lunulae re-use or reworking, and supports a prolonged life span for individual lunulae. It also challenges the idea of a chronological development from unaccomplished to classical. Taylor (1980) therefore considered the unaccomplished and classical forms to be contemporary, and differ only in terms of quality. Their distribution is solely in Ireland, more specifically around the northern centre of classical lunulae (Figure 2.7).

Provincial lunulae are distinctive due to their geographic distribution that contrasts with that of the classical and unaccomplished forms; all but one have been found outside Ireland. The provincial lunulae are significantly thicker than the other two forms, decoration is increasingly sparse, and they have deeply concentric or three quarter moon shaped terminals (Taylor, 1980). The extreme thickness means that they stand out from the neck even more so than the unaccomplished forms. Two types of decoration can be found on the provincial lunulae: dot line and linear. Taylor (1980) recognised stylistic affinities to both Beaker goldwork and earlier Beaker pottery motifs, although differences in the techniques used to apply decoration are also highlighted. Further links to Beaker society are made; excluding northern Germany their distribution is consistent with areas of strong Beaker influence.

Of the lunulae discovered in Ireland, 45 have details recorded regarding their discovery (Eogan, 1994; Taylor, 1994; Kelly and Cahill, 2010). Although the recently re-discovered Coggalbeg lunula was apparently found in association with two gold discs, lunulae are typically found as isolated single finds and when accompanied by other artefacts these are usually further lunulae (Eogan 1994). There has been one find of four lunulae, two finds of three, and three finds of two (although two lunulae from the west coast of Co. Mayo may have also been found together). Of these lunulae, 17 were found in bogs and 22 were found in dry or agricultural land (13 of which were placed by standing stones and other prominent landmarks). Four have uncertain associations with graves, and this lack of direct burial association contrasts with the depositional context of the typologically similar spacer necklaces elsewhere (Eogan, 1994). It also led Taylor (1980) to propose that the lunulae were not owned by individuals, and instead belonged to groups or communities. The situation is no clearer outside Ireland. The Orbliston lunula from Scotland was reportedly recovered from a barrow, yet details pertaining to its discovery are unclear and this context remains unproven (Taylor, 1980). The two Cornish lunulae from Harlyn Bay were deposited in a barrow, although the depositional contexts of the remaining Cornish lunulae are less certain (Mattingly et al., 2009). The three lunulae found together at Kerivoa, Brittany, were associated with other gold objects. However these objects were not finished artefacts, they were a piece of sheet gold and what is believed to be the beginnings of a lunulae; a gold rod with beaten lunulae-like terminals. It has therefore been interpreted as a worker's hoard (Taylor, 1980).

The lack of archaeological context or association with other artefacts has helped to make the lunulae one of the more enigmatic artefact forms of the EBA, and has significantly hindered secure dating. Despite these difficulties, they have long been considered of EBA date. There is a tentative association between the Orbliston lunulae and a barrow that also contained a basket-ornament (Taylor, 1980; Needham, 1996). If this association is correct, an age contemporary with the basket ornaments could be inferred. A more reliable association is found with the lunulae from Harlyn Bay, Cornwall, although Needham (1996) does caution against the poor nineteenth century documentation. Here, two lunulae were associated with a class 3 flat axe which Needham (1996) describes as 'broadly Migdale type'. This suggests a date in period 2 of the Bronze Age, c.2200-2000 BC. The Coggalbeg lunula was reportedly found in association with two gold discs. If true, this supports a chronological relationship between the two artefact forms and provides further evidence that lunulae were in circulation between 2300 and 2000 BC (Kelly and Cahill, 2010).

The practice of using geometric designs to decorate pottery spread across Britain and Ireland with the Beaker assemblage (Figure 2.10). This style of decoration continued on subsequent forms of pottery such as Food Vessels, with styles evolving into insular traditions. Taylor (1980) carried out a comparative study of the motifs found on lunulae and those decorating British and Irish Bronze Age pottery. It was concluded that every motif found on the lunulae was paralleled on Beaker pottery or goldwork, and therefore a close chronological link between the two was proposed. More specifically the earliest lunulae are seen to correlate with Clarke's (1970) N_2 and N_3 beaker groups rather than any of the later traditions. This all points towards a date earlier in the EBA, by Needham's (1996) period 2 c.2200-2000 BC. Eogan (1994) was cautious of this conclusion because the classical lunulae were an Irish type, and most of the comparative Beaker material was British. Eogan (1994) appeared to favour an Irish bowl food vessel origin for the lunulae motifs and highlights the similarities between the two, yet Irish Food Vessels were included in the study by Taylor albeit with a caution on the limited published corpus available at the time. It is also important to note that although this would change the stylistic origins of the lunulae, the age is likely to remain towards the end of the 3rd millennium BC due to the earlier inception of food vessels in Ireland relative to Britain (see Needham, 1996).

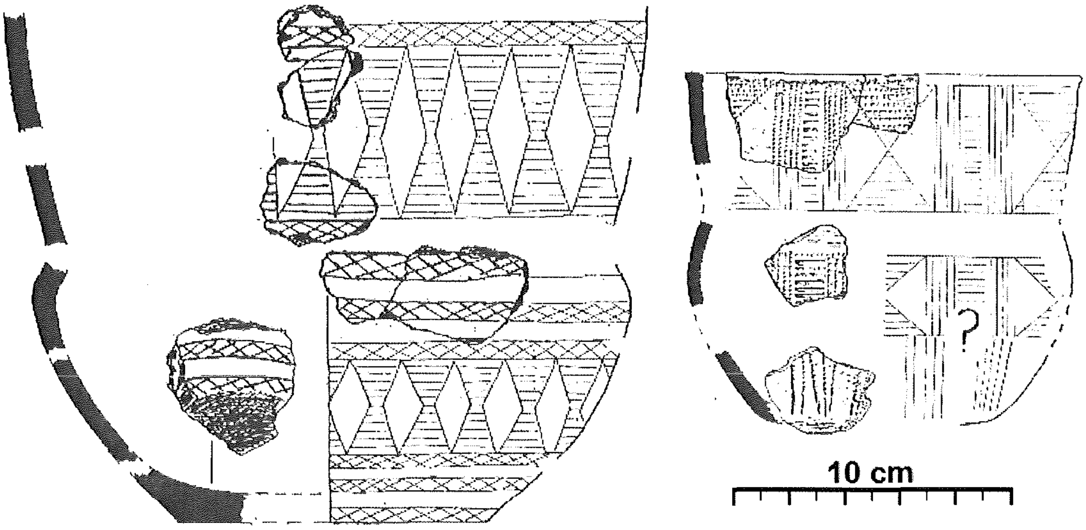


Figure 2.10: Beaker pottery from Dalkey Island, Co. Dublin, decorated with motifs comparable to those incised in EBA gold lunulae. From Liversage (1967/1968) plate 7, fig. 11, page 210 (left) and plate 179, fig. 12, page 209 (left).

Similarities between the lunulae ornamentation and that found on some EBA Irish axes (e.g. Figure 2.11) were also highlighted by Eogan (1994). Comparable geometric designs can be found on flat and flanged axes of Ballyvally and Derryniggin type (Harbison, 1969), suggesting an age after c.2000 BC. As with this type of comparative analysis, it is not always clear which artefact form stimulated which, and can only highlight broad chronological correlations.

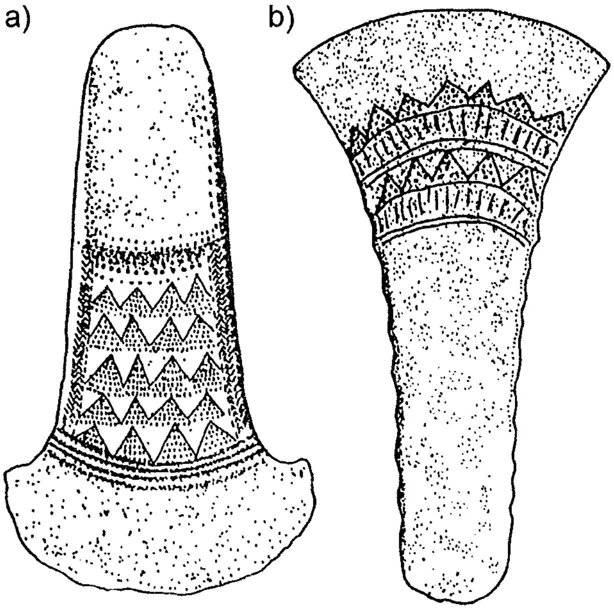


Figure 2.11: Examples of decorated Irish EBA Derryniggin (a) and Ballyvally (b) axe heads. From Harbinson (1969) plate 70 no. 8, and plate 38 no. 20 respectively.

The weight of archaeological evidence therefore suggests that the lunulae were in circulation by c.2200 BC, and lasted for a number of centuries. This theory has gained further support from one radiocarbon date. The Crossdoney lunula, Co. Cavan, was discovered in an alder box, which produced a radiocarbon age of 2460-2040 cal BC (Cahill, 2006). This date places the lunulae firmly in the EBA, although as highlighted by Cahill (2006) this does not provide a start or end date for their production. Equally, it can not be known how long the Crossdoney lunula was in circulation for before the alder tree used to produce the box was felled. Perhaps the possible association of a lunulae and basket earring at Orbliston is more likely than once thought. It should also be noted that a fragment of sheet gold found associated with a secondary series Collared Urn at Pendleton, Lancashire may have once been part of a lunulae (Needham, 1996). If true this suggests continued deployment well into the 2nd millennium BC, albeit in apparently fragmentary form perhaps as heirlooms.

The origin of the artefact form can also be discussed. An association between the lunulae and the EBA spacer-plate necklaces of jet and amber has long been accepted (Craw, 1928-29; Taylor, 1980; Eogan, 1994; Needham, 1996). However these were not predecessors of the lunulae because they are chronologically later, for example a burial at Risby, Suffolk, which contained a jet spacer-plate necklace, can be assigned to Needham's period 3 of the Bronze Age c.1950-1750/1700 BC (Needham, 1996). If lunulae continued into phase 3, then a temporal overlap in the use of lunulae and the spacer-plate necklaces did exist. This idea is supported by the differing geographic foci of these ornaments; lunulae are concentrated in Ireland, the amber spacer-plate necklaces in Wessex, and jet spacer-plate necklaces in Yorkshire, Derbyshire and Scotland (Eogan, 1994). As discussed by Eogan (1994), they could be part of a widespread fashion for cresentic neck ornaments, where different regional trends preferred different raw materials.

In conjunction with the origins of the lunulae motifs, Taylor (1980) prefers a Beaker source for the concept of crescentic neck ornaments. More specifically, the metal-working assemblage that Beaker using people acquired from central Europe included a lunette shaped pectoral ornament. Eogan (1994) also does not favour an Irish origin. Sheet bronze collars from Germany and oar-ended ornaments from Denmark are two of the examples cited, and the range of crescentic neck ornaments from continental Europe that date to the Beaker Period or EBA suggests Europe could have provided the stimulus for the creation of gold lunulae. Eogan (1994) even speculates that gold lunulae could have developed on the continent, spawning numerous traditions such as those found in Portugal, Scandinavia, and Taylor's provincial group. Provincial style lunulae were seen as a potential stimulus for the Irish classical and unaccomplished forms, and in agreement with Taylor (1980) it was believed that these were manufactured from Irish gold.

The purpose of the gold lunulae has often been discussed (Taylor, 1980; Eogan, 1994; Cahill, 2006), and the potential for a prolonged life span has already been alluded to. They may have been worn by people around the neck or on the forehead (Eogan, 1994), or could have been reserved for statues (Taylor, 1980). An association with celestial bodies has been proposed (Cahill, 2006), thus in line with other exotic materials, links to the supernatural are possible. A further interesting feature of the lunulae is that many of them were rolled-up or folded in antiquity (Taylor, 1980; Cahill, 2006). Although few have been recorded as being discovered in rolled-up form, a significant number show evidence for this practice during their life-span, and sometimes on more than one occasion (Cahill, 2005, 2006). This is seen as an indication for long term curation by Cahill (2006), and there is further evidence for long life histories: the Ballinagroun lunula and two further lunulae show evidence for redecoration, use-wear has been identified on a number of examples (Taylor, 1980), and others were stored in containers such as the Crossdoney lunula. Although some lunulae have a fresh appearance suggesting infrequent or rare use (Taylor, 1980), the apparent long duration of others is further support for a more communal function.

Discs and associated goldwork

The circulation of gold discs continued beyond the primary Beaker phase. Case (1977) proposed that the type B discs were from this later period, and they are typified by a change in the style of decoration; ladder-patterned cruciforms were replaced with dot-decorated cruciforms, and zig-zag or dot patterned circumferential bands. Dating these later discs has proved difficult. The majority have been found in Ireland and few records of their discovery exist; the Tedavnet discs (e.g. Figure 2.12) were found by the roots of a tree, and the Sparrograda (formerly Ballydehob) disc was discovered in a rock cleft (Case, 1977). The Ballyvourney disc, Co. Cork, was found in association with a gold pin (Case, 1977). This pin is considered to be of EBA date because of affinities to bone pins from Lough Gur, Co. Limerick, and Caltragh, Co. Galway (Case, 1977), whilst Cahill (2006) highlighted similarities with a gold pin from Areia, Aveiro, Portugal. An EBA date for this disc (and associated pin) therefore seems likely.

Figure 2.12: Gold disc from Tedavnet, Co. Roscommon (1872:35). Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

The Banc Tynddol disc was discovered in a grave located near to an EBA copper mine in Wales (Timberlake et al., 2004). Its design is consistent with the type B discs, yet Timberlake (2004) links the style of decoration to the basket ornaments the primary Beaker goldworking phase and an age of 2500 to 2100 BC was preferred. This is supported by design similarities with Chalcolithic discs from Brittany (see Eluère, 1982), and therefore raises doubts over the chronological separation of the type A and type B discs by Case (1977). Whether the type A discs do predate the type B discs or not does not change the fact that this artefact form was in circulation throughout the EBA; the Knowes of Trotty discs, Orkney, have been dated to 2030-1770 BC (2σ) based on radiocarbon dating of associated human bone (Sheridan and Bradley, 2007).

The goldwork of Co. Cork has been discussed in detail by Cahill (2006), and represents the highest concentration of early goldwork in Ireland. Out of the six gold discs discovered in the county, one is particularly significant due to its high copper content. This is the Sparrograda disc, a type B disc with cruciform design. Its copper concentration of 6.2% (Hartmann, 1970) is exceptionally high for EBA goldwork, a level more typical of later Bronze Age gold artefacts (Warner, 1993). However the disc was discovered with a bronze armlet identified as being similar to those found in the Migdale hoard (Cahill, 2006). This would corroborate an EBA date, with Migdale metalwork also dating to phases 2 to 3 of Needham's (1996) chronology of the Bronze Age (c.2200 to 1900 BC). Additionally the copper content of the Chilbolton and Amesbury Archer basket ornaments exceeded 1%, therefore EBA goldwork did on occasion contain copper concentrations greater than naturally occurring gold alloys (Russel, 1990; Cahill, 2006; La Niece, 2011).

The Sparrograda disc is the only Irish disc to have near all-over decoration; the cruciform itself and the voids between the arms are all filled with a linear decoration applied using the reversible relief technique and only a narrow outer border is left plain. Cahill (2006) noted that it shares most affinities with a trapezoidal plaque from Knockane, also Co. Cork. The Knockane plaque (Figure 2.13) is a rare example of an Irish gold artefact found in association with a burial (Cahill, 2006 citing Crofton Croker, 1824), an association more typical for EBA gold in Britain. Indeed the edges of both the disc and plaque have been folded over in a way that resembles the plaques of EBA Wessex and Britain, and the style of infilling the voids on the Sparrograda disc is seen to resemble the base of the Upton Lovell (Wiltshire) sheet gold cone (Cahill, 2006).

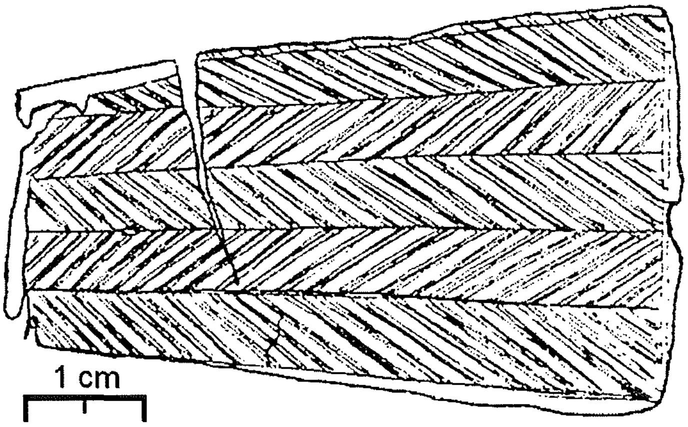


Figure 2.13: Trapezoidal plaque from Knockane, Co. Cork (SA1913.131). From Armstrong (1933) plate X no. 57.

Unlike earlier discs, the Sparrograda disc does not have any central perforations, and combined with the thin nature of the two artefacts and the over-turned edges, Cahill (2006) interpreted these two artefacts as decorative covers. This draws further parallels with the goldwork of Wessex, in particular the gold button and stud covers. In addition, Cahill (2006) highlighted affinities between the trapezoidal shape of the Knockane plaque and the amber plaques and rectilinear gold foils from some Wessex burials. The Knockane inhumation was also reportedly associated with amber beads; a further parallel with British EBA graves (Crofton Croker, 1824; Case, 1977; Cahill, 2006). Consequently there is a strong typological case for links to the goldwork of Wessex. This would suggest that the Knockane plaque and Sparrograda disc date to late in the EBA, contemporary with the Wessex linear style. Despite these affinities, there are still strong Irish connections; the decoration on the Knockane plaque resembles the patterns found on the base of some Irish vases (Cahill, 2006).

A further similarity between the Sparrograda disc and the Knockane plaque is that the plaque also has an unusually high copper concentration. A third artefact, the Ballyvourney pin, can also be included in this group (Hartmann, 1970; Cahill, 2006). As previously discussed, it seems likely that these artefacts are all of EBA date, and the fact that one of the Chilbolton basket ornaments also has high copper proves that high copper gold artefacts did exist in the EBA. This indicates that either deliberate or accidental alloying infrequently occurred during the EBA, and Cahill (2006) proposed that these artefacts could represent the first experimentation by goldsmiths at creating gold-copper alloys in Ireland. The proximity to well known copper sources such as Ross Island and Mount Gabriel may lend support to this theory.

Hilt bands

Gold hilt bands are typically found in Scotland (for example the Skateraw and Blackwaterfoot hilt bands) and although they are not considered part of the Wessex linear style, they are broadly contemporary with it (Taylor, 1980). A gold hilt band has been found in Ireland at Topped Mountain, Co. Fermanagh, associated with a Food Vessel grave (Taylor, 1980), whilst a recent discovery at Forteviot, Perth and Kinross, was found in a cist burial that produced a radiocarbon date of 2199-1977 cal BC (Noble and Brophy, 2011).

Wessex linear

The goldwork of Wessex (southern Britain) has been introduced as a comparative form to the atypical Irish artefacts from Sparrogr噶da and Knockane. This style of goldwork is known as the Wessex linear style because of its concentration in Wessex barrows, and it consists of geometric decoration produced by linear grooves often enhanced using pointillé techniques (Needham, 2000a). The Wessex goldwork is typically used in conjunction with other materials such as bronze, amber and shale; the gold itself usually acting as a cover for other objects (Needham, 2000a). This style of goldwork is part of the Wessex I grave series, which Needham (1996, 2000a; see also Needham and Woodward, 2008) dates to c.1950 to 1700 BC based on associated grave goods and rare radiocarbon dates. As with the British Beaker goldwork, the Wessex linear style is typically found in burial contexts (round barrows), with examples being Bush Barrow, Wilsford G8 and Upton Lovell in Wiltshire, along with the Clandon Barrows and Hengistbury Head in Dorset (Eogan, 1994). Although the number of gold artefacts is relatively small (the weight of all the Wessex gold equals that of roughly two lunulae; Eogan, 1994), they include a large range of artefact forms including beads, bosses/stud covers for mace heads, dagger hilt studs or pins, lozenge shaped plaques, a belt hook cover, button covers, and disc, cone or 'horned' pendants (Taylor, 1980; Eogan, 1994; Needham and Woodward, 2008; Needham et al., 2010a).

Based on the style of decoration, Taylor (1980) recognised the work of a single craftsman in a large proportion of the Wessex goldwork, whilst the Upton Lovell G2a burial contained what has been interpreted as a metalworkers toolkit by Shell (2000);

the grave contained a polished stone and a slate burnisher with traces of gold. The origins of the Wessex linear goldwork are not clear. Artefacts such as the gold belt hook and lozenges from Bush Barrow have parallels in materials including cannel coal and jet else where in Britain (Needham and Woodward, 2008), and Taylor (1980) preferred a predominantly insular development. Conversely the gold pin-inlaid dagger hilts, along with other Wessex I artefact forms such as bone baton mounts, are also found in Brittany (Taylor, 1980; Needham, 1996). This highlights interactions between the two regions, and a possible source area for some of the artefact forms. Relating to the source of the gold itself, it also poses a problem for Taylor (1980, p.45) because of the assumption that 'the economic centre for continental trade in metal definitely lies in the Hiberno-Scottish domain'.

The Wessex type linear goldwork has also been found outside the region of Wessex. In England, the gold boxes found at Little Cressingham, Norfolk, have been linked to the Wessex assemblages, along with finds from Bircham, Norfolk and Rochford, Essex (Taylor, 1980; Needham, 2000a). The Lannion gold 'box' from Brittany is seen to parallel the finishing on some of the Wessex goldwork by Taylor (1980), again highlighting possible Wessex-Breton links. In Scotland, two finds have been linked to the Wessex linear style: the Knowes of Trotty discs, and the button covers from Broughty Ferry, Barnhill, Angus (Needham, 2000a). The Knowes of Trotty discs are thought to correlate to the Wessex linear style rather than the Irish type discs previously discussed based on their geometric decoration and an interpretation that they were originally conical in form (Needham, 2000a).

The classical Únetice culture of central Europe was contemporary with Wessex 1, and has produced dendrochronology dates as early as the mid 20th and mid 19th centuries BC (Gerloff, 2007). A series of richly furnished graves belonged to this culture, examples being Leubingen, Helmsdorf and Dieskau, and grave goods included a solid gold axe, solid gold fluted torcs, and gold pins with cast heads (Gerloff, 2007). Rich burials are also a feature of the Breton EBA, for example the burial of Kernonen en Plouvorn (Eluère, 1982). These too contained items of gold including the Breton daggers with gold nail decoration, bracelets, pins and beads (Eluère, 1982; Gerloff, 2007).

Embossed tradition

The final style of EBA gold working is the embossed goldworking tradition, and its emergence has been discussed in depth by Needham (2000a). A number of exceptional gold artefacts from Britain can be included in this tradition, including the Lockington armlets, the Rillaton and Ringlemere cups, and the Mold cape.

The two Lockington armlets were discovered as part of a hoard on the edge of a funerary zone that also included a copper dagger and pottery (Needham, 2000a). The embossed decoration consists of multiple ribs separated by flat sections, and one of the armlets contained regular lentoid 'swellings' along the ribs and pointillé decoration on the flat zones (Needham, 2000a). Needham (2000a) dated these embossed ornaments to the EBA because of the accompanying finds. The ceramics consist of sherds of Beaker pottery and an upturned Beaker or Collard Urn, whilst the copper dagger is an Armorican 'Quimplerlé' type which dates from c.2200 to 1900 BC. This early age was supported by radiocarbon dating, and highlights an embossed goldworking tradition that began in the EBA. Two further (now lost) embossed gold armlets have been recorded in Britain and Ireland: one from Whitfield, Co. Waterford, which was described as repoussé rather than embossed by Eogan (1994); and one from Cuxwold, Lincolnshire (Needham, 2000a). The Scottish Melfort type bronze armlets are similar to the Lockington gold examples, and date to a similar EBA date pre c.1900 BC. These were proposed as one of two possible stylistic stimuli for the gold armlets by Needham (2000a), with the alternate being the fusiform beads of jet and other materials which are paralleled by the lentoid bosses that decorate the armlets.

Two embossed gold cups have been discovered in Britain; the Rillaton cup (Cornwall), and the Ringlemere cup (Kent). Absolute dating of the Ringlemere cup was not possible, however detailed excavation of the find area revealed that it was deposited with an amber pendent in a late Neolithic to EBA monument complex (Needham et al., 2006). The amber pendent has parallels in Wessex and Brittany that suggest an age contemporary with Wessex 1, c.1950 to 1700 BC, therefore indicating that the Ringlemere cup could pre-date the Rillaton cup (Needham, 2006b). The Rillaton cup was found in a burial context associated with a Wessex 2 Camerton-Snowshill dagger indicating an age from c.1750/1700 to 1500 BC (Needham, 2000a). However its poor condition might represent a prolonged life history, thus the date of manufacture could have been more consistent with that of the Ringlemere cup (Needham, 2006b). These embossed gold cups were produced using similar goldworking techniques to the embossed armlets (Needham, 2000a). As described by La Niece in Needham et al. (2006), they were created using sheet gold techniques; a flat sheet of gold would have been raised up around a stake by hammering to form the hollow shape of the vessels, and the embossing could be created by working the gold against a former held inside the cup. Annealing would have also been required, along with surface finishing, while the handle strips could be fastened on using gold rivets. Yet La Niece does state that despite the high quality of the goldworking, no advanced tools would have been required.

The two British gold cups were part of a more widespread tradition of precious cups that stretched from Cornwall and Brittany in the west, to the Rhineland in the east (Needham, 2006b). Including the Rillaton and Ringlemere examples, a total of seven cups were made of gold, with further examples manufactured in silver (two), amber (two) and shale (five). The diversity of the cups is highlighted, not only in the material used for manufacture, but also in capacity, decoration and form. A possible chronology for the development of the precious cup tradition was presented by Needham (2006b). After continental origins in either the Rhineland or the Rhône Culture from ceramic handled cup traditions that already existed in these areas, the tradition reached Britain after the emergence of embossed goldwork (as evidenced by the Lockington armlets). Thus local interpretation of the precious cup tradition resulted in the embossed British examples.

The Mold Cape is a unique embossed gold object from Flintshire, north-east Wales. Powell (1953) believed it was beaten from a single ingot attached to an internal bronze frame, and that it would have had a leather or cloth backing. As Needham (2000a) discussed, its find context was poorly recorded therefore dating has had to rely on stylistic analysis. Powell (1953) highlighted similarities with both the EBA embossed armlets and the continental hats/cones, therefore an age of c.1400 BC in the Early to Middle Bronze Age transition was preferred. Both Taylor (1980) and Eogan (1994) settled on similar ages as late as the 13th to 12th centuries BC. However since these publications the tradition of embossed goldwork has been pushed back to an earlier phase of the Bronze Age, thus Needham (2000a) prefers an EBA date c.1900 to 1700 BC. The cape was discovered as part of an inhumation burial under a cairn which Needham (2000a) speculated could be an EBA cist burial, whilst its sheetwork manufacture is more typical of Early Bonze Age goldworking techniques. The majority of the embossed motifs found on the cape (generally lentoid, conical or sub-conical) are paralleled in other EBA artefacts and therefore do not challenge an EBA date, whilst the composition of the gold is consistent with known EBA metalwork. It should be noted that this early age for the Mold cape is still debated, with Gerloff (2007) preferring a date c.1400 to 1300 BC.

The origin of the embossing technique was also discussed by Needham (2000a), with two plausible ideas presented. The first is that embossing could have developed from the repoussé or reversible relief style that was applied to some of the EBA Irish type B discs. The second is that the origins could lie in the gold hilt bands of Scotland, notable for being the same region in which the Melfort type embossed bronze armlets were found. The hilt bands have rows of small scale and symmetrical corrugations, a style that if enlarged could have led to the type of embossing found on the gold armlets. Needham (2000a) proposed that the tradition developed c.2050 BC therefore making it contemporary with both the Wessex linear and the Scottish hilt band traditions. A geographical pattern is also emphasised, with these three apparently contemporaneous traditions all focussed in different geographical regions of Britain and Ireland; embossed goldwork is typically found across the midlands of Britain and further west. There is clear evidence for the existence of an embossed goldworking tradition in Britain and Ireland during the EBA, and thus it may have stimulated the emergence of the later continental embossed goldwork tradition (Needham, 2000a).

Contemporary with the advanced stages of the embossed goldworking tradition were the artefacts found in Wessex II (c.1750/1700 to c.1500 BC) and late Únetice contexts (Gerloff, 2007). The use of gold pins for decorating dagger pommels continued in Britain (for example the pommel of a Camerton-Snowshill dagger from Hammeldon, Devon; Gerloff, 1975, 2007), however overall there was however a marked decline in the amount of gold deposited as grave goods from the preceding Wessex I (Braithwaite, 1984). The Nebra hoard of the late Únetice culture also dates to this period (Ehser et al., 2011), indicating the continued use of gold in continental Europe. This hoard included two bronze swords with gold hilt bands and the Nebra Sky disc, a copper disc with gold inlays thought to represent certain astronomical bodies (Schlosser, 2005).

2.3.1.4 Middle Bronze Age

The MBA witnessed the appearance of a number of new gold object forms. Within the Early Tumulus culture of central Europe, broad bodied bracelets with double spiral terminals and penannular bracelets with lozenge shaped cross sections were in fashion (Eogan, 1994). The aforementioned embossed sheet gold tradition reached new heights of technical accomplishment with the appearance of domed discs and hats/cones on continental Europe between c.1400 and 1300 BC (Eogan, 1994; Gerloff, 2007). These developments stimulated emerging gold artefact forms in northern Europe including gold discs, bowls and ladles, and penannular bar-twisted bracelets; the impressive Danish gold assemblages also belong to this period (Eogan, 1994).

In Ireland and Britain this diversification occurred during the Early Bishopsland and Taunton metalworking phases respectively (Waddell, 1998), following an apparent hiatus in goldworking during the Killymaddy-Acton Park phases (Eogan, 1994). This led Eogan (1994) to propose that the MBA goldworking traditions of Britain and Ireland were a result of stimulus from continental Europe, an inspiration that created a significant increase in both the number and variety of gold objects under production compared to that seen in the EBA. The Early Bishopsland-Taunton range included six varieties of bracelets (for example the bar twisted and ribbed sheet types), four varieties of neck ornaments (such as the three-flanged torcs, non-flanged bar torcs, rare ribbon torcs; Figure 2.14), two varieties of earrings, along with tress rings, ribbed rings, finger rings and composite rings (Eogan, 1994; Waddell, 1998; Warner, 2004). A single gold disc, known as the Landsdown disc, also dates to the Taunton metalworking phase. Decoration with concentric circles and a central star shaped motif sets it apart from the discs of the British EBA, and suggests links with Danish or north German origins (Eogan, 1994).

The greatest numbers of both bar and flange-twisted torcs have been found in Britain, closely followed by Ireland, whilst further examples are known from continental Europe (Eluère, 1982; Waddell, 1998). Eogan (1994) cites these distribution patterns to suggest insular development for a number of the MBA artefact forms. Ireland's impressive Derrinboy hoard dates to this period, and its contents define the goldwork of Ireland's Early Bishopsland phase (Warner, 2004). It should also be noted that although some ribbon torcs appear to date to this period of goldworking, the majority are in fact Iron Age (Warner, 2004).

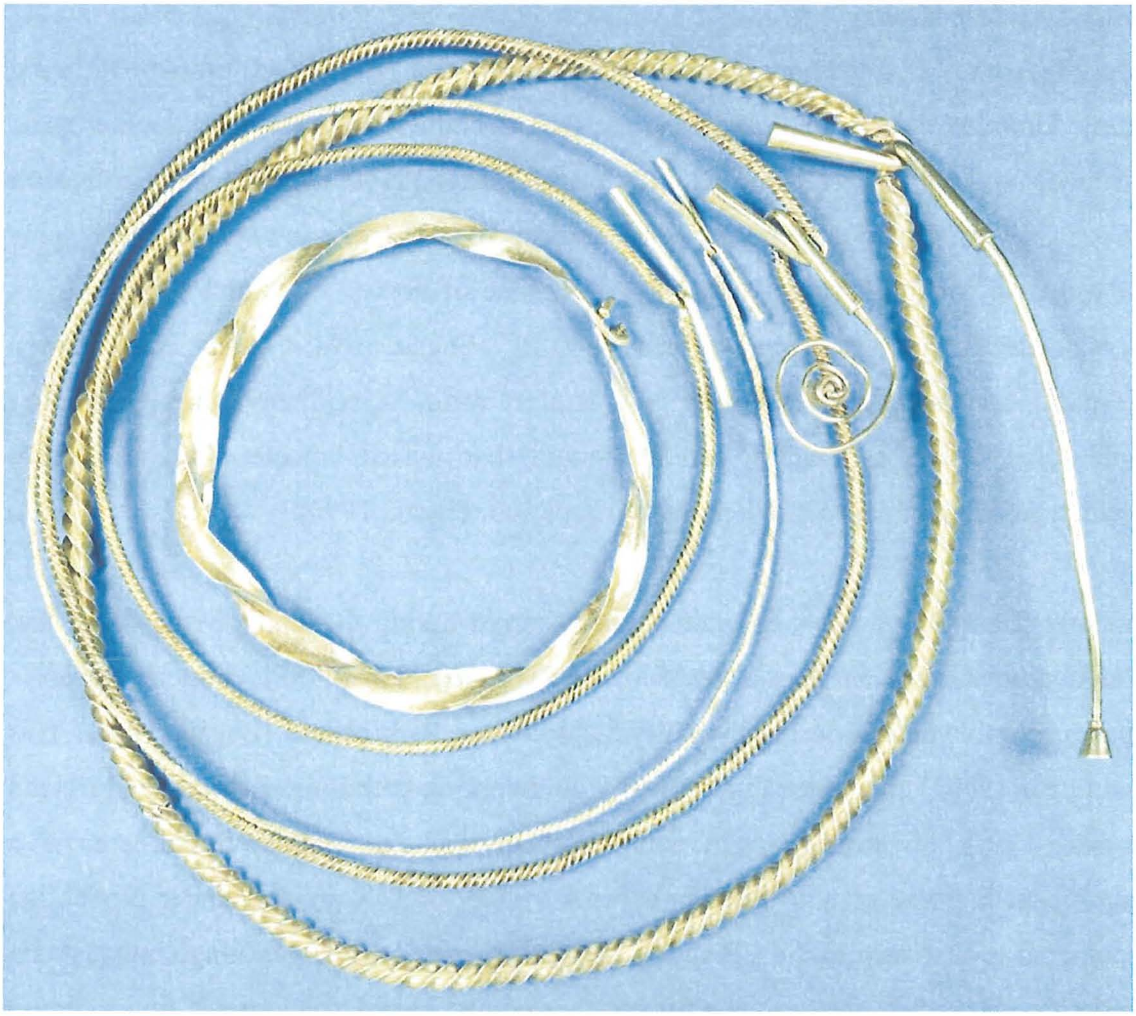


Figure 2.14: A selection of MBA Irish gold torcs. Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

From this array of artefacts it is clear that bar techniques had now joined sheetworking in the technological repertoire of goldsmiths (Taylor, 1980; Eogan, 1994). This new technique was practised by shaping gold bars through hammering and twisting. Unfinished examples have been found in the Derrinboy and Cappeen hoards, whilst further decoration through incision or engraving is rare (Eogan, 1994).

Some of these artefact forms continued into the subsequent Late Bishopsland and Penard metalworking phases of Ireland and Britain, including earrings, plain and twisted bracelets, non-flanged bar torcs (Eogan, 1994; Gerloff, 2007). These were joined by the four-flanged torcs, whilst penannular rings (also known as hair rings or ring money) are compositionally consistent with this group although they are traditionally dated to the LBA (Warner, 2004). Barwork now dominated technologically, and the primary method of decoration was by twisting (Eogan, 1994).

The distribution of MBA gold artefacts suggests metalwork was originally concentrated near the southern coast of England, whilst bronze was more commonly used for ornament manufacture in Britain (Eogan, 1994). Goldwork eventually spread northwards, however societies in Scotland and the north of England still did not wear gold ornaments to the same degree as their southern counterparts during this period (Eogan, 1994). In Ireland, bronze ornaments were rare, and the comparatively large number of gold ornaments led Eogan (1994) to propose that Ireland again became a leading centre of production. Hoards of MBA metalwork have been discovered in both Ireland and Britain, and of the Irish examples the vast majority consist of new goldwork. Eogan (1994) therefore proposed a ceremonial aspect to these formal depositional practises, and that the amount of gold reveals the wealth of MBA societies.

2.3.1.5 Late Bronze Age

Traditionally there is little evidence for goldworking in the Roscommon-Wilburton phase of the LBA, although in Britain the Thirsk hoard (including an embossed or corrugated gold bracelet and ring) and potentially the Monkston Park hoard (two bar torcs and three bracelets) date to this period (Needham, 1990, 2003). Furthermore, recent consideration of goldwork from the site of Rathgall, Co. Wicklow, suggests some Irish goldwork may also date to this period (Warner in press), and admittedly there were similarities in both the manufacturing techniques and the choices of decorative motifs used either side of the Roscommon-Wilburton phase (Eogan, 1994). It is therefore possible that the Late Bishopsland and Dowris-A goldworking traditions merged together.

The Dowris-A-Ewart Park tradition saw the zenith of developments in Bronze Age ornament manufacture; there was a marked increase in both the amount of gold in circulation and the variety of object forms under production (Eogan, 1994; Waddell, 1998). A range of new ornaments appeared including gorgets, dress/sleeve fasteners, lock rings, bowls, boxes, balls, expanded bracelets, collars, and probably the penannular rings (Taylor, 1980; Eogan, 1994; Waddell, 1998; Warner, 2004). There was a resurgence in sheetwork techniques, and technologically advanced goldworking skills such as hollow casting were employed for the production of artefacts such as dress/sleeve fasteners and some penannular bracelets (Eogan, 1994). Lock rings were constructed by soldering multiple pieces of gold together including wires averaging 1 mm in diameter, whilst the gorgets (e.g. Figure 2.15) are composite ornaments consisting of a broad, ribbed, cresentic collar stitched to decorated circular terminals by rivets or gold thread (Eogan, 1994; Waddell, 1998). Contrasting with continental Late Urnfield goldwork, decoration was common in Ireland where both angular and circular style were incorporated by both incision and embossing (Eogan, 1994).

Figure 2.15: Gorget from Gorteenreagh, Co. Clare. Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

The range of gold ornaments deployed in Ireland was more extensive than that of Britain (Eogan, 1994). A number the aforementioned LBA artefact types were uniquely Irish; all gorgets have been discovered near the Shannon estuary, whilst the distribution of others such as dress fasteners (Figure 2.16) strongly centres on Ireland (Waddell, 1998). The distribution patterns of Irish LBA goldwork also suggest regional traditions. The high density of gorgets and lock rings around the Shannon estuary, or sleeve fasteners in the north-east may indicate centres of production or regional identities (Eogan, 1994; Waddell, 1998). Those gold ornaments found in Britain includes objects of probable Irish origin such as dress fasteners and Irish type bracelets, and ornaments universal in both regions such as lock rings (Eogan, 1994). Nine styles of penannular bracelet have been characterised as typically British, all of which were made from bar gold, usually have solid terminals, and were probably influenced by the Late Urnfield culture of west-central Europe (Eogan, 1994). The number of artefacts found in Britain, along with the weight of gold used, suggests that sufficient amounts were available for British goldworking traditions (Eogan, 1994).

Figure 2.16: Dress fastener from Clones, Co. Monaghan (1963:1). Photograph reproduced with the permission of the National Museum of Ireland, copyright National Museum of Ireland.

Whilst the British artefacts can be linked to continental styles, the origins of the Irish artefacts are less clear. The lack of clear forerunners led Eogan (1994) to propose insular development for a number of the ornament forms including the gorgets and boxes, whilst the modification of imported types probably led to the development of others such as the Irish type penannular bracelets and dress fasteners. Coinciding with the new artefact forms that appeared in this goldworking tradition, there was also a return to the practise of depositing personal ornaments in hoards, a custom that was not practised in the preceding Wilburton (or Roscommon) phase (Eogan, 1994).

2.3.1.6 Summary

The earliest goldworking in Ireland and Britain coincided with the appearance of Beaker material culture during the Chalcolithic period from c.2500 BC. Artefacts were rare, and manufactured using sheet gold techniques. The two most common artefact types were the discs and basket shaped ornaments, whilst other objects including beads, rivet caps and oval plaques were also produced. The deployment of basket shaped ornaments was centred in Britain where gold artefacts were typically deposited in burial contexts. Conversely, the majority of the early discs have been found in Ireland where gold objects were rarely placed in such contexts. Few recorded details regarding the deposition of early Irish goldwork survive and only the Ballyshannon discs have a possible association with a grave (Eogan, 1994). The distributional focus of both discs and basket ornaments suggests insular production, although a source outside the region for at least some of this early gold is still discussed (e.g. Fitzpatrick, 2011). Associations with Iberian Chalcolithic goldwork have been proposed, whilst France, northern and central Europe have also been mooted as possible regions of stylistic influence. It is clear that that gold was beginning to play in important role in society from the mid 3rd millennium BC.

In Britain and Ireland the primary Beaker goldwork evolved into the goldworking traditions of the EBA. The production of discs continued, whilst new styles of sheetwork appeared. The most notable of these were the lunulae, whose distributional focus provides further evidence that Ireland had become a manufacturing centre of gold artefacts and has helped support theories of an Irish EBA gold source. The vast quantity of EBA goldwork found in this country is testament to the importance of gold in its societies, and suggests a vibrant goldworking industry was in existence. Association of two Cornish lunulae with Migdale axes and a single radiocarbon from the Crossdoney lunulae box supports the view that the lunulae tradition emerged by the Killaha-Migdale metalworking phases that commenced c.2200 BC (Needham's Period 2), whilst evidence exists for continued deployment well into the 2nd millennium BC perhaps as heirlooms.

The end of the core lunulae phase corresponds with the emergence of the principle British goldworking traditions of the EBA, highlighting a potential shift in the importance of goldworking from Ireland to Britain. Whilst the Scottish hilt band tradition may have commenced as early as c.2100 BC, the Wessex linear style and the embossed traditions began c.2050 to 1950 BC. The amount of gold in the Wessex burials was significantly less than that seen in the lunulae tradition, however it still indicates a change in the regional deployment of gold. By period 4, c.1750/1700 to 1500 BC, goldwork had become rare in Britain and was almost absent from Ireland (Eogan, 1994) despite its continued production in continental Europe. Gold pins were used to decorate dagger pommels in southern Britain, whilst the Rillaton cup and potentially the Mold cape also date to this period. Reasons behind this apparent decline in gold production are unclear; it could have resulted from changes in society, exotic fashion, or the ability to procure the raw material. Understanding why this decline occurred, especially in relation to Ireland, is important when investigating the deployment of gold in the EBA. The continuation of embossed goldwork into the MBA suggests goldworking did not cease completely, rather that gold was manufactured into a smaller number of more impressive artefact forms. Even if this contributed to a bias in the archaeological record, patterns of gold deployment in both Ireland and Britain had clearly changed from earlier periods.

As the MBA began, there was an apparent hiatus in goldworking in Britain and Ireland. The embossed tradition reached new heights on continental Europe with the production of the gold hats/cones and related artefacts, whilst new forms of bracelets were produced and numerous artefacts were in circulation in northern Europe. These continental developments stimulated a new tradition of goldworking in Ireland and Britain, during the Early Bishopsland-Taunton metalworking phases from c.1400 BC. New forms to appear included bar torcs, 3-flanged torcs, earrings, ribbed rings and bracelets, and evidence suggests the majority were insular developments and of local manufacture. With the onset of the Late Bishopsland-Penard metalworking phases (c.1300/1250 BC to 1150 BC) new artefact types appeared including the 4-flanged torcs, whilst others including bar torcs and bracelets continued from the preceding tradition. The MBA saw the appearance of new goldworking techniques, most notably the casting and working of gold bar.

There is little evidence for goldworking at the beginning of the LBA, and it was not until c.950 BC and the Dowris-A-Ewart metalworking phases that a resurgence was seen. This tradition witnessed the peak of Bronze Age goldworking, both in terms of the amount of gold in circulation and the number of artefacts in production. New ornament types appeared, such as gorgets, dress/sleeve fasteners, lock rings, bowls, boxes, balls, expanded bracelets, and collars. This zenith of gold working also saw renaissance in sheet working, and technological developments including hollow casting.

The first exploitation of gold coincided with a significant increase in the deployment of exotic materials during the Chalcolithic/EBA. These important early goldworking traditions were surpassed during the Middle and Late Bronze Ages when far greater quantities of gold were transformed into a multitude of artefact forms, mirroring the increasingly complex societies that began to emerge in the latter half of the 2nd millennium BC. Gaining an understanding of the role materials such as gold played in Bronze Age societies, and how this changed over time, may help to explain the new social structures that emerged during this period. Critical to this research aim is an understanding of control. Controlling materials, particularly exotics, is seen as a source of power to individuals or groups, and a potential mechanism for the creation of elites. Managing the procurement of a raw material is a key method of regulating its deployment, thus discerning the number and locations of exploited gold sources is of vital importance to Bronze Age archaeology.

2.3.2 The sources of Chalcolithic and Bronze Age gold

2.3.2.1 Introduction

Locating the sources of Chalcolithic and Bronze Age gold has typically relied on the distribution of gold artefacts, yet an association between the two is not obligatory. A significant proportion of goldwork has been discovered in Ireland, and in conjunction with the numerous natural gold deposits throughout the country, the belief of an Irish source has often been hypothesised (Calvert, 1853; Taylor, 1980; Eogan, 1994). The alluvial gold deposits of Co. Wicklow were frequently seen as the most likely candidate due to known exploitation during the 18th and 19th centuries (Armstrong, 1933), whilst the potential of other locations in the north and west have also been discussed (Taylor, 1980; Eogan, 1994). No direct archaeological evidence for the exploitation of Irish gold has been found to date. As a result, the application of scientific provenance studies has become the primary means of locating the sources of Bronze Age gold. These have focussed on the elemental composition of both artefacts and native gold deposits, yet it still remains unclear which gold deposits were exploited during this period. Sections 2.3.2.2 to 2.3.2.4 overview these studies, and highlight the need for a provenance study that employs a new technique independent to elemental composition.

2.3.2.2 Major element compositional analysis

Hartmann and the "Prähistorische Goldfunde aus Europa" project

The first attempt to provenance European Bronze Age goldwork through scientific analysis was carried out by Hartmann in the "Prähistorische Goldfunde aus Europa" project (1970, 1982). This study employed optical-emission spectrometry (OES), although silver concentrations were typically calculated using the specific gravity of the artefact or gravimetric analysis of an artefact sample. Metal groups were proposed based on elemental composition (principally the concentrations of silver, copper and tin), typology and the age of the artefacts. A number of natural gold samples were also analysed, and attempts made to link the metal groups with known gold deposits.

Hartmann found that Chalcolithic and EBA goldwork contained silver and copper concentrations mirroring that found in natural gold, whilst from the MBA onwards increased levels of copper suggested alloying with copper or bronze was practiced. In relation to Irish goldwork, the compositional groups correlated well with the accepted chronology. Table 1 presents an overview of the key Hartmann groups in relation to Irish Bronze Age goldwork.

Table 1: The compositional ranges (and means in parenthesis) of Hartmann's metal groups for Irish Bronze Age goldwork. Means from Warner (1993).

Metal Group	Period	Natural or alloy?	% Ag	% Cu	% Sn
L	EBA	Natural	4 – 22% (12%)	0.01 – 1% (0.2%)	0 - 0.45% (0.1%)
M	MBA	Alloy?	5 – 23% (12%)	0.8 - 2.2% (1%)	0.08 - 0.3% (0.2%)
OC	MBA	Alloy	6 – 35% (17%)	2.5 – 23% (7%)	0.15 – 1% (0.4%)
MC/NC	LBA	Alloy	5.5 – 30% (14%)	2.8 - 17.5% (8%)	0.02 - 0.8% (0.2%)

Before discussing these groups, it is worth noting that some Irish (and British) EBA artefacts were categorised in three other Hartmann metal groups. The earliest compositional assemblage was known as B metal. It was free of tin, usually contained less than 10% silver, and an Eastern Mediterranean source was postulated (Hartmann and Sangmeister, 1972). The artefacts assigned to this group were predominantly found in Czechoslovakia and the former Yugoslavia, however some artefacts from as far away as Britain and Ireland were also included (including some Irish lunulae). Metal group A_3 also dates to the EBA and is marked by its higher silver content, averaging at 26%.

Distribution of this metal is centred on the middle Danube, and therefore a link to the Transylvanian gold deposits was proposed (Hartmann and Sangmeister, 1972). This group also includes some objects found further afield in north and west Europe, for example the handle of the Rillaton cup. Hartmann's S metal had detectable tin and <0.08% copper, and its predominance in Iberia was seen to indicate the source region (Hartmann, 1978). Some lunulae from Brittany, Britain and Ireland along with other artefacts such as the Mere discs also fall into this compositional group (Hartmann, 1978).

A key difficulty encountered when characterisation relies solely on compositional analysis is that different gold deposits from different regions can have the same compositional ranges. Therefore although long distance trade may have occurred, conclusions on provenance should be made with caution until local sources have also been characterised. The inclusion of Irish and British artefacts into metal groups predominantly found in distant regions such as south-east Europe implies a direct association which is not necessarily true.

The vast majority of British and Irish Chalcolithic to EBA gold artefacts fall into Hartmann's L metal classification. The composition of this group ranges from c.4% to 22% silver, c.0.01% to 1% copper and c.0% to 0.45% tin. It includes the majority of the lunulae along with the basket ornaments, discs, oval plaques, and hilt bands, along with the Wessex gold and embossed items such as the Mold cape and the Rillaton cup (excluding its handle). This group was divided into four sub-groups based on varying copper concentrations: L_1, L_2, Q_1, Q_2, with the latter two including significant numbers of artefacts from continental Europe such as the gold hats/cones of Schifferstadt and Ezelsdorf. Some of these artefacts have no recorded tin concentration and therefore demonstrate compositional overlap with B metal. Moreover the majority of the Irish artefacts assigned by Hartmann to the B and S metal groups fall within the compositional range of L metal, and consequently are perhaps more likely to be part of the L metal group. The classification of the Topped Mountain hilt band can also be queried. It was assigned by Hartmann to the "Restgruppe", the group of artefacts that were not assigned to one of the defined metal groups, yet its composition of c.16% silver, 0.45% copper and 0.56% tin could easily place it with the L metal along side the Scottish hilt bands. Questions can therefore be raised about how Hartmann's devised the metal groups, and subsequently assigned artefacts to them.

M metal correlates to the goldwork of the Early Bishopsland phase of Irish archaeology (Raftery, 1971; Warner, 1993; Warner, 2004), contemporaneous with the British Taunton phase c.1400 to 1300/1250 BC (Warner, 2004; Gerloff, 2007). Silver and tin concentrations are essentially the same as the L metal, whilst the M metal can be distinguished by its higher average copper value of 1%.

OC metal correlates with the Late Bishopsland phase of Irish archaeology (Warner, 1993), contemporaneous with the British Penard phase c.1300/1250 to 1150 BC (Warner, 2004; Gerloff, 2007). It contains a significant proportion of copper (averaging 7%), suggesting the practice of alloying gold with copper or bronze had begun (Hartmann, 1970). The average silver and tin concentration are also markedly higher; 17% and 0.4% respectively (Warner, 1993). Raftery (1971) believed the OC metal was imported into Ireland, and draws parallels with Egyptian artefacts similar to the penannular rings. However if the copper (and tin) is a function of alloying, then only the silver content is characteristic of the gold source, and this is consistent with numerous gold deposits in north-west Europe including some located in Ireland (see Chapman et al., 2000a, 2000b, 2006).

The final principle metal group of interest is Hartmann's MC/NC. This correlates with the Ireland's Dowris-A phase (Warner, 1993), and dates to the LBA c.950-800/750 BC (Warner, 2004; Gerloff, 2007). The average silver and tin contents are both lower than the OC metal (14% and 0.2% respectively), while the copper concentration is similar at 8% (Warner, 1993).

The tin concentrations for the majority of the Bronze Age artefacts are typically higher than that found in natural gold, therefore its presence led Hartmann to suppose its incorporation as cassiterite from an alluvial source (Hartmann, 1970; Raftery, 1971). This may in fact only be true for the earlier artefacts apparently made from natural gold alloys. From the MBA onwards copper was deliberately alloyed to the gold. If this copper was added in the form of bronze, then the tin may be a function of alloying rather than the gold source itself. Alluvial gold from Co. Wicklow was also analysed by Hartmann, yet the relatively low silver content meant that the majority of the L metal artefacts, and indeed the chronologically later groups, were inconsistent with a Co. Wicklow source. Due to this non-match, Hartmann concluded that the majority of L metal originated outside Ireland (with Iberia or central Europe favoured as the most likely source region; Hartmann, 1978), thus most of the gold used to manufacture Irish goldwork was seen to be imported.

Initial criticisms of the "Prähistorische Goldfunde aus Europa" project

It was this conclusion that stimulated a number of critical reviews. Harbison (1971) argued that until the importation theory could be proven, there was no reason to consider that the majority of Irish goldwork originated outside the country. The key reasons for this were:

- The majority of the Hartmann gold groups that were interpreted as imports into Ireland were not linked to specific gold deposits elsewhere (only regions based on the artefact distribution patterns).
- The samples of Wicklow gold analysed may not be the only gold type present in the region, and there is no certainty that they are characteristic of the gold exploited during the past.
- Co. Wicklow may not have been the only potential source of prehistoric gold in Ireland.
- An Irish source could have been exploited in the past and leave no trace in the present.

These are all important points, yet perhaps the most significant is that Co. Wicklow may not have been the only potential gold source in Ireland. This argument was developed by Scott (1976), who highlighted the existence of a number of Irish gold deposits located in areas other than Co. Wicklow. This view has been supported by more recent reviews of gold mineralisation throughout Ireland (McArdle et al., 1987; Stanley et al., 2000). Scott (1976) also criticised the attempted characterisation of Wicklow gold through the analyses of only five samples, and suggested that characterisation of the artefacts should be based on more than one analysis. Additionally this highly critical review questioned both the accuracy of the analytical programme and the reliability of the metal groupings; the results were described as 'suspect' and 'requiring revision'. The issue of artefact recycling was also raised, which has the potential to combine the compositions of more than one gold source thus making provenancing difficult. This unfavourable assessment prompted Scott (1976) to call for a completely new investigation that needed to include the collection and analysis of as many native gold samples as possible from multiple locations, and a repeat of the analyses programme.

"Prähistorische Goldfunde aus Europa": sample re-analysis

Warner (1993) presented a more favourable overview of Hartmann's data; the principle typological and chronological groupings are identifiable by their chemical composition. However after re-analyses of the returned Hartmann samples alongside the analyses of further artefacts, it was determined that the accuracy of Hartmann's silver data were both poor and unreliable (Warner, 2004; Warner and Cahill, 2011). Hartmann's copper and tin data were shown to be accurate, but a relative uncertainty of 25% (1 S.D.) was recommended for the silver analyses (Warner and Cahill, 2011). This is particularly problematic because the silver concentration is key for characterising gold alloys.

It was noted that Hartmann's metal groups are still apparent when using only the copper and tin concentrations. Furthermore, it was shown that although Hartmann's silver data do not reflect accurate silver concentrations for individual artefacts, the average silver values for each metal group are in fact reasonably accurate; group means are within 2% of those calculated from the recent program of re-analyses (Warner, 2004). Consequently it was argued that Hartmann's data still has some validity, although re-analyses of artefacts to collect new silver data was recommended (Warner and Cahill, 2011). Additional criticisms centred on the statistical methodologies employed in creating analytical groups (Warner, 2004).

With this programme of re-analysis, Warner (2004) was able to draw a number of conclusions. The lunulae and discs of the Irish EBA formed one compositional group based on the silver (means of 10% and 12% respectively) and copper (mean of 0.3%) concentrations (L- and D-gold respectively). The tin varied from low values characterised by the discs (mean of 0.01%) to high values characterised by certain lunulae (ranging from undetected to 0.35%) found predominantly in the Irish north-west and south midlands (L-gold). Despite this it was concluded that D- and L-gold represent one compositional group, and the potential that those with high tin were a result of tin addition, either intentionally or accidentally, was discussed. Similar average silver concentrations suggested a common gold source for Irish, Cornish and Scottish gold was possible, along with the Wessex gold of southern England. This metal group equates to Hartmann's L metal.

In agreement with Hartmann, two distinct metal groups were distinguished that date to the Irish MBA. The first, B-gold or mba1 gold alloy, equates to Hartmann's M metal and is characterised by the following mean concentrations: 11% silver, 1% copper and 0.13% tin. This dates to the early Bishopsland period (c.1400 to 1300/1250 BC), and includes bracelets (plain, twisted and ribbed varieties), torcs (three-flanged, bar and some ribbon varieties), and tress rings. The silver concentration is not distinguishable from the EBA gold, therefore the possible exploitation of the same source of gold was highlighted. The copper and tin concentrations of this gold plot as a tight cluster too homogenous to represent the signature of natural gold, therefore this was seen as evidence for the addition of both. The second of the MBA alloys is termed F-gold or mba2 gold alloy, equates to Hartmann's OC metal, and dates to the later Bishopsland phase (c.1300/1250 to 1150 BC). It is characterised by significantly higher silver (mean 16%), copper (mean 5%) and tin (mean 0.3%) concentrations and includes bar and four-flanged torcs. The penannular rings also fall into this metal group although these are traditionally dated to the LBA; no explanation for this inconsistency was offered. The levels of copper and tin again suggested deliberate addition, whilst it could not be ruled out if the silver was a deliberate alloy as well. If the silver was inherited from the gold, it indicates a new high silver source was being exploited. Differences between the gold alloys worked in Ireland and Britain were also highlighted, suggesting different pools of metal were in circulation. A regular ratio of copper to tin suggested that bronze may have been deliberately alloyed for the manufacture of the British goldwork, and whilst the alloying of bronze and gold was not favoured in an Irish context, the ratio of copper to tin suggests this was a possibility.

The LBA goldwork, termed G-gold or lba gold alloy, was also distinguishable; mean concentrations were 13% silver, 6% copper and 0.14% tin. All traditionally LBA artefacts plot close to the focus of this compositional group except for the penannular rings already discussed, leading Warner (2004) to propose the existence of a single gold working industry. The copper and tin were again deliberate additions (although not as bronze), whilst the difference in silver concentration indicated the exploitation of a different source to the MBA.

A distinction between objects of different sizes was also highlighted. The copper and tin concentrations of larger objects belonging to the F- and G-gold tend to plot near to the average or core values, whilst smaller objects are more variable and cluster around the focus. A possible explanation for this pattern was put forward by Warner (2004). If small quantities or ingots of gold were alloyed with copper and tin to different degrees, possibly relating to the requirements of different workshops, then smaller artefacts would reflect this variance. Larger artefacts manufactured from multiple ingots or smaller pieces of gold would produce a homogenised signature that would be nearer to the mean concentration of the metal group.

Warner (2004) also briefly discussed the ribbon torc artefact class. These are particularly problematic because they vary compositionally; some are consistent with B-gold of the MBA, however the majority match the composition of Iron Age goldwork with high silver averaging at c.22% and trace levels of platinum. This may indicate the exploitation of a high silver source of gold, although the possibility that silver was deliberately alloyed also exists.

To summarise, Hartmann's vast study of hundreds of prehistoric gold artefacts has in general received poor reviews. Whilst recent studies lend support to the existence of the compositional groupings and highlight the good accuracy of the copper and tin analyses, the silver concentrations, perhaps the most important element for gold characterisation, are highly inaccurate. Furthermore, characterisation of a significant proportion of the possible gold sources was not achieved and the attempts made by Hartmann to link the artefact metal groups to known gold deposits were based on very small datasets from few gold deposits. Regarding the gold source, Hartmann favoured a continental origin for gold from all periods. A programme of re-analyses has confirmed the existence of gold alloy groups that are generally consistent with the perceived chronology of the Bronze Age. In conjunction with the characterisation of potential gold sources, this vast dataset could help to identify the gold deposits that were exploited throughout this period.

2.3.2.3 Laser ablation ICP-MS trace element analysis

Irish and British Bronze Age goldwork

Trace element characterisation using laser ablation inductively-coupled plasma mass-spectrometry was applied to Irish and British Bronze Age gold artefacts in order to further explore the question of provenance (Taylor et al., 1997; Watling et al., 1999). By concentrating on just Irish and British artefacts, a more focussed study of potential gold sources was possible; samples from over twenty alluvial sites were analysed. Initially the alluvial deposits were shown to be relatively homogenous and it was possible to distinguish between them (Taylor et al., 1997). However when the study was widened to include a larger number, there was increased overlap and some sites demonstrated greater heterogeneity (Watling et al., 1999). Additionally, experimental work recorded the loss of more volatile elements.

Chapman et al. (2006) highlighted two key problems with this technique. The first was that the method relied on the assumption that the chemical signature of the natural gold is unaffected by the fabrication process. However as the authors discussed, some degree of contamination, for example from ash or crucibles, is likely. Moreover, the process of alloying would incorporate impurities from the alloy thus further complicating the trace element signature. Gold grains liberated from bedrock into alluvial systems can also undergo chemical changes, and can collect particles of other heavy minerals whose composition varies due to local geology. When focussing on the major elements such as silver and copper, this is not a significant problem because any change is likely to be small relative to the overall concentrations. Conversely, any variation of trace elements could be significant due to their inherently low abundances.

The second problem discussed by Chapman et al. (2006) relates to the internal heterogeneity of natural gold grains, a common feature due to the presence of mineral inclusions and the natural variation of the alloy composition. The authors argue that although reproducible results may be produced within individual phases of a gold grain, they are not necessarily representative of the grain as a whole. Consequently gold from a single location can display heterogeneity due to natural compositional variation whilst alluvial deposits can be a combination of more than one source. Finally, it was cautioned that characterisation of gold deposits based on small sample sets and the analyses of small grain volumes could produce misleading results.

A further problem existed with the work of Taylor et al. (1997) and Watling et al. (1999), and that is the lack of data quantification. The authors clearly stated this, and claimed it was due to technical reasons; the analysis of native gold produced varying crater morphologies that created significant differences in the laser coupling efficiency and variable amounts of debris (Watling et al., 1999). The lack of quantification was not seen to be an issue for the aims of the work; elemental characterisation was based on the presence or absence of elements and the association or lack of association of certain element suites. However interpretive discussions utilised ternary plots that directly compare the relative contribution of three chosen elements, which effectively quantifies the elements in question using the intensities of the other two. Accurate quantification not only turns isotopic intensities into actual concentrations, but also calibrates for processes such as elemental fractionation, varying mass responses of the ICP-MS, and differences in ablation yields between samples and standards (Jackson, 2008). If the elements chosen for the ternary plot comparisons behave differently throughout laser ablation and mass spectrometry, then the unquantified intensities used to plot the elements may be inaccurate.

In addition to the ternary plots, the direct comparison of raw intensity spectral plots and raw count data plots were utilised. Although the presence/absence of particular elements was used for interpretation, a significant number of elements appear on the different spectra to varying degrees and appear to have been used for interpretive discussions. An example of this is the comparison of the Bracks Farm torc and County Antrim artefacts in figures 4 and 5 of Watling et al. (1999), and led the authors to claim different gold sources were responsible. The relative concentration peaks of arsenic and mercury are key in differentiating between the artefacts. Both the Co. Antrim artefacts and Bracks Farm torc have peaks for these elements, it is only by comparing the relative concentration that the difference emerges. Without quantification of the data, these peaks could simply represent differences in the analysis of mercury and arsenic on the day or time of data collection. Watling et al. (1999) does discuss the use of external standards that would allow the normalisation of data collected on different days, and in-house gold reference materials were also analysed for cross-referencing. Applying a normalisation correction would at least account for day to day variations in signal intensities; however the plots are called *raw* spectral data plots or *raw* count data plots, therefore it is unclear if any normalisation was applied.

Taylor et al. (1997) and Watling et al. (1999) did not link any of the analysed artefacts to a named gold deposit, whilst Watling et al. (1999) stated that future work would focus on establishing the element suits that could assist in this aim. Unfortunately no further publications emerged that have achieved this.

The Nebra Sky Disc

Ehser et al. (2011) also employed laser ablation trace element analysis techniques to provenance the gold used on the Nebra Sky Disc, a bronze disc with gold inlays discovered in central Germany. In this study, quantified concentration data for a suite of elements was used to characterise both artefact and natural gold. Furthermore only elements characterised by high stability under both metallurgical and geological processes were used, therefore negating against potential changes in geochemistry between ore source and artefact.

The basic elemental composition of the gold from the Nebra Sky Disc is consistent with Hartmann's A_3 group, whose distribution was thought to be centred in south-eastern Europe (Hartmann and Sangmeister, 1972). However comparisons of the artefact's trace element signature to over 150 gold deposits from both south-east and central Europe failed to highlight a potential source (Schmiderer, 2009). Haustein et al. (2010) presented data that suggest the tin used in the manufacture of the bronze disc may have originated in Cornwall, England, therefore this region was seen as a potential source for the gold as well. Consequently, seven Cornish gold deposits were characterised for their major and trace element signature.

No Cornish deposit matched the artefact gold for every element analysed. The combined compositional variation of two placer deposits from the River Carnon provided the best correlation, therefore Ehser et al. (2011) proposed Cornwall as the most likely source of the gold incorporated onto the Nebra Sky Disc; a region already postulated as a source of Bronze Age gold by Penhallurick (1986, 1997). Correlation with a mix of two deposits highlights a key issue with compositional studies, yet is a valid interpretation. If alluvial deposits were being exploited, it is highly likely that gold would be collected from a number of locations in the same river system. Consequently it is perhaps more accurate to treat their compositional range as that of one gold deposit, and therefore an association to the combined signature is legitimate.

Although the River Carnon provided the most likely Cornish source for the artefact gold, correlation for every element was not achieved; both copper and platinum were found to be lower in the alluvial gold. Ehser et al. (2011) linked the inconsistency in copper and platinum to the presence of micro inclusions or unintended contamination with heavy minerals during processing. Micro inclusions can be characterised therefore it should be possible to judge if these are a possible explanation. It is widely accepted that tin is incorporated into EBA goldwork due to its association with gold in alluvial deposits, therefore it is possible that the same could be said for platinum or even copper. This hypothesis could be tested by documenting the composition of the heavy mineral fraction that accompanies alluvial gold in Cornish streams. However the high copper signature of the artefact gold (0.52%) would require a significant proportion of copper minerals being present compared to tin which seems unlikely. Further investigations to help explain the differences in copper and platinum concentrations are therefore a priority, because an alternative explanation for the inconsistency in the copper and platinum data is that the gold on the Nebra Sky Disc did not originate in the River Carnon.

2.3.2.4 Microchemical Characterisation

Irish goldwork from the Early, Middle and Late Bronze Age

Chapman (2006) took a geological approach when investigating the question of provenance. Microchemical characterisation is a technique employed when investigating the sources of alluvial gold deposits, and characterises populations of gold grains using their natural alloy composition and suit of mineral inclusions. Building on previous exploration work (Chapman et al., 2000a, 2000b), a total of 62 Irish gold deposits were characterised providing a comprehensive database of possible gold sources. The silver concentration of natural gold was variable, and was primarily influenced by the host terrane with increasing silver content found in lode gold from the south to the north of the country (albeit with some exceptions). Analyses of 180 Irish gold artefacts, ranging from the EBA to Iron Age in date, suggested a pattern of exploitation for a small number of Irish sources throughout the Bronze Age, with their importance changing over time.

It was found that the artefacts could be variable in their alloy composition and inclusion suite. EBA artefacts showed little internal variation suggesting either a homogenous charge or a homogenising process during manufacture. Experimental work highlighted the difficulties in producing a homogenous melt, therefore the former was preferred; an indication of source homogeneity (Chapman et al., 2006). The LBA artefacts demonstrated greater internal variation in both silver and copper. This point is perhaps surprising because many of the later artefacts were cast rather than sheet worked, yet it may relate to the extra alloying processes involved during manufacture during this period.

Chapman et al. (2006) concluded that artefacts dating to the EBA and MBA were most likely to have originated from the same single source. The silver concentration of these artefacts typically falls in the range of 9.7% to 12.7%, and this is consistent with a source hosted by the Southern Uplands Terrane (present in both Ireland as the Longford Down inlier and in Britain). Two alluvial deposits from the Mourne Mountains provided the best match with the artefacts from gold sources within Ireland, although it was stated that these deposits may not have had the potential to account for the amount of gold in circulation at this time. Similar silver concentrations were also documented in grains from the Southern Uplands terrane of Scotland, highlighting this area as a possible source region. In line with previous analytical work, the copper concentrations of the EBA artefacts were consistent with natural gold deposits, whereas the Middle Bonze Age artefacts (that equate to Warner's B-gold) demonstrated copper concentrations from 1% to 2%. This is inconsistent with natural gold, therefore it was suggested that the practice of alloying had begun.

Significantly higher silver concentrations of the LBA artefacts (usually within the range of 12.6% to 16.3%) led Chapman et al. (2006) to propose that a new source was under exploitation (in this study the LBA artefact group includes those of Warner's F-gold composition that date to the MBA). Although this range of silver values is consistent with a number of gold deposits across the north of Ireland, the majority were deemed as too small to account for the vast amounts of artefacts produced at this time. Therefore the site of Croagh Patrick, a major gold resource in Co. Mayo, was highlighted as a possible source deposit. The high copper of the LBA artefacts (typically 2% to 8%) suggested the continuation of alloying, yet now with greater quantities of copper. Those Middle and Late Bronze Age artefacts that were alloyed with copper also contained higher levels of tin. Although the inclusion of tin due to a cassiterite bearing alluvial source could not be ruled out, the potential that the tin was incorporated due to the alloying with bronze was stressed. The silver content of the Iron Age artefacts (typically 19.3% to 27%) was shown to be inconsistent with any plausible Irish gold source, therefore the view that gold was imported during this period was put forward.

The mineral inclusion suite of the EBA artefacts was similar to those found in natural gold, namely quartz and the occasional calcium-rich phase. The Middle and Late Bronze Age artefacts contained inclusions that are not found in natural gold. Chapman et al. (2006) therefore proposed that they were incorporated during the fabrication process, with potential sources including charcoal ash and fluxes. These suggested increasingly complex metallurgical processes were employed as the Bronze Age progressed.

Irish Early Bronze Age goldwork and the Mourne Mountains, Co. Down, Ireland

This work was further developed by Warner et al. (2009, 2010a, 2010b). The source of EBA gold was explored in more detail, with work focussing on the Mourne Mountains of the Longford Down Inlier, Co. Down. The silver and copper composition of Mourne Mountain alluvial gold, and its association with cassiterite in placer deposits, made it the only likely source of EBA gold in Ireland (Warner et al., 2009). It should be noted that some Co. Wicklow alluvial gold are characterised by atypically high silver concentrations for south-east Ireland, consistent with the EBA artefacts (Chapman et al., 2006). There are known cassiterite deposits in the region (Jackson, 1979), therefore they represent a potential source for EBA gold. However Chapman et al. (2006) noted that the largest modern day gold resource in this area has silver concentrations inconsistent with these artefacts, and it is unlikely that this would have been missed in favour of smaller deposits. Although there is a possibility that the higher silver deposits were richer in the past and exploitation has changed their relative abundances, it is considered unlikely that these south-eastern deposits were exploited in the Chalcolithic or Bronze Age.

The potential for a non-Irish source was also considered. The majority of the EBA artefacts contain 7% to 12% silver with appreciable tin, and this signature is consistent with gold from the Mourne Mountains. Those artefacts that possessed silver either higher or lower than this range were seen to have lower tin levels or lack this element completely. Therefore it was deemed likely that these artefacts were manufactured from a different gold source.

One of the key problems with the Mourne Mountain theory is the present day low abundance of gold in the region (Chapman et al., 2006; Meighan, 2011). This may be due to the exploitation of as yet undiscovered bedrock mineralisation, or overexploitation of the alluvial deposits in the past (Warner et al., 2010a). A further explanation was discussed by Warner et al. (2010b), where parallels were drawn to the Wicklow gold rush of the 18th to 19th centuries AD. In this example, rather than the exploitation of the active sediment load, gold-bearing fluvial deposits were dug from the river valleys followed by extraction via sluicing. Rich deposits hosted by fluvial sequences have been located by streams with apparently low abundances, therefore the abundance of panned gold today may not be an accurate indication of abundances in adjacent sediments.

Warner et al. (2010a, 2010b) also presented the hypothesis that rather than the cassiterite simply being a contaminant, it may also have been actively exploited. The lunulae were seen as the first native Irish gold artefacts, and contain the higher tin levels that suggest a link with the Mourne Mountains deposits. Some of the earliest goldwork in Ireland were the gold discs which are not characterised by significant tin concentrations. These date in part to the Chalcolithic period before the exploitation of tin had begun, therefore the possibility that they were imports was proposed. The fact that the emergence of insular artefacts with higher tin levels coincided with the start of tin exploitation was seen as possible evidence for the exploitation of both cassiterite and gold from the same alluvial deposits, with the Mourne Mountains able to account for both.

Possible features relating to streaming activities have also been identified adjacent to the Ballincurry River in the south-west Mourne Mountains. Banks and regular channels near the head of the river were interpreted as potential waste mounds and races or sluice-gullies respectively, whilst a deep and wide gully further down stream was seen as a possible extraction pit (Warner et al., 2010a). Although numerous features in this valley were explained as natural run-off channels, the regularity of some of the aforementioned features is suggestive of human activity. This particular stream is more prevalent in gold rather than cassiterite, therefore it was suggested that if these features are evidence for streaming, gold was the more likely target. Further research is needed to confirm what these features are. If they are related to streaming activities then dating them is a priority; documented evidence for the arrival of Cornish miners in the 19th century (Warner et al., 2010a) raises the possibility that these features may not be prehistoric in date.

In a critique of the Mourne Mountains theory, Meighan (2011) also highlighted a number of more general issues that are often used to criticise compositional based provenance studies. The effects of melting and potential changes in the geochemistry of gold grains after liberation from a bedrock source was referred to, however both of these issues were previously discussed by Chapman et al. (2006). A further issue raised relates to the mixing of different gold deposits. This complicates direct comparisons of natural alloys with artefact alloys, yet by concentrating on the earliest artefacts this problem should be minimised assuming fewer deposits were exploited during the earliest period of goldworking.

Finally, Meighan (2011) dismissed the hypothesis of a Mourne Mountain source on geological grounds and claimed that the presence of substantial gold mineralisation in the Mourne Mountains is unlikely. Economic gold deposits (i.e. their exploitation will create a significant profit) tend to be associated with destructive plate margins, whereas the Mourne Mountain granites are part of a series of intrusions relating to the opening of the Atlantic Ocean (known as the British Tertiary Igneous province). However it is difficult to judge whether a gold source would have been considered 'economic' during prehistory, and deposits could instead have been exploited for other more esoteric reasons. Consequently deposits that would not be exploited in the modern day may have been exploited in the past.

Meighan (2011) proposed that the gold of the Mourne Mountains could instead have been glacially transported from more auriferous regions such as Co. Tyrone, and concluded that the source of Irish EBA gold remains a mystery. However Warner (2009, 2010a, 2010b) never proposed a direct association between the emplacement of the Mourne granites and the local gold mineralisation, and gold relating to orogenic processes is present elsewhere in the same geological terrane (Chapman et al., 2012). Additionally, the microchemical signature of the Mournes gold is inconsistent with derivation from a Sperrin Mountains source, therefore the Mourne Mountains alluvial gold is of local origin and remains the most likely Irish source of EBA gold based on the current evidence (Chapman et al., 2012).

2.4 A Lead Isotope Provenance Study of Irish Chalcolithic and Bronze Age Gold

Recognising the source locations of Chalcolithic and Bronze Age exotic materials is crucial for understanding the controls of their procurement, trade and exchange, and could help to explain the increasingly complex societies that formed during this period. Significant quantities of goldwork dating to these periods have been discovered in Ireland, however procurement of the raw material exploited by Irish goldworking industries is poorly understood. This is primarily due to the lack of archaeological evidence for gold extraction, both within Ireland and neighbouring regions of north-west Europe. As a result, scientific provenance studies are of critical importance if any understanding of gold procurement, and consequently the role that gold played in Bronze Age societies, is to be achieved.

Despite almost 50 years of research focussing on the elemental composition of EBA gold, no scientific provenance study has been able to conclusively establish the sources exploited for their manufacture. Debate continues today, thus the application of a new provenance technique independent from elemental characterisation is required. This would allow critical evaluations of interpretations presented by previous studies such as the Mourne Mountain hypothesis. Lead isotope analysis is often employed in archaeological provenance studies (recent overviews of this technique available in Cattin et al., 2009; Stos-Gale and Gale, 2009), yet it has never been applied to the study of Bronze Age gold. This study will therefore develop both solution and laser ablation mass spectrometry techniques able to analyse the lead isotope signatures of artefact and natural gold, and apply them in a lead isotope provenance study of gold artefacts from the Irish Bronze Age.

Chapter 3: Geological Setting and Lead Isotope Analysis

3.1 Synopsis

The ability to differentiate between possible ore sources is critical to the success of archaeological provenance studies. The variations in the isotopic signatures of different ore deposits relate to differences in source age and source rock composition (e.g. Marcoux et al., 2002, Tornos and Chiaradia, 2004), therefore a geological understanding of the study region is key. Due to the generally accepted opinion that an Irish gold source was exploited in the Bronze Age, and the current hypothesis regarding the Mourne Mountains of Co. Down, the focus of this provenance study is on the gold deposits of Ireland. Consequently the present chapter provides the relevant geological background required for this study.

A general overview of the geology of Ireland is provided in Section 3.2. The principle styles of global gold mineralisation are then outlined (Section 3.3), followed by an introduction to the gold deposits of Ireland (Section 3.4). Lead isotope analysis is introduced in Section 3.5. This consists of a discussion on the fundamentals of lead isotope systematics (3.5.1), an overview of published lead isotope investigations studying Irish mineral deposits (3.5.2) and the applicability of lead isotope analysis to archaeological provenance studies (section 3.5.3). Finally, Section 3.6 details and briefly discusses the key aims of this project.

3.2 Geological overview of Ireland

3.2.1 Introduction

The geology of Ireland (Figure 3.1) demonstrates a long and complex history, with rocks dating from as far back as the Palaeoproterozoic (Daly, 2001). The present day landmass of Ireland formed when two palaeocontinents collided during the Caledonian Orogeny c.470 Ma to c.390 Ma (Holdsworth et al., 2000). As the Iapetus Ocean closed, the Avalonian Plate (including the basement of south-east Ireland and henceforth referred to as the south-east terrane or SET after Max and Long, 1985) collided with the Laurentian Plate (including the basement of north-west Ireland and referred to as the north-west terrane or NWT). Although the exact location of the Iapetus suture (dashed black line on Figure 3.1) is unclear, in the present day it runs approximately from the

Shannon estuary in the south-west of Ireland to Balbriggan on the east coast of Ireland (Todd et al., 1991).

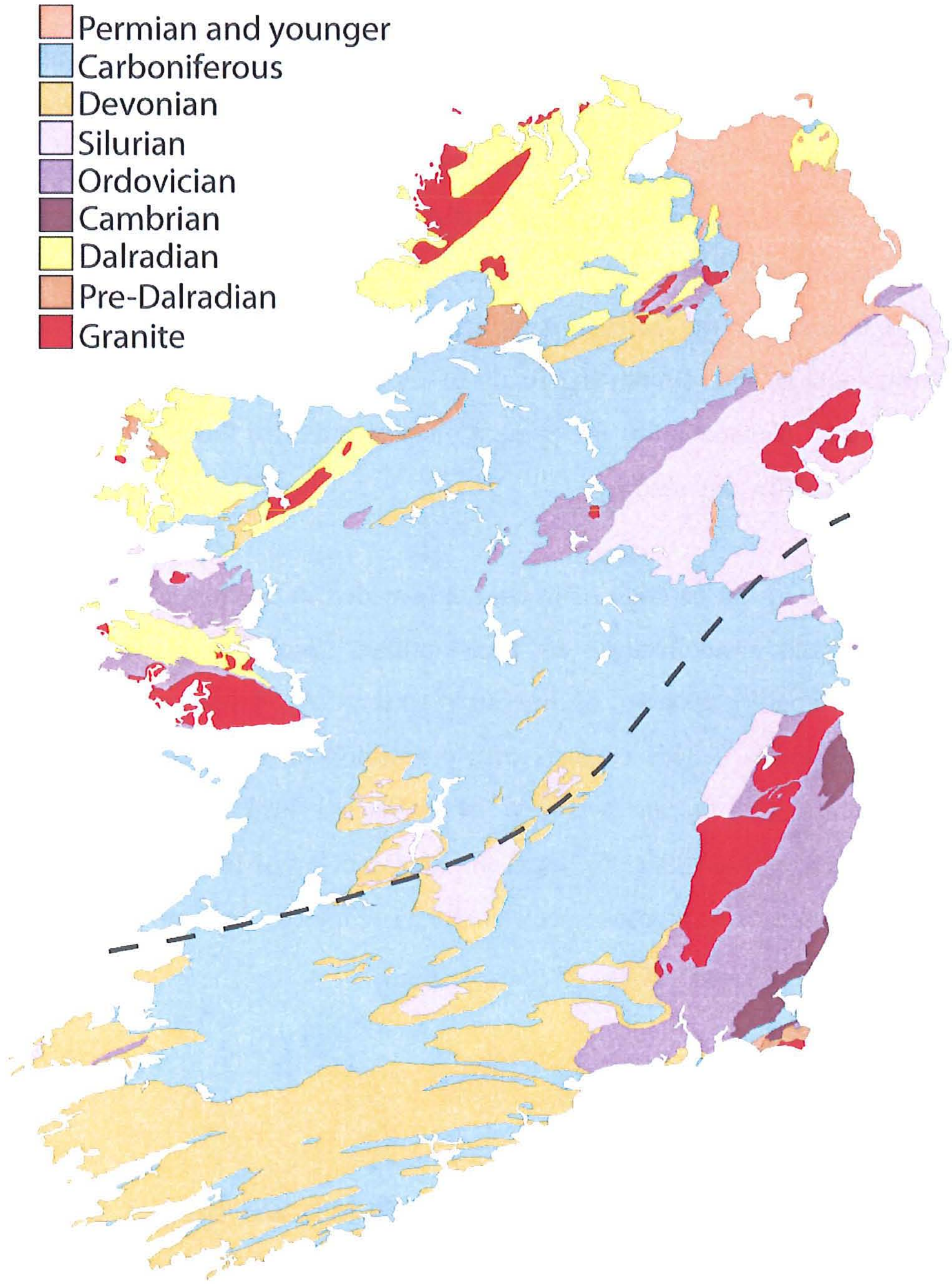


Figure 3.1: Simplified geological map of Ireland based on the Geological Survey of Ireland's 1:250,000 bedrock series map. Dashed black line represents the approximate trace of the Iapetus suture.

3.2.2 Precambrian basement

The Precambrian sequence of Ireland is far from continuous (Woodcock and Strachan, 2000), and examples from both north and south of the Iapetus suture outcrop in Ireland (see Figurer 3.2 for a geological timescale). As described by Daly (2001), rocks from the Rhinns Complex (Palaeoproterozoic), the Slishwood Division (Meso- to Neoproterozoic) and the Dalradian Supergroup (Neoproterozoic) are all found in Co. Donegal. Further Dalradian geology outcrops in north-east Co. Antrim and in the Central and Lack Inliers of Co. Tyrone. In the west of Ireland, there are outcrops of Precambrian geology in Co. Mayo and Co. Sligo, such as the Slishwood Division and Neoproterozoic Dalradian of the Ox Mountains and at Rosses Point, and the Annagh Gneiss Complex (Palaeoproterozoic). Rocks of Dalradian age are also found throughout Connemara in Co. Galway. In the far south-east of Ireland Precambrian lithologies belonging to the Rosslare Complex (Neoproterozoic or older) have been documented.

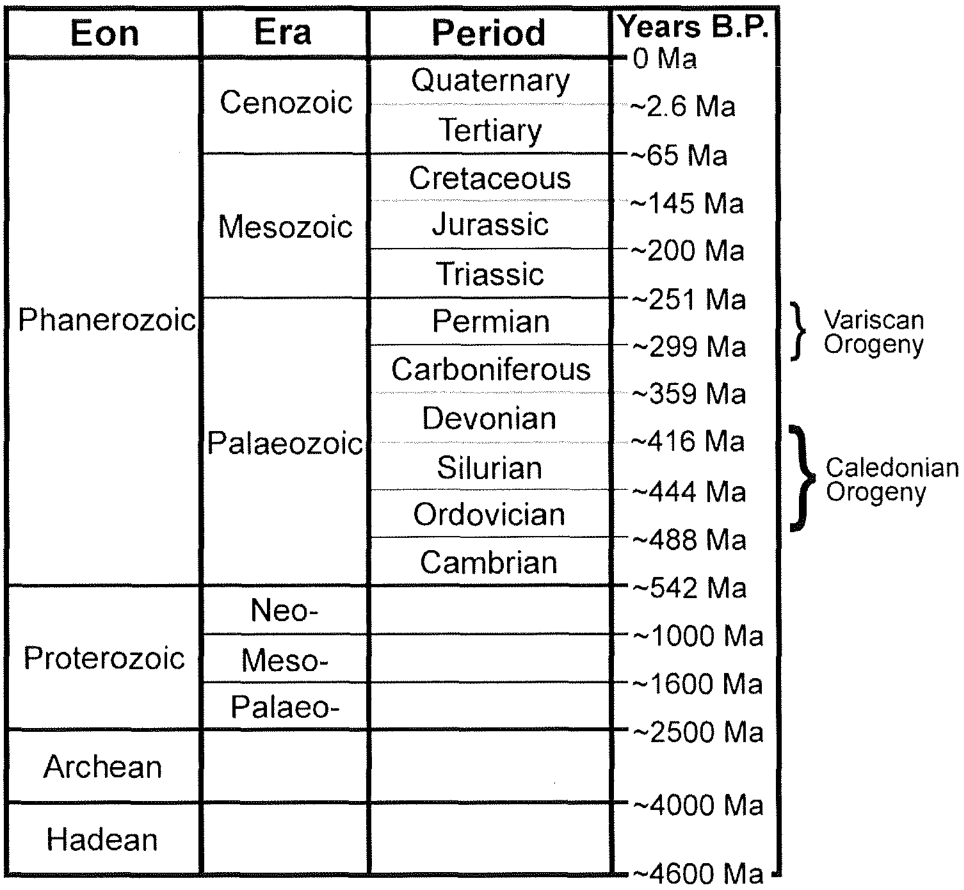


Figure 3.2: Geological timescale after U.S. Geological Survey Geologic Names Committee (2010). Ages presented as B.P. (before present) in Ma (million years).

3.2.3 Lower Palaeozoic

Lower Palaeozoic rocks of Cambrian, Ordovician and Silurian age overlie the Precambrian basement across much of Ireland, and outcrop in four key regions (see Figure 3.1): the Longford Down inlier of north-eastern Ireland (Ordovician to Silurian); southern Co. Mayo (Ordovician to Silurian); the Leinster Massif of south-east Ireland

(Cambrian to Silurian); and as numerous inliers in southern central Ireland (Silurian). They consist of ocean floor (Iapetus) and turbidite sequences with interbedded volcanics; sedimentary lithologies including greywackes, mudstones, shales, siltstones and sandstones have been identified along with both basic and mafic igneous rocks (Stillman and Williams, 1978; Morris, 1987; Max et al., 1990; Aherne et al., 1992; Thompson et al., 1992; Everett et al., 2003). These Lower Palaeozoic sequences are associated with the Caledonian orogeny (c.470-390 Ma) and were subjected to both deformation and metamorphism, the peak of which occurred c.470 Ma. In the NWT this peak Caledonian event is often referred to as the Grampian orogeny (Fettes et al., 1985; Powell and Phillips, 1985; Hutton, 1987; Holdsworth et al., 2000; Chew et al., 2010).

3.2.4 Upper Palaeozoic

Devonian sedimentation is focussed in the Munster Basin of south-west Ireland, although sequences are also present to a lesser degree further north (Figure 3.1). Terrestrial Old Red Sandstone (ORS) facies dominate with alluvial and fluvial sequences, while marine facies began to develop by the late Upper Devonian in the south of this region (Clayton et al., 1980; MacCarthy, 1990). Igneous activity also occurred in the Early Devonian during the closing stages of the Caledonian orogeny, with the emplacement of large granitic plutons such as the Donegal granites, Connemara granite, Leinster granite, and Newry granite, along with smaller granitic bodies including the Corvock granite of Co. Mayo (O'Connor, 1975; O'Connor, 1989; O'Connor and Brück, 1978; Halliday et al., 1980; Murphy, 1987).

The marine transgression of the late Upper Devonian continued into the Lower Carboniferous. Shale and siltstone deposits from the Lower Tournasian were overlain by thick limestone sequences famous for hosting Pb-Zn mineralisation, while depositional environments ranged from moderately deep waters of a few hundred metres, to shallow, high energy marine settings in a stable marginal shelf to subsiding basin environment (LeHuray et al., 1987; Banks et al., 2002; Wilkinson, 2003). These Carboniferous marine sequences cover vast areas of central Ireland (Figure 3.1). Metamorphism and mineralisation associated with Late Devonian to Carboniferous crustal extension ended with the onset of the Variscan Orogeny (Meere, 1995; Kinnaird et al., 2002). This was the result of the closure of the Rheic Ocean and the collision between the continents of Laurasia (which included the old Laurentian and Avalonian land masses) and Gondwana, and was associated with deformation, low grade metamorphism and further episodes of mineralisation (Cooper et al., 1986; Graham, 2001; Kinnaird et al., 2002). The collision itself is most likely to have occurred during the Upper Carboniferous to Lower Permian, with the effects primarily focussed in the south of Ireland (Graham, 2001).

3.2.5 Post-Variscan

Post-Variscan lithologies are relatively rare in Ireland. Sedimentary deposits from this period are primarily found in the Rathlin Trough and Lough Neagh-Larne Basin of north-east Ireland, where Permian, Triassic, Jurassic and Cretaceous sequences have all been identified (McCann, 1988; McCann, 1990; Naylor, 1992). Elsewhere in Ireland they are even more restricted: Permo-Triassic deposits have been recorded in the Kingscourt Graben of Co. Cavan and in the Wexford Outlier; Jurassic sediments have been identified in the Cloyne Syncline of Co. Cork; Upper Cretaceous lithologies are present in the Ballydeenlea Outlier of Co. Kerry; while there are also several small Tertiary deposits scattered across the country (Naylor, 1992).

Tertiary igneous complexes are also present in the north-east of Ireland, and relate to the rifting of North America and Eurasia and the opening of the Atlantic Ocean (Jolley and Bell, 2002; Stevenson and Bennett, 2011). The Mourne granites of Co. Down were emplaced c.56 Ma (McCormick et al., 1993; Stevenson and Bennett, 2011), whilst the vast Tertiary basaltic lavas of Co. Antrim formed at a similar time (Lyle, 1980; Lyle and Preston, 1993).

3.3 Gold Mineralisation

3.3.1 Introduction

The average abundance of gold in the earth's crust is 4-5 ppb, thus to produce an economic deposit (in today's terms) of around 5 ppm, an enrichment factor in the order of 1000 is required (McArdle et al., 1987; Robb, 2005). Ore forming processes that involve the concentration of a particular metal or mineral into a viable ore deposit include (Skinner, 1997):

- A source of the dissolved constituents, for example disseminated gold at a low, crustal, concentration.

- A hydrothermal solution that can dissolve the disseminated source. This may comprise of metamorphic fluids, magmatic fluids, surface water, ground water, or connate water.
- Crustal structures such as fractures and faults that facilitate the transport of the gold-bearing solution.
- A mechanism for the precipitation of the gold into a concentrated ore deposit, for example changes in temperature, pressure or chemistry.

There are numerous geological settings in which these processes can occur, and this has led to the identification of a number of different gold deposit types or classes. A brief overview of the principle types follows.

3.3.2 Orogenic

Orogenic lode gold deposits tend to be hosted in thick (several kilometres) marine sedimentary sequences associated with convergent plate margins, and are usually structurally controlled with quartz gold lodes located in fault and shear systems (Bierlein and Crowe, 2000). The host rocks can be Archaean, Proterozoic or Phanerozoic in age and tend to be metamorphosed to greenschist facies (Stanley et al., 2000), whilst associations with volcanogenic rocks that relate to spreading, arc formation, plate collision or subduction are common (Bierlein and Crowe, 2000). The ore forming fluids are CO_2-rich and relate to orogenic metamorphism with mineralisation thought to closely follow the peak metamorphism of the host rock, while the mineralised suite can include carbonate, feldspar, mica, tourmaline and As, Cu, Fe, Pb, Sb and Zn sulphides (Bierlein and Crowe, 2000).

3.3.3 Skarn

Skarn deposits form due to regional or contact metamorphism of limestones, and to a lesser degree shales and sandstones, that have been intruded by granitoids (Stanley et al., 2000). The associated plutons tend to be of Phanerozoic age and at depths of ≤ 5 km, while the mineralising fluids are high temperature (400°C to 600°C) moderate salinity magmatic brines (Meinert, 2000).

3.3.4 Epithermal

Epithermal gold deposits are associated with extrusive volcanic settings (felsic to intermediate) and form at shallow depths within the earth's crust; <1-2 km (Cooke and

Simmons, 2000; Stanley et al., 2000). Two classes of epithermal deposits exist: low sulphidation and high sulphidation. Regarding low sulphidation, mineralisation tends to occur a few kilometres above the site of magmatic intrusion, with volatiles showing a magmatic source yet water indicating a meteoric source (Cooke and Simmons, 2000). High sulphidation deposits mineralise closer to the magmatic intrusion (typically calc-alkaline), with waters of a magmatic origin (Cooke and Simmons, 2000). These deposits tend to be found in oceanic arc, continental arc or back-arc basin tectonic settings, and are generally of Phanerozoic (predominantly Tertiary) age (Stanley et al., 2000).

3.3.5 Volcanic-hosted massive sulphide (VHMS)

VHMS gold deposits are formed within sub-aqueous volcanic sequences situated in back-arc rift basins or mid-ocean ridge settings (Stanley et al., 2000). The gold mineralisation tends to be associated with mineralisation of either copper or zinc. Gold associated with copper is thought to have formed from acidic, high-temperature oxidising fluids, and is generally found towards the base of the sulphide lens (Huston, 2000). Conversely, gold associated with zinc tends to form from lower temperature near-neutral fluids, and is found towards the top of the massive sulphide lens (Huston, 2000).

3.3.6 Iron oxide copper gold (IOCG)

IOCG deposits tend to be restricted to Proterozoic settings, and form from variable fluid chemistries in a broad range of crustal and tectonic settings (Partington and Williams, 2000). Although the host rocks can be igneous or sedimentary, there does seem to be a temporal and spatial relationship with granites (Stanley et al., 2000).

3.3.7 Banded iron formations (BIFs)

Gold mineralisation associated with BIFs is found in metamorphosed sediments indirectly related to volcanism, and frequently has epigenetic features such as stringer zones and veins (McArdle et al., 1987). It is associated with and often in-fills sulphide minerals such as pyrrhotite, pyrite, arsenopyrite, chalcopyrite and galena, and can be linked to phases of hydrothermal alteration that post date the formation of the BIF deposit (McArdle et al., 1987; Ixer et al., 1990).

3.3.8 Porphyry (Cu-Au)

Porphyry gold mineralisation is associated with the emplacement of sub-volcanic I-type calc-alkaline intrusions into oceanic or continental arc settings (McArdle et al., 1987; Stanley et al., 2000). Hydrothermal alteration and mineralisation plays an important role in this type of gold deposit, with zoning radiating out from the porphyry due to interactions between the gold and copper bearing brine, acidic volatiles, the wall rocks, and meteoric and connate fluids (Sillitoe, 2000). The gold mineralisation is contemporary with the intrusion of the igneous body, and can be found within vein networks or as disseminations (McArdle et al., 1987).

3.3.9 Intrusion related

Intrusion related gold deposits are associated with the emplacement of reduced granitoids, (generally I-type), and mineralisation styles vary considerably due to the depth of formation, distance from the intrusion, and structural controls; mineralisation can occur as flat or sheeted veins, breccias, stockworks, or disseminations (Stanley et al., 2000; Thompson and Newberry, 2000). They are found in continental tectonic settings, and can be associated with Bi-Te-As mineralisation, along with W-Sn-Mo-Sb (Stanley et al., 2000; Thompson and Newberry, 2000).

3.3.10 Carlin

Carlin type gold mineralisation is Tertiary in age and is hosted by carbonaceous silty limestones or carbonate rich siltstones in extensional tectonic settings aligned along deep crustal faults that relate to rifting (Hofstra and Cline, 2000; Stanley et al., 2000). They generally form at depths of >2 km from reduced acidic fluids at temperatures of 150°C to 250°C that precipitated minerals due to both cooling and chemical reactions with the host rocks (Hofstra and Cline, 2000).

3.3.11 Sedimentary exhalative (Sedex)

Sedex deposits are hosted in sedimentary basins within rift systems, and are formed from locally derived basin brines (Emsbo, 2000). Sedex deposits are generally known for Zn-Pb-Ba mineralisation; however they are now known to contain gold mineralisation in certain cases. This appears to be a function of differing hydrothermal solution compositions, with gold mineralisation occurring when the mineralising brines are H_2S rich, SO_4 poor and more reduced in oxidation state (Emsbo, 2000).

Related to the Sedex deposits, low temperature saline fluids are increasingly being connected to gold mineralisation. The Au-Pd mineralisation located around the Permo-Triassic basins of south-west England has been linked to such low temperature brines (86 ± 13 °C, ~16 wt% salinity), with metal precipitation associated with either calcic brine mixing, dilution by groundwater, or interaction with reduced lithologies (Shepherd et al., 2005). In a similar fashion, Lusty et al. (2011) have favoured an association between the gold mineralisation at Bohaun, western Ireland, and low temperature Carboniferous basinal brine-type solutions.

3.3.12 Witwatersrand

Witwatersrand type gold deposits occur in conglomerate sections of fluviatile sedimentary basins, for example the type deposit in South Africa (Stanley et al., 2000). The origin of the gold is not entirely clear. Placer or modified placer models were originally preferred. However more recently hydrothermal models, which include gold transport into the host rocks from underlying crustal rocks during metamorphism, have been proposed (Phillips and Law, 2000).

3.4 The gold mineralisation of Ireland

3.4.1 Introduction

Numerous gold occurrences have been recorded in Ireland (Figure 3.3), and mineralisation tends to be associated with Lower Palaeozoic to Dalradian geology. Six principle gold bearing regions of Ireland can be defined: the Dalradian of north-west Ireland; the Longford Down inlier of north-east Ireland; the Lower Palaeozoic and Dalradian of Co. Galway-Co. Mayo; the Leinster massif of south-east Ireland; the Lower Palaeozoic inliers of central southern Ireland; and the ORS hosted copper deposits of south-west Ireland. An introduction to each region will now be provided.

3.4.2 The Dalradian of north-west Ireland

The Dalradian of north-west Ireland hosts numerous gold occurrences (Figure 3.3). Alluvial and bedrock deposits have been recorded throughout the Dalradian of Co. Donegal, Co. Londonderry and Co. Tyrone, and the region is seen as an attractive target for orogenic gold mineralisation (Moles and Schaffalitzky, 1992; Chapman et al., 2000a, 2000b; Stanley et al., 2000; Lusty et al., 2009). This is in part due to the existence of two economic grade orogenic style gold prospects in the Sperrin Mountains of Co. Tyrone: Cavanacaw and Curraghinalt.

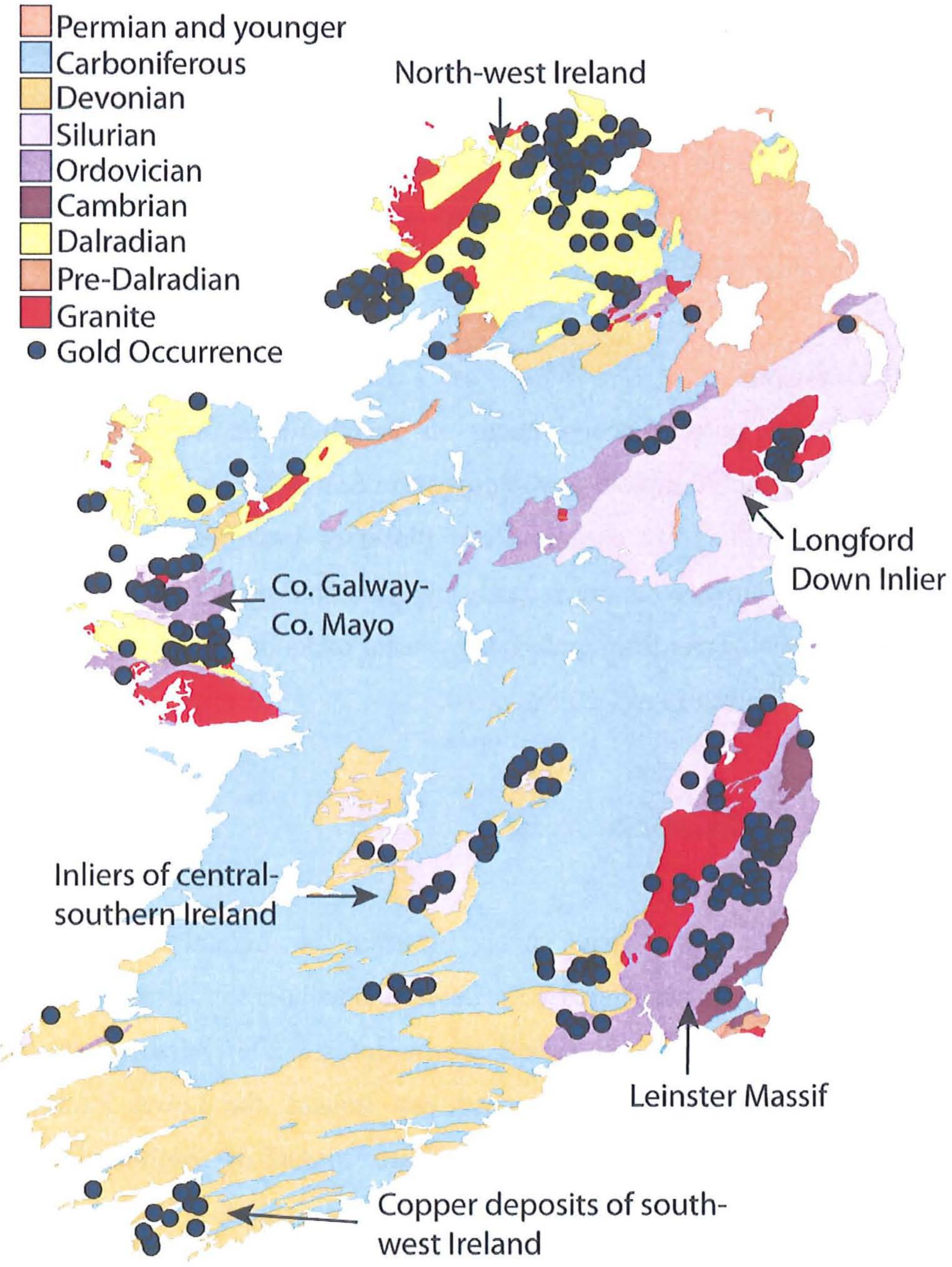


Figure 3.3: Recorded gold occurrences in Ireland. Locations primarily from GSI Gold in Ireland CD-ROM (2005). Additional locations from Earls et al. (1997), Chapman et al. (2000a, 2000b, 2006), and Moles et al. (in press).

Two principle rock groups are associated with the gold mineralisation of the Sperrin Mountains: the aforementioned Dalradian metasediments and the Tyrone igneous complex of Ordovician age. The Tyrone igneous complex consists of two distinct units: the Tyrone ophiolite of MORB origin and the Tyrone volcanic group consisting of basaltic, andesitic and rhyolitic volcanics and granitoid rocks (Cliff and Wolfenden, 1992; Earls et al., 1997; Parnell et al., 2000). Gold mineralisation is principally hosted within the Dalradian metasediments, although there is one occurrence at Cashel Rock within the Tyrone igneous complex (Parnell et al., 2000) which underlines the association between gold mineralisation and this Ordovician igneous complex. Earls et al. (1997) and Parnell et al. (2000) both proposed that Caledonian magmatism was the key process behind gold mineralisation in the region, with Caledonian deformation creating large scale faults and associated veins which provided space for the transport and precipitation of gold bearing fluids originating in the Tyrone igneous complex. There is also evidence for the remobilisation of gold in the Sperrin Mountains by Carboniferous basinal brines (Parnell et al., 2000), and Rb-Sr and K-Ar studies of fault gouge at both Cavanacaw and Curraghinalt suggest Variscan faulting or re-activation of pre-existing faults occurred, highlighting the prolonged history of the deposits.

Lusty et al. (2009) discussed the potential for further orogenic gold mineralisation elsewhere in the Dalradian of north-western Northern Ireland. Similar geology also extends to the north-west into Co. Donegal, therefore highlighting the potential that the numerous recorded gold occurrences in the Dalradian of north-west Ireland have a similar genesis. By employing microchemical characterisation, Chapman et al. (2000a, 2000b) identified a second possible style of gold mineralisation at the location of Balwoges in south-west Co. Donegal. The presence of copper sulphide inclusions and a significantly higher copper concentration distinguished the gold grains from the more typical Co. Donegal signature. A magmatic influence was hypothesised, and an association with a nearby granitic intrusion was seen as a possible explanation (Moles et al., in press).

3.4.3 The Longford Down inlier

The Longford Down inlier comprises greywacke dominated Ordovician to Silurian sequences (Morris, 1987) intruded by Caledonian and Tertiary granites (Murphy, 1987; McCormick et al., 1993; Stevenson and Bennett, 2011). Alluvial gold has been recovered from streams in and around the western Mourne Mountains of Co. Down (Chapman et al., 2006; Moles et al., in press), while a number of gold prospects exist to the south-west such as Clay Lake in Co. Armagh and Clontibret in Co. Monaghan (Morris et al., 1986; Steed and Morris, 1986; Steed and Morris, 1997).

The gold mineralisation at Clontibret is part of an antimony-arsenic-gold deposit. It is hosted in Mid to Late Ordovician greywackes, and consists of several lode zones which post date regional Caledonian metamorphism (Morris et al., 1986; Steed and Morris, 1986). Two principle episodes of mineralisation were identified by Morris et al. (1986): arsenopyrite-pyrite within the lode zones and disseminated in adjacent wallrock, and localised stibnite mineralisation. Gold principally occurs as a lattice constituent in the arsenopyrite, and to a lesser degree in the pyrite, with native grains proving to be very rare. The stibnite was dated to 360 ± 7 Ma by K/Ar dating (Halliday and Mitchell, 1983) indicating emplacement by the end of the Devonian. This was interpreted as evidence for Late Caledonian mineralisation contemporary with local microdiorite intrusions (of presumed Late Caledonian age). A spatial association between arsenic-gold mineralisation and mafic composition greywackes was recognised by Morris et al. (1986) thus indicating the greywackes of the Longford Down inlier may in part be the source of the metals, however Steed and Morris (1986) ruled out significant remobilisation of sulphides from a synsedimentary source due to a lack of known sulphide enrichments within the Clontibret district. Sulphur, oxygen and carbon isotope analysis by Steed and Morris (1997) suggested that ore fluids derived from a deep homogenous source region, consistent with an igneous association, and local diorite sills and areas of hornfels are seen to indicate the presence of larger scale concealed intrusions in the area.

The alluvial gold of the Mourne Mountains is poorly understood, and no bedrock source has been located to date. Ongoing research into the microchemical signature of alluvial gold grains from the Mourne Mountains by Moles et al. (in press) has begun to shed light on the style of gold mineralisation responsible. The inclusion mineralogy of alluvial gold grains principally corresponds with orogenic gold elsewhere in the host terrane, however the signatures of sub-populations indicates that either atypical orogenic or intrusion related mineralisation is also present.

3.4.4 The Lower Palaeozoic and Dalradian of Co. Galway-Co. Mayo

Co. Galway-Co. Mayo is another important gold bearing region of Ireland (Figure 3.3). Auriferous quartz veins are hosted by metamorphosed quartzite at Croagh Patrick, south of Clew Bay in Co. Mayo (Aherne et al., 1992). The gold is coarse grained and associated with minor sulphides and oxides; the highest concentrations of gold have been found in the A- and C-veins (mineralised structures to the north and south of the

Croagh Patrick anticline core), whilst alluvial gold is also present in streams draining the location (Aherne et al., 1992). Aherne et al. (1992) related the mineralisation to Late Caledonian movement on the Clew Bay fault zone, and postulated that the Caledonian age Corvock granite (with associated porphyry, appinite and lamprophyre intrusions) could have been important in providing a heat source for the mobilisation of mineralising fluids. A volcano-sedimentary pile, ophiolitic, or more deep seated source was also discussed.

The Cregganbaun shear zone, an east-west trending zone that stretches from the Atlantic coast to the Sheeffry Hills in southern Co. Mayo, is host to multiple gold occurrences. Gold mineralisation is generally confined to zones of intense shearing within altered tuff bands of the Sheeffry and Derrylea turbiditic formations. Visible gold is common within quartz veins, although gold mineralisation also occurs within altered tuff shear vein complexes (Aherne et al., 1992; Thompson et al., 1992). The mineralisation is also thought to be structurally controlled, with Aherne et al. (1992) linking it to movement on the Maam Valley fault zone and suggesting similar mechanisms to those responsible for the Croagh Patrick deposit. Thompson et al. (1992) proposed that the Grampian age collision between the Laurentian margin and the South Mayo arc/basin led to shearing through both the overlying turbiditic sediments and the underlying ophiolitic basement at Cregganbaun, and an association between the gold and local lamprophyre intrusions was put forward as a possible mechanism for a deep crustal or mantle source.

Gold mineralisation is also present further south in Co. Galway. The Dalradian Connemara terrane hosts numerous gold occurrences (Stanley et al., 2000), whilst the gold deposit of Bohaun is hosted by Silurian rocks that unconformably overly this terrane and have undergone low grade metamorphism. Mineralisation is within a brecciated and silicified fault zone, and displays multiple growth stages and a number of epithermal style textures (Lusty et al., 2011). Lusty et al. (2011) preferred an association with Carboniferous or later mineralising fluids, and the lack of pre-existing Caledonian gold mineralisation was used to rule out remobilisation on a deposit scale. Low temperature basinal brines similar to those seen in red-bed Au-Pd or Irish base metal deposits was therefore proposed as a possible mechanism for mineralisation.

3.4.5 The Leinster massif

The Leinster massif is an inlier of Lower Palaeozoic (Cambrian to Silurian) sediments and volcanics intruded and deformed by the Caledonian Leinster granite (Max et al., 1990). Numerous gold occurrences have been recorded in the Leinster massif (Figure 3.3), from Co. Kildare in the north, through Co. Wicklow and Co. Wexford, to Co. Waterford in the south-west (Stanley et al., 2000; Chapman et al., 2006). The large number of known gold occurrences and the region's geological association with the Caledonian Orogeny means that the Leinster massif is seen to have serious potential for hosting economic grade orogenic and VHMS gold deposits (Stanley et al., 2000).

Co. Wicklow is perhaps the most famous gold-bearing region of Ireland due to an 18th Century gold rush that centred on the Goldmines River (Stanley et al., 2000). Numerous other alluvial deposits have been recorded across Co. Wicklow and Co. Wexford, although the bedrock source of the majority of these deposits remains obscure. Ixer et al. (1990) recorded mineralised gold in magnetite-chalcopyrite-pyrite rich bedrock samples within Upper Ordovician volcanics (Duncannon Group) close to the Goldmines River. Gold was found within chalcopyrite infilling of pyrite minerals, highlighting magnetite-chalcopyrite ores as a potential source for the local alluvial gold. Primary mineralisation of the magnetite-chalcopyrite ore is related to low grade Caledonian metamorphism, although the actual gold mineralisation itself is linked to a phase of hydrothermal alteration which remobilised the gold and associated minerals from earlier phases. Ixer et al. (1990) concluded that this alteration was associated with Early Devonian doleritic dyke emplacement, or fracturing and faulting relating to the emplacement of the Leinster granite which has been dated to 404 ± 24 Ma (O'Connor and Brück, 1978).

Gold mineralisation is also recorded at Kilmacoo within the Avoca mining district of Co. Wicklow. Mineralisation occurs in sulphide rich tuffs within Ordovician metasediments; the typical hosts of chalcopyrite-pyrite ores elsewhere in Avoca (Milner and McArdle, 1992). Milner and McArdle (1992) proposed a two stage evolution for the gold deposit. In the Ordovician, low grade gold was deposited with the volcanogenic massive and disseminated sulphides. Fluid movements in the Caledonian orogeny then remobilised the gold and deposited it concentrated in veined and sheared rocks.

Although Co. Waterford plays host to well known copper deposits such as Bunmahon, gold occurrences have also been recorded in the county (Stanley et al., 2000; Chapman et al., 2006). The Bunmahon copper deposit is hosted by Duncannon Group volcanic rocks (McArdle and Kennan, 1992), the same stratigraphical unit that has been linked to the Goldmines River gold deposits by Ixer et al. (1990). The gold bearing streams of Co. Waterford drain metasedimentary rocks of the Campile Formation, a division of the Duncannon Group, and both felsic and rhyolitic volcanics belonging to this formation are found in the immediate area. The similarity between the type and age of bedrock at the Co. Waterford locations and the gold bearing streams of Co. Wicklow-Co. Wexford may suggest that a similar phase and style of mineralisation produced the alluvial gold found in both regions

Gold mineralisation has also been identified in Silurian greywackes (Carrighill Formation) to the north-west of the Leinster granite. The region has been the focus of vein-hosted, shear-hosted and stratabound gold mineralisation exploration after the discovery of gold nuggets in the 1990s (Minco, 2003). It is also worth noting here that there are minor gold occurrences on the Dingle Peninsula, Co. Kerry (Chapman et al., 2006). They are associated with similar Lower Palaeozoic lithologies that host the gold mineralisation of the Leinster massif. Alluvial gold locations in the Slieve Mish Mountains drain the Ordovician Annascaul Formation which has been correlated to the Ribband Group of south-east Ireland by Todd et al. (2000). Finally, gold has been recorded at the western tip of the Dingle Peninsula (Chapman et al., 2006) where later Silurian lithologies are present.

3.4.6 The Lower Palaeozoic inliers of central southern Ireland

Alluvial gold is associated with the Lower Palaeozoic inliers of central southern Ireland, for example it has been recorded in streams draining the Galtee Mountains, the Slieve Bloom and the Slieve Aughty (Stanley et al., 2000; Chapman et al., 2006). These inliers are located within the central Carboniferous basin and consist of Silurian sedimentary lithologies (similar to those that host gold mineralisation the north-west Leinster massif and the Longford Down inlier) surrounded by ORS (Figure 3.3). Little is known about the source of this gold mineralisation; however the spatial association with the Silurian lithologies may suggest a link with Silurian hosted deposits elsewhere in Ireland.

3.4.7 The ORS hosted copper deposits of south-west Ireland

Historical reports of gold associated with copper-barite mineralisation in south-west Ireland have been documented (McArdle et al., 1987; Stanley et al., 2000; Pracht and Sleeman, 2002). Reilly (1986) proposed that the copper was leached from the surrounding ORS sediments, and therefore remobilisation from ORS hosted palaeoplacers was seen as a possible source for the gold by McArdle et al. (1987). However as noted by numerous authors including McArdle et al. (1987) and Cowman and Reilly (1988), the dubious accuracy of some of these historical reports casts doubt on the true potential of the region. Ni Wen et al. (1999) reported the presence of gold as inclusions in copper minerals at the Ballycummisk copper mine. This suggests at least some of the reports have a basis in truth.

3.5 Lead isotope analysis: applications to geology and archaeology

3.5.1 The fundamentals of lead isotope analysis

There are four naturally occurring isotopes of lead: ^{204}Pb is less radiogenic, whilst ^{206}Pb, ^{207}Pb and ^{208}Pb are radiogenic and result from the radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively (Herz and Garrison, 1998). As discussed by Faure (1986), the isotopic composition of Pb varies throughout the Earth's evolution. Different geological environments, such as crustal or mantle rocks, are characterised by different U/Pb and Th/Pb. Processes including magma generation/mixing, metamorphism, and weathering can modify these ratios. The decay of uranium and thorium creates further variations, with ancient U- or Th-bearing rocks and minerals becoming depleted in these elements as radiogenic Pb is produced through radioactive decay.

Mineralising fluids dissolve disseminated metals including Pb from different regions within the Earth. These source regions are effectively reservoirs of metals, whose components can be transported through cracks and fissures to precipitate as concentrated mineral deposits. Reservoirs may also include the uranium and thorium parent isotopes of ^{206}Pb, ^{207}Pb and ^{208}Pb, and consequently Pb isotopic ratios evolve or grow over time as more radiogenic Pb is produced. The isotopic evolution of Pb can be plotted (Pb growth or evolution curves) using the decay constants of ^{238}U, ^{235}U and ^{232}Th if the starting compositions of Pb, U and Th are all known. A more detailed overview of Pb isotope systematics is available in Faure (1986), however in essence when Pb is transported away from a reservoir it can become isolated from the uranium and thorium parent isotopes and produce conformable ore deposits consisting of minerals containing common Pb, i.e. with low U/Pb and Th/Pb, such as galena or feldspar. When this is the case, no further significant Pb growth occurs and the minerals take on the Pb isotope signature of the reservoir from which they crystallised at the time of isolation.

Lead isotope signatures can therefore indicate the source age of a mineral, i.e. the age at which Pb became separated from a uranium and thorium bearing reservoir, and can be used to date conformable mineral deposits through the calculation of model Pb ages (see Faure, 1986). If more than one ore deposit originates from the same reservoir yet at different times, they will plot on the same growth curve, with the younger deposit demonstrating more evolved Pb isotope ratios (Figure 3.4). As each stage of a Pb growth curve represents a point in time, isochrons can be constructed by drawing a line through points of equal age for multiple Pb growth curves (Figure 3.4). Samples that plot on an isochron, and share a common yet heterogeneous source, can be dated using the slope of their isochron along with the decay constants and natural abundances of the parent isotopes. This technique is also applicable for rocks and minerals that undergo continued Pb growth due to high U/Pb and Th/Pb, and is classically used to date crustal rocks. When mineral deposits are not conformable, and therefore have an input of radiogenic crustal Pb after removal from a reservoir or are the product of source mixing, isotopic signatures may not be consistent with individual growth curves or isochrons.

Numerous models have attempted to explain the evolution of Pb within the Earth. The Holmes-Houtermans model, presented in Figure 3.4, is a simplified model created from the independent work of Holmes (1946) and Houtermans (1946). This model is based on the principle that the Earth was originally both fluid and homogenous, with uniformly distributed U, Th and Pb, and a unique Pb isotope composition. Differences in the U/Pb (and Th/Pb) ratios then developed as the Earth began to solidify and differentiate into layers. This produced a number of reservoirs with different compositions, and subsequent changes of U/Pb and Th/Pb within each reservoir was due to radioactive decay only.

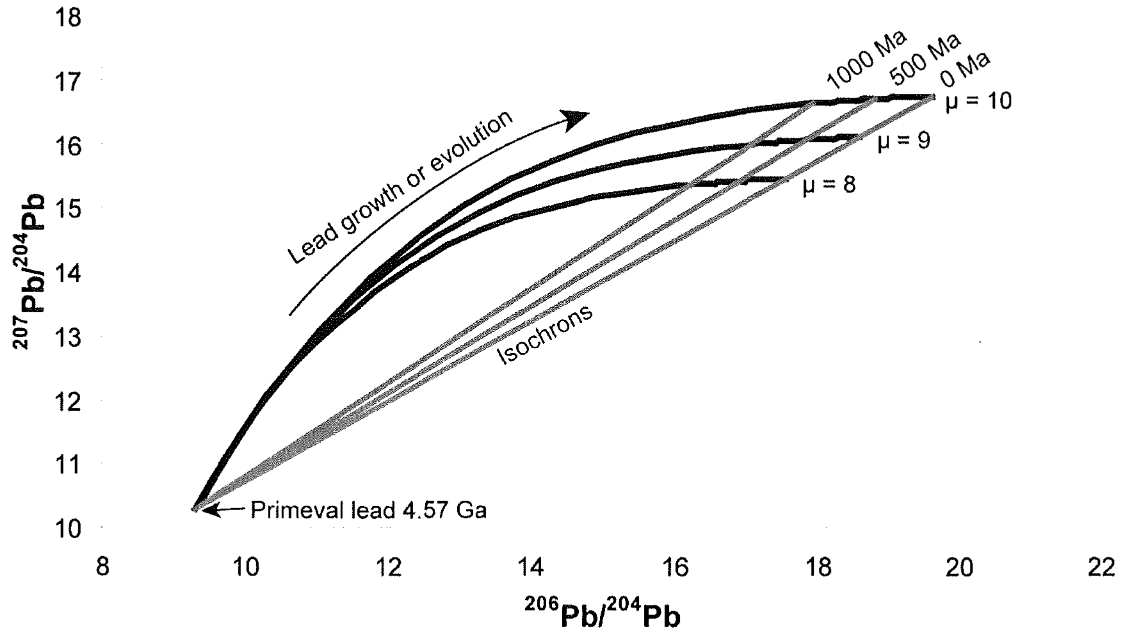


Figure 3.4: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of the Holmes-Houtermans single-stage model of Pb evolution, adapted from Faure (1986). Examples of three Pb growth curves for reservoirs with primeval Pb composition and μ ($^{238}U/^{204}Pb$) = 8, μ = 9 and μ = 10 are plotted, along with isochrons for 0 Ma, 500 Ma and 1000 Ma.

The Holmes-Houtermans model is only valid if the Pb in question had a single-stage history, and in reality this is rarely the case. This was highlighted by discrepancies between the model Pb ages of conformable ore deposits uncontaminated by radiogenic crustal Pb and their known geological ages determined by other dating techniques. Consequently Stacey and Kramers (1975) proposed a two-stage model of Pb evolution, summarised in Figure 3.5. In this model Pb evolved from 4.57 Ga to 3.7 Ga in a reservoir with uniform U/Pb and Th/Pb (stage one). At 3.7 Ga, these ratios were changed by chemical differentiation creating reservoirs with varying U/Pb and Th/Pb which then evolved undisturbed to the present day (stage two).

Stacey and Kramers (1975) found that this model generates ages in agreement with known geological ages for both conformable ore deposits and feldspars of all ages. In fact it is still relevant for mineral deposits uncontaminated by radiogenic crustal Pb, and is often referred to in studies of ore mineralisation today (Tornos and Chiaradia, 2004; Gloaguen et al., 2007; Neiva et al., 2008). Nevertheless, Stacey and Kramers (1975) did state that this is a model for average Pb and exceptions do exist.

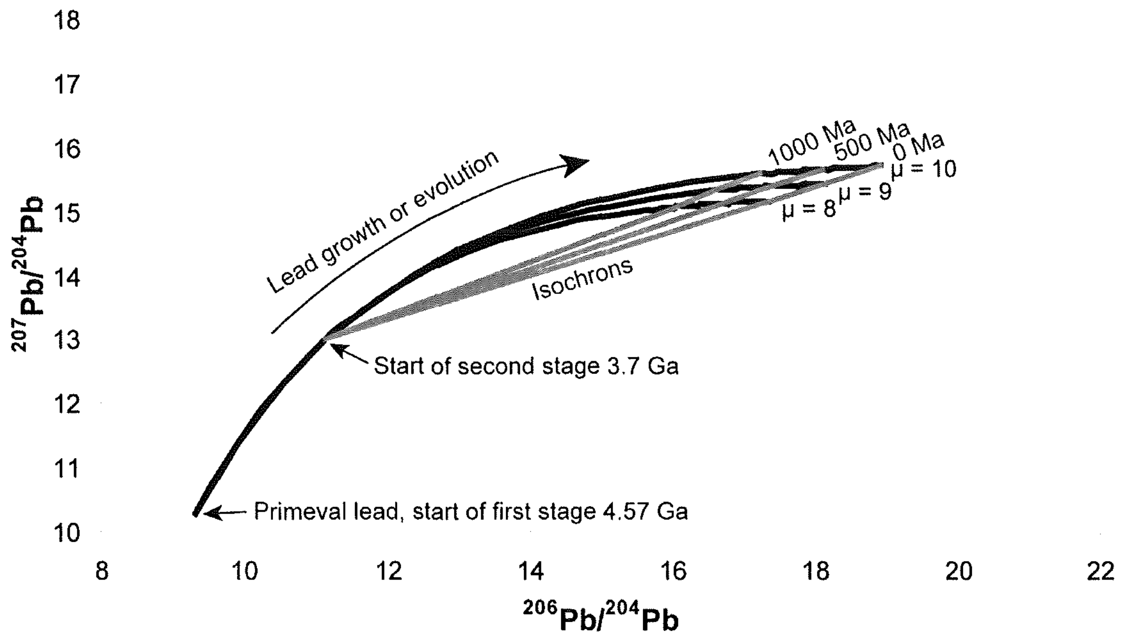


Figure 3.5: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of the two-stage Pb evolution model by Stacey and Kramers (1975). Examples of three Pb growth curves for reservoirs with primeval Pb composition and μ ($^{238}U/^{204}Pb$) = 8, μ = 9 and μ = 10 are plotted, along with isochrons for 0 Ma, 500 Ma and 1000 Ma.

These points were further developed in the plumbotectonics model of Pb evolution by Zartman and Doe (1981). These authors calculated Pb evolution curves for four key geochemical reservoirs: the upper continental crust, the lower continental crust, the orogene (a hypothetical mixing reservoir required to account for the overall terrestrial isotopic pattern) and the mantle (Figure 3.6). The Pb isotope composition of any sample could then be interpreted in terms of different mixing between these reservoirs.

A fundamental aspect of all models is that they simplify reality, and regarding Pb isotope systematics, they model average ratios. Numerous other attempts to model Pb evolution exist (Cumming and Richards, 1975; Amov, 1983; Kramers and Tolstikhin, 1997), however the models outlined above demonstrate the fundamentals of how Pb isotopes evolve within the earth and explain why differences in the source age and composition of rocks and minerals result in variations in their Pb isotope signatures.

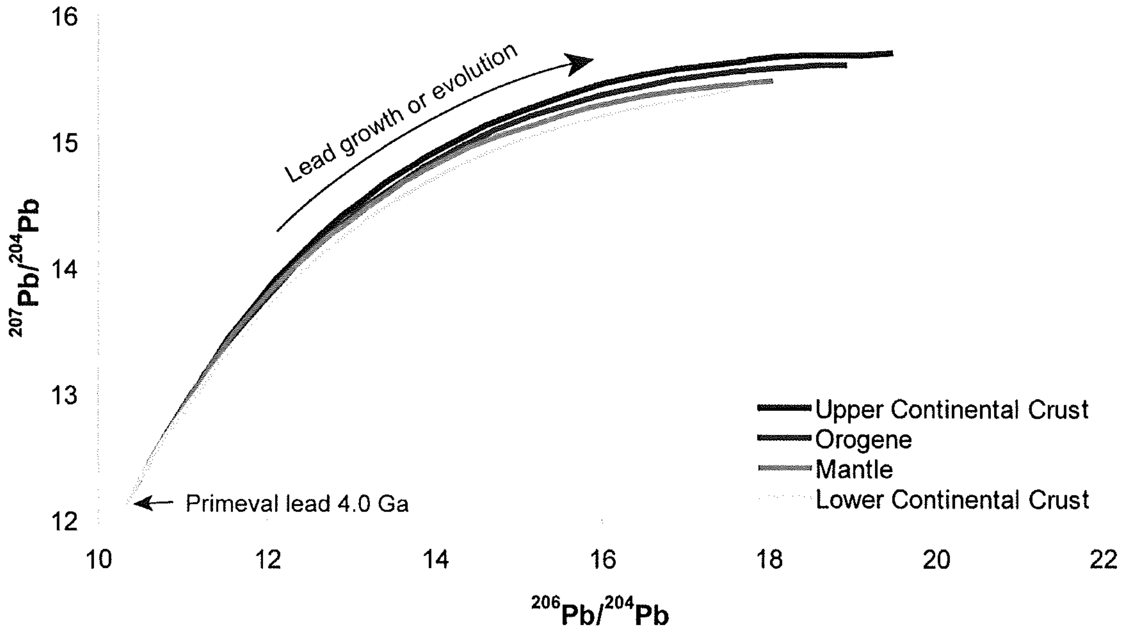


Figure 3.6: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of the plumbotectonics model by Zartman and Doe (1981), showing the evolution of four key geochemical reservoirs.

3.5.2 Lead isotope studies of Irish mineral deposits

3.5.2.1 Introduction

Carboniferous basinal brines played an important role in the metallogenic history of Ireland. Evidence is widespread; they were responsible for the extensive base metal (Zn-Pb) deposits found throughout central Ireland (O'Keeffe, 1986; LeHuray et al., 1987). Due to their economic importance extensive studies have targeted these deposits, and these investigations have included programmes of Pb isotope analysis (Boast et al., 1981; Boast, 1983; O'Keeffe, 1986; LeHuray et al., 1987; Dixon et al., 1990; Everett et al., 2003).

3.5.2.2 Palaeozoic hosted massive sulphide mineralisation and Carboniferous and Palaeozoic hosted Pb-Zn mineralisation

Initial Pb isotope studies focussing on the genesis of the Irish Pb-Zn deposits centred on two principle deposit groups: Palaeozoic hosted massive sulphide mineralisation of Early Caledonian age; and Carboniferous and Palaeozoic hosted Pb-Zn mineralisation of Carboniferous or Variscan age (Figure 3.7).

Carboniferous to Permian age Pb-Zn mineralisation hosted by both Carboniferous and Lower Palaeozoic lithologies (grey domain on Figure 3.7) plot as a linear array where variation is geographically controlled; the least radiogenic isotope compositions are found in the north-west and Pb isotope signatures becomes progressively more radiogenic towards the south-east (O'Keeffe, 1986; LeHuray et al., 1987). The slope of this array may represent the age of the source rock that the Pb was mobilised from, however an age of 3.2 Ga calculated by O'Keeffe (1986) is not consistent with the age of the postulated underlying basement. It was therefore concluded that this array represents an isochron created by the mixing of two discrete source components.

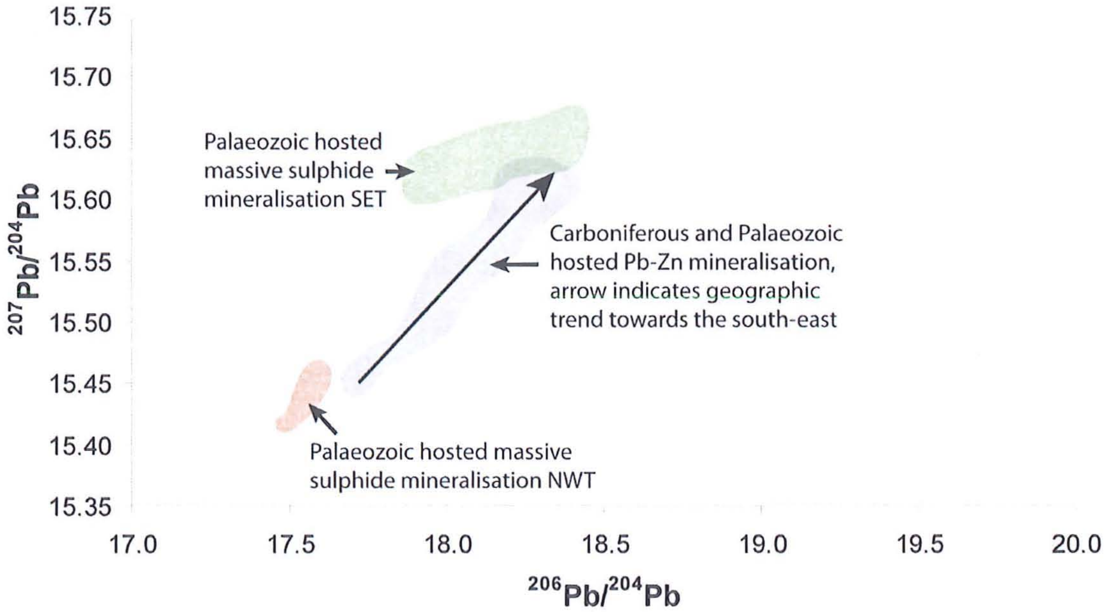


Figure 3.7: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Irish Palaeozoic and Carboniferous hosted ore deposits. The arrow located within the Carboniferous and Palaeozoic hosted Pb-Zn mineralisation data field represents a geographic trend towards the south-east. Data from Boast et al. (1981); Boast et al. (1983); O'Keeffe (1986) including citations of unpublished data from P. O'Connor; LeHuray et al. (1987); Dixon et al. (1990); Rohl (1996); Wilkinson et al. (2005).

These two source regions were defined by the analysis of massive sulphide deposits located in both the NWT and the SET. The Pb isotope signature of the Charlestown massive sulphide deposit of the NWT (red domain on Figure 3.7) plots at the less radiogenic end of the Carboniferous and Palaeozoic hosted Pb-Zn mineralisation. It also falls to the left of this array indicating older source material, with O'Keeffe (1986) calculating a model Pb age of 470 Ma (based on the two-stage model of Stacey and Kramers, 1975). This was interpreted as a mineralisation age by O'Keeffe (1986), therefore the Charlestown deposit was seen to represent Early Caledonian mineralisation originating from the NWT source region which also supplied the more less radiogenic Pb component to the later Carboniferous Pb-Zn deposits (O'Keeffe, 1986). This Early Caledonian age is supported by independent studies that dated the Charlestown deposit to the Arenig stage of the Ordovician (Cummins, 1954; O'Connor and Poustie, 1986). The Pb isotope signature of galenas from massive sulphide deposits have been shown to record the isotopic signature of their volcanic host rock at the time of mineralisation (LeHuray et al., 1988), therefore as the deposit is hosted by an Arenig volcanic series, an Early Caledonian age is credible. The source of this less radiogenic Pb was believed to be of mantle origin because the calculated μ ($^{238}U/^{204}Pb$) of 9.15 (based on Stacey and Kramers, 1975) is best typified by a mantle-type environment (O'Keeffe, 1986).

Multiple massive sulphide deposits were also analysed from the SET (green domain Figure 3.7). These demonstrate a more radiogenic Pb source, and plot as a linear trend that intersects with the radiogenic end of the Carboniferous and Palaeozoic hosted Pb-Zn mineralisation data array. O'Keeffe (1986) interpreted this trend as a Pb growth curve because volcanic arc data typically lie on a growth curve and yield meaningful ages. A model Pb age of 440 Ma was calculated for the Avoca deposit of the SET (again using the two-stage model of Stacey and Kramers, 1975), indicating another Early Caledonian age. This is consistent with the accepted mineralisation age of the deposit; it is associated with a Llandeilo-Ashgill age acid volcanic arc sequence (Williams et al., 1986). This SET Pb source is seen to be upper crustal in nature due to the higher μ of 10.09 (again based on Stacey and Kramers, 1975), and is believed to be the source of the more radiogenic Pb incorporated into the Carboniferous Pb-Zn deposits (O'Keeffe, 1986).

Further investigation by LeHuray et al. (1987) concluded that the Pb from both sources was derived locally from the underlying pre-Caledonian basement, although it could not be ascertained if the source was the pre-Caledonian rocks themselves, or detritus derived from these rocks and incorporated into the later Caledonian lithologies. The increasingly radiogenic signatures to the south-east were linked to the increasing importance of the Later Proterozoic upper crustal basement rocks of the SET, however the less radiogenic signatures to the north-west were linked to the increasing influence of Lewisian basement.

The mixing of these two sources was seen to have occurred by the Late Caledonian based on the isotopic signature of stibnite samples from the Sb-As mineralisation at

Clontibret (O'Keeffe, 1986). The stibnites plot to the left of a line of best fit through the Carboniferous and Palaeozoic hosted Pb-Zn mineralisation data array on the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot. O'Keeffe (1986) interpreted this less evolved isotopic signature as evidence for an earlier mineralisation event, and one that is consistent with a proposed link to Late Caledonian intrusives. Although the Clontibret samples do plot to the left of the line of best fit, they are not clearly distinguishable from the Carboniferous Pb-Zn deposit field. Additionally, a K/Ar age of 360±7 Ma was derived from clay minerals associated with the stibnite phase of mineralisation (Halliday and Mitchell, 1983). Therefore an Early Carboniferous age is also plausible. As the Clontibret samples fall between the two massive sulphide data fields adjacent to the Pb-Zn mixing line, the mixing of the NWT and SET Pb sources must have occurred before the mineralisation of the Clontibret deposit (O'Keeffe, 1986), irrespective if it is of Late Caledonian age or later.

It is also worth noting that three deposits located by the north-west coast of Ireland and analysed by O'Keeffe (1986) form a Pb isotope array distinct from other Irish samples when their $^{208}Pb/^{206}Pb$ are plotted. Two of the deposits are located in Co. Donegal and are hosted by Dalradian lithologies, while the other is a Carboniferous hosted deposit in Co. Sligo. Their calculated source Th/U ratios are lower than the Carboniferous and Palaeozoic hosted Pb-Zn mineralisation further to the south-east, indicating a different source with a relative depletion in thorium. This raises the possibility of second source region in the far north-west of Ireland that is not characterised by the massive sulphide deposit of Charlestown.

3.5.2.3 An Irish model of lead evolution

Dixon et al. (1990) proposed that three isotopically distinct end members contributed to the Pb isotope signatures of the ore deposits: (1) old less radiogenic basement in north-west Ireland, (2) Ordovician arc material from north-west Ireland, and (3) Ordovician arc material from south-east Ireland. The basement source of north-west Ireland contributed directly to the north-western Ordovician arc sediments, whilst the north-west and south-east Ordovician arcs both contributed to later Silurian sediments to varying degrees, as a function of their geographic location. Dixon et al. (1990) cited sedimentological and petrological evidence for the incorporation of south-eastern and north-western derived material into the Silurian rocks of Ireland to further support this theory (Hutton and Murphy, 1987; Morris, 1987). The two Ordovician arcs were therefore seen as the key isotopic end members for a model of Irish Pb evolution, and the isotope signature of galenas from massive sulphide deposits have been shown to record the isotopic signature of their volcanic host rock at the time of mineralisation (LeHuray et al., 1988). Therefore the isotopic evolution of these end members was modelled using the isotopic compositions of galenas hosted by local massive sulphide deposits: Avoca for the SET and Charlestown for the NWT (Figure 3.8).

The present day Pb isotope signatures of some Caledonian host rocks were also determined by Dixon et al. (1990). The Pb isotope ratios of Ordovician and Silurian greywackes from the Longford Down inlier (NWT) plot as a linear array (Figure 3.8) that is sub-parallel to the Carboniferous ore deposits; they are more radiogenic and also become increasingly radiogenic towards the south-east. The only Ordovician hosted whole rock sample (empty blue circle on Figure 3.8) plots at the radiogenic end of the NWT Pb evolution curve, whilst three Silurian whole rock samples (filled blue circles Figure 3.8) plot between the radiogenic ends of the NWT and SET Pb evolution curves. This supports the proposed theory that the Ordovician rocks of Ireland were derived directly from basement material specific to the geological terrane they resided on, whereas the Silurian rocks were derived from varying mixtures of NWT and SET material relative to their geographic position. When the Longford Down inlier whole rock ratios are age corrected to 350 Ma (i.e. the proposed time of base metal mineralisation), using μ values stated in Figure 3.8, they plot within the array of Carboniferous and Palaeozoic hosted Zn-Pb ore deposits. The whole rock samples are therefore interpreted to reflect a similar mixing line to that recorded by the Carboniferous base metal deposits (of the SET and NWT Pb reservoirs), which has subsequently evolved to present day compositions. These whole rock data act as a control on, and further supports, the Pb evolution model proposed for the base metal deposits of Ireland. It should be noted that the μ values employed in this model are significantly different from those typically discussed in global models of Pb evolution. This can be explained by the different time scales involved; they were chosen to enable the evolution of Pb from the massive sulphide compositions at 470 Ma and 450 Ma respectively to the whole rock linear array at 0 Ma, via the base metal linear array at 350 Ma.

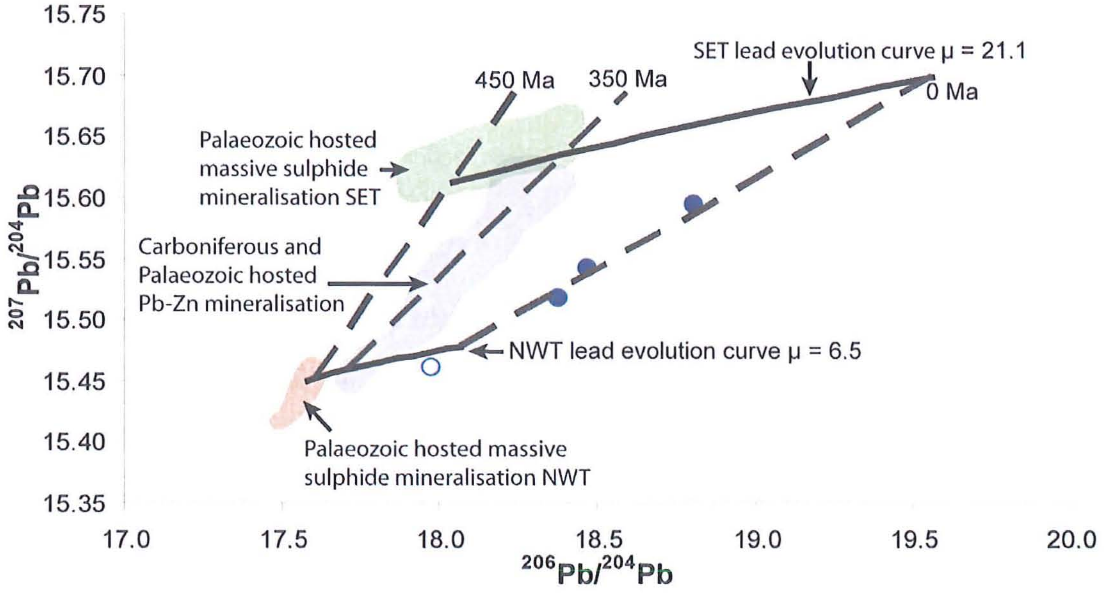


Figure 3.8: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot showing the model for Irish base metal Pb evolution of Dixon et al. (1990), with 0 Ma, 350 Ma and 450 Ma isochrons (dashed grey lines) and Pb evolution curves for the south-eastern Ordovician arc ($\mu = 21.1$) and the north-western Ordovician arc ($\mu = 6.5$). ○ Longford Down (NWT) whole rock Ordovician; ● Longford Down (NWT) whole rock Silurian.

Dixon et al. (1990) linked the less radiogenic end member to the Lewisian basement. The radiogenic end of the NWT Pb evolution curve, i.e. the present day isotopic signature, was shown to plot as a continuation of present day Pb isotope ratios of Lewisian whole rocks from Scotland (Lewisian data from Whitehouse and Moorbath, 1986). The present day mixing line between the NWT and SET Pb evolution curves plots sub-parallel to the Lewisian basement trend, highlighting the increasing input of a non-Lewisian source from the SET terrane. The association of Lewisian basement to the less radiogenic NWT basement is made despite the fact that the majority of north-west Ireland overlies Grampian or North-west terrane basement, and pre-Grampian basement has only been recorded at a few Irish locations such as Inishtrahull off the north coast of Co. Donegal (Daly, 2001). Published Pb isotope data exist for the Grampian terrane (Blaxland et al., 1979; Marcantonio et al., 1988), and plots within the radiogenic end of the Lewisian field (further Lewisian data from Chapman and Moorbath, 1977; Whitehouse, 1993). Thus the Grampian terrane may itself be derived from the Lewisian material and the two can not be distinguished using Pb isotopes. O'Keeffe (1986) preferred a mantle-like source for the NWT end member, however it is difficult to distinguish a typical mantle signature from the Lewisian derived basement because they are both characterised by less radiogenic Pb isotope signatures, thus both scenarios are consistent with the data. Other isotopic data can distinguish between mantle and lower crustal sources (e.g. sulphur isotopes; Parnell et al., 2000). Therefore when discussing the lead isotope signature of Irish gold deposits, it may be possible to distinguish between crustal and mantle source regions when appropriate literature data is available.

When devising this model, Dixon et al. (1990) assumed a common mineralisation age of 350 Ma for all the Carboniferous deposits. However, the timing of the Irish base metal mineralisation remains a controversial issue (Wilkinson, 2003). In a review of the available evidence, Wilkinson et al. (2003) suggested that the age of mineralisation was 355-345 Ma, yet palaeomagnetic data from the Lower Carboniferous carbonate-hosted Lisheen Zn-Pb deposit indicated an age of 277 ± 7 Ma (Pannalal et al., 2008). This Early Permian age supports other palaeomagnetic studies on the Silvermines and Galmoy deposits, although doubt was raised over the methodologies employed (Wilkinson, 2003). Consequently uncertainty remains over the age of these deposits, and it is likely that base metal mineralisation relates to both Carboniferous basin extension and Variscan compression during the Permian (Kinnaird et al. 2002). The isochron defined by the base metal Pb data may therefore represent a common source age rather than a common mineralisation age, and if the continued evolution of the Longford Down inlier host rocks is accepted, a significant contribution of Pb originating from a deeper source region may be inferred. The model of Irish Pb evolution may only be relevant for a) mineralisation that shares the same (or comparable) source to the analysed massif sulphide deposits (hosted by the Leinster Massif and Charlestown inlier respectively) or b) mineralisation that was sourced from the Longford Down inlier metasediments.

3.5.2.4 Copper mineralisation of south-west Ireland

Lead isotope data from Irish copper mineralisation is added to the massive sulphide and Pb-Zn mineralisation data in Figure 3.9 (data from O'Keefe, 1986; Rohl, 1996; Rohl and Needham, 1998; Kinnaird et al., 2002; Kinnaird et al., 2002 citing Rohl, 1995). Carboniferous hosted copper mineralisation (light blue array Figure 3.9) plots within the Carboniferous and Palaeozoic hosted Pb-Zn array. However ORS hosted mineralisation (dark blue array, Figure 3.9) demonstrates a very different isotopic pattern that represents mixing between two lead components. Disseminated mineralisation is consistent with this trend, and Kinnaird et al. (2002) interpreted it as a mix between basement sources (represented by the Carboniferous Pb-Zn array) and a more radiogenic component presumed to be granitic derived material. Minor veinlets were isotopically more restricted and it was suggested that these represent fluid flow homogenisation of the disseminated sulphides, whilst major quartz veins demonstrate a clustered signature consistent with a basement source and minor contamination from red-beds (Kinnaird et al., 2002). Those samples consistent with the Pb-Zn array were seen to represent basement sources due to the presence of mineralisation within basement fractures located some distance from Carboniferous hosted deposits, and evidence for fluid flow in the Lower Palaeozoic basement itself. Two phases of mineralisation were postulated: Carboniferous basin extension associated c.360 to 340 Ma and Variscan compression associated c.290 to 270 Ma (Kinnaird et al., 2002).

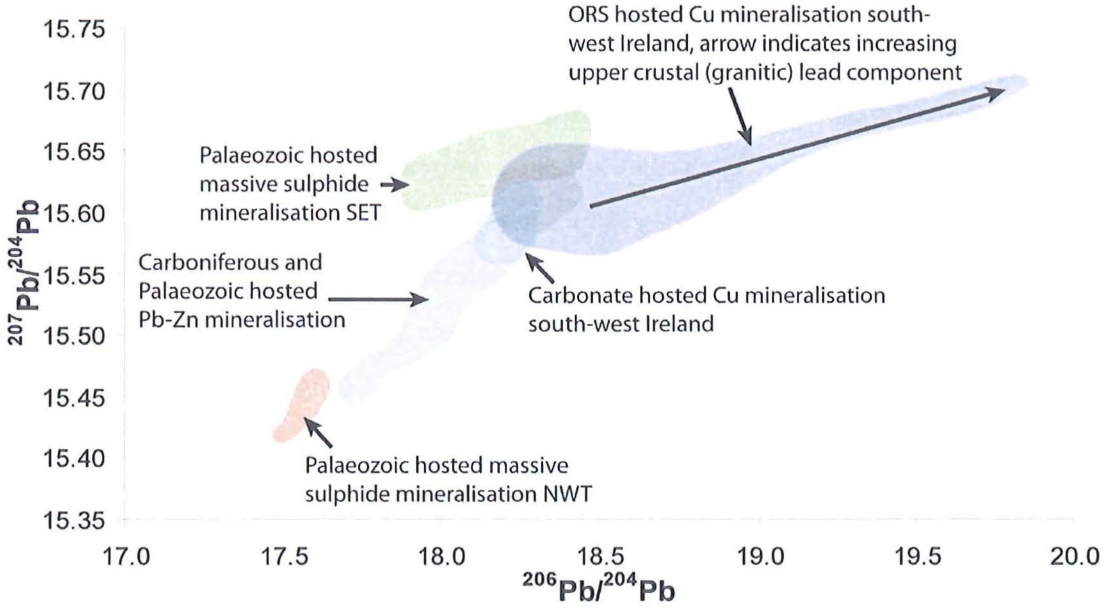


Figure 3.9: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ of Irish sulphide mineralisation, showing the data for base metal and copper deposits. Copper mineralisation Pb isotope data from O'Keefe (1986); Rohl (1996); Rohl and Needham (1998); Kinnaird et al. (2002); Kinnaird et al. (2002) citing Rohl (1995).

Everett et al. (2003) presented further evidence that linked the radiogenic component to granitic derived material within the ORS lithologies. The mineralogy of the ORS, along with the presence of igneous clasts, is consistent with a significant contribution from a granitic source, and this conclusion is supported by studies investigating ORS elsewhere in the Munster basin (Everett et al., 2003). Feldspars are particularly useful in Pb isotope analysis because they incorporate minimal U and Th into their crystal lattice. As a result, their Pb isotope composition primarily reflects the isotopic composition at the time of formation. Everett et al. (2003) used published feldspar Pb isotope data from the Leinster Massif Caledonian S-type granites (O'Keeffe, 1986) to model the present day composition of granite detritus, and these data supports the conclusion that the Caledonian granite is the primary control on the Pb isotope signature of the ORS sediments. The large isotopic variation visible in the ORS hosted copper mineralisation data results from varying degrees of input from the more radiogenic Caledonian granite-derived Pb at the time of mineralisation. Mixing with S-type granite-derived Pb is therefore a possible explanation for isotopic trends that point towards a more radiogenic value as demonstrated by the ORS hosted copper mineralisation.

3.5.2.5 A summary of Irish mineral deposit lead isotope studies

Two principle sources, distinct in their isotopic signatures, contributed to Irish mineralisation. Early Caledonian massive sulphide deposits of the NWT inherited relatively less radiogenic Pb from the mantle and/or a lower crustal source (red field, Figure 3.9), whilst Early Caledonian massive sulphide mineralisation of the SET inherited more radiogenic Pb from the upper crustal basement (green field, Figure 3.9). Early Caledonian mineralisation such as Charlestown (NWT) and Avoca (SET) therefore demonstrate significantly different isotopic signatures. These two sources were combined through mixing by the Late Caledonian (physical mixing of south-eastern and north-western derived material by the Silurian has been proposed based on sedimentological and petrological evidence, e.g. Morris, 1987; Hutton and Murphy, 1987), resulting in any mineral deposits of this age or younger inheriting Pb isotope signatures derived from both source regions. Different degrees of mixing relating to the geographic position of the mineral deposits resulted in the Pb isotope array seen in the Carboniferous and Palaeozoic hosted Pb-Zn mineralisation (grey field, Figure 3.9). Deposits hosted by ORS lithologies inherited varying degrees of upper crustal radiogenic Pb resulting in a trend towards a more radiogenic signature (dark blue field, Figure 3.9). Any mineral deposits incorporating significant components of similar upper crustal Pb are likely to follow this trend. There is also some evidence for a third, albeit minor, source region in the far north-west of Ireland that is relatively depleted in Th. Due to the lack of deposits associated with this source little else can be inferred, however it is worth highlighting its presence due to the multiple gold occurrences in this region.

3.5.3 Lead isotope analysis and archaeology

Section 3.5.1 demonstrated why the lead isotope signatures of rocks and minerals can vary. Although lead isotope analysis does not provide a unique fingerprint for every mineral deposit, variations are created if they are derived from different source regions or become isolated from their uranium and thorium bearing source at different points in geological time. Further variation can be added if the genesis of an ore deposit involves some degree of mixing between more than one lead composition, for example an involvement of more radiogenic upper crustal material. It is therefore possible to characterise ore deposits using their Pb isotope signature. Section 3.5.2 explained how the lead isotope signatures of Irish sulphide deposits vary, suggesting that characterisation of Irish gold deposits based on their Pb isotope signatures should also be possible. This is critical for archaeological provenance studies because mineral deposits need to be distinguishable from each other to some degree.

Lead isotope analysis can be performed on archaeological materials containing major or trace levels of lead. By comparing the isotopic signature of artefacts and potential ore sources, inferences about provenance can be made. Pb isotope analysis was first employed in archaeological provenance studies by Brill and Wampler (1965) and Grögler et al. (1966), who focussed on the analysis of metallic lead and glass. Since its inception, numerous investigations have continued to use lead isotope analysis in provenance studies of these two materials, along with copper and silver (e.g. Stos-Gale et al., 1995; Rohl and Needham, 1998; Northover et al., 2001; Niederschlag et al., 2003; Ponting et al., 2003). During the course of this study, the first investigation to employ lead isotope analysis to gold artefacts was also published (Bendall et al., 2009).

A key criticism of elemental provenance studies is that the preferential loss of more volatile elements during fabrication will create discrepancies between the raw material and resulting artefacts. A critical feature of Pb is that its isotope ratios do not significantly fractionate during the manufacturing process (i.e. melting, smelting, refining, cupellation), therefore the isotopic signature of an ore is inherited unaltered by the artefacts. A number of studies have demonstrated this to be the case. Barnes et al. (1978) heated galena with charcoal and produced samples of metallic lead, litharge, potassium lead silicate glass and yellow lead antimonate pigment. The isotopic signatures of all four samples were within error (±0.05%) of the galena, therefore no significant fractionation was recorded.

Lead is a volatile element, and can be lost during fabrication. Pollard and Heron (2008) noted that the amount of Pb lost during the experiments of Barnes et al. (1978) did not exceed c.5%, therefore it was still possible that fractionation could occur if greater quantities of Pb were lost. Consequently Stos-Gale and Gale (2009) reviewed a number of publications that reported no significant changes in lead isotope compositions during fabrication where large lead loss is recorded. However these publications typically did not report the isotopic data behind these conclusions. Stos-Gale and Gale (2009) therefore carried out lead isotope analysis on a series of Greek silver coins along with minerals from the Lavrion ore deposit which was linked to their production in literary sources. These coins contained 0.5% to 3% Pb yet were produced from argentiferous galena ore, therefore the amount of lead loss during production far exceeds the 5% of Barnes et al. (1978). The isotopic signatures of the coins were consistent with production from the mine in question. Providing the literary sources were accurate, the study offers further evidence to suggest no significant fractionation of lead isotopes occurs during fabrication even when large amounts of lead loss occurs.

Although fractionation is not an issue for lead isotope provenance studies, mixing and recycling are. Artefacts can be produced with raw material from more than one ore deposit, and consequently the isotopic signature of the artefact will not reflect that of a single source but will be a mix of all those involved. This is also the case if alloying with a second metal type is involved. In reality it is difficult to know how many sources contribute to an artefact's isotopic signature, therefore this is a significant drawback to the technique that has to be taken into consideration. Compositional analysis can indicate if the practice of alloying was employed, and direct evidence for the mixing of isotopic signatures allows this to be taken into account during interpretive discussions of the data. Similarly artefacts do not have to be manufactured from new metal, and the practices of complete or partial recycling must also be considered. The likelihood that an artefact's isotopic signature is the result of recycling can at least be tested if the isotopic signatures of metal pools already in circulation are characterised.

During the early 1990s a heated debate focussing on the validity of lead isotope provenance studies took place in the journals *Archaeometry* and the *Journal of Mediterranean Archaeology*. This primarily arose from inconsistencies between the interpretations of lead isotope data in some studies and the accepted archaeological consensuses, and an overview of these debates was presented by Budd et al. (1995). A number of the problems highlighted are applicable to most forms of provenance studies, including source mixing, artefact recycling, and the existence of unknown ore deposits. There were also two key issues specific to lead isotope provenance studies. The first related to the isotopic variations within and between ore deposits; variation within most proved to be greater than originally expected and as a result the isotopic signature of different sources could overlap. The second related to the use of statistics to help link artefact to source, namely multivariate analysis and discriminant function analysis. There are only three variables in lead isotope analysis, therefore Budd et al. (1995) see the use of multivariate approaches as unnecessary, whilst discriminant function analysis is also unfavoured because it assumes that all the possible ore sources have been fully characterised. The authors therefore believed statistical approaches are superfluous, and simply plotting the isotopic data in three dimensions is sufficient for interpretation. Validating interpretations with statistical analysis can be misleading because potential sources that have not been analysed or have not been fully characterised results in inaccurate statistical outputs. Consequently no statistical analysis will be performed in this study unless clearly defined ore deposits can be fully characterised. Despite the limitations discussed, Budd et al. (1995) did conclude that lead isotope analysis is a useful technique relevant to archaeology. It was the interpretation of the data, not the data itself that caused the lead isotope debate, and if the true complexity of lead isotopes, ore deposits and metal circulation are taken into account then the technique can be of use (Budd et al., 1995).

3.6 Project Aims

Bronze Age society was one of increasing complexity. It witnessed a shift from small family based agricultural communities living in dispersed hamlets or farmsteds, to societies characterised by settlement organisation, increased social stratification and greater specialisation. This pattern is mirrored in the deployment of exotics and metalwork, with the consumption of materials such as amber and jet increasing significantly alongside the exploitation of new materials such as gold. Crucial in discerning the role that exotic materials played in these increasingly complex societies is an understanding of their procurement and control.

A significant proportion of Chalcolithic and Bronze Age goldwork has been found in Ireland, whilst the vast number of native gold deposits in the country means that the exploitation of local sources is reasonable. Recent compositional and microchemical characterisation studies have highlighted the Mourne Mountains of Co. Down as the most probable Irish source of EBA gold (Warner et al., 2009, 2010a, 2010b), however it is unclear if these deposits could account for the quantity of gold in circulation during this period (Meighan, 2011). The application of a method for provenancing gold independent from element compositional analysis is therefore desired. Lead isotope analysis has been successfully employed in a number of archaeological provenance studies that investigated the source of metallic artefacts. Consequently the principle objective of this project was to provenance a series of Irish Chalcolithic and Bronze Age gold artefacts using lead isotope analysis. In order to achieve this objective, the following project aims were devised:

- Develop solution and laser ablation inductively-coupled plasma mass-spectrometry techniques that can analyse the lead isotope signature of gold.
- Characterise the lead isotope signatures of potential Irish gold sources.
- Characterise the lead isotope signatures of a set of Irish Chalcolithic and Bronze Age gold artefacts.

Completing these three key aims will enable a discussion on the sources of Irish Bronze Age gold, including the number of gold sources that were exploited, where they were located, and how this changed over time. Understanding the patterns of gold procurement will allow further questions to be addressed. Does the distribution of gold sources demonstrate patterns of long distance movement? Is this consistent with the deployment of other exotic materials during the Chalcolithic and Bronze Age, and can the value of gold be attributed to notions of exoticness, economic wealth or an additional reason? Are the patterns of gold exploitation indicative of centralised/controlled procurement and/or distribution, or could gold be procured in an *ad hoc* fashion from numerous locations whenever required? What were the reasons behind a) any changes in the source of gold, and b) any changes in the deployment of gold? These new insights will help to explain the role that gold played in Bronze Age society, and how the deployment of this material related to the new social structures that formed at this time.

Chapter 4: Analytical Techniques

4.1 Synopsis

Lead isotope analysis has been employed to investigate the source of Irish Chalcolithic and Bronze Age gold. When this project commenced, methodologies for this analytical technique did not exist. Eugaster et al. (1995) had performed lead isotope analysis on alluvial and vein gold, however detailed information regarding methodologies were not published. Solution and laser ablation lead isotope analysis of gold was later presented by Bendall et al. (2009) who demonstrated that the two techniques were in agreement, and quantified the reproducibility of the laser ablation methodology. However the authors did not discuss the accuracy and reproducibility of the solution methodology, including ion exchange chromatography, and no ^{204}Pb data were presented for the laser ablation analyses due to the isobaric interference of ^{204}Hg.

As a result, the first aim of this project was to develop both solution and laser ablation MC-ICP-MS (multi-collector inductively-coupled plasma mass-spectrometry) Pb isotope methodologies, and prove both their accuracy and reproducibility. Development was carried out on two gold reference materials; RAuGP3 and RAuGP5 (SPEX CertiPrep Ltd) with 34.1 ± 0.5 ppm Pb and 129 ± 4 ppm Pb respectively (certified concentrations, 2 standard deviation (S.D.) errors). Solution analysis requires ion exchange chromatography, therefore a two stage methodology similar to Bendall et al. (2009) was devised. Repeat analyses of RAuGP3 and RAuGP5 yielded an external precision of <150 ppm for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb and <250 ppm for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb. Laser ablation analyses yielded external precision of <600 ppm for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb, however due to the low abundance of ^{204}Pb and the isobaric interference of mercury on this mass the external precision for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb was significantly lower at <1640 ppm when ^{204}(Pb+Hg)/^{202}Hg is >1. Critically the techniques agree within error and therefore both can be employed in the same study. These methodologies have been published in Standish et al. (2013).

Section 4.2 outlines the solution MC-ICP-MS techniques, including the two stage ion exchange chromatography methodology. Section 4.2 details the laser ablation MC-ICP-MS techniques and demonstrates that the solution and laser ablation methodologies are directly comparable. Major element compositional analysis was also performed on the artefact samples using an electron probe microanalyser (EPMA), whilst mineral inclusions within the artefact samples were characterised using a scanning electron microscope (SEM). These two techniques are outlined in sections 4.4 and 4.5 respectively. Section 4.6 briefly discusses the presentation of errors.

4.2 Solution Mass Spectrometry

4.2.1 Reagents and Labware

The following reagents were used during analytical work:

- Fisher Scientific analytical grade HNO_3.
- Romil SpA HNO_3.
- Romil UpA HBr.
- VWR AnalaR NORMAPUR HCl.

Ion exchange chromatography and sample dissolution was carried out using Romil UpA HBr, Romil SpA HNO_3, and twice distilled AnalaR HCl unless otherwise stated. Labware cleaning procedures employed analytical grade HNO_3 and undistilled AnalaR HCl. Table 4.1 presents typical Pb blanks for these reagents (and 18.2 MΩ-cm water; henceforth referred to as ultrapure water).

Table 4.1: Typical Pb blanks for reagents employed during ion exchange chromatography.

Reagent	Pb Blank (pg/ml)
0.4 M HBr from Romil	19.85
Concentrated twice distilled AnalaR HCl	13.91
Concentrated Romil HNO_3	63.45
Ultrapure water	10.24

Acid was stored in nalgene bottles, cleaned using the following procedure. Bottles were fluxed with 7 M HNO_3 for ≥2 days including two hours on a hotplate at 80°C, emptied and rinsed three times with ultrapure water, fluxed with 6 M HCl for ≥2 days including two hours on a hotplate at 80°C, emptied and rinsed three times in ultrapure water.

Samples were processed in 7 ml Teflon vials. Before use, the vials were cleaned using the following procedure. Each vial was individually filled half full with 6 M HCl and fluxed on a hotplate at 130°C for ≥1 hour, emptied and rinsed inside and out three times with ultrapure water, then placed in a large one litre Teflon beaker with lids unattached and fluxed in 7 M HNO_3 for ≥2 days at 130°C. The acid was decanted and the vials rinsed three times with ultrapure water before being fluxed in dilute HNO_3 (2-4 ml of concentrated Romil HNO_3 in one litre of ultrapure water) for ≥1 day. They were then rinsed three times in ultrapure water and stored ready for use. Immediately before samples were placed inside, a final cleaning stage consisted of individually filling each vial half-full with 6 M HCl and fluxing on a hotplate at 130°C for ≥30 minutes before being rinsed four times with ultrapure water.

During the analytical procedures, 1000 μl pipette tips, 200 μl pipette tips and 2 ml centrifuge tubes were also used. These were all cleaned by fluxing in a beaker filled with 6 M HCl for ≥1 week, then rinsing three times in ultrapure water.

Ion exchange columns of 80 μl or 50 μl volume and AG1-X8 resin, a strongly basic anion exchange resin (Bio-Rad), were used for ion exchange chromatography. The AG1-X8 resin had a mesh size of 100-200, which equates to particle diameters of 150 μm to 75 μm. Before use, the resin was cleaned in a nalgene bottle by repeatedly cycling ten times in 6 M HCl then ten times in ultrapure water. Resin was stored in ultrapure water.

The ion exchange columns were made by heat shrinking 9.5 mm diameter Teflon tubing (Shrinktek) onto stainless steal moulds using a heat gun. The diameter of the column reservoir remains at 9.5 mm, while the column itself shrinks approximately by a factor of 4 to a maximum diameter of 2.44 mm. Columns were cleaned by first submerging them in acetone for one hour before being rinsed with ultrapure water three times. They were then fluxed in 7 M HNO_3 on a hotplate at 80°C overnight and off the hotplate for a further two days. The frits were bored from porous polyethylene and once inserted into the columns to produce the required volume, the columns were again cleaned by fluxing in 6 M HCl followed by 7 M HNO_3 for at least two days per stage. Columns were cleaned and stored between uses in 6 M HCl.

4.2.2 Concentration Analysis

Element concentration analysis was required for calibrating the ion exchange chromatography methodology and to determine the Pb concentration of procedural blanks. Analysis was performed on a Thermo Fisher Scientific Element 2; a high resolution, single-collector, fast scanning magnetic-sector inductively-coupled plasma mass-spectrometer. Samples were introduced in solutions of 2% HNO_3 unless otherwise stated. The Element 2 detects ions using a secondary electron multiplier, which produces a signal in counts per second (cps) proportional to the concentration of the element under analysis. Typical operating conditions are summarised in Table 4.2. Take up times per analysis were 75 seconds, whilst preceding wash times (that clean the system of the previous analysis) were 120 seconds.

Table 4.2: Typical operating conditions for the Element 2.

Instrument	Thermo Fisher Scientific Element fast scanning magnetic-sector ICP-MS
RF Power	1356 W
High Vacuum	1.56×10^{-7} mbar
Cones	Nickel Skimmer (H) and Platinum Sample
Argon Gas Flows	
Cool Gas	15.84 l/min^{-1}
Auxiliary Gas	0.83 l/min^{-1}
Sample Gas	1.069 l/min^{-1}
Sample Introduction	Glass spray chamber
Nebuliser tip	Elemental Scientific PFA Microflow, ~50 ul min^{-1}

Lead concentration analysis provided quantified data and was carried out in low resolution mode. Blocks of six samples, all spiked with 5 ppb Tl (CPI International single element standard solution) and diluted to roughly 1 ppb Pb, were preceded by three Pb standards (NIST SRM981) at concentrations of 0.1 ppb, 1 ppb and 10 ppb respectively. Linear regression of these standards allowed the conversion of sample Pb signals (cps) into concentrations (ppb):

$$\mathrm{Pb_{ppb}} = \left(\mathrm{Pb_{cps}} - \mathrm{intercept}\right)/\mathrm{slope} \tag{4.1}$$

The calculated concentrations were then corrected for their dilution factors and converted to ppm:

$$\mathrm{Undiluted\ Pb_{ppm}} = \left(\mathrm{diluted\ Pb_{ppb}} \bullet \mathrm{dilution\ factor}\right)/1000 \tag{4.2}$$

An internal correction (to account for matrix effects and instrumental drift) was applied using the Tl spike by multiplying the Pb concentration by a correction factor. Correction factors were calculated for each individual sample by dividing the expected 5 ppb Tl cps by the measured 5 ppb Tl cps. The expected 5 ppb Tl cps was calculated by first using the slope and intercept of the three Pb standards on mass 206 to calculate the total measured cps per ppb Pb:

$$\text{cps per ppb total Pb}_{\text{measured}} = \left(\left({}^{206}\text{Pb}_{\text{slope}} + {}^{206}\text{Pb}_{\text{intercept}}\right) \bullet 100\right) / {}^{206}\text{Pb}_{\text{abundance\%}} \qquad (4.3)$$

then by correcting for the abundance of ^{205}Tl to calculate the expected cps per 5 ppb ^{205}Tl:

$$\text{cps per 5 ppb } {}^{205}\text{Tl}_{\text{expected}} = \left(\left(\text{cps per ppb total Pb}_{\text{measured}} \bullet {}^{205}\text{Tl}_{\text{abundance\%}}\right) / 100\right) \bullet 5 \qquad (4.4)$$

When calibrating ion exchange chromatography it was necessary to collect data to characterise the behaviour of the sample matrix. Concentration data for these elements were unquantified; data outputs in cps acted as a guide to which elements were present in a particular sample. The following corrections were applied to the signal: a blank correction ($\text{cps}_{\text{sample}} - \text{cps}_{\text{blank}}$); a dilution correction ($\text{cps}_{\text{sample}} \bullet$ dilution factor); and an isotopic abundance correction ($\text{cps}_{\text{sample}}/\text{isotope}_{\text{abundance\%}} \bullet 100$). The signals of different elements were then directly comparable. Masses were analysed in low, medium or high resolution depending on the element in question.

4.2.3 Lead Isotope Analysis

4.2.3.1 Operational details

In the past, Pb isotope analysis was typically performed using thermal ionisation mass-spectrometry (TIMS, e.g. Gale and Stos-Gale, 1981, 2000; Woodhead et al., 1995; Powell et al., 1998), where overall reproducibility was typically 1000 ppm (2 S.D.) on all ratios (Woodhead, 2002; Baker et al., 2006). Multi-collector inductively-coupled plasma mass-spectrometers (MC-ICP-MS) have since become the mass spectrometer of choice because they demonstrate improved accuracy and precision over TIMS, and they are faster and more cost effective to run (Niederschlag et al., 2003; Baker et al., 2006).

For this study, solution Pb isotope analysis was performed on a Thermo Fisher Scientific Neptune mass-spectrometer; a high resolution multi-collector inductively-coupled plasma mass-spectrometer. Samples were introduced in 2% HNO_3 using a Cetac Aridus desolvating nebuliser with PFA spray chamber after Pb fractions were isolated from samples through column chromatography. Typical operating conditions are summarised in Table 4.3 (and Standish et al., 2013).

Table 4.3: Typical operating conditions for solution MC-ICP-MS Pb isotope analysis.

Instrument	Thermo Fisher Scientific Neptune MC-ICP-MS
RF Power	1200 W
Cones	Nickel skimmer (X) and nickel sample
Argon Gas Flows	
Cool gas	15 l min^{-1}
Auxiliary gas	0.7-0.8 l min^{-1}
Sample gas	0.78 l min^{-1}
Sample Introduction	Cetac Aridus desolvating nebuliser
Nebuliser tip	Elemental Scientific PFA Microflow, ~50 ul min^{-1}
Argon sweep gas	c.5 l min^{-1}
Nitrogen	c.4 ml min^{-1}

Ion detection employed nine Faraday cup detectors; the cup configuration used is presented in Table 4.4 (and Standish et al., 2013). Prior to every session, 'gain' and 'baseline' calibrations were performed to calibrate the faraday cup resistors and calculate the background electronic signal respectively.

Table 4.4: Faraday cup configuration employed during solution MC-ICP-MS Pb isotope analysis.

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass	-	202	203	204	205	206	207	208	-

Tuning to optimum conditions was performed using NIST SRM981, a Pb isotope standard solution. An example of a typical solution peak centre on mass 208 is presented in Figure 4.1, and an example of a typical solution peak scan on all masses is shown in Figure 4.2. A peak centre was automatically performed every third NIST SRM981 standard throughout an analyses sequence.

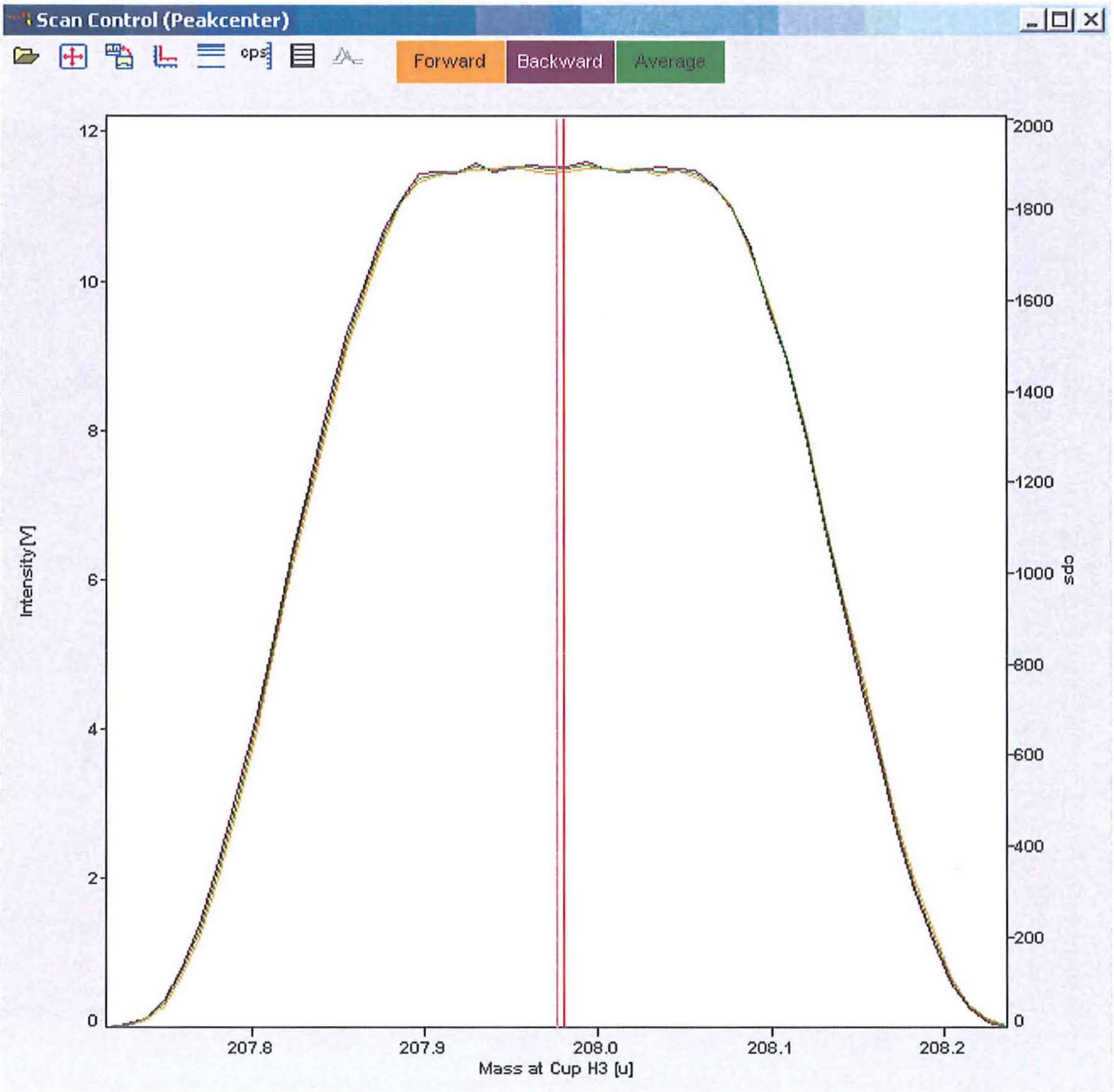


Figure 4.1: Example of a typical solution peak centre of mass 208 on cup H3 after tuning with NIST SRM981.

Samples and standards were analysed at 20 ppb concentrations providing a typical signal intensity of 9 to 10 volts on mass 208. When low Pb restricted analysis to below 20 ppb, standards were diluted to match the concentrations of the samples.

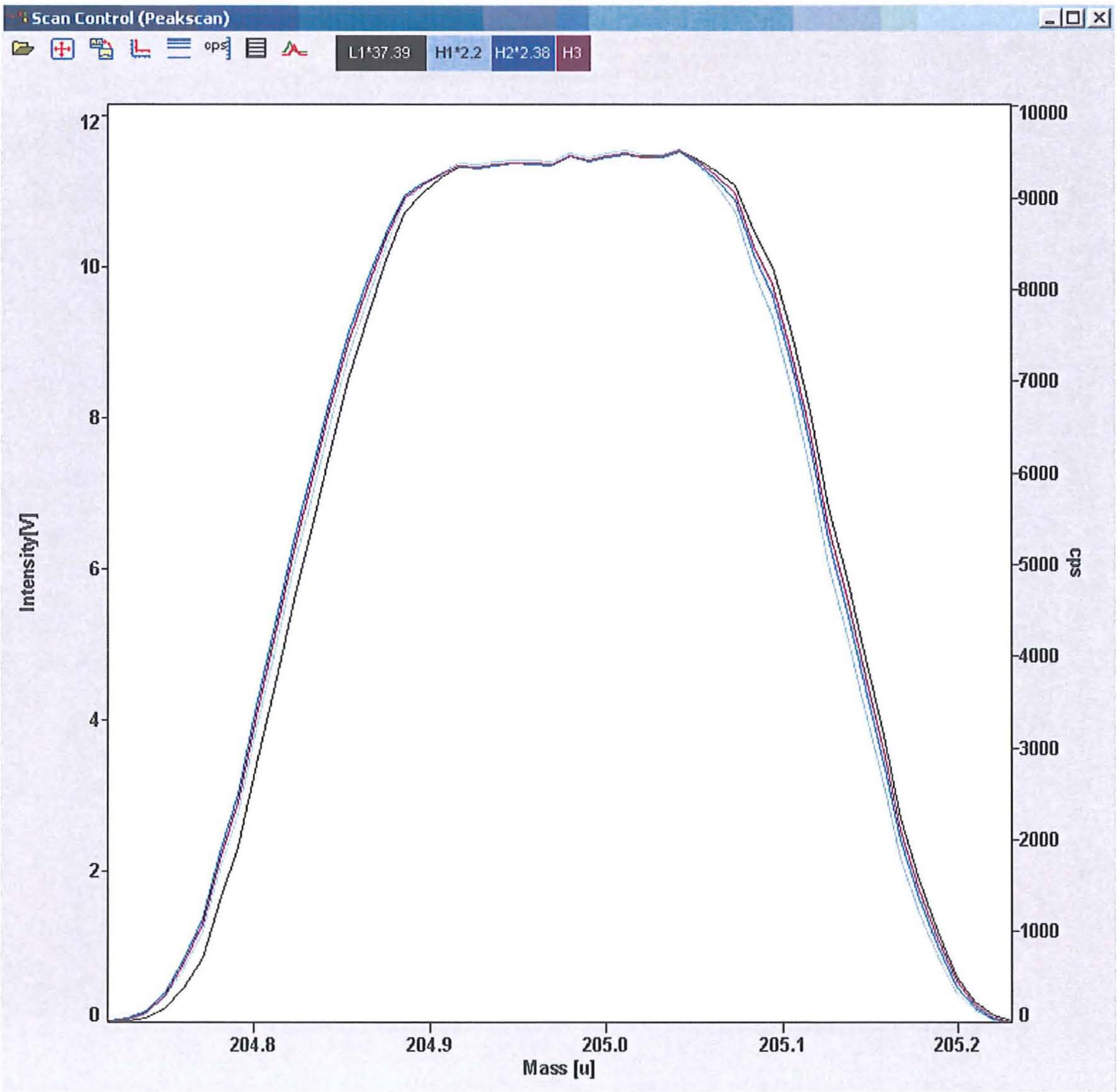


Figure 4.2: Example of a typical solution peak scan after tuning with NIST SRM981.

Samples were analysed using the standard sample bracketing technique. An analysis sequence consisted of alternating NIST SRM981 with samples of unknown isotopic composition. Samples were analysed in pairs with a machine blank (2% HNO_3) in place of every third sample to allow the monitoring of background intensities. A typical block therefore consisted of blank, standard, sample, standard, sample, standard. This was repeated throughout the sequence, whilst a 'wash out' using 2% HNO_3 was automatically performed before each analysis to remove any analyte remaining from the preceding analysis. NIST SRM982 was analysed throughout the sequence as a secondary standard. Its data were reduced in the same way as an unknown sample to act as a consistency standard and a control on the data reduction methods employed. Two gold reference materials, RAuGP3 (34.1 ± 0.5 ppm Pb) and RAuGP5 (129 ± 4 ppm Pb) from SPEX CertiPrep Ltd. were also run with every sequence as a further consistency guide. These were processed through ion exchange chromatography and thus acted as a guide to the reproducibility of the whole analytical procedure.

Each individual sample, standard or blank processed was analysed over five blocks of ten cycles (one cycle equalling 4.2 seconds of integration). The isotopic ratio quoted is the mean of these five blocks after the exclusion of any cycle greater than three standard deviations from the mean. Typical internal precisions (two relative standard errors (S.E.) of the mean of the 50 cycles comprising one analysis) for 20 ppb solutions were <50 ppm for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, and <20 ppm for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb (Standish et al., 2013).

The averaged data for each sample was reduced offline by applying a series of corrections: a blank correction, a Hg correction, and finally a mass bias correction. Blank corrections were applied by subtracting the voltage of a particular isotopic mass in the preceding blank from the voltage of said mass in the sample or standard in question. A Hg correction was applied on mass 204 due to the isobaric interference of ^{204}Hg. The intensity of ^{204}Hg was calculated and subtracted from the total measured intensity at mass 204, henceforth referred to as ^{204}(Pb+Hg). The ^{204}Hg/^{202}Hg$_{\text{measured}}$ was first calculated for bracketing NIST SRM981 analyses using the following equation:

$$\left[\frac{^{204}\text{Hg}}{^{202}\text{Hg}}\right]_{\text{measured}} = \left[\frac{^{204}\text{Hg}}{^{202}\text{Hg}}\right]_{\text{true}} \bullet \left(\frac{\left[\frac{^{208}\text{Pb}}{^{206}\text{Pb}}\right]_{\text{measured}}}{\left[\frac{^{208}\text{Pb}}{^{206}\text{Pb}}\right]_{\text{true}}}\right)^{\left(\frac{\ell n\left(m_{204\text{Hg}}/m_{202\text{Hg}}\right)}{\ell n\left(m_{208\text{Pb}}/m_{206\text{Pb}}\right)}\right)} \tag{4.5}$$

where m denotes atomic mass, [^{204}Hg/^{202}Hg]$_{\text{true}}$ = 0.230074, and ^{208}Pb/^{206}Pb$_{\text{true}}$ is the value published in Baker et al. (2004), see Table 4.5. The ^{204}Hg intensity could then be calculated by multiplying [^{204}Hg/^{202}Hg]$_{\text{measured}}$ by the measured ^{202}Hg intensity. For unknown samples, the mass bias of [^{204}Hg/^{202}Hg]$_{\text{true}}$ was calculated using the means of the two bracketing NIST SRM981 analyses (Standish et al., 2013).

Table 4.5: NIST SRM981 isotopic ratios used as 'true' values in this study. As presented in Baker et al. (2004), these values represent the average of all MC-ICP-MS double spiked analyses from Baker et al. (2004) and Thirlwall (2002).

^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
16.9416	15.4998	36.7249	0.91489	2.16775

4.2.3.2 Mass bias correction and external precision

One of the main constraints on the quality of isotopic data is the need to accurately correct for instrumental mass bias. MC-ICP-MS mass bias, typically at a level of 1% per amu, is thought to be a product of 'space-charge' effects in the ICP-MS interface (Woodhead, 2002). Lighter ions migrate away from the centre of the plasma, and consequently are focussed less efficiently into the mass analyser (White et al., 2000). The most common method used to correct for mass bias effects in mass spectrometry is internal normalisation. However with respect to Pb, this is not possible because it requires an isotopic ratio of the element in question with a known and constant value. As a result, mass bias corrections of Pb isotope analysis typically employs one of three methods: Tl doping (e.g. Walder and Furuta, 1993; Hirata, 1996; Woodhead, 2002), double spiking (e.g. Thirlwall, 2002; Baker et al., 2004), or sample standard bracketing (e.g. Belshaw et al., 1998). Woodhead (2002) achieved external precision of <173 ppm for ^{206}Pb/^{204}Pb, <312 ppm for ^{207}Pb/^{204}Pb and <520 ppm for ^{208}Pb/^{204}Pb (2σ, two year period) on a range of sample types (NIST SRM981 pure Pb solution, NIST SRM 610 silica rich glass, and USGS BCR-1 basaltic reference material) by employing the Tl doping technique. Superior external precision has been achieved with the double spiking method; Thirlwall (2002) generated precision of 87 ppm-245 ppm on the ^{208}Pb/^{204}Pb ratio by employing a ^{208}Pb/^{204}Pb spike, whilst Baker et al. (2004) generated precision of <102 ppm on all ratios after employing a ^{207}Pb/^{204}Pb spike.

Double spiking requires the careful mixing of a solution containing two isotopes of the element in question, and the accurate determination of their isotopic ratio. In simple terms, the difference between the known isotopic ratio of the spike and the analysed ratio then allows for a mass bias correction. This technique clearly offers the best precision for Pb isotope analysis, however it requires each sample to be run twice; once spiked and once unspiked. Due to the small sizes of the samples processed as part of this study, and their variable and often very low Pb content, many will only contain enough Pb to run once. Consequently, standard-sample bracketing was employed because this method is time efficient, entails little set up, and does not require the sample to be analysed more than once. Every sample was preceded and followed by a Pb standard of similar concentration and with a known isotopic composition. The average offset of the bracketing standards from the measured value to the true is then used to correct the sample for mass bias:

$$S_t = S_m B_t / ((B1_m + B2_m)/2) \qquad (4.6)$$

where S = sample, B = bracket (NIST SRM981), $_t$ = true (values published in Baker et al., 2004, see Table 4.5), $_m$ = measured. This method does assume that the degree of mass bias is the same in the standards and the unknown samples, however the external precision or reproducibility (expressed as two relative standard deviations of the mean) for repeat analyses of NIST SRM982 is comparable to that of the Tl doping method and only slightly lower than double spiking: ^{206}Pb/^{204}Pb = 218 ppm, ^{207}Pb/^{204}Pb = 197 ppm, ^{208}Pb/^{204}Pb = 233 ppm (n = 131, 18 month period). Within session external precision was typically <130 ppm for ^{206}Pb/^{204}Pb, <160 ppm for ^{207}Pb/^{204}Pb, and <215 ppm for ^{208}Pb/^{204}Pb. Changes in the mass bias between the bracketing standards and the sample can therefore be considered insignificant. Accuracy is also comparable to that of literature data; analyses of NIST SRM982 are within error of published values in Doucelance and Manhès (2001), Thirlwall (2002) and Baker et al. (2004).

Table 4.6 and Figure 4.3 and Figure 4.4 summarise published values of NIST SRM982 along with the mean value from this study, highlighting the accuracy and precision achieved. The data define linear trends, however these are not solely a function of mass bias and other factors may in part be responsible.

Table 4.6: Mean NIST SRM982 Pb isotope composition from published sources and this study. Errors are ±2 S.D. in the last decimal place. Note that values in italics are not quoted in the original publications and have been calculated using the ratios provided to allow comparison with this study.

NIST SRM982	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb	n
This Study	36.7480±48	17.1648±26	36.7545±66	0.467092±23	1.00018±8	131
Baker et al. (2004)	36.7432±17	*17.1622*	*36.7491*	0.467084±17	1.00016	7
Doucelance and Manhès (2001)	36.7485±27	*17.1645*	*36.7496*	0.467080±10	1.00016	5
Thirlwall (2002)	36.7437±68	*17.1625*	*36.7544*	0.467087±12	1.00016	7
Todt et al. (1996)	36.7498±27	*17.1630*	*36.7557*	0.467023±19	1.00016	11

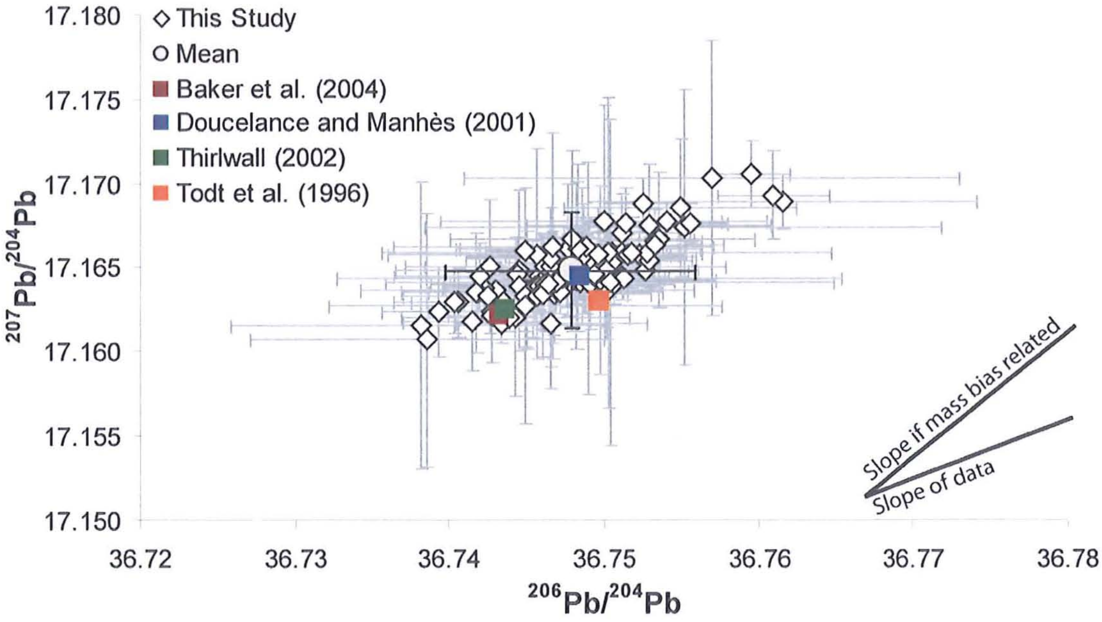


Figure 4.3: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb compilation plot of 131 analyses of NIST SRM982 ±2 S.E. of the mean of 50 integration cycles (light grey error bars). The mean value for this study ±2 S.D. (black error bars) and mean values (without errors) for selected literature publications are also presented.

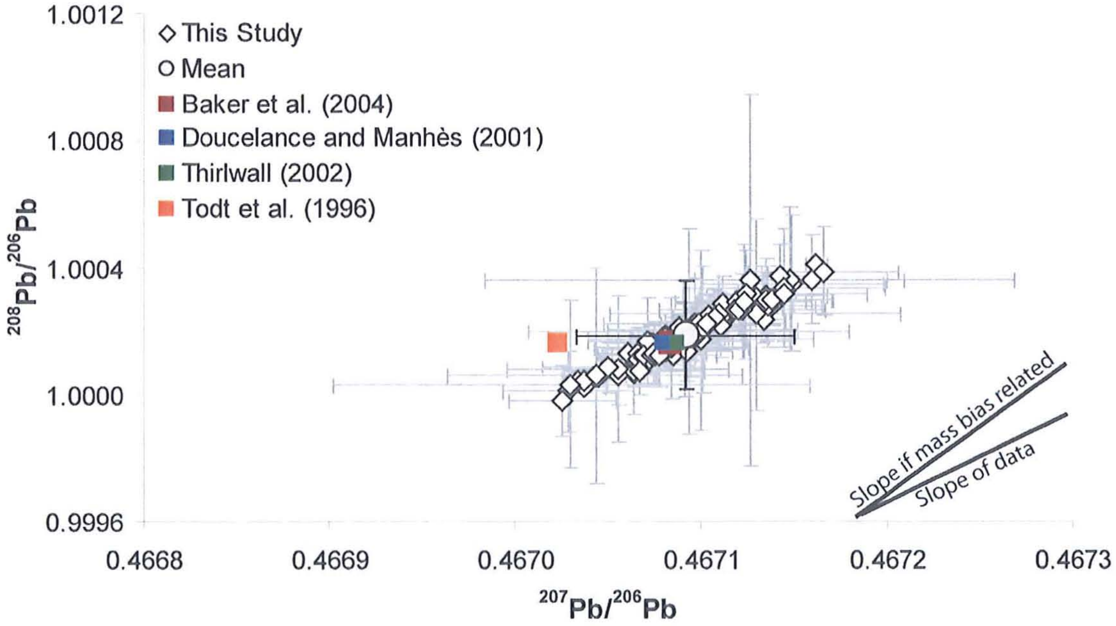


Figure 4.4: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb compilation plot of 131 analyses of NIST SRM982 ±2 S.E. of the mean of 50 integration cycles (light grey error bars). The mean value for this study ±2 S.D. (black error bars) and mean values (without errors) for selected literature publications are also presented.

4.2.3.3 Ion exchange chromatography: separation of lead from a gold and silver rich matrix

Method development

Numerous methods have been developed for the separation of Pb from geological materials using ion exchange resins. AG1-X8 (Bio-Rad), a strongly basic anion exchange resin, has long been employed to isolate Pb from a range of matrices (Korkisch and Hazan, 1965; Strelow and Toerien, 1966; Strelow, 1978; Manton, 1988), while methods using the ion exchange resins Sr.Spec^{TM} (Horwitz et al., 1992; Gale, 1996; Vajda et al., 1997) and Pb.Spec^{TM} (Horwitz et al., 1994) have also been developed (Eichrom). Pb.Spec^{TM} resin was developed from Sr.Spec^{TM} after the latter was found to have strong retention of Pb as well as the intended Sr (Horwitz et al., 1994). However for this study Sr.Spec^{TM} was preferred because the extreme retentivity for Pb on Pb.Spec^{TM} means consistently achieving low chemistry blanks can be difficult, and some elements such as Bi tend to remain with Pb throughout the whole procedure (Gale, 1996). Consequently both AG1-X8 and Sr.Spec^{TM} were explored during the development of an ion exchange chromatography methodology for the separation of Pb from a gold and silver rich matrix.

Method development was undertaken using fine gold reference materials RAuGP3 (34.1 ± 0.5 ppm Pb) and RAuGP5 (129 ± 4 ppm Pb) from SPEX CertiPrep Ltd. Two-hundred milligram globules were dissolved in *aqua regia* (three parts HCl to one part HNO_3), dried down, then re-dissolved and stored in 2 M HCl. Five milligram aliquots were doped with AAS specpure 1000 µg/ml Ag standard solution (Alfa Aesar) to reflect Ag concentrations of 5%, 10% and 20%; concentrations typical of naturally occurring gold alloys (Chapman et al. 2000a, 2000b, 2006), thus producing a matrix matched reference material (Standish et al., 2013).

Three key problems were encountered during method development. The first relates to the insolubility of the AgCl residue which first forms when Ag rich samples are dissolved in *aqua regia*: $Ag^+ + Cl^- = AgCl$ (Scott, 1983). Dissolution is possible in 6 M HCl; higher molarities allow the formation of the complex anion $(AgCl_4)^{3-}$: $AgCl + 3Cl^- = (AgCl_4)^{3-}$ (Scott, 1983). However Pb will not load onto either of the ion exchange resins investigated when introduced in this acid, therefore separation is unsuccessful. The second is that classic HBr methods of Pb separation can not be used due to the formation of a Au precipitate throughout the column length and reservoir. This results in reduced Pb yields and potential fractionation of the Pb isotope ratios. The final problem is that if a sample is successfully loaded onto Sr.Spec^{TM} in a more dilute HCl or HNO_3 acid after the physical separation of AgCl residue, then Pb can not be separated from Au unless large volumes of acid are passed through the columns. This is undesirable due to the resulting increase in the Pb blank and decrease in time efficiency.

Single stage ion exchange chromatography techniques are unable to separate high yields of lead from a gold and silver rich matrix using minimal quantities of acids. Therefore a two stage column chromatographic methodology similar to Bendall et al. (2009) was developed. An initial column separates the gold from the remaining sample, allowing classic HBr methods to be employed to isolate the lead from the remaining matrix in the second. Silver was physically removed in the form of AgCl residue.

Column 1: separation of lead from a gold rich matrix

The first column (80 μl volume) employs AG1-X8 resin in the chloride form, and samples are loaded in 6 M HCl at volumes of 0.5 to 2 ml so that complete dissolution is achieved (including the silver component). The volume of loading acid required is dependant on silver content rather than sample mass. The distribution coefficient (K_D) of Au in 6 M HCl is c.3500 (Marhol, 1982), therefore it is strongly retained on the resin. In contrast, the K_D of Pb is <10 (Marhol, 1982) and only small quantities are retained on the resin. The loading volume of acid is collected, and this elutes c.67% of the Pb. By passing two further aliquots of 400 μl 6 M HCl, a total Pb yield of 95% can be achieved (Figure 4.5). Further elution of the Pb tail was deemed unnecessary due to the low recovery rate.

Natural gold typically contains a significant silver content, and in Ireland this ranges from c.0.5% to c.20% (Chapman et al. 2000a, 2000b, 2006). Other elements that can make up significant components of natural gold are copper, tin, mercury and palladium, all of which can be as high as a few percent depending on the mineralisation style. As silver will be physically separated, it was these elements that had to be isolated during ion exchange chromatography. All but mercury were quoted as being present in the gold reference materials used to develop this column methodology at either c.130 ppm (RAuGP5) or c.30 ppm (RAuGP3). Mercury was known to be present at similar concentrations based on analysis by laser ablation, therefore it has been possible to determine the behaviour of all these elements. Mercury is not eluted in the lead fraction, while only background levels of Cu, Sn and Pd were present. Arsenic, Cr, Se and Na, along with small amounts of Au, were eluted in the Pb fraction (Figure 4.6).

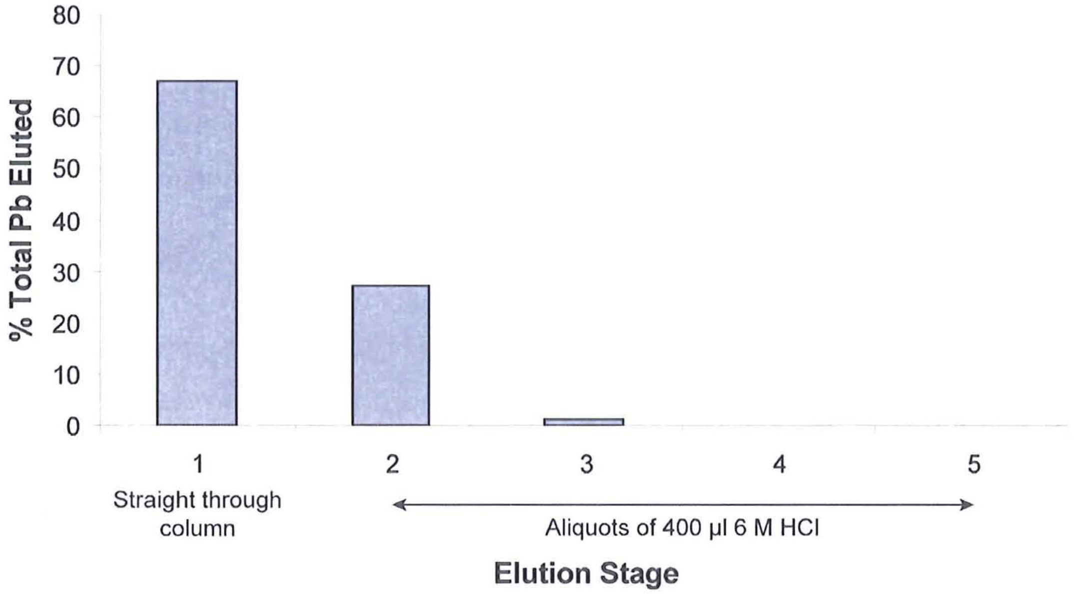


Figure 4.5: Column 1 % total Pb eluted versus elution stage.

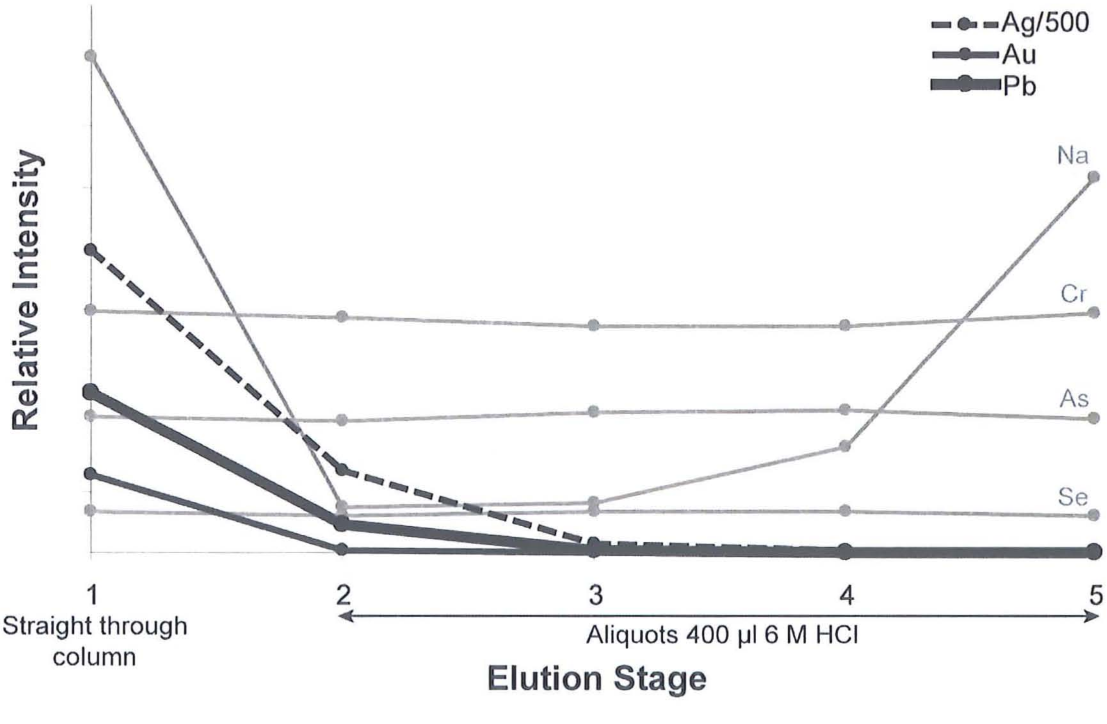


Figure 4.6: Column 1 relative signal intensity for selected elements versus elution stage.

Removal of silver as a silver chloride residue

As discussed, silver is a significant component of most natural gold alloys. On dissolution in *aqua regia* a residue of AgCl forms which can be dissolved in 6 M HCl for loading onto column 1. However at this molarity, Ag has a similarly low K_D to that of Pb (<10; Marhol, 1982), and thus the majority elutes through the column with the Pb fraction. The AgCl residue precipitates out when the sample is dried down and will not re-dissolve in 0.4 M HBr for loading onto the second column. Consequently Ag was physically separated from the samples as a AgCl residue.

The first column stage required sample loading in 6 M HCl, therefore separation would be performed after the samples were processed through this column stage. The same volume of HCl could then be used to achieve both total sample dissolution of the AgCl residue and column loading, thus helping to keep the Pb blank as low as possible. As the column 1 Pb fractions were dried down, AgCl precipitated out. The samples could then be re-dissolved in an acid where AgCl is insoluble; 500 µl of 7 M HNO_3. This was fluxed on a hot plate for 30 minutes to allow dissolution of soluble elements before the samples were transferred into centrifuge tubes and centrifuged for 10 minutes at 13400 rpm. The supernatant was pipetted back into the sample vial along with one ultrapure water wash of the residue; the AgCl residue remained in the centrifuge tubes. The samples were now free of the majority of the Ag, and could be dried down and complexed with HBr for loading onto column 2.

Regarding the removal of the AgCl residue, two key questions needed to be addressed. The first was to determine if the formation of the residue incorporated significant quantities of Pb. If it did, then the second was to see if the loss of this element caused significant fractionation of the Pb isotope ratios. In order to test this, three samples of the gold reference material RAuGP5 were each spiked with silver to 5%, 10%, and 20% of the total sample mass (5 mg) respectively (Alfa Aesar AAS spec-pure Ag standard solution). These were processed through the ion exchange chromatography currently being outlined, and Ag was separated using the method outlined above. The AgCl residues were then analysed for their Pb concentration, and the sample Pb fractions were analysed for their Pb isotope composition.

The Pb concentrations of the residues were analysed as set out in section 4.2.2, however they were analysed in 6 M HCl rather than the usual 2% HNO_3 to enable dissolution of the AgCl residues. The standards were also run in 6 M HCl thus their analysing conditions matched those of the samples. The silver chloride residues incorporated quantities of Pb directly proportional to the Ag content of the samples (Figure 4.7). The average Pb yields of the AgCl residues were 3% of the total Pb for 5% Ag, 6% of the total Pb for 10% Ag, and 10% of the total Pb for 20% Ag.

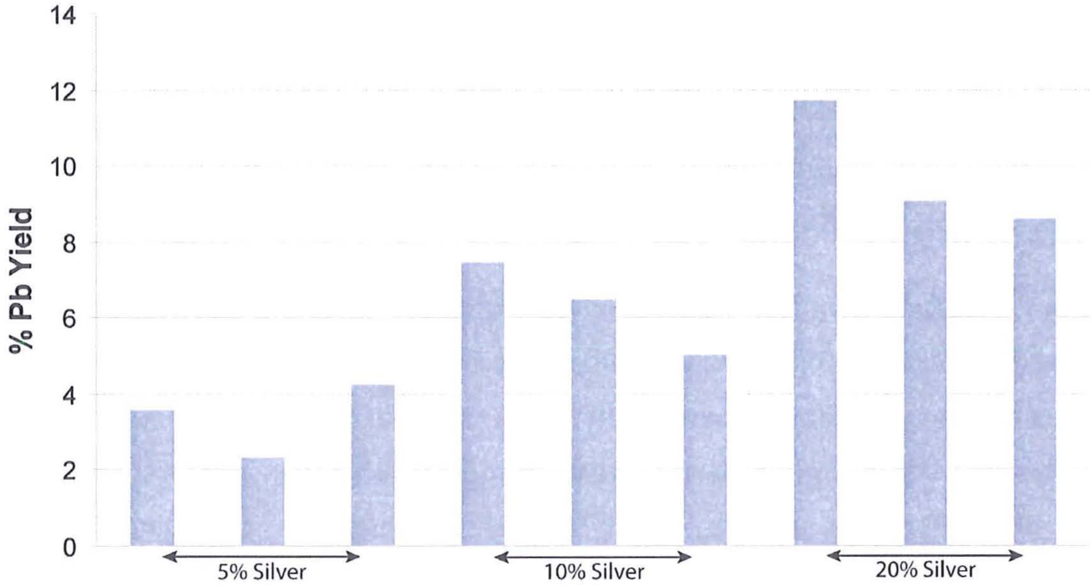


Figure 4.7:% total sample Pb incorporated into AgCl residues.

It was therefore important to check if this Pb loss caused fractionation of the Pb isotope ratios. Table 4.7 presents the typical isotopic deviation in ppm of the Ag-doped RAuGP5 from the Pb isotope signature of undoped RAuGP5 after chemical separation. This deviation takes into account the Pb concentration and isotopic composition of the Ag standard solution. There is no significant fractionation of the Pb isotope ratios (maximum deviation of ±502 ppm for the 206Pb/204Pb; and Standish et al., 2013), and the deviation is in general within the external precision of the repeat analyses of gold reference material RAuGP3 (Table 4.9). Consequently, no correction is required.

Table 4.7: Typical isotopic deviation of RAuGP5 (SPEX CertiPrep Ltd) after Ag-doping (Alfa Aesar AAS Specpure Ag standard solution) and Ag separation through the precipitation of AgCl residue. Expressed as the relative difference in ppm from ratios measured on undoped aliquots of the same standard (see Table 4.9) Analytical errors (2σ) are typically <180 ppm for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb and <50 ppm for ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb respectively.

% Ag	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
5%	-67	84	56	149	123
10%	-153	146	79	294	231
20%	-502	-68	-236	423	262

Column 2: separation of lead from the remaining sample matrix

The second column (80 µl volume) employs classic HBr techniques to isolate the Pb fraction from the remaining sample matrix. AG1-X8 resin is again used, however this time it is converted to the HBr form. Serious tailing can occur when elements are eluted using dilute HBr acids, therefore HBr-HNO_3 acid mixtures can be employed instead (Strelow and Toerien, 1966). The HNO_3 acts as a non-complexing acid and contains a relatively strongly adsorbed anion which competes for exchange sites on the resin. This is successful in eliminating the tailing and therefore improves the separation of different elements (Strelow, 1978). The work of Strelow and Toerien (1966) and Strelow (1978) found that the K_D of Pb increases with HBr concentration to a peak of 821 at 0.5 M HBr before slowly decreasing again. The K_D also decreases with increasing nitric acid concentration. Samples are therefore loaded in 500 µl 0.4 M HBr and Pb is retained on the resin (K_D c.800). A solution of 0.2 M HBr and 0.5 M HNO_3 (solution A) is used to elute the majority of the remaining matrix elements while Pb remains on the resin (K_D of 106). In fact Strelow (1978) shows that this solution will elute most elements including Al, Cu, Fe, Mn, Zn, the alkali metals and alkaline earths because they have little tendency to form bromide complexes. Pb can then be eluted with a solution (solution B) of 0.03 M HBr and 0.5 M HNO_3 (K_D of 4.1). The average Pb yield remains at 95%, indicating negligible Pb is retained on the resin during this column stage (Figure 4.8).

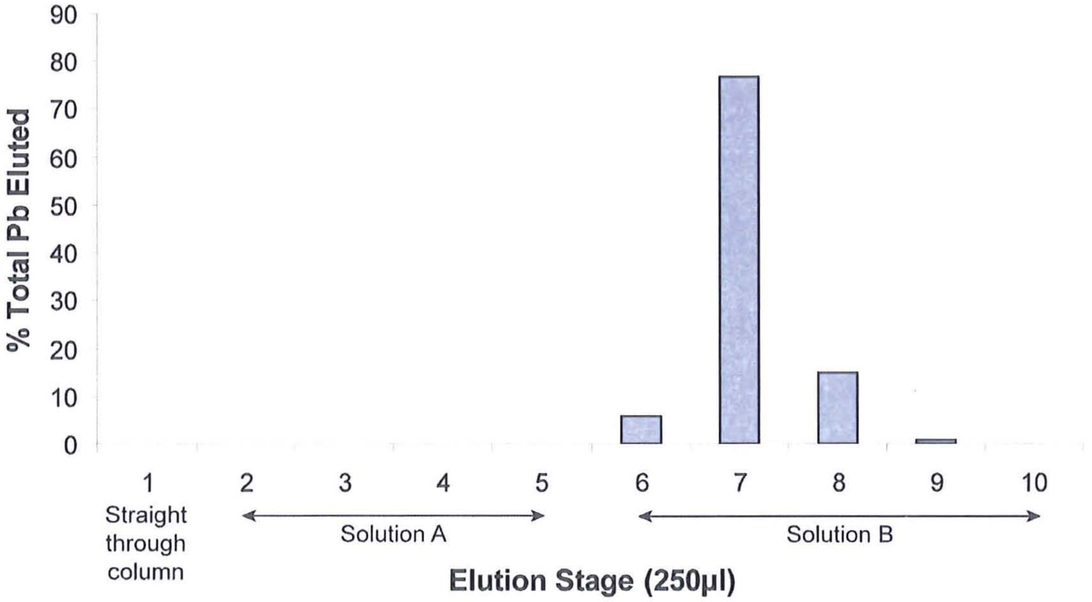


Figure 4.8: Column 2 % total Pb eluted versus elution stage.

Regarding the matrix elements that may still be present in the sample, the majority are easily separated from the Pb fraction due to their low K_D in solution A (Figure 4.9). Elements such as Bi, Cd, Au, Hg, Pt, Pd and Tl are strongly retained on the resin during loading, however their K_D is significantly higher than that of Pb for solution B. Additionally, the majority of these elements do not pass through the first column as they have a high K_D in 6 M HCl when AG1-X8 is in the chloride form. The elements that were eluted with the Pb fraction during column 1 are therefore not present in the Pb fraction after column 2 to any significant degree. The remaining Au, along with Ar, Cr and Se are all at background levels, while only Na is present with the Pb at any quantity. This is not expected to cause any major interferences when samples are analysed for their Pb isotope ratios due to the low relative abundance of Na compared to Pb in natural gold alloys, and because its mass range of 22 to 23 amu is far from those of Pb. If gold samples have high levels of the other major components identified earlier such as Cu or Hg, then it is worth noting that this second column procedure will also separate them from the Pb too. Any Ag remaining after the removal of the AgCl residue passes straight through the column and thus is not eluted with the Pb fraction.

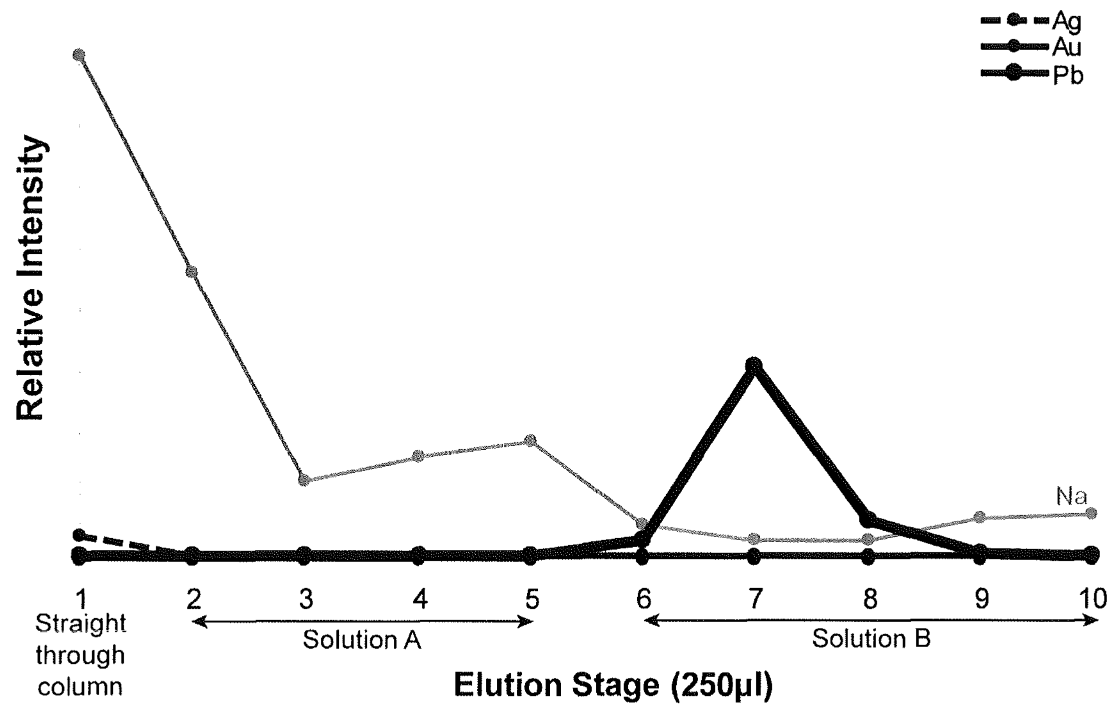


Figure 4.9: Column 2 relative signal intensity for selected elements versus elution stage.

Summary of ion exchange chromatography procedure: separation of lead from natural gold samples

As presented in Standish et al. (2013), samples were first weighed (typically mass between 2 and 10 mg) then placed in a pre-cleaned 7 ml Teflon vial. They were cleaned by ultrasonication in acetone for ten minutes followed by three washes with ultrapure water, then a further ten minutes ultrasonication in 2 M HCl followed by three ultrapure water washes. Samples were then dissolved in 800 µl *aqua regia* (600 µl concentrated HCl and 200 µl concentrated HNO_3) over c.48 hours on a hot plate at 130°C. Once total dissolution of the gold was achieved, the samples were dried down and re-dissolved in 0.5 to 2 ml 6 M HCl to dissolve any AgCl residue that had formed throughout the dissolution process. The samples were then ready for processing through column 1.

Eighty microlitre columns were rinsed in ultrapure water then loaded with pre-cleaned AG1-X8 resin. The resin was cleaned again by elution of 800 µl 6 M HCl (10x column volume) followed by 400 µl ultrapure water (5x column volume). Resin was conditioned with 500 µl 6 M HCl before the samples were loaded in 6 M HCl. Lead was not retained on the resin due to its low K_D, and so passed directly through the column where it was collected. Any remaining Pb that remained in the column was then eluted by two 400 µl aliquots of 6 M HCl. Samples were dried down on a hot plate ready for the physical separation of Ag.

As the samples dried down, AgCl residue precipitated out of the solutions. The samples were re-dissolved in 500 µl 7 M HNO_3 and fluxed for 30 minutes. The AgCl residues were insoluble, while the remaining sample dissolved. Once cooled, these samples were transferred into pre-cleaned 2 ml centrifuge tubes and centrifuged for 10 minutes at 13400 rpm. The supernatant was pipetted into the sample vial along with one wash of ultrapure water. The supernatant was dried down then complexed with HBr by dissolution in 100 µl 0.4 M HBr, before being dried down and re-dissolved in 500 µl HBr. After fluxing at 120°C overnight, they were ready for processing through column 2.

The same 80 µl columns as used for column 1 were rinsed in ultrapure water before being loaded with new, pre-cleaned AG1-X8 resin. The resin was again cleaned by eluting 800 µl 6 M HCl (10x column volume) and 400 µl ultrapure water (5x column volume). Resin was then conditioned by passing through 200 µl 0.4 M HBr. The samples were loaded in 500 µl 0.4 M HBr, and while the waste elution stages were carried out, the sample vials are filled with 6 M HCl and fluxed at 140°C for 30 minutes and rinsed four times in ultrapure water as a final cleaning stage before the lead fractions are collected. Four 250 µl aliquots of solution A (0.2 M HBr and 0.5 M HNO_3) were passed through to elute the remaining matrix, before the sample vials were replaced beneath the columns and 1x 250 µl then 2x 375 µl aliquots of solution B (0.03 M HBr and 0.5 M HNO_3) were passed through the columns to elute the Pb fractions. Samples were then dried down for storage until analyses by mass spectrometry.

Chromatography blanks

One column blank was processed with every batch of samples through all the stages of chemistry from initial dissolution to analysis on the mass spectrometer. This allows monitoring of the background levels of Pb and thus can highlight any contamination from the environment or from reagents and labware. The concentration of these blanks range from 20 pg to 114 pg Pb, with an average of 57 pg (Figure 4.10). With the sample Pb concentration typically between 50 ng and 100 ng, the blank contribution is three orders of magnitude lower and therefore has a negligible affect on the isotopic ratios calculated.

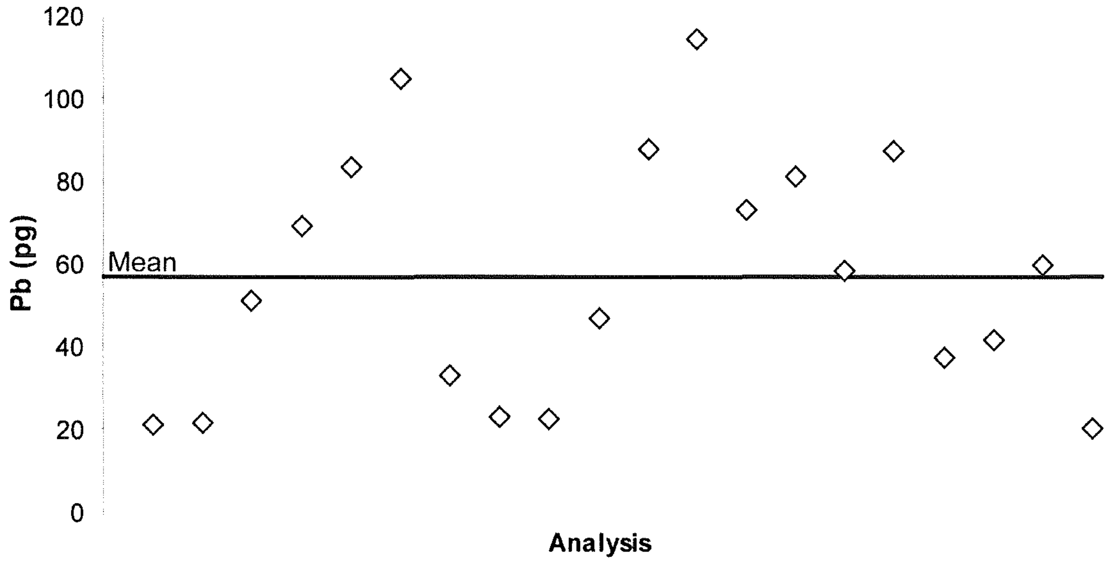


Figure 4.10: Column blank Pb concentrations (2 S.E. smaller than symbols).

Accuracy and external precision

This column procedure successfully collects c.95% of the total Pb within a sample. Given that this means 5% of the Pb is lost, it is important to check that there is no fractionation of the Pb isotope ratios. There are no published solid gold standards with known Pb isotope compositions, therefore three samples of BCR2, a powdered basaltic rock standard (USGS) that does have published Pb isotope data, were run through the two column procedure (Standish et al., 2013). Table 4.8 and Figure 4.11 detail the resulting Pb isotope ratios, along with published values from Baker et al. (2004) and Woodhead and Hergt (2000).

Table 4.8: BCR2 mean Pb isotope composition from published sources and this study. Errors are ±2 S.D. in the last decimal place.

Reference	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Baker et al. (2004) n=8	18.765±11	15.628±5	38.752±22	-	-
Woodhead and Hergt (2000) n=4	18.750±22	15.615±6	38.691±42	-	-
This Study n=6	18.760±7	15.627±2	38.739±11	0.83299±35	2.0650±4

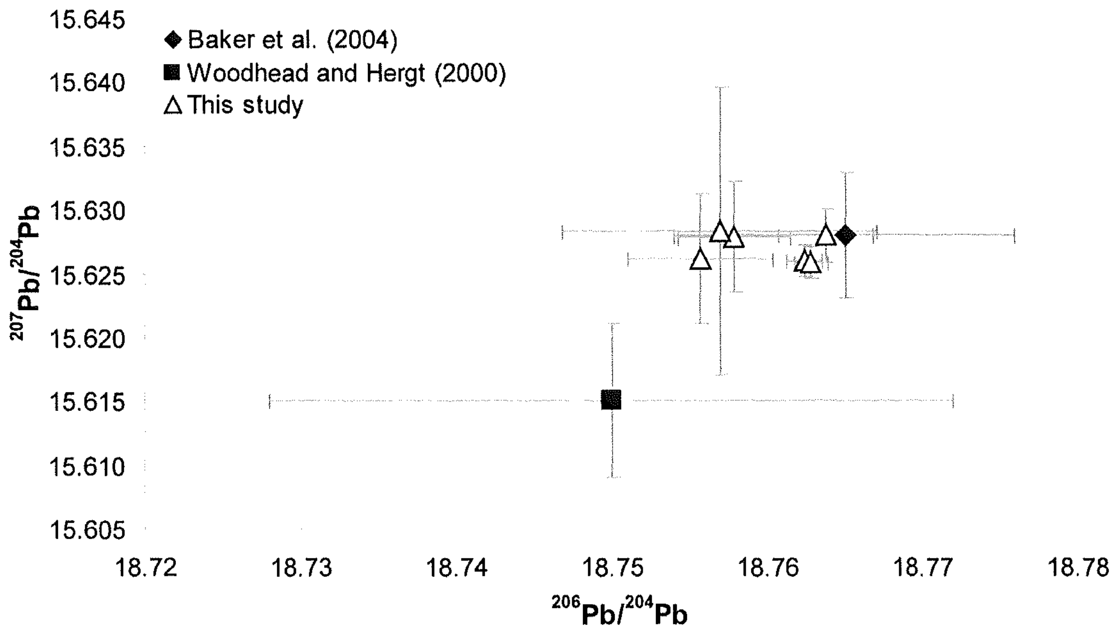


Figure 4.11: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of BCR2 published data (mean ±2 S.D.) and analyses from this study (±2 S.E. of the mean of 50 integration cycles).

The BCR2 that were processed through this two stage column procedure plot between and within error of the published data, therefore they are in agreement and demonstrate good accuracy and precision. There is no significant fractionation during the column procedure. The gold reference materials RAuGP3 and RAuGP5 (which have not previously been characterised for their lead isotope signature), with no Ag doping, were therefore processed through column chromatography and repeatedly analysed for their Pb isotope signature over an 18 month period (Standish et al., 2013). Table 4.9 details their mean isotopic values, and Figure 4.12 and Figure 4.13 plot a compilation of all analyses.

Table 4.9: Mean isotopic ratios of reference materials RAuGP3 and RAuGP5. Samples were not doped with silver standard solution. Errors are ±2 S.D. in the last decimal place.

	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
RAuGP3 n=24	17.110±4	15.520±3	36.862±9	0.90710±11	2.15448±32
RAuGP5 n=26	17.070±2	15.514±2	36.854±7	0.90886±5	2.15910±18

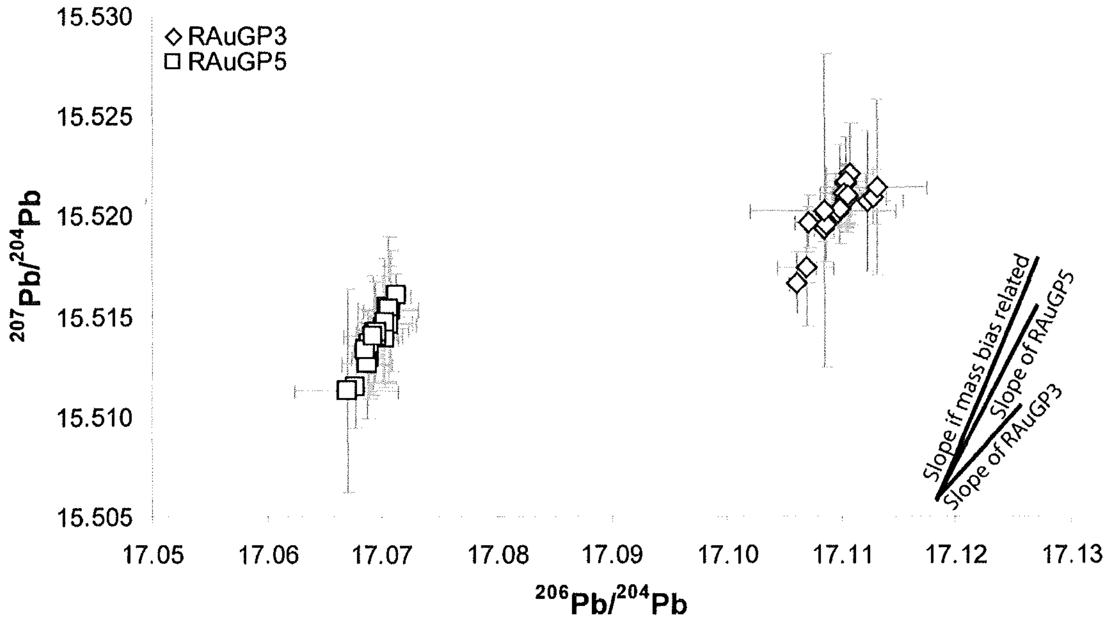


Figure 4.12: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ compilation plot of reference materials RAuGP3 and RAuGP5 ±2 S.E. of the mean of 50 integration cycles.

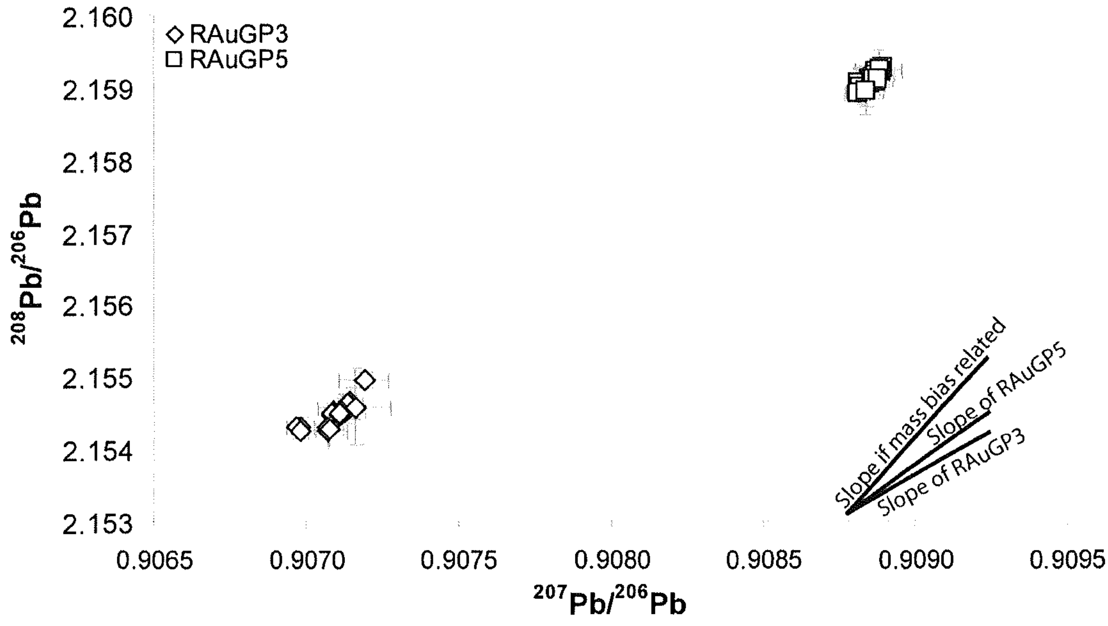


Figure 4.13: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ compilation plot of reference materials RAuGP3 and RAuGP5 ±2 S.E. of the mean of 50 integration cycles.

The data trends in Figure 4.12 are not simply mass bias related, and in part are likely to relate to the analysis of ^{204}Pb, and the interferences of ^{204}Hg on this mass. Due to the internal precision, correcting for this linear spread will not greatly improve the reproducibility of the data. The external precision, or reproducibility, of RAuGP3 expressed as two relative standard deviations of the mean is <250 ppm on $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ and <150 ppm on $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. Greater external precision is achieved for RAuGP5 due to its higher lead content; <190 ppm on $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ and <80 ppm on $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. For high silver samples, i.e. Ag ~20% or above, external precision is reduced on the majority of isotopic ratios due to the precipitation of AgCl residue.

4.2.3.4 Ion exchange chromatography: separation of lead from sulphide minerals

Sulphides from Au bearing mineralisation were also analysed for their Pb isotope ratios. Single stage ion exchange chromatography using classic HBr techniques was employed, adapted from Darling (2010). Samples were first weighed (typically 0.4 mg for Pb sulphides and 2-4 mg for other sulphides) then cleaned using the same method outlined previously. They were dissolved in 1000 µl 7 N HNO3, then all the samples except Pb sulphides were dried down and complexed with HBr by dissolving in 100 µl 0.4 M HBr. Twenty microlitre aliquots of the Pb sulphides were taken and complexed with HBr due to their high lead content. Samples were then re-dissolved in 500 µl 0.4 M HBr for column loading.

Fifty microlitre columns were cleaned in ultrapure water then loaded with pre-cleaned AG1-X8 resin. The resin was further cleaned by eluting 500 µl 6 M HCl and 300 µl ultrapure water. The resin was conditioned by eluting 200 µl 0.4 M HBr. The samples were loaded in 500 µl 0.4 M HBr, and while the waste elution stages were carried out, the sample vials were filled with 6 M HCl and fluxed at 140°C for 30 minutes and rinsed four times in ultrapure water. Four 250 µl aliquots of solution A (0.2 M HBr and 0.5 M HNO_3) eluted the remaining matrix, before the sample vials were replaced beneath the columns and 1x 150 µl then 1x 400 µl aliquots of solution B (0.03 M HBr and 0.5 M HNO_3) eluted the Pb fractions. Samples were then dried down for storage until Pb isotope analysis was performed.

4.3 Laser Ablation Mass Spectrometry

4.3.1 Materials and Labware

Samples were mounted in epoxy resin and left to set over two to three days. They were polished using a series of graded sand papers (P800, P1200, P4000) and a synthetic textile polishing cloth with 1 µm diamond solution until a smooth and flat finish to the samples was produced. This removes any scratches or relief that may act as a trap for surface contamination. The mounted samples were then cleaned by ultrasonication in acetone followed by ultrasonication in 2% HNO_3, before being rinsed three times in ultrapure water. Samples were then ready to be analysed, and were wiped with isopropyl alcohol before each session.

4.3.2 Lead Isotope Analysis

4.3.2.1 Operational details

Laser ablation MC-ICP-MS allows in situ analysis of a sample in solid form. Although precision and accuracy tend to be lower than solution techniques due to matrix effects and decreased ion beam stability, it can be advantageous because minimal sample preparation is required.

Laser ablation is frequently used for trace element analysis of gold artefacts (Watling et al., 1994; Guerra et al., 1999; Guerra and Calligaro, 2004; Brostoff et al., 2009). More recently it has been adapted to Pb isotope studies; Ponting et al. (2003) demonstrated this application in a study of Roman silver coins and gained improved reproducibility over the more traditional TIMS methodology (150 ppm compared to 400 ppm on $^{207}Pb/^{206}Pb$ at 2σ). Laser ablation ICP-MS was first applied to Pb isotope analysis of gold by Bendall et al. (2009), however no ^{204}Pb data was presented due to the isobaric interference of mercury.

Laser ablation Pb isotope mass spectrometry was performed on a Thermo Fisher Scientific Neptune MC-ICP-MS. Samples were delivered by a New Wave Research UP193HE Deep-UV (193 nm) Excimer laser ablation system. Typical operating conditions are summarised in Table 4.10, and the faraday cup configuration is detailed in Table 4.11 (see Standish et al., 2013). Sample introduction was through a mix of Ar, He and N. He rather than Ar was used to transport the sample out of the laser ablation cell because it reduces the amount of particles deposited around the ablation pits (Günther and Heinrich, 1999). The He carrier gas was then mixed with Ar because an Ar-He mix leads to an increase in signal intensities (Günther and Heinrich, 1999). A small amount of N was also mixed into the carrier gas at this point because it enhances the sensitivity of heavier elements (Hirata and Nesbitt, 1995).

Table 4.10: Typical operating conditions for laser ablation MC-ICP-MS Pb isotope analysis

Instrument	Thermo Fisher Scientific Neptune MC- ICP-MS
RF power	1100 W
Cones	Nickel skimmer (X) and sample
Gas Flows	
Cool gas	15 l min^{-1}
Auxiliary gas	0.7-0.8 l min^{-1}
Helium ablation cell carrier gas	0.89 l min^{-1}
Additional nitrogen	0.004 l min^{-1}
Argon make-up gas	0.93 l min^{-1}
Ablation conditions	
Laser power density	6-8 J cm^{-2}
Laser repetition rate	4 Hz
Laser spot size	150 µm – 187 µm

Table 4.11: Faraday cup configuration for laser ablation MC-ICP-MS Pb isotope analysis.

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass	-	200	201	202	204	206	207	208	-

Tuning to optimum conditions was performed on NIST SRM610, a glass with a known Pb concentration of 426±1 ppm (Jochum et al., 2011). As with solution analysis, a 'gain' calibration was performed before every session. Laser ablation is typically less stable than solution methodologies, and Figure 4.14 presents a representative laser ablation peak centre on mass 208.

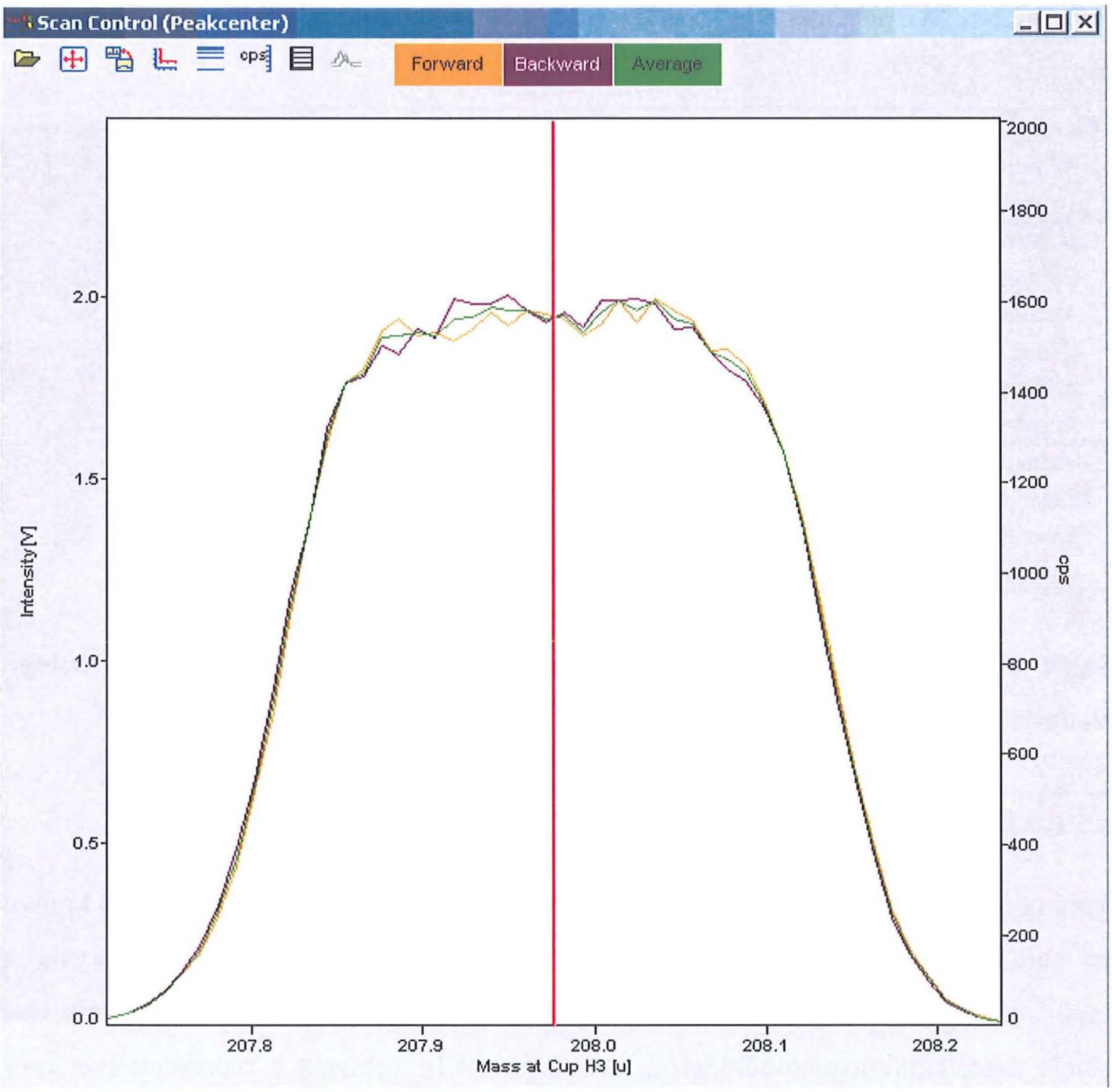


Figure 4.14: Example of a typical laser ablation peak centre of mass 208 on cup H3 after tuning with NIST SRM610.

Each individual sample or standard processed was analysed over 180 cycles, where one cycle comprises one second of integration. This included 40 cycles of pre-ablation to allow signal stabilisation and to prevent the analysis of surface contamination. Any cycles greater than three standard deviations from the mean were excluded, and if the signal died mid analysis, the number of cycles integrated was further reduced. The data quoted is therefore an average of $\leq$140 cycles. A scanning electron microscope (SEM) image showing the morphology of a typical laser ablation crater in gold reference material RAuGP5 is presented in Figure 4.15 (Standish et al., 2013, Fig. 4).

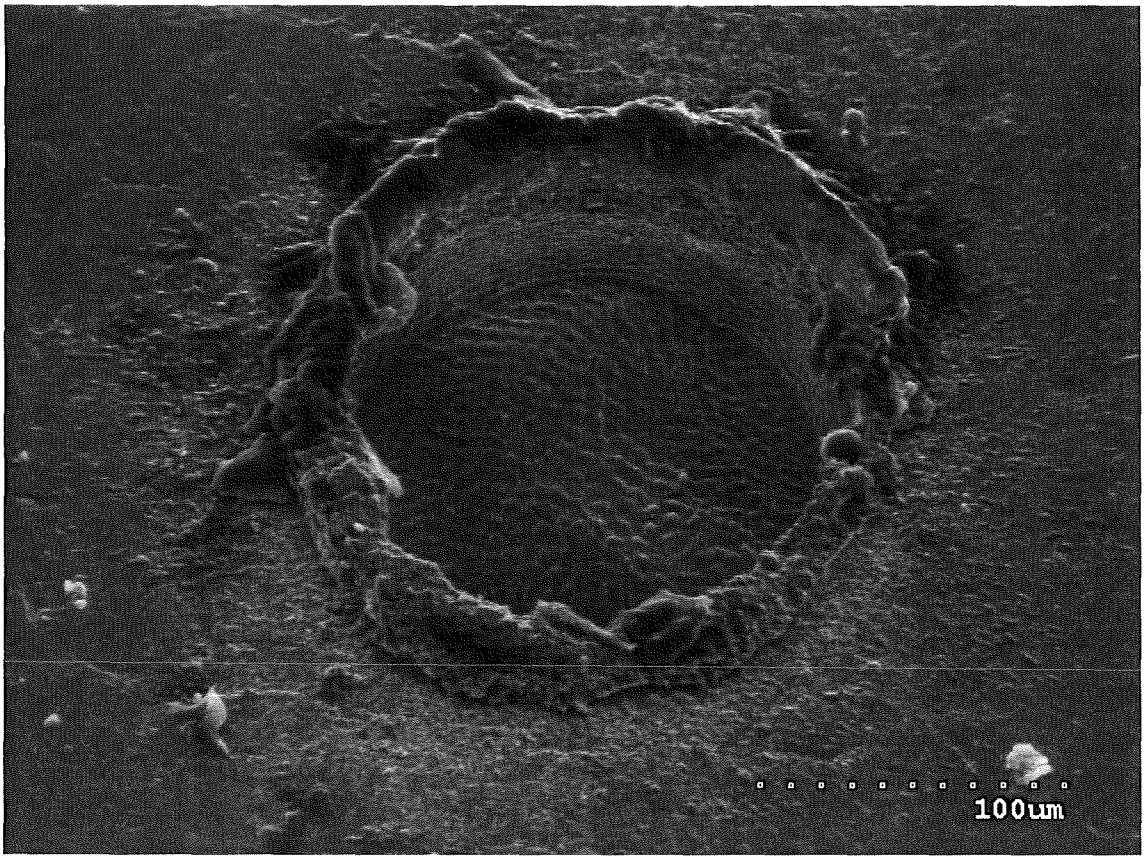


Figure 4.15: SEM image of a typical laser ablation crater in gold reference material RAuGP5.

An on-peak gas line 'wash out' and gas 'blank' (both consisting of 45 cycles) were analysed before every standard or sample, and a blank correction was applied. Internal precision at this point varied between samples due to a) differences in Pb concentrations, b) varying degrees of homogeneity, and c) differences in Hg contents. Table 4.12 demonstrates typical internal precisions for NIST SRM610, NIST SRM612, RAuGP3, and RAuGP5 (see also Standish et al., 2013).

Table 4.12: Typical internal precision (ppm) for laser ablation Pb isotope analysis (two relative S.E. of the mean of the 140 cycles comprising one analysis) before a Hg correction is applied.

	Pb (ppm)	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
SRM610	426±1	<200	<200	<200	<40	<40
SRM612	38.57±0.2	<1500	<1500	<1500	<150	<120
RAuGP3	34±0.5	<3800	<3800	<5000	<170	<170
RAuGP5	129±4	<1300	<1300	<1300	<130	<130
Samples	-	<2000	<2000	<2000	<150	<150

Internal precisions are comparable to that achieved in other laser ablation Pb isotope studies (such as Walder et al., 1993; Gagnevin et al., 2005; Bendall et al., 2009). It is clear from Table 4.12 that the internal precisions of gold samples are substantially lower than the NIST glasses on the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, yet is comparable to them on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios. Although the gold standards and samples do tend to demonstrate increased heterogeneity over the NIST glasses, this is primarily due to their higher and more variable Hg content (Figure 4.16). It is worth noting here that the internal precisions quoted for the gold samples reflect the internal precisions for samples where ratios including ^{204}Pb are accepted as accurate. In many cases, the Hg content is too high for the resulting Hg correction to be deemed as reliable, and internal precision in the tens of thousands is not uncommon. As a guide to the amount of Hg in a sample relative to the amount of Pb, the $^{204}(Pb+Hg)/^{202}Hg$ ratio was also calculated. When this value was <1, the Hg correction was deemed unreliable and no mass 204 data was used. An explanation of this is provided in section 4.3.2.3.

Mercury corrections were applied to account for the isobaric interference on mass 204. Sample introduction by laser ablation involves the direct analysis of solid samples and there is no chemical separation of different elements prior to analysis. Isobaric interferences are therefore more problematic than during solution analysis where the interference elements can be reduced to background levels during ion exchange chromatography. Mercury has a natural affinity to gold, and can be a significant component in both natural and artefact gold. An accurate mercury correction is therefore necessary if analysis of ^{204}Pb is required. Numerous different methods of applying a mercury correction were investigated. Techniques that used different stable mercury isotope ratios with known values were expected to provide the most accurate correction, however this was not the case. As with solution analysis, a correction that utilised the $^{208}Pb/^{206}Pb$ ratio of the bracketing standard was most appropriate (equation 4.5). This was favourable because it provided continuity between the different methods of analysis. In equation 4.5, $^{208}Pb/^{206}Pb_{true}$ now reflects the analysis of NIST SRM610 and the preferred working values published in Baker et al. (2004), see Table 4.13.

Table 4.13: NIST SRM610 and SRM612 isotopic ratios used as 'true' values in this study (Baker et al. 2004).

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
SRM610	17.052±2	15.515±2	36.991±5	0.90986±5	2.1694±1
SRM612	17.099±3	15.516±2	37.020±7	0.90745±4	2.1651±1

This correction improved the typical internal precision for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ to <1000 ppm for RAuGP3 and <400 ppm for RAuGP5. The blank and mercury corrections are presented graphically in Figure 4.16 (Standish et al., 2013, Fig. 5), a plot of a laser ablation analysis of RAuGP3. The varying mercury intensities and the $^{206}Pb/^{204}Pb$ ratios before and after the blank and mercury corrections are plotted over 180 cycles of analysis.

Instrument induced mass bias was corrected using the standard sample bracketing technique (equation 4.6) producing consistency with the solution methodologies (see also Standish et al., 2013). NIST glass SRM610, which has a known Pb isotopic composition, was employed as the bracketing standard. The true values referred to are again those published by Baker et al. (2004), see Table 4.13. RAuGP5 was run as a matrix matched consistency standard and data were reduced using the same methods applied to unknown gold samples. RAuGP3 was also analysed during each session to act as a further consistency standard, whilst NIST glass SRM612 (38.57±0.2 ppm Pb) has also been characterised as a guide to accuracy.

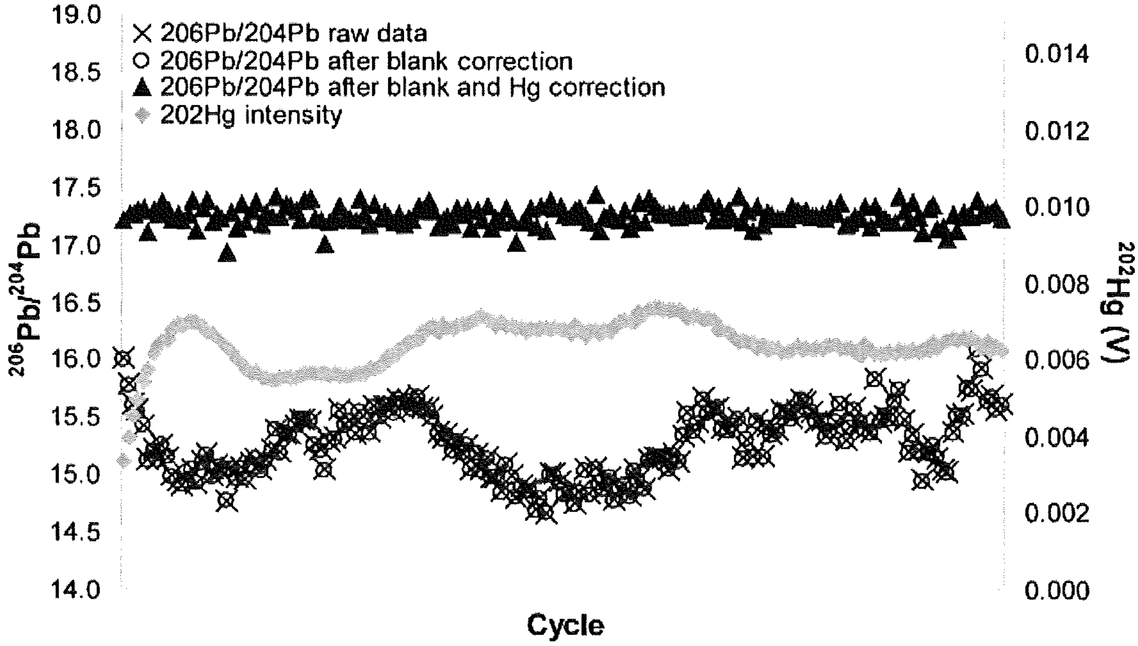


Figure 4.16: Laser ablation MC-ICP-MS analysis of gold reference material RAuGP3 over 180 cycles.

This method does assume that the degree of mass bias is the same in the standards and the unknown samples, and considering the different composition of the standards and samples this could be an issue. Ødegård et al. (2005) and Klemme et al. (2008) have highlighted the fact that using non-matrix matched standards for calibration in elemental studies can be problematic due to the differences in the composition of the materials involved. Indeed, the compositions of the NIST glasses, along with their physical properties, are very different to those of gold. However Jackson (2008) found that accurate results could be produced for elemental studies by using non matrix matched standards, particularly when using shorter wavelength lasers such as the 193 nm laser used in this study. Nevertheless, a trial utilising RAuGP5 as the bracketing standard was carried out. No significant difference in accuracy or reproducibility was recorded. NIST glass SRM610 was therefore preferred due to the more stable signal that it produced and the fact that it allowed RAuGP5 to be run as a consistency standard.

4.3.2.2 Accuracy and external precision

The accuracy and precision of this method has been demonstrated by the analyses of a secondary NIST glass standard SRM612, and the two gold reference materials first characterised by solution analysis; RAuGP3 and RAuGP5. The analysis of NIST glass SRM612 is presented in Figure 4.17 and Figure 4.18. The mean values ± 2 S.D. of NIST SRM612 from this study are as follows: $^{206}Pb/^{204}Pb = 17.091 \pm 21$, $^{207}Pb/^{204}Pb = 15.508 \pm 19$, and $^{208}Pb/^{204}Pb = 36.995 \pm 44$. These are comparable to the values presented in Baker et al. (2004).

External precisions based on repeat analyses of the solid gold reference materials are <600 ppm for RAuGP3 (n = 30) and <450 ppm for RAuGP5 (n = 145) on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ (2σ, see also Standish et al., 2013). This is slightly lower than studies that employed thallium for mass bias corrections; Gagnevin et al. (2005) achieved 200 ppm on the $^{207}Pb/^{206}Pb$ and 170 ppm on the $^{208}Pb/^{206}Pb$ after correction factors were calculated by analysing the $^{205}Tl/^{203}Tl$ ratio in NIST glass SRM610 run regularly throughout the analysis sessions. However the external precisions quoted here were calculated from long term data compilations over a 12 month period. For the ratios where mercury is an isobaric interference to mass 204, the external precision is lower; <1640ppm for RAuGP3 and <900 ppm for RAuGP5 on the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$. This is due to the relatively high mercury content and low ^{204}Pb abundance of gold rather than the method of mass bias correction employed, and therefore is unlikely to be significantly improved by using alternative mass bias correction methodologies. Within session external precision (2σ) based on repeat analysis of

RAuGP5 is slightly higher at <1000 ppm for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ and <230 ppm for $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$.

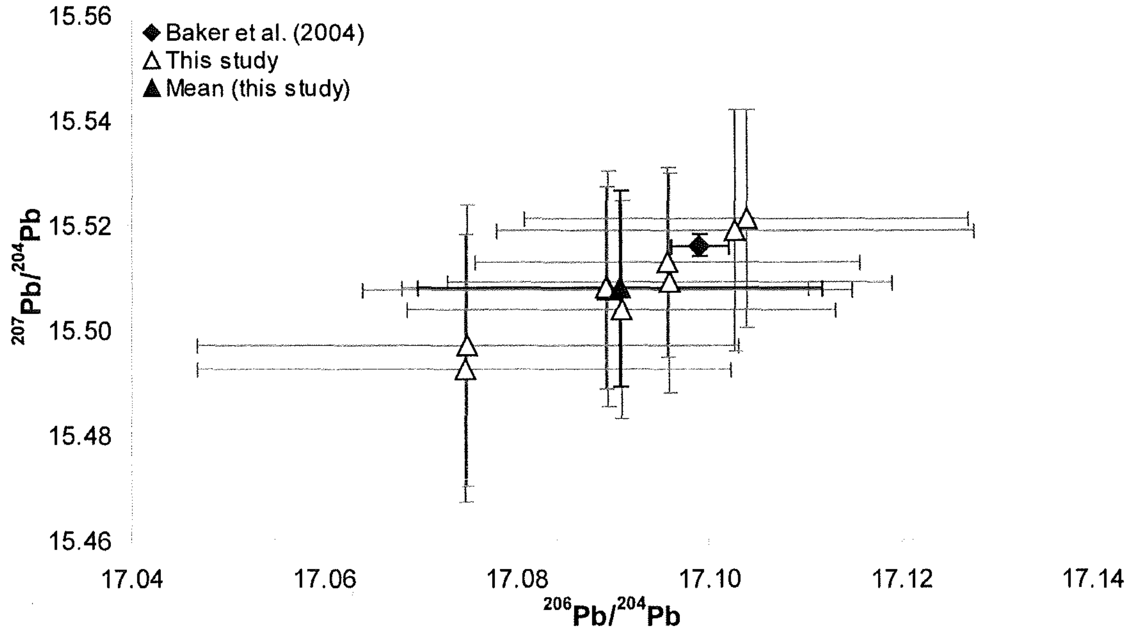


Figure 4.17: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ compilation plot of NIST SRM612 analysed by laser ablation MC-ICP-MS. Individual analyses represented by open black triangles ±2 S.E. of the mean of 140 integration cycles (light grey error bars), mean value from this study represented by filled black triangle (±2 S.D. black error bars), and mean value from Baker et al. (2004) represented by filled black diamond (±2 S.D. black error bars).

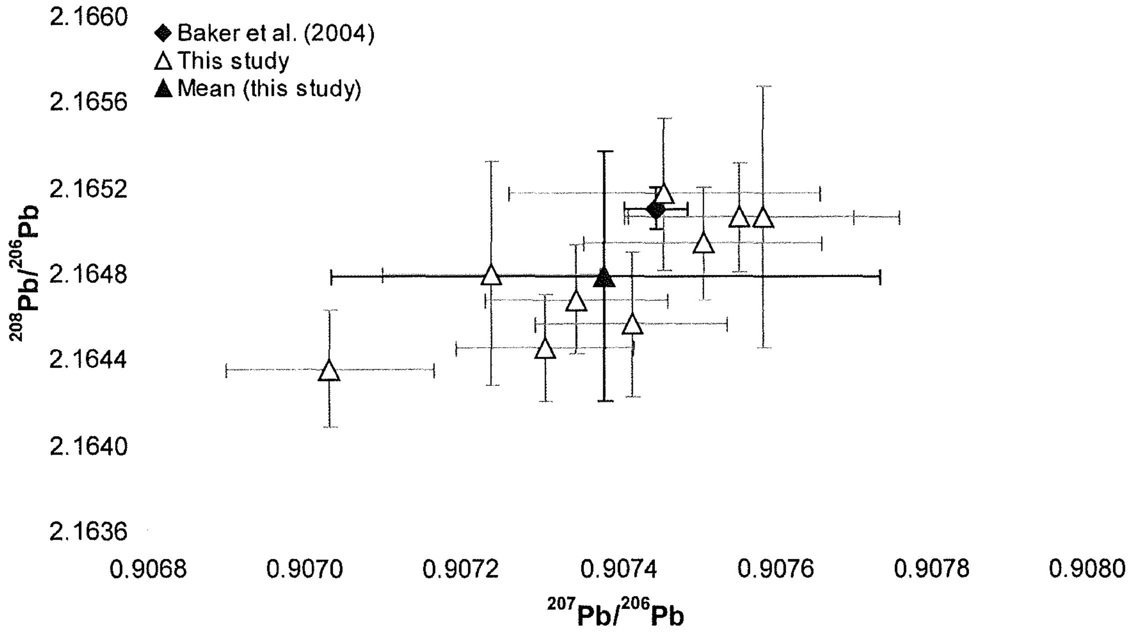


Figure 4.18: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ compilation plot of NIST SRM612 analysed by laser ablation MC-ICP-MS. See Figure 4.17 caption for details.

The accuracy and external precision of both gold reference materials are demonstrated in Figure 4.19 and Figure 4.20 (see also Standish et al., 2013). Accuracy is also lower for 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb compared to 207Pb/206Pb and 208Pb/206Pb. The 'true' ratios were determined by cutting a small piece off the solid gold globule that was to be used as a laser standard before mounting, and processing it using the solution MC-ICP-MS techniques outlined previously. These ratios are presented in Table 4.14, along with the mean ratios from laser ablation analysis. Again the data trends are not solely mass bias related, and other factors may be involved. Regarding Figure 4.19 they are more likely to relate to the analysis of 204Pb, and the high interferences of 204Hg on this mass. Due to the internal precision of the data, correcting for the linear spread will not greatly improve the reproducibility of data. It is worth noting that this laser ablation technique can distinguish between the isotopic signatures of certain Irish gold ore fields (see Chapter 5).

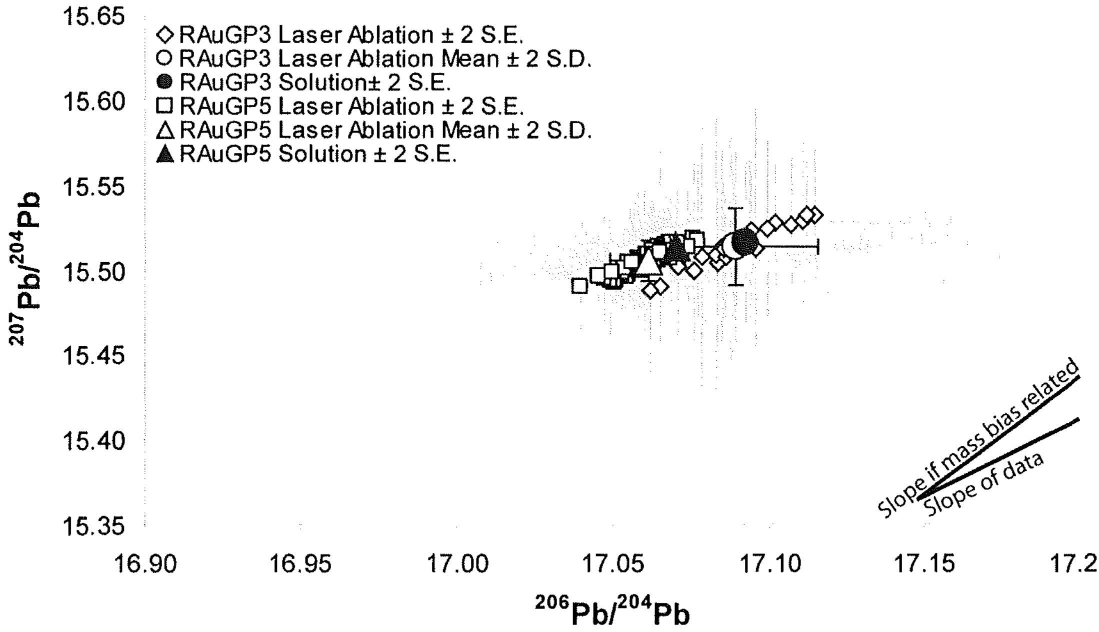


Figure 4.19: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ compilation plot of gold reference materials RAuGP3 and RAuGP5 analysed by laser ablation MC-ICP-MS, ±2 S.E. of the mean of 140 integration cycles (light grey error bars). Means are represented by the large open symbols ±2 S.D. (black error bars). Solution analysis of the laser ablation reference materials are represented by the large filled symbols. Solution analysis errors are not shown since they are smaller than the symbols.

Table 4.14: Mean isotopic ratios (±2 S.D. in the last decimal place) of reference materials RAuGP3 and RAuGP5 analysed by laser ablation MC-ICP-MS. Solution analysis (±2 S.E. in the last decimal place) of the specific reference material globules employed in laser ablation analysis are also provided for comparison.

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	n
RAuGP3 'true'	17.093±1	15.516±2	36.857±4	0.90776±2	2.1563±1	1
RAuGP3 laser ablation	17.089±26	15.513±22	36.846±58	0.90770±38	2.1560±12	27
RAuGP5 'true'	17.070±1	15.514±1	36.855±4	0.90883±2	2.1591±1	1
RAuGP5 laser ablation	17.061±13	15.505±12	36.832±32	0.90880±28	2.1590±9	145

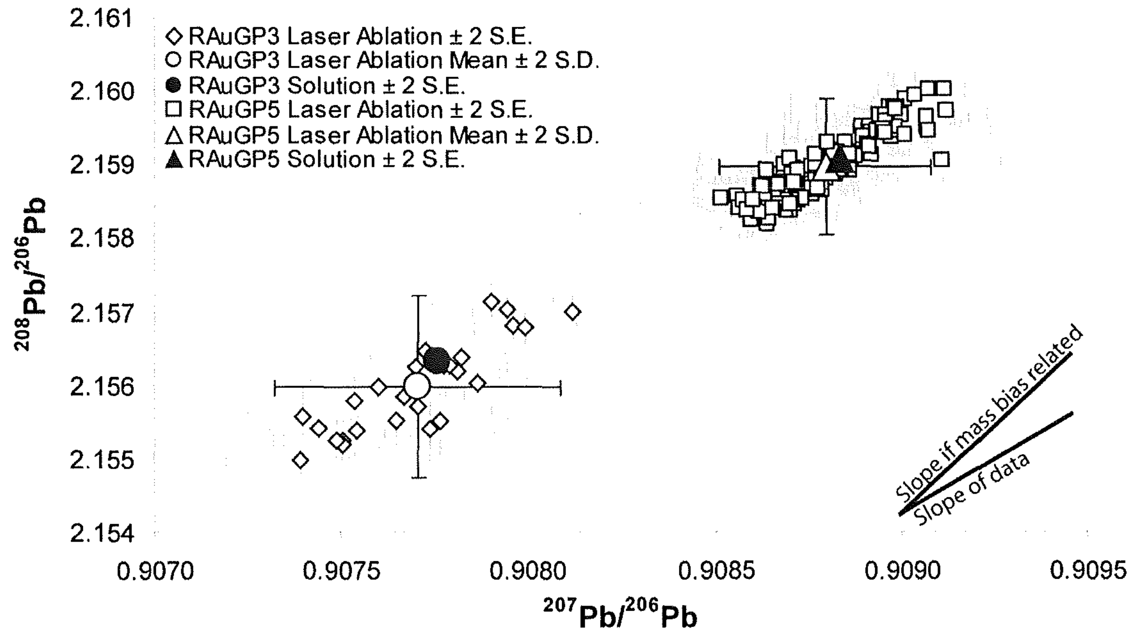


Figure 4.20: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ compilation plot of gold reference materials RAuGP3 and RAuGP5 analysed by laser ablation MC-ICP-MS, ±2 S.E. of the mean of 140 integration cycles (light grey error bars). Means are represented by the large open symbols ±2 S.D. (black error bars). Solution analysis of the laser ablation reference materials are represented by the large filled symbols. Solution analysis errors are not shown since they are smaller than the symbols.

4.3.2.3 Isobaric interference of mercury on mass 204

It is clear that both accuracy and external precision are lower for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ due to the isobaric interference of Hg on mass 204 and the low natural abundance of ^{204}Pb. The ratio $^{204}(Pb+Hg)/^{202}Hg$ has been used to monitor the effect of the low abundance of ^{204}Pb on the efficiency of the mass 204 mercury correction (Standish et al., 2013). For RAuGP5 this ratio is typically 6.6 to 63.4 compared to 1.5 to 3.7 for RAuGP3, a reflection of differences in Pb concentration between the two reference materials. Figure 4.21 (see also Standish et al., 2013, Fig. 8) demonstrates to what extent both the accuracy and external precision varies as a function of the ^{204}(Pb+Hg)/^{202}Hg ratio. The external reproducibility of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb is clearly enhanced for high ^{204}(Pb+Hg)/^{202}Hg values. It is typically <1640 ppm when ^{204}(Pb+Hg)/^{202}Hg = 1-5 (n = 27), <900 ppm when ^{204}(Pb+Hg)/^{202}Hg = 5-20 (n = 78), and <810 ppm when ^{204}(Pb+Hg)/^{202}Hg = >20 (n = 67).

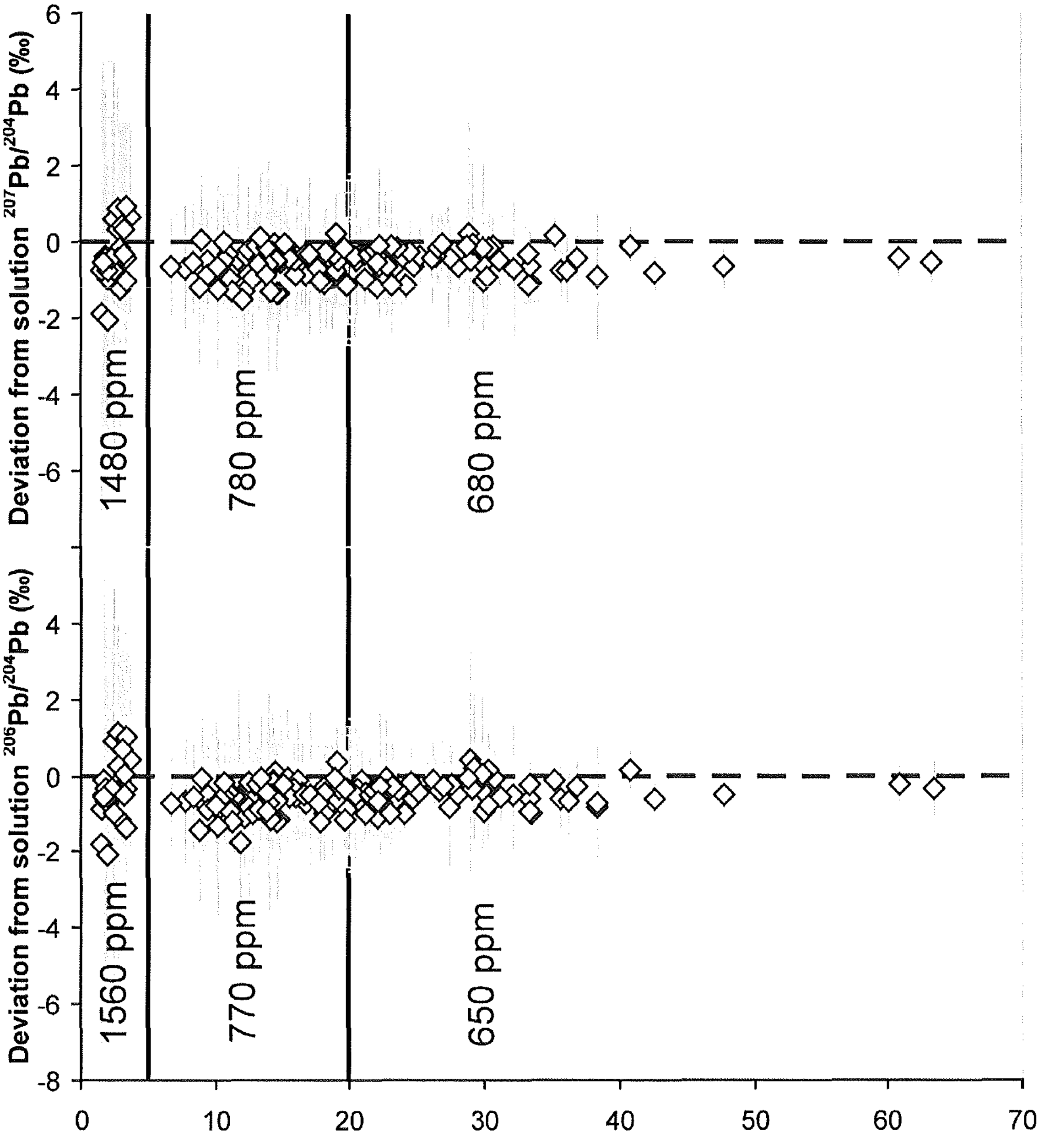


Figure 4.21: Deviation of RAuGP3 and RAuGP5 206Pb/204Pb and 207Pb/204Pb from 'true' values (presented in Table 4.14) as a function of 204(Pb+Hg)/202Hg. External precision presented for 204(Pb+Hg)/202Hg 1-5, 5-20 and >20 respectively.

Figure 4.21 also shows the data are accurate within error for the entire range of $^{204}(Pb+Hg)/^{202}Hg$, therefore ^{204}Pb data may be of use to some applications such as archaeological provenance studies and laser ablation Pb isotope analysis has the potential to distinguish between certain deposits of natural gold presented in Chapter 5. As a result, and based on the demonstrated accuracy and precision of measurements of these standards, samples with $^{204}(Pb+Hg)/^{202}Hg > 1$ can reasonably be assumed to have their Pb isotope ratios determined within the quoted accuracy. As accuracy cannot be characterised for $^{204}(Pb+Hg)/^{202}Hg < 1$ using these reference materials, ^{204}Pb data quality cannot be assured for samples with $^{204}(Pb+Hg)/^{202}Hg < 1$.

4.3.2.4 Laser ablation and solution MC-ICP-MS: a comparison

It has been demonstrated that both accuracy and precision are reduced when sample introduction employs laser ablation systems. A further comparison between the two techniques can be made by considering the relative ionisation efficiency, i.e. the number of ions detected relative to the number of Pb atoms introduced. Because ions can also be lost during transmission through the mass spectrometer, a more appropriate term for this calculation is the sample ion yield.

Due to the unknown concentration of samples, the sample ion yield has been calculated using the two external standards run throughout solution and laser ablation MC-ICP-MS; NIST SRM981 (mean signal on mass 208 of 9.14 V) and NIST SRM610 (mean signal on mass 208 of 1.66 V). NIST SRM981 was introduced at a concentration of 20 ppb Pb and a flow rate of 50 μl per second. The calculated sample ion yield is 0.98%. NIST SRM610 (426 ppm Pb) was introduced by laser ablation at an ablation rate of 0.5-1 μm per second and produced craters of 150 μm diameter. The calculated sample ion yield ranges from 0.35% to 0.18% depending on ablation rate. Clearly the sample ion yield is lower for laser ablation MC-ICP-MS, although it can not be determined if this is a result of reduced ionisation efficiency, reduced transmission efficiency, or a combination of both.

Solution MC-ICP-MS is therefore favourable over laser ablation MC-ICP-MS due to increased accuracy, precision and ion sample yields, and is consequently the preferred methodology for the Pb isotope analyses undertaken in this study. However when investigations require the analyses of culturally important, precious, or rare samples, considerations regarding how much sample is destroyed must be made. Laser ablation allows analysis on small sample masses, as indicated by the size of crater left behind (typically with diameters on the tens to hundreds of micron scale). In order to sample such small quantities using solution techniques, micro-drilling of the sample would be required. However due to the physical properties of gold, this technique can not be employed; rather than removing material from a sample, drilling causes the gold to deform. As a result, when analysing archaeological artefact samples laser ablation MC-ICP-MS will be the preferred analytical technique thus sample destruction is kept to a minimum.

4.4 Electron Probe Microanalyser (EPMA)

Quantitative major element analysis of artefact samples was performed using a JEOL JXA 8600 Superprobe fitted with four wavelength dispersive (WD) spectrometers and an Oxford Instruments PCXA2 energy dispersive spectrometer housed in the microbeam laboratory at the Department of Earth Sciences, University of Bristol.

Samples were first mounted in epoxy resin, polished and cleaned as set out in section 4.3.1 for laser ablation MC-ICP-MS analysis, then were carbon coated to a thickness of 15 nm. This is a prerequisite for EPMA analysis, and is required so that the samples are conductive thus preventing issues relating to charge build-up. The EPMA was operated at 20 KV and 19.98 nA, with counting times varying between 10 and 40 seconds depending on the element in question. The following elements were analysed: Ag, As, Cu, Fe, Hg, Pb, Pd, S, Sb, Si, and Sn. Gold abundance was calculated by subtracting the sum of all these elements from 100%. Quantified concentrations were calculated through the use of pure metal standards, and the typical limits of detection for each element are displayed in Table 4.15.

Table 4.15: Limits of detection (LoD) for the elements analysed by EPMA.

	Ag %	As %	Cu %	Fe %	Hg %	Pb %	Pd %	S %	Sb %	Si %	Sn %
LoD	0.074	0.076	0.029	0.03	0.182	0.224	0.068	0.098	0.187	0.03	0.044

Each sample was analysed three times, and the data presented is the following chapters are the averages of these analyses. Errors are % analytical errors calculated by the EPMA software. Arsenic, Fe, Pd, S, Sb, and Si tend to fall below the detection limit for the majority of samples and thus were not of use for interpretation. Hg and Pb proved to be very variable and when present above the limit of detection, they were typically very close to it. Consequently only Ag, Cu and Sn were of use for artefact characterisation.

4.5 Scanning Electron Microscope (SEM)

The mineral inclusion suites of artefact samples were characterised using a Hitachi S-3500N variable pressure microscope equipped with an EDAX Genesis energy dispersive spectrometer (EDS x-ray detector) also housed in the microbeam laboratory at the Department of Earth Sciences, University of Bristol. The sample preparation techniques are the same as set out for the EPMA in section 4.4. Data were not quantified, instead the inclusion's major elements were determined by x-ray detection. Energy dispersive spectrums were generated on the SEM under operating conditions of 10 Kv and 23μA.

4.6 Presentation of Errors

4.6.1 Analytical errors

A brief note on the presentation of errors is required. All artefact and natural gold Pb isotope data analysed using solution techniques are presented ±2 S.E. of the mean of 50 integration cycles. Artefact samples analysed by laser ablation Pb isotope analysis and EPMA were typically analysed more than once. When this was the case, errors are ±2 S.E. of the mean of the multiple analyses. If only one analysis could be performed for laser ablation Pb isotope analysis, then the error remains ±2 S.E. of the mean of ≤ 140 integration cycles.

4.6.2 Lead isotope analysis error propagation

Regarding both solution and laser ablation Pb isotope analysis, the external precision (a measure of analytical reproducibility over multiple sessions of analyses) is often greater than the internal precision (a measure of reproducibility throughout one analysis). When this is the case, analytical errors that only reflect the internal precision are not an accurate representation of the true reproducibility of these methodologies. Consequently for cases when external precision exceeded internal precision, errors were propagated for external precision.

In order to determine if error propagation was required, a reduced chi square test was performed and the mean square weighted deviation (MSWD) was calculated for each standard compilation (both solution and laser ablation). Firstly, the MSWD critical value was calculated using the CHINV function on Microsoft Excel, with a probability of 0.05 and one degree of freedom:

$$\text{MSWD critical value} = \text{CHINV}(\text{probability}, \text{degrees of freedom})/(\text{n} - 1) \tag{4.7}$$

The MSWD for each data set could then be calculated, where x_i have 1σ errors and $\bar{x}_w$ is the weighted mean:

$$\text{MSWD} = \frac{1}{n-1}\sum_{i=1}^{n}\frac{(x_i - \bar{x}_w)^2}{\sigma_i^2} \tag{4.8}$$

The weighted mean was calculated accordingly:

$$\bar{x}_w = \sum_{i=1}^{n}\frac{x_i}{\sigma_i^2} \Big/ \sum_{i=1}^{n}\frac{1}{\sigma_i^2} \tag{4.9}$$

Based on the differing number of analyses carried out on each standard, the MSWD critical values varied between 1.18 and 2.21. The calculated MSWDs all came out above these critical values except for the laser ablation ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb analyses of BCR2, NIST SRM612 and RAuGP3 (where internal precision was lower due to the low intensity of ^{204}Pb and the isobaric interference of ^{204}Hg). This highlighted the need for error propagation. The value of the required extra error (Table 4.16) was independently calculated for each isotopic ratio per standard by creating a new error value that changes the MSWD to equal one, i.e. below the critical values (using Microsoft Excel's solver function). This new error value was then propagated with the original analytical error to create a new 2σ absolute error:

$$2\,\text{S.E.} = \sqrt{x^2 + y^2} \bullet 2 \tag{4.10}$$

where x is the original analytical error at 1σ and y is the added error at 1σ. The values for the gold reference material RAuGP3 (solution and laser ablation respectively) were used for the 'unknown' gold samples because they are of similar matrix and lead concentration.

Table 4.16: Absolute errors (1σ) propagated with analytical errors to account for external precision.

Standard	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
Solution:					
BCR2	0.003327	0.005	0.003558	0.000221	0.000123
NIST SRM982	0.000025	0.001114	0.002682	0.000025	0.000069
RAuGP3	0.001675	0.001129	0.003597	0.000059	0.000155
RAuGP5	0.000511	0.000654	0.001984	0.000015	0.00005
Laser ablation:					
BCR2	n/a	n/a	n/a	0.001109	0.002713
NIST SRM612	n/a	n/a	n/a	0.00016	0.000245
RAuGP3	n/a	n/a	n/a	0.000209	0.000696
RAuGP5	0.001893	0.002876	0.012474	0.000124	0.000489

Chapter 5: The Characterisation of Irish gold through lead isotope analysis

5.1 Synopsis

No widespread Pb isotope study has previously been carried out on Irish gold mineralisation, although there are Pb isotope data for sulphides from the Cavanacaw (Parnell et al., 2000) and Clontibret (O'Keeffe, 1986) prospects. An essential aspect of an archaeological provenance study is that ore deposits can be distinguished from each other. Therefore Chapter 5 investigates the degree to which Pb isotopes can be used to characterise and discriminate the numerous gold deposits found across Ireland. The sampling strategy employed to collect samples of native gold, and the locations of the sample sites, are outlined in Section 5.2. Lead isotope data are presented in Section 5.3, together with a discussion of the source(s) of Pb incorporated into Irish gold mineralisation. Results are interpreted in Section 5.4, using the global two-stage Pb evolution model of Stacey and Kramers (1975) and the Irish model of Pb isotope evolution by Dixon et al. (1990). Each of the gold deposits investigated is thoroughly characterised in Section 5.5, before the data are brought together to create a spatial/temporal model of Irish gold mineralisation in Section 5.6. Finally, the degree to which Pb isotope analysis can be used to discriminate the gold deposits of Ireland is summarised in Section 5.7. Data for Glencurry Burn and Goldmines River East are published in Standish et al., 2013.

5.2 Sampling strategy

Samples of native Irish gold or associated sulphide minerals were collected from all the key gold-bearing regions of Ireland, and the locations of sample sites are summarised in Figure 5.1. Alluvial deposits were sampled for their heavy mineral fraction using panning techniques. Specimens of gold-bearing veins and lodes were also collected, and these whole rock samples were crushed using a jaw crusher before the heavy mineral fractions were gravitally isolated using a Wilfley® concentrating table. Gold grains and sulphide minerals were then hand picked from the heavy fractions under a microscope.

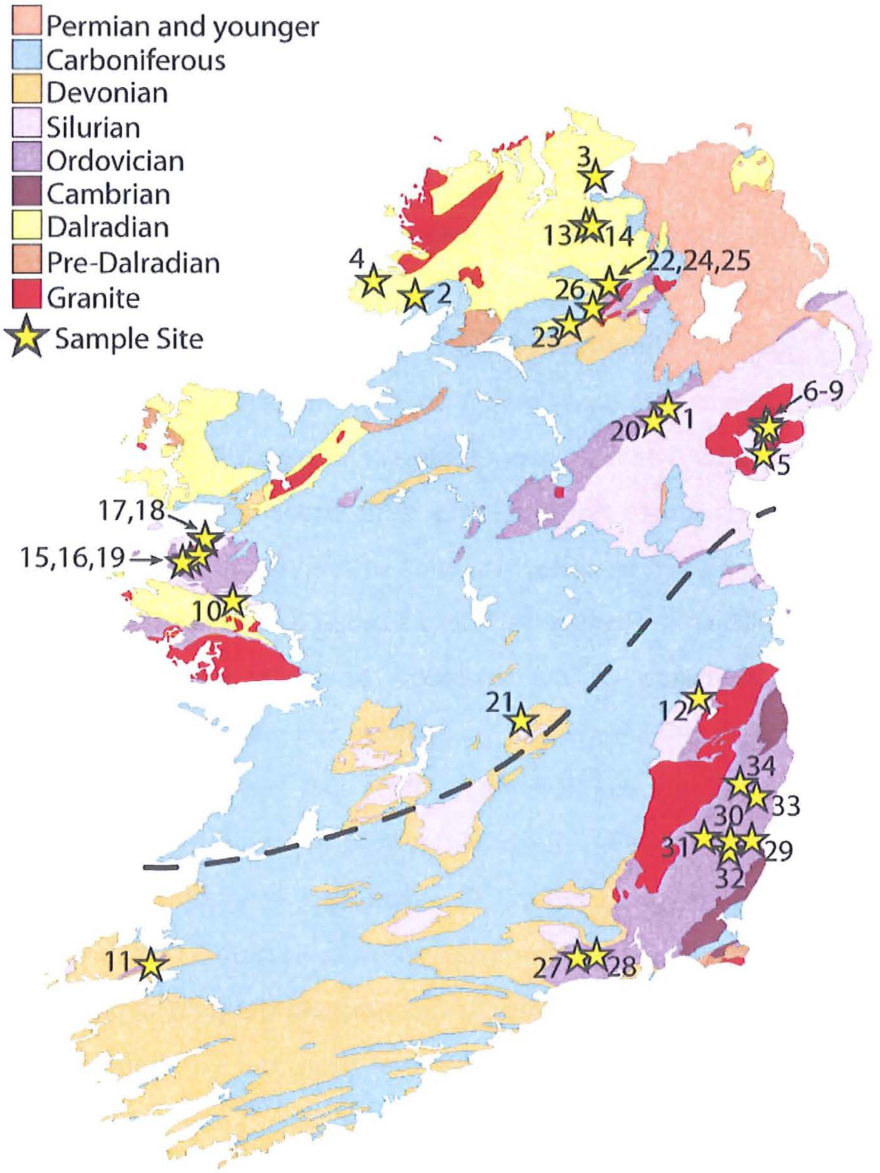


Figure 5.1: Location of Irish native gold and sulphide sample sites. 1 Clay Lake (Co. Armagh), 2 Balwoges, 3 Cabry River, 4 Lougheraherk (Co. Donegal), 5 Ballincurry River, 6 River Bann, 7 Leitrim River (lower), 8 Leitrim River (upper), 9 Rocky River (Co. Down), 10 Bohaun (Co. Galway), 11 Knockmore (Co. Kerry), 12 Walishtown (Co. Kildare), 13 Berry Burn, 14 Burntollet River (Co. Londonderry), 15 Bunowen River, 16 Carrownisky River, 17 Croagh Patrick, 18 Lecanvey Stream, 19 Shraroosky (Co. Mayo), 20 Clontibret (Co. Monaghan), 21 Camcor River (Co. Offaly), 22 Attagh Burn, 23 Cavanacaw, 24 Curraghinalt Burn, 25 Curraghinalt, 26 Glencurry Burn (Co. Tyrone), 27 Ballybrack, 28 Whelanbridge (Co. Waterford), 29 Ballykale, 30 Boley, 31 Gibbett Hill, 32 Millshoge (Co. Wexford), 33 Goldmines East River, 34 Ow River (Co. Wicklow). Dashed black line represents approximate trace of the Iapetus suture.

5.3 The sources of lead in Irish gold mineralisation

Pb isotope data of 109 gold samples from 31 Irish gold deposits (Appendix A1) are variable, ranging from 17.287–18.679 for the ^{206}Pb/^{204}Pb, 15.382–15.661 for the ^{207}Pb/^{204}Pb, and 37.517–38.635 for the ^{208}Pb/^{204}Pb (Figure 5.2).

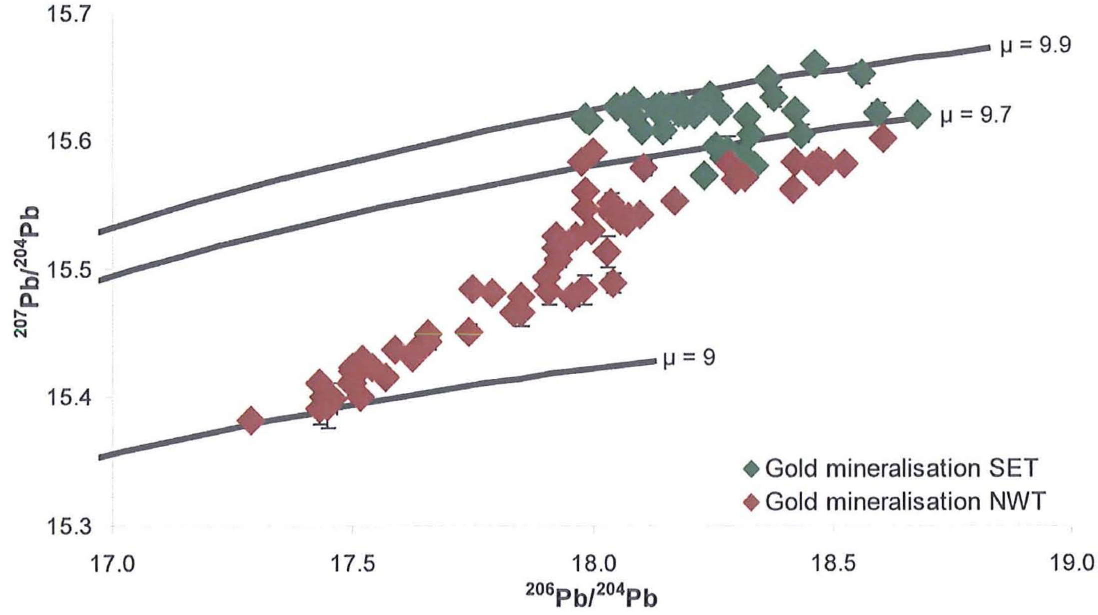


Figure 5.2: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Irish gold mineralisation as a function of the basement geology, i.e. the north-west terrane (NWT) located NW of the Iapetus suture, and the south-east terrane (SET) located SE of the Iapetus suture. The lead evolution growth curves of Stacey and Kramers (1975) for μ (^{238}U/^{204}Pb) = 9, μ = 9.7 and μ = 9.9 are plotted for comparison.

On the ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb diagram, the data plot between the Stacey and Kramers (1975) lead evolution curves calculated for μ = 9 and 9.9 (Figure 5.2). In addition, the isotope variation defined by the data tend to overlap with the evolution curves for the Earth's 'key' geochemical reservoirs, such as the mantle and the continental crust (Figure 5.3). This suggests that more than one Pb source were involved in the formation of the Irish gold.

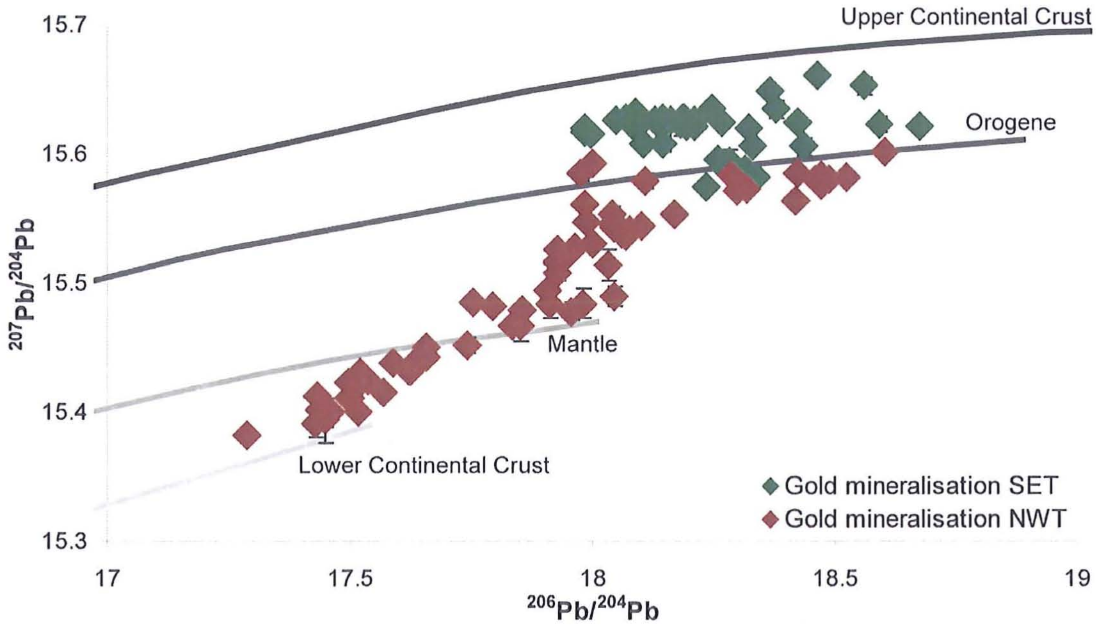


Figure 5.3: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Irish gold mineralisation relative to the lead evolution curves defined by Zartman and Doe (1981) for some Earth's key geochemical reservoirs.

The gold deposits of Ireland can be divided into two groups as a function of their basement geology: those that are underlain by Laurentian basement, (NWT) and those that are underlain by Avalonian basement (SET). These two groups show contrasting Pb isotope compositions. Deposits located overlying the NWT (red diamonds) are characterised by a variable Pb isotope composition (e.g., Figures 5.2 and 5.3). On the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram, NWT deposits plot between the Stacey and Kramers (1975) growth curves for $\mu = 9$ and $\mu = 9.7$ (Figure 5.2), whilst they overlap with the lower continental crust, mantle, and orogene (a hypothetical short lived reservoir of mixed derivation) evolution curves of Zartman and Doe (1981). The Pb isotope compositions of the NWT deposits may therefore be interpreted by variable mixing between 1) a less radiogenic source constituted by the mantle and/or the lower continental crust and 2) a more radiogenic source with an upper crustal origin (Figures 5.3 and 5.4).

In Figure 5.4, NWT samples are be plotted along with data for lower continental crust xenoliths, mid-ocean ridge basalts (MORB), ocean island basalts (OIB) and upper continental crust fluvial and turbidite sediments. NWT samples are encompassed by the domain defined by both MORB and OIB (which constitutes a proxy for mantle-derived Pb), and some data also overlap the fields defined by pre- and post-Archaean lower continental crust, and the upper crust (Figure 5.4). The lead incorporated into NWT gold mineralisation may therefore be regarded as a mixture, in variable proportions, between mantle Pb and crustal Pb of lower and/or upper crustal origin. Possible source regions are therefore oceanic volcanic rocks with a mantle like isotopic signature, or the Laurentian basement which has a less radiogenic lead isotope signature and has been proposed as the source region for lead incorporated into other Irish metal deposits (LeHuray et al., 1987; Dixon et al., 1990).

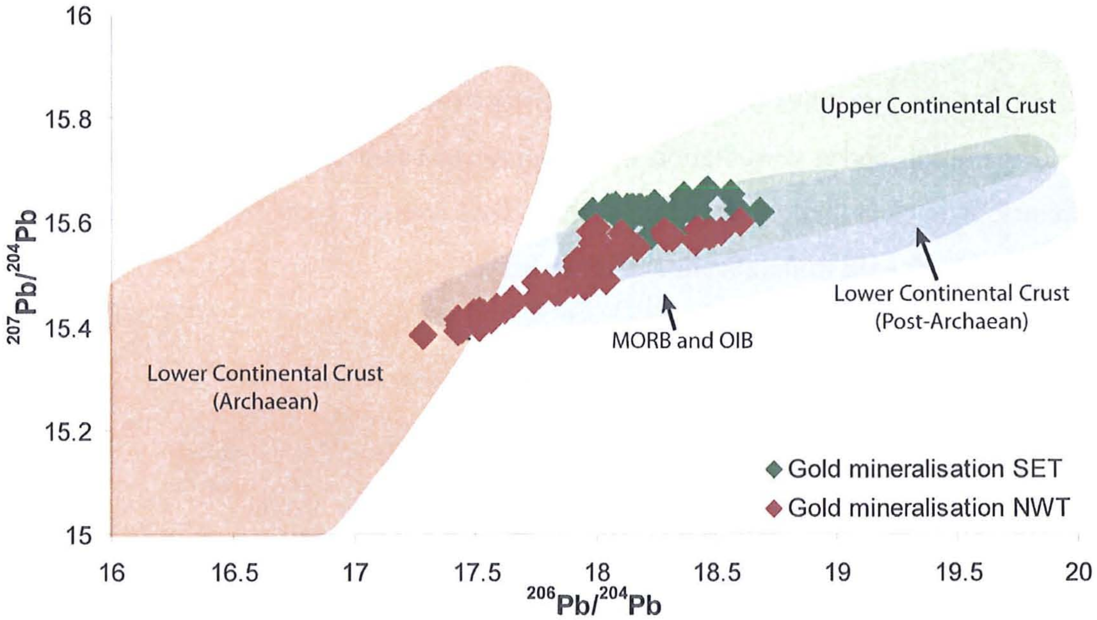


Figure 5.4: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Irish gold mineralisation relative to published present day literature data for pre- and post-Archaean lower continental crust, MORBs, OIBs and upper continental crust. Crustal xenoliths are used as a proxy for the composition of the lower crust. Fluvial and turbidite sediments are used as a proxy for the composition of upper crust. Data compiled from the GEOROC database.

SET deposits (green diamonds) can be distinguished from the NWT data by higher and less variable $^{207}Pb/^{204}Pb$ (e.g., Figures 5.2 to 5.4). They plot along the μ = 9.9 evolution curve of curve of Stacey and Kramers (1975), and proximal to the upper continental crust growth curve of Zartman and Doe (1981); Figure 5.2 and Figure 5.3 respectively. This suggests the Pb source of the SET gold mineralisation received a greater contribution from an upper crustal reservoir. Importantly, an origin from a unique source reservoir can be inferred due to the distribution of the data along the μ = 9.9 evolution curve.

In Figure 5.4, SET data is consistent with the field of the upper crust, and some data are overlapped by post-Archaean lower crust field and to a lesser extent the MORB/OIB field. This supports the idea that the source of the Pb within SET gold mineralisation includes a greater contribution from an isotopically enriched crustal reservoir compared to the source of Pb within NWT gold mineralisation. This crustal reservoir may either be upper continental crust or post-Archaean lower continental crust. The basement of the SET consists of Late Proterozoic upper crustal rocks (LeHuray et al., 1987), therefore the pre-Caledonian basement or associated Lower Palaeozoic lithologies represent viable sources for the lead incorporated into SET gold mineralisation.

The lead isotope signatures of Irish gold deposits have been compared to global models of lead evolution and a compilation of literature data that characterises different lead reservoirs. It is clear that at least two distinct lead sources contributed to the isotopic signature of Irish gold mineralisation (Figure 5.5).

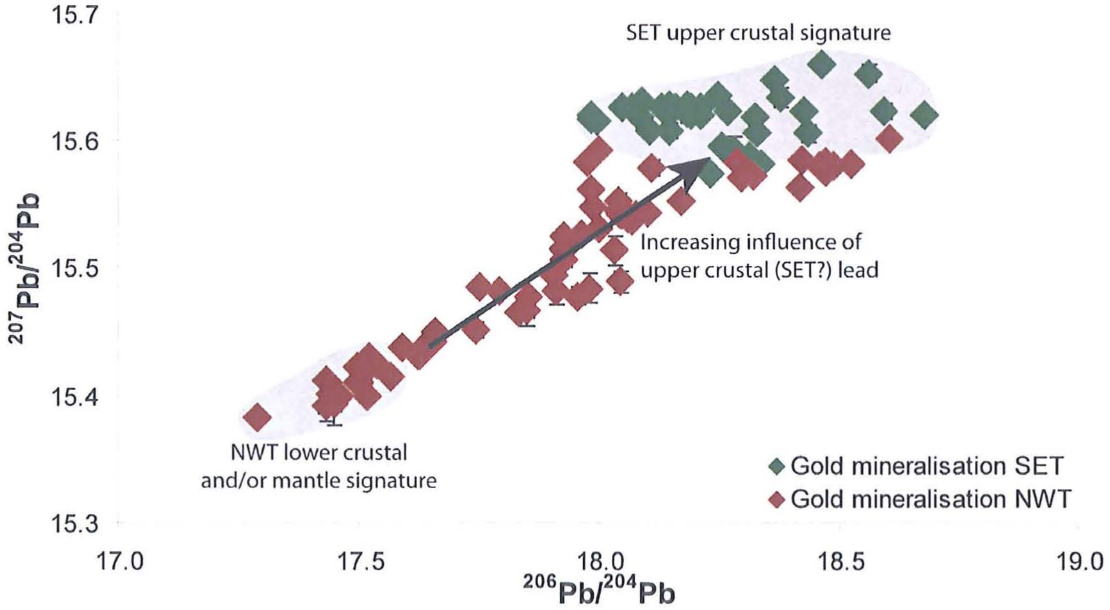


Figure 5.5: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ summary plot of NWT and SET isotopic end members, including possible upper crustal mixing.

The SET mineralisation exhibits an upper crustal or post-Archaean lower crustal isotopic signature and is consistent with a SET upper crustal basement source. The NWT mineralisation exhibits a mixed isotopic signature that can be explained by lead contributions from an upper crustal more radiogenic lead source (the SET reservoir is a possible explanation) and a less radiogenic end member consistent with a mantle or lower crustal derived lead source. Possible source regions for this less radiogenic end member are oceanic crust volcanic rocks, or the lower crustal NWT basement.

5.4 Models of Irish lead evolution

5.4.1 The two-stage lead evolution model of Stacey and Kramers (1975)

Model Pb ages are often used in Earth Sciences for dating whole rocks and minerals. The most common method of calculating Pb ages for individual mineral grains is by employing the two-stage lead evolution model of Stacey and Kramers (1975). This model is outlined in Section 3.5.1 and Figure 3.5, and in essence, minerals with low U/Pb can be dated because their lead isotope ratios represent the time at which they were removed from a source reservoir. Post-crystallisation Pb growth occurs in minerals with high U/Pb, therefore model lead ages will not be truly representative of source age and will reflect minimum possible ages. Gold grains typically contain low U/Pb (i.e. $\mu < 1$; Eugster et al., 1995; Pettke et al., 1997), however they can include U-rich inclusions (Eugster et al., 1995) which may increase the bulk U/Pb ratios in the gold grains. Additionally the two-stage model of Stacey and Kramers (1975) is an idealised situation which does not take into account complex geological processes such as crustal recycling and plate tectonics. These processes are responsible for the mixing, on a very large scale, of the main Earth's geochemical reservoirs. For this reason, individual Pb ages of mineral deposits may not always reflect the true age of their source. Yet when multiple analyses are carried out, broad patterns relating to the ore forming events can become apparent. For example, by analysing lead isotopes in 26 different mineral deposits, Tornos and Chiaradia (2004) were able to correlate mineralisation events in the Iberian Peninsula to the Cadomian and Variscan orogenies.

Model Pb ages based on Stacey and Kramers (1975) have been calculated for each sample using their $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios (Appendix A1), and the distribution of these ages is shown in Figure 5.6. Four main peaks can be identified, and they correlate with the four principal Irish mineralisation events that occurred during the Early Caledonian, the Late Caledonian, the Carboniferous and the Late Permian (or Variscan). This is generally consistent with the preferred ages of mineralisation for Irish gold deposits (e.g. Ixer et al., 1990; Parnell et al., 2000; Lusty et al., 2011)

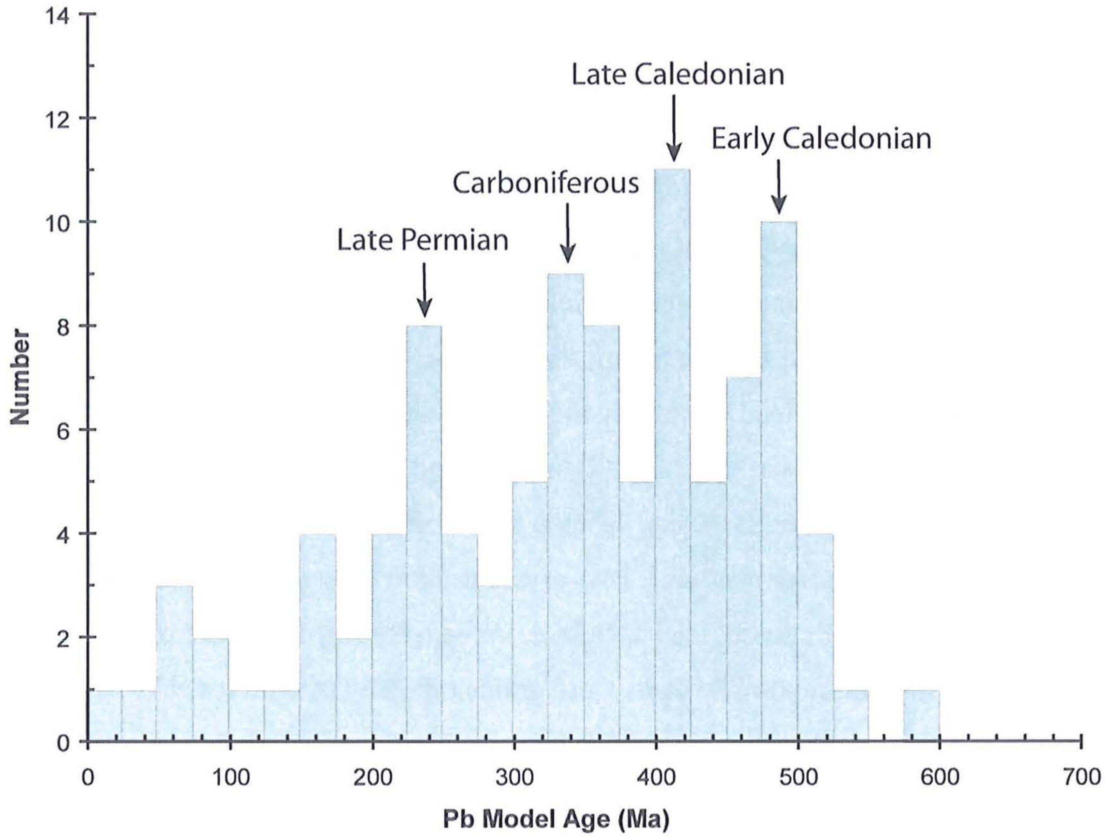


Figure 5.6: Distribution of Pb model ages for the gold deposits of Ireland calculated after the two-stage lead evolution model of Stacey and Kramers (1975).

In Figure 5.7 all the analysed gold samples are plotted along with the Pb evolution curves of Stacey and Kramers (1975) for $\mu = 9$ and $\mu = 9.9$, and isochrons for 300 Ma, 400 Ma, and 500 Ma. Two gold mineralisation regions produce Pb ages from around 500 Ma; the Co. Wicklow-Co. Wexford region of south-east Ireland (Figure 5.7 open green diamonds, Pb ages range from 528 Ma to 0 Ma), and the Sperrin Mountains of Northern Ireland (Figure 5.7 open red diamonds, Pb ages range from 526 Ma to 434 Ma, with one outlier at 583 Ma).

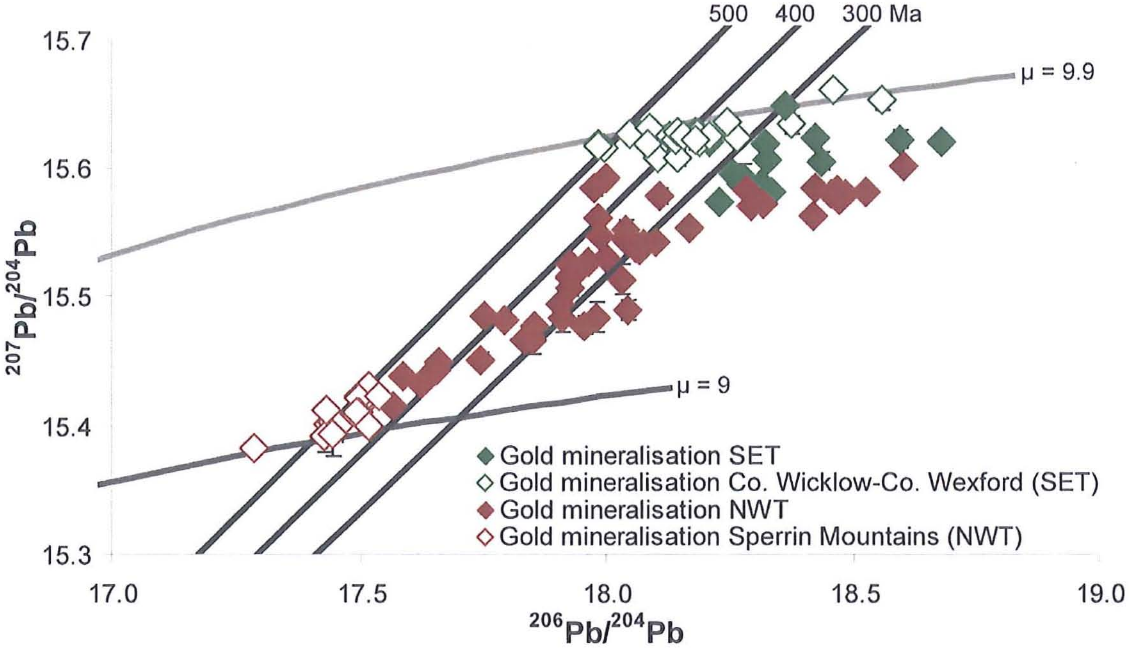


Figure 5.7: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of SET and NWT Irish gold mineralisation with the Co. Wicklow-Co. Wexford and Sperrin Mountain gold deposits identified by open symbols. Data are plotted relative to lead growth curves of Stacey and Kramers (1975) for $\mu = 9$ and $\mu = 9.9$, and isochrons for 300 Ma, 400 Ma, and 500 Ma.

The Grampian phase of the Caledonian Orogeny has been dated at 480-455 Ma (McKerrow et al., 2000), and this time span represents the initial collision between a volcanic arc and the Laurentian plate prior to the Avalonian-Laurentian collision. This event is thought to be responsible for a number of Irish gold deposits, and thus the correlation in dates between the Grampian orogeny and the earliest Pb ages for the gold mineralisation of the Sperrin Mountains may indicate a Grampian age of mineralisation. Contemporaneously, oceanic crust was being subducted beneath the Avalonian crust (Max et al., 1990), and so the Co. Wicklow-Co. Wexford samples may indicate a similar Early Caledonian age of mineralisation. Indeed Early Caledonian ages have been proposed for gold deposits in both these regions based on evidence from stratigraphical studies, mineralisation style and texture, fluid inclusions studies and geological setting (e.g. Ixer et al., 1990; Parnell et al., 2000).

The heterogeneous signatures of the Co. Wicklow-Co. Wexford mineralisation define a sub-linear array on the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ graph (Figure 5.5). As mentioned in Section 3.5.1, lead isotope trends can result from lead growth, compositional heterogeneity (and therefore the trend represents a source isochron), or mixing between two or more sources. Regarding the Co. Wicklow-Co. Wexford trend, the $^{207}Pb/^{204}Pb$ ratios show little variability compared to the $^{206}Pb/^{204}Pb$, therefore the data can not define an isochron. In Figure 5.7, there is excellent consistency between the distribution of the data points and the Stacey and Kramers (1975) Pb evolution curve for $\mu = 9.9$, with the majority of the samples plotting between the 500 Ma and 350 Ma isochrons (although a few samples show slightly more radiogenic values). The Pb isotope composition of the Co. Wicklow-Co. Wexford deposits may therefore be interpreted as the product of a series of mineralisation events between c.500-300 Ma ago, during which the Pb was repeatedly extracted from a unique crustal reservoir with $\mu = 9.9$. The times at which the main mineralisation events occurred are best represented by the main cluster of samples that plot between the 500 Ma and 300 Ma isochrons. An initial event in the Early Caledonian produced isotopic signatures that indicate source ages c.500 Ma. A second mineralisation event by c.300 Ma is characterised by a more evolved lead isotope signature, and this remobilised and mixed with some of the earlier mineralisation to varying degrees producing isotopic ratios that plot between the two end members. The U concentrations of the gold samples were not analysed, therefore the U/Pb is unknown. However as U/Pb in gold is typically low, the more radiogenic data can be explained by the presence of U-rich inclusions derived from more radiogenic fluids.

All other analysed Irish gold deposits (Figure 5.7 filled green and red diamonds) plot to the right of the 500 Ma isochron suggesting younger source ages, and they also plot sequentially closer together implying increased mixing between the two main source reservoirs defined previously. After the Caledonian collision, a series of successor basins formed. These filled with Silurian sedimentary sequences that consist of both NWT and SET derived material (Hutton and Murphy, 1987; Murphy, 1987), consequently physical mixing of the two source reservoirs had begun to occur by this time. These two reservoirs could also undergo mixing if mineralising fluids passed through the suture zone and dissolved constituents from both terranes. Gold bearing regions such as Co. Waterford and the Longford Down Inlier have Pb ages starting from c. 390-360 Ma, which suggests a Late Caledonian mineralisation event. Deposits such as Bohaun in Co. Galway, the Camcor River (Co. Offaly), and Croagh Patrick are all consistent with Variscan ages (oldest ages range from 334-298 Ma), while the oldest Pb date for the Kildare mineralisation is 244 Ma.

The two-stage evolution model of Stacey and Kramers (1975), used for these calculations, assumes the constant evolution of two reservoirs (i.e. SET and NWT) since 3.7 Ga without any interaction or mixing with another lead source. This is unlikely due to processes such as crustal recycling, and the great diversity of lithologies of varying sources and ages that ore-bearing fluids can pass through. Consequently, when regional studies use global models of lead evolution, Pb isotope data should be used primarily as a guide to mineralisation phases. The following summary of gold mineralisation based on the interpretation of Pb isotope analysis and the model of Stacy and Kramers (1975) can therefore be given.

Two initial lead sources can be distinguished because they originate from two different geological terranes. The SET (Avalonian) deposits are more radiogenic, and display an upper crustal signature. The Late Proterozoic upper crustal rocks of the SET basement are therefore the most likely SET source region. The NWT (Laurentian) deposits are less radiogenic and display lower crustal and/or mantle signatures. Oceanic volcanics and/or the less radiogenic Laurentian basement are therefore likely NWT source regions. The NWT and SET sources were incorporated into gold mineralisation during an early phase of mineralisation in the early stages of the Caledonian Orogeny, and produced deposits with distinct Pb isotope signatures. Over time there was mixing between Pb from these two reservoirs and thus the Pb isotope signatures of each terrane gradually combined. This pattern is recorded in the isotopic signatures of gold deposits that mineralised at later stages of geological history, and relate to Late Caledonian and Carboniferous to Variscan mineralising events. Significantly more SET lead was incorporated into this later mineralisation, therefore deposits hosted by the NWT took on a more upper crustal signature.

5.4.2 The Irish model of lead evolution

Due to the ongoing interaction of different geochemical reservoirs, it is advantageous if lead isotope data can be interpreted within smaller scale or local lead evolution models. There is a wealth of Pb isotope data from Irish mineral deposits due to a series of investigations that examined the genesis of the economically important Carboniferous base metal deposits (Boast et al., 1981; Boast, 1983; Caulfield et al., 1986; O'Keeffe, 1986; LeHuray et al., 1987; Dixon et al., 1990; Kinnaird et al., 2002; Everett et al., 2003). A summary of these studies has been provided in Section 3.5.2. Five key isotopic fields can be defined: 1) Palaeozoic hosted massive sulphide deposits of the SET (Early

Caledonian); 2) Palaeozoic hosted massive sulphide deposits of the NWT (Early Caledonian); 3) Carboniferous and Palaeozoic hosted Zn-Pb mineralisation (Variscan); 4) Carbonate hosted copper mineralisation of SW Ireland (Variscan); and 5) ORS hosted copper mineralisation of SW Ireland (Variscan). These fields are plotted in Figure 5.8, together with the isotopic data for Irish gold mineralisation analysed in this study.

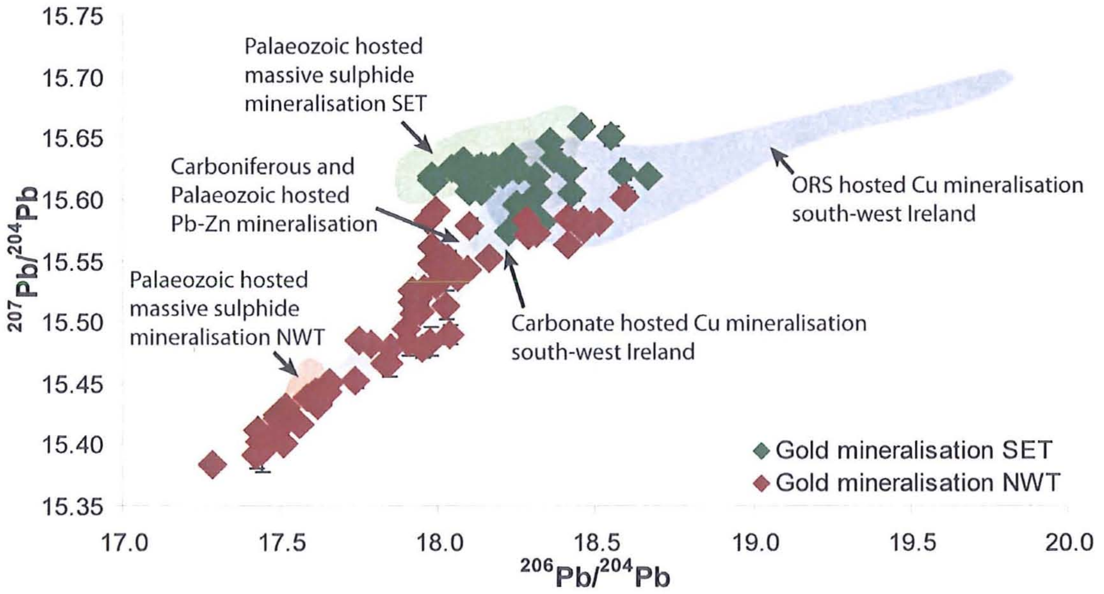


Figure 5.8: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Irish gold mineralisation (this study) and published Irish lead isotope data (references in Section 3.5.2).

Figure 5.8 shows striking correlations between the Pb isotope signatures of Irish gold (red and green diamonds) and the published data for sulphide minerals, represented by the five shaded domains. This suggests that similar sources were involved in both the sulphide and the gold mineralisation. For this reason, the model of Irish lead evolution devised by Dixon et al. (1990) and explained in Section 3.5.2.3, is also applicable to Irish gold mineralisation to some degree. This model is presented in Figure 5.9, together with the Irish gold and sulphide data.

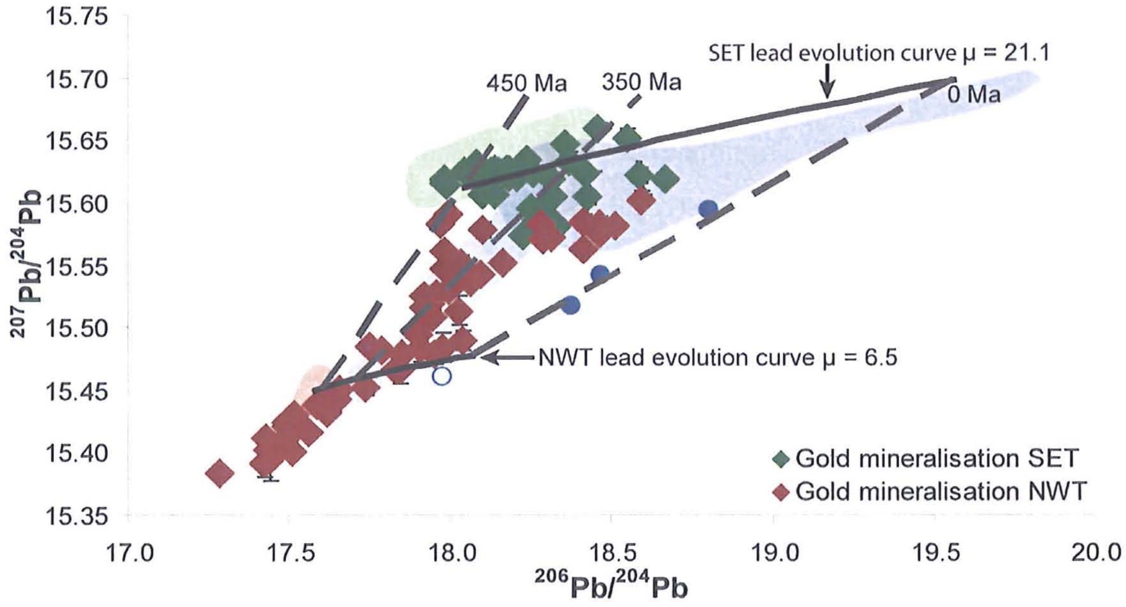


Figure 5.9: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ of Irish gold mineralisation and the model of Irish lead evolution by Dixon et al. (1990). Isochrons of 0 Ma, 350 Ma and 450 Ma age (dashed grey lines) and lead evolution curves for the south-eastern Ordovician arc (μ = 21.1) and the north-western Ordovician arc (μ = 6.5) are plotted. ● = Longford Down whole rock Silurian; ○ = Longford Down whole rock Ordovician. Sulphide domains are same as Figure 5.8.

It is generally accepted that the Late Proterozoic upper crustal basement of the SET is the most likely source region of SET sulphide mineralisation (O'Keeffe, 1986; LeHuray et al., 1987; Dixon et al., 1990). The correlation between SET gold and sulphide mineralisation (and associated Pb growth curve; Figure 5.9) suggests a similar upper crustal basement source was also responsible for the gold mineralisation. The NWT Pb growth curve derived from sulphide data is consistent with some samples of NWT gold mineralisation, again suggesting similarities in lead source. However this lead growth curve is not consistent with the least radiogenic gold samples, thus indicating the involvement of lead from an alternative source region. When comparing the NWT evolution curve to the Pb isotope fields defined in Figure 5.4, it falls within the MORB and OIB domain supporting a significant mantle derived input. The least radiogenic gold samples trend into the Archaean lower continental crust domain (Figure 5.4), thus it seems likely that those gold samples characterised by lead less radiogenic than the NWT Pb growth curve incorporated a greater degree of lower crustal lead relative to the NWT massive sulphide deposits. This is consistent with the work of Dixon et al. (1990)

who proposed that the NWT end member had an input from both Ordovician volcanic arc rocks and Lewisian basement.

Published Pb isotope data from both the Grampian and Lewisian basement (present day compositions) are plotted together with the data for Irish gold mineralisation in Figure 5.10. The basement of the NWT (Figure 5.10 triangles) is on average less radiogenic than the Irish gold samples, thus is a likely end-member source for the least radiogenic Pb. The slope of the Carboniferous sulphide mineralisation data indicates a basement source age of 3.2 Ga (O'Keeffe, 1986) which is inconsistent with the basement underlying central Ireland. As many of the data points representing gold mineralisation are consistent with this literature data, they also do not reflect basement age.

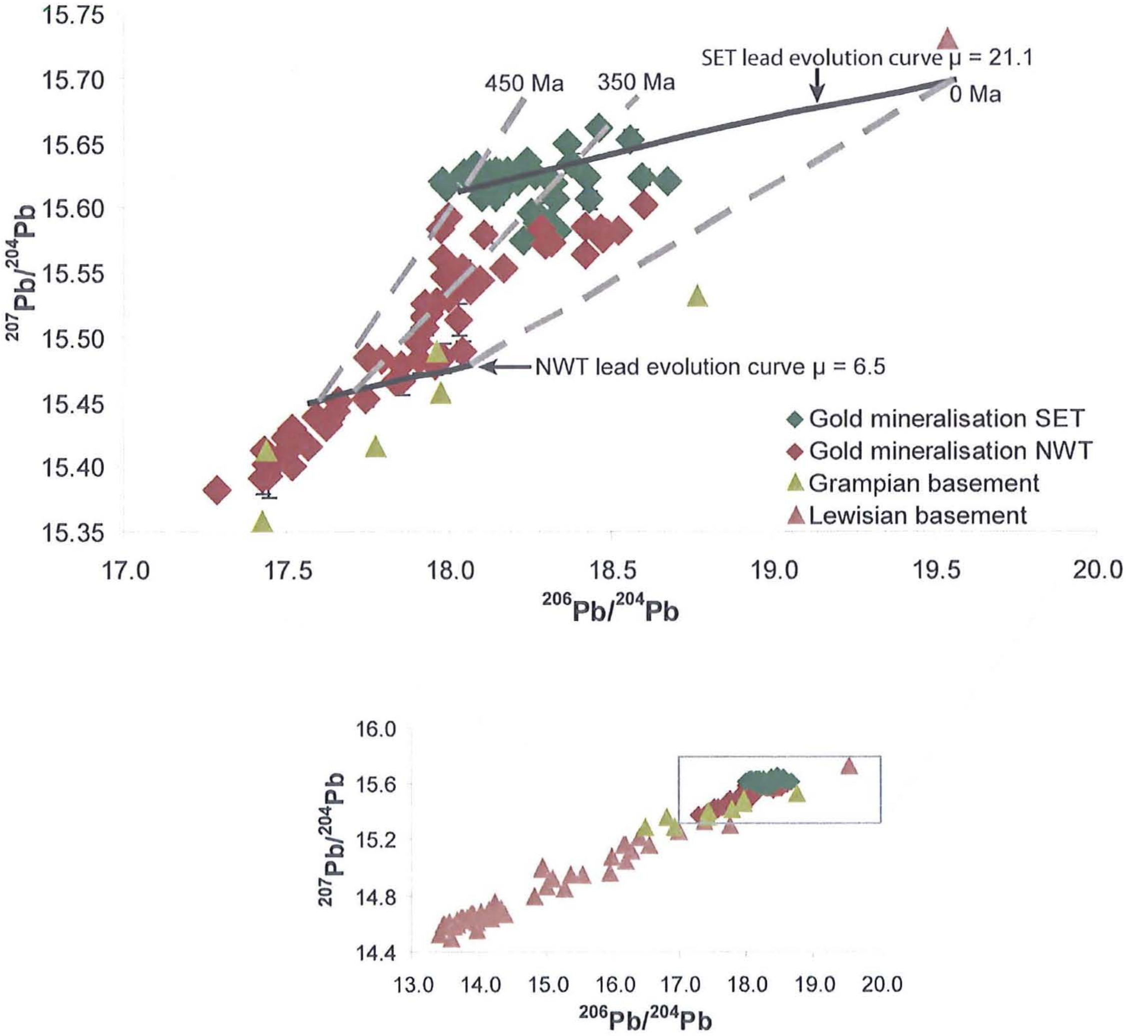


Figure 5.10: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb of Irish gold mineralisation along with present day isotope compositions of Grampian and Lewisian basement rocks. Data from Chapman and Moorbath (1977), Blaxland et al. (1979) Whitehouse and Moorbath (1986), Marcantonio (1988) and Whitehouse (1993).

Despite the shift from a global to regional scale, the same broad patterns exist. Certain gold deposits overlying both the SET and NWT plot consistent with Grampian source ages from c.470 Ma (Figure 5.9), whilst further examples are consistent with later Caledonian ages. A number of the gold deposits are consistent with Carboniferous to Variscan base metal deposits. This implies a contribution from the same sources of Pb, however whether this is a reflection of similar source ages or mineralisation ages requires further discussion. Further consistency between some gold samples and the ORS hosted copper mineralisation highlights an association with secondary upper crustal Pb. As discussed in section 3.5.2, the radiogenic Pb incorporated into ORS hosted copper mineralisation has been linked to Pb derived from Late Caledonian S-type granites (Kinnaird et al., 2002; Everett et al., 2003).

The growth curves that form the basis of the Irish model are based on analysed Irish samples of known age, therefore any reservoir mixing or recycling prior to the start of the model (c.470 Ma) is taken into account. This is a significant advantage over global models of lead evolution. The two growth curves calculated by Dixon et al. (1990) characterise lead growth associated with mineralisation in the Leinster Massif and Charlestown inlier respectively, therefore any gold deposits hosted by these (or genetically related) terranes should conform to the Irish model. However mineralisation hosted by, or derived from, other geological terranes or reservoirs may not conform to this model. As a result, it might not always be relevant to interpret gold mineralisation data using this model of Irish lead evolution.

5.5 Gold bearing regions of Ireland

5.5.1 Introduction

Interpreting the isotopic data of Irish gold mineralisation in both global and regional models of lead evolution highlights the same broad patterns. The data advocates multiple stages of mineralisation (Early Caledonian through to the Variscan) that incorporated Pb from a number of different source regions (i.e. lower crustal, upper crustal, and mantle derived). The NWT and SET gold mineralisation groups can be further divided into a series of distinct gold bearing regions based on their geographic location and mineralisation style (Figure 5.11). Each of these gold bearing regions will now be discussed in greater detail, allowing a full understanding of why Irish gold deposits inherited their Pb isotope signature to be achieved. This will be followed by a synthesis that summarises the genesis of Irish gold deposits as inferred through Pb isotope analysis, and the degree to which Irish gold deposits can be characterised for provenance studies will become apparent. In the following sections all isotopic data are plotted in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ space only, however the $^{208}Pb/^{204}Pb$ variations will be discussed when relevant. The data are plotted using all available ratios at the end of this chapter (Figure 5.29, Figure 5.30 and Figure 5.31).

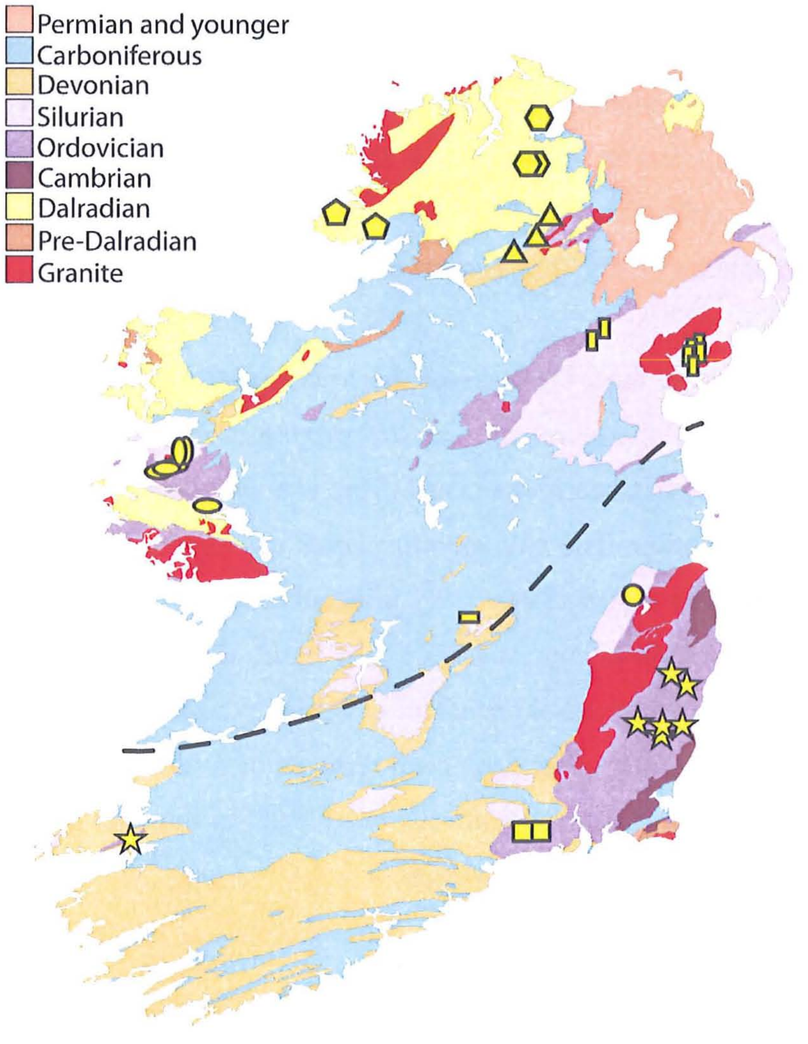


Figure 5.11: Map of gold bearing regions discussed in section 5.5. Triangles: Dalradian hosted deposits of the Sperrin Mountains; stars: Palaeozoic hosted deposits of Co. Wicklow-Co. Wexford and Co. Kerry; horizontal and vertical ellipses: Palaeozoic hosted mineralisation of Co. Galway-Co. Mayo; squares: Palaeozoic hosted mineralisation of Co. Waterford; hexagons: Dalradian hosted mineralisation of north-east Co. Donegal and Northern Sperrins; circles: Palaeozoic hosted deposits of Co. Kildare; pentagons: Dalradian hosted mineralisation of south-west Co. Donegal; vertical rectangles: Palaeozoic associated deposits of the Longford-Down inlier; horizontal rectangles: Palaeozoic hosted mineralisation of the central southern Irish inliers. Dashed black line represents approximate trace of Iapetus suture.

5.5.2 Dalradian hosted gold in the Sperrin Mountains: NWT Early Caledonian mineralisation

Dalradian metasediments and the Tyrone igneous complex are the two principle rock groups associated with the gold mineralisation of the Sperrin Mountains (Figure 5.11, yellow triangles). During the Grampian orogeny the Tyrone igneous complex was obducted onto the Dalradian sediments which were metamorphosed to greenschist facies (Alsop and Hutton, 1993; Parnell et al., 2000). Gold mineralisation is principally hosted within the Dalradian metasediments, (Parnell et al., 2000), and samples from three deposits have been analysed: bedrock gold from the Kearney vein at Cavanacaw; alluvial gold from Curraghinalt (Attagh Burn and Curraghinalt Burn); and alluvial gold from Glencurry Burn (Figure 5.1). Lead isotope signatures of gold from the Sperrin Mountains are the least radiogenic of all the Irish gold deposits (Figure 5.12, red dots; and Appendix A1).

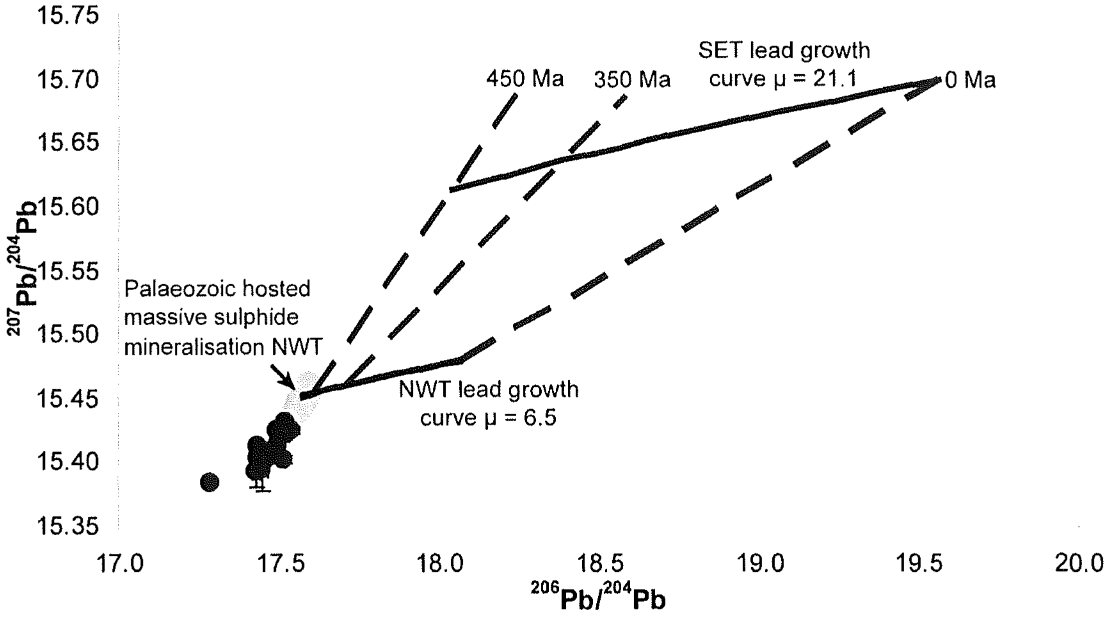


Figure 5.12: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Sperrin Mountain gold mineralisation (red dots) relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide field.

Parnell et al. (2000) proposed that the Tyrone Igneous Complex was the source of Pb at Cavanacaw because of the isotopic similarity between the Charlestown (hosted by an Ordovician volcanic complex; red domain in Figure 5.12) and Cavanacaw deposits. However the Sperrin Mountain signature is in general less radiogenic than the Charlestown deposit, suggesting slightly different Pb sources. As discussed previously (section 5.4.2), the Charlestown deposit (form which the NWT Pb evolution curve was calculated by Dixon et al., 1990) show typical signatures of a mantle Pb source. The slightly less radiogenic signature of the Sperrin Mountain gold mineralisation may indicate a greater contribution from a lower crustal component, with the Grampian/Lewisian basement (Figure 5.10) constituting a possible source region.

The Pb incorporated into the gold mineralisation of the Sperrins Mountains is therefore derived from two source regions: 1) a source with a mantle origin similar to that of the Charlestown massive sulphide deposit, and that can be associated with the Tyrone Igneous Complex (Parnell et al., 2000); and 2) a source with an increasingly lower crust origin, represented by the Dalradian metasediment host terrane (see also Standish et al., 2013). LeHuray et al. (1987) and Dixon et al. (1990) concluded that the NWT Pb source was the pre-Caledonian basement, whereas O'Keeffe (1986) preferred a mantle origin. The most likely scenario is a combination of the two, with the NWT less radiogenic end-member deriving from both less radiogenic NWT basement and mantle-derived sources. A more detailed isotopic investigation of the region may help to elucidate this further.

Pb model ages of Sperrin Mountain gold range from 584 Ma to 435 Ma (Appendix A1), and are consistent with Early Caledonian mineralisation. The older pre-Caledonian ages can be explained by the postulated contributions of less radiogenic crustal Pb. This Early Caledonian age is supported by the general consistency of the Sperrin Mountain gold mineralisation with the Charlestown massive sulphide deposit and start of the NWT Pb evolution curve (the Charlestown deposit has been dated to the Arenig stage of the Ordovician; Cummins, 1954; O'Connor and Poustie, 1986). It is also consistent with proposals favouring Caledonian magmatism as the key process behind gold mineralisation in the region (Earls et al., 1997; Parnell et al., 2000), and the origin of the Tyrone ophiolite dated to 472 ± 4 Ma by Hutton et al. (1985).

On a site specific scale, four analyses of gold mineralisation from the Kearney vein at Cavanacaw define a tight cluster in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ space (Figure 5.13, filled blue circles). They plot along the 450 Ma isochron in the Irish Pb evolution model, suggesting Grampian age mineralisation. Galena and pyrite minerals from the Kearney vein (open blue circles, n = 7) show Pb isotope ratios in agreement with those of the vein gold. The slightly higher $^{207}Pb/^{204}Pb$ of the Cavanacaw mineralisation relative to the other Sperrin Mountain deposits can be explained if there was less contribution from a lower crustal source.

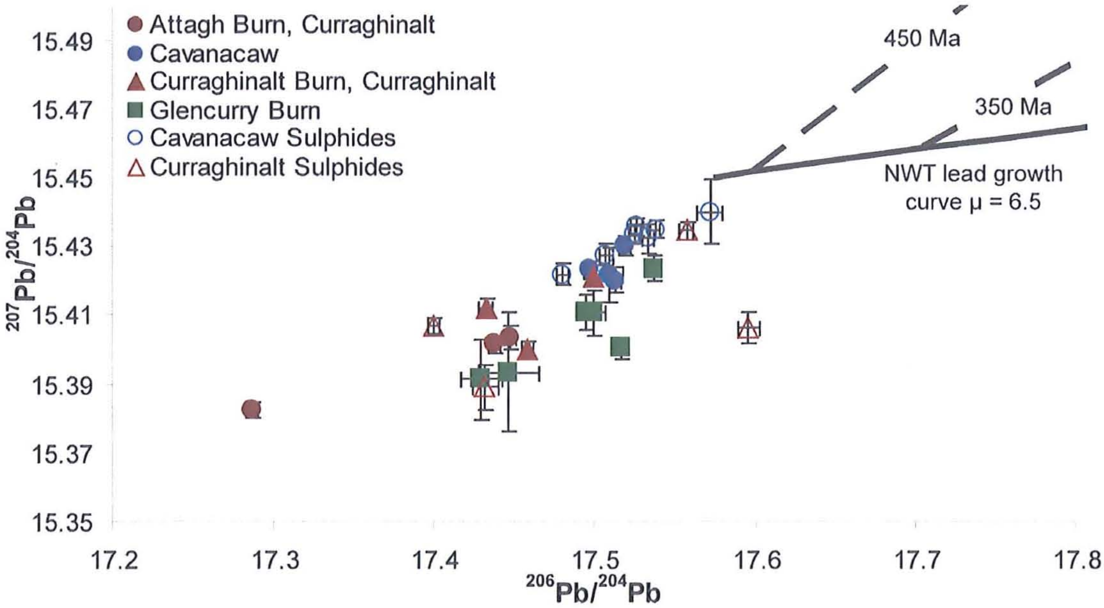


Figure 5.13: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Sperrin Mountain gold mineralisation and associated sulphides.

In contrast, gold from Attagh Burn and Curraghinalt Burn at the Curraghinalt prospect (Figure 5.14, red filled triangles; n = 6) are characterised by slightly more variable and less radiogenic signatures (Appendix A1). Arsenopyrite and pyrite minerals from the same location (T17 vein, open red triangles) have Pb isotope signatures broadly similar to the alluvial gold deposits, although they tend to show a greater variation in both ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb. In the context of the Irish Pb evolution model, samples from Attagh Burn and Curraghinalt Burn define a primary Grampian age of mineralisation (assuming that older ages are related to contributions from less radiogenic crustal Pb). However a number of the samples plot with significantly higher ^{206}Pb/^{204}Pb ratios indicating a more radiogenic lead component. Gold from Glencurry Burn (filled green squares, n = 6, see also Standish et al., 2013) is characterised by isotope signatures similar to Curraghinalt (open and filled red triangles), which indicates similar Pb sources and mineralisation styles for both Glencurry Burn and Curraghinalt gold. This contrasts with the microchemical investigation by Chapman et al. (2000b) who link Glencurry Burn to the mineralisation at Cavanacaw based on composition and mineral inclusions.

There is evidence for the remobilisation of gold in the Sperrin Mountains by Carboniferous basinal brines, and Rb-Sr and K-Ar studies of fault gouge at both Cavanacaw and Curraghinalt suggest that re-activation of pre-existing faults occurred during this period (Parnell et al., 2000). A contribution of these Carboniferous fluids in the source of gold may explain higher $^{206}Pb/^{204}Pb$ ratios seen in some of the Sperrin Mountain samples such as the Curraghinalt T17 vein sulphides because Carboniferous related ore deposits have more radiogenic Pb (for example in the grey domain in Figure 5.8). Remobilisation of gold by these Carboniferous fluids would lead to mixing between Grampian Pb (less radiogenic) and Carboniferous Pb (more radiogenic).

To summarise, the Pb isotope signatures of the NWT Sperrin Mountains gold deposits indicate that mineralisation primarily incorporated lead from a mantle-derived source, with varying degrees of contamination from the lower crustal host lithologies. In agreement with Earls et al. (1997) and Parnell et al. (2000), the Tyrone igneous complex is seen to have played a major role in the mineralisation. A primary Grampian age of mineralisation c.470–450 Ma is favoured.

5.5.3 Palaeozoic hosted gold deposits of Counties Waterford, Wexford, Wicklow (and Kerry): SET Early and Late Caledonian mineralisation

Numerous gold occurrences have been recorded in the Lower Palaeozoic lithologies of south-east Ireland (Stanley et al., 2000), and gold occurrences located on the Dingle Peninsula, Co. Kerry, are spatially associated with related lithologies (e.g. Stanley et al., 2000; Chapman et al., 2006).

The Co. Wicklow-Co. Wexford (and Co. Kerry) gold deposits (Figure 5.11 yellow stars) plot along the less radiogenic end of SET Irish lead evolution curve on a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Figure 5.14). These samples define a field which is broadly encompassed by the field defined by the SET massive sulphide deposits (green domain). As previously discussed (Sections 5.3 and 5.4), the underlying later Proterozoic upper crustal basement rocks or associated Lower Palaeozoic lithologies are the most likely source region (see also Standish et al., 2013). Eight samples from the Goldmines East River (Standish et al., 2013) and seven from the Ow River were analysed from Co. Wicklow, while four alluvial deposits were sampled from Co. Wexford: Ballykale (n = 1), Boley (n = 2), Gibbett Hill (n = 2), and Millshoge (n = 2). There are no clear differences between the Pb isotope ratios of gold from the different locations (Appendix

A1), indicating a similar lead source for the entire region. All sample sites drain Ordovician metasedimentary lithologies, whilst there is also a spatial relationship with the Campile Formation comprising of felsic, intermediate and rhyolitic volcanics along with metasediments.

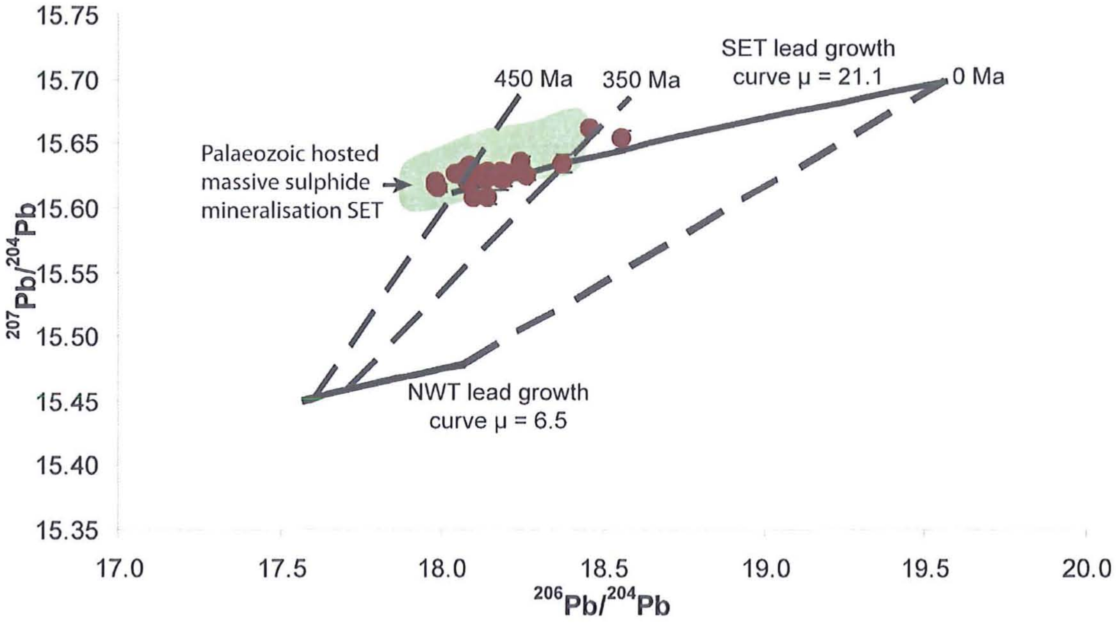


Figure 5.14: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Co. Wicklow, Co. Wexford and Co. Kerry gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide field.

As discussed in section 5.4.1, Pb model ages are variable but primarily range between 500 Ma and 300 Ma (Appendix A1). This suggests the occurrence of at least two mineralisation events; the first c.500 Ma and the second by c.300 Ma. In the context of the Irish model of lead evolution, the majority of the samples (n = 18) plot between 470 Ma and 400 Ma along the SET Pb growth curve. This growth curve was calculated using sulphide deposits hosted by the same geological terrane that hosts the gold mineralisation currently under discussion, therefore these ages can be considered more robust than the model Pb ages calculated previously. Early Caledonian source ages can be proposed for the primary phase of gold mineralisation c. 470 to 450 Ma, an age that is broadly contemporaneous with the host rock formation and local massive sulphide deposits (green domain, Figure 5.14). The spread in ages along the SET Pb evolution curve is too large to result from in situ decay of U and Th based on the typical U/Pb and Th/Pb of gold. Therefore a second mineralisation event is postulated to have occurred by c.400 Ma (Late Caledonian). This event remobilised the Early Caledonian mineralisation and mixed it with more evolved fluids creating the documented isotopic trend.

This two-stage model consisting of Early and Late Caledonian source ages is consistent with the proposals of both Ixer et al. (1990) and Milner and McArdle (1992) for the gold mineralisation by the Goldmines Rivers and at Kilmacoo respectively. Both studies concluded that initial Ordovician mineralisation relating to Early Caledonian metamorphism was followed by later Caledonian remobilisation and alteration related to fluids associated with the emplacement of Early Devonian doleritic dykes, or the Late Caledonian Leinster granite. The Leinster granite has been dated to 404 ± 24 Ma (O'Connor and Brück, 1978), therefore the second stage of mineralisation may have been associated with the emplacement of this granite or associated intrusions.

Three Ow River samples and one Millshoge sample have higher $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ than other samples from this region (Appendix A1), yet they plot along the SET Pb evolution curve in Figure 5.14. A possible explanation is that these resulted from in situ decay of U- and Th-rich inclusions inherited during the second stage of mineralisation. The Leinster granite is a S-type granite formed by partial melting of a Lower Palaeozoic immature sedimentary source (Sweetman, 1987). As previously discussed (Sections 5.3 and 5.4), the Lower Palaeozoic rocks of SE Ireland are upper crustal in nature, and it has been demonstrated that Pb associated with the S-type granites of SE Ireland is characterised by increasingly radiogenic signatures (Kinnaird et al., 2002; Everett et al., 2003). Consequently partial derivation from the Leinster granite (or other related intrusions) is a potential source for this radiogenic material and U- and Th-rich inclusions.

One sample of alluvial gold was analysed from the Dingle Peninsula, Co. Kerry. It was collected from the site of Knockmore in the Slieve Mish Mountains. Isotopically, the Knockmore sample plots within the Co. Wicklow-Co. Wexford field, and on the 450 Ma isochron of Irish lead evolution. This suggests a similar upper crustal Pb source and Grampian age of mineralisation, hence it could conceivably be part of the same mineralisation event that produced the widespread gold occurrences of Co. Wicklow-Co. Wexford. Gold has also been recorded at the western tip of the Dingle Peninsula (Chapman et al., 2006) where later Silurian lithologies are present, however no gold was recovered from this locality for analysis.

The gold bearing streams of Co. Waterford drain metasedimentary rocks of the Campile Formation, a division of the Duncannon Group, and both felsic and rhyolitic volcanics belonging to this formation are found in the immediate area. The similarity in the type and age of bedrock underlying the gold bearing streams of Co. Waterford and the gold bearing streams of Co. Wicklow-Co. Wexford suggests a similar phase and style of mineralisation may have produced the mineralisation found in both regions. Alluvial gold was collected from two streams in Co. Waterford (Figure 5.11, yellow squares), at the locations of Ballybrack (n = 6) and Whelanbridge (n = 3). The two deposits have indistinguishable Pb isotope ratios, as shown in Figure 5.15 and Appendix A1.

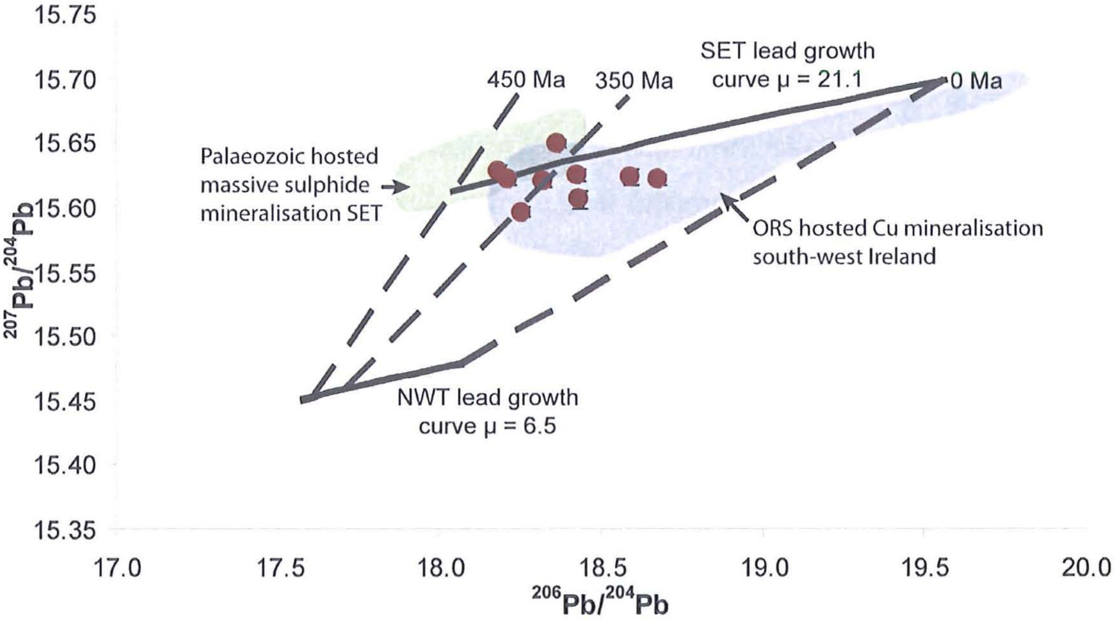


Figure 5.15: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Co. Waterford gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide fields.

The Co. Waterford gold deposits plot along the SET Pb evolution curve, suggesting that lead originated from the same crustal source reservoir as the Co. Wicklow-Co. Wexford gold deposits (the later Proterozoic upper crustal basement or overlying sediments), albeit with more evolved isotopic ratios. Pb model ages date from 388 Ma (Appendix A1) suggesting a later minimum source age, whilst if interpreted within the Irish model of lead evolution, a source age by c.400 Ma can be proposed. Both models therefore suggest mineralisation by the Late Caledonian. The c.404 Ma Leinster granite (see above) is located c.25 km to the north-east of the gold bearing streams of Co.

Waterford, therefore its emplacement may have also triggered mineralisation in this area. Alternatively, other more local Late Caledonian intrusions may have played a role during mineralisation processes.

There is further evidence that links the Co. Waterford gold mineralisation with the Late Caledonian intrusives. The Co. Waterford samples are consistent with the ORS hosted copper deposit field (dark blue domain in Figure 5.15) which has been linked to upper crustal lead associated with the Leinster granite by Kinnaird et al. (2002) and Everett et al. (2003). Additionally a uranium oxide inclusion has been identified in a grain of gold from one of the Co. Waterford locations (Chapman, pers. comm.) suggesting radiogenic source material and providing a possible explanation for the more radiogenic samples of Co. Waterford gold.

In summary, the Co. Waterford and Co. Wicklow-Co. Wexford gold deposits are associated with similar upper crustal lead sources. In agreement with Zn-Pb deposit investigations (e.g. O'Keeffe, 1986; LeHuray et al., 1987; Dixon et al., 1990) the underlying later Proterozoic upper crustal basement is seen as the ultimate source for the lead, although whether the mineralising fluids mobilised Pb from the basement, or the overlying Ordovician lithologies is unclear. The model of Irish lead evolution suggests that primary gold mineralisation in Co. Wicklow and Co. Wexford occurred during the Early Caledonian orogeny c. 470 Ma to 450 Ma, consistent with Early Caledonian metamorphism. A second phase of mineralisation that inherited Pb from the same source occurred later in the Caledonian by c.400 Ma.

5.5.4 Palaeozoic hosted gold deposits of Cregganbaun and Bohaun: NWT Late Caledonian and Variscan mineralisation in western Ireland

Co. Galway-Co. Mayo is an important gold bearing region of Ireland with a number of potentially economic grade gold deposits (Aherne et al., 1992; Thompson et al., 1992; Lusty et al., 2011). Lead isotope data for the Cregganbaun and Bohaun deposits (Figure 5.11, horizontal yellow ellipses) are presented in Figure 5.16 and Appendix A1. In this figure, the samples plot along the NWT Pb evolution in the context of Irish model of lead evolution, and trend away from the Charlestown massive sulphide deposit, (red domain) towards the Carboniferous to Variscan Zn-Pb mineralisation field (grey domain). This suggests lead was derived in part from a lead reservoir of similar composition as the Charlestown massive sulphide deposit; a source with a significant mantle derived component. Further support for this is provided by the consistency with Zartman and Doe's (1981) mantle lead evolution curve. The variation of the data is indicative of mixing with a secondary lead component; lead that originated from the same source yet was evolved to a younger age, or one containing some degree of upper crustal lead.

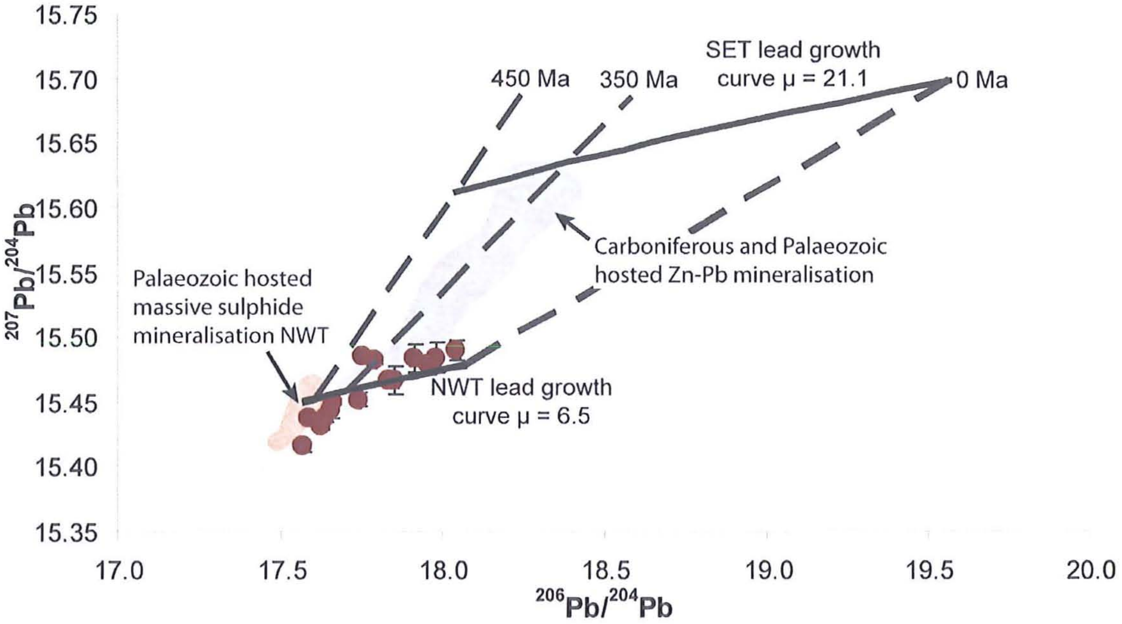


Figure 5.16: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Co. Galway-Co. Mayo gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide fields.

In detail, the Cregganbaun gold mineralisation is represented by the Bunowen River alluvial gold (filled red circles in Figure 5.17, n = 2), the Carrownisky River alluvial gold (filled blue circles in Figure 5.17, n = 10), the Shraroosky vein gold (filled green circles in Figure 5.17, n = 2) and Shraroosky vein sulphide (open green circles Figure 5.17, galena n = 2). Aherne et al. (1992) suggested that local volcano-sedimentary formations may have been the source of the gold in this region, and mineralisation in the Cregganbaun area (Sheeffry Hills) is associated with Ordovician rocks containing a significant component of ophiolitic material. This would be consistent with the apparent mantle association identified through Pb isotope analysis. The mean Pb model age of the Cregganbaun samples is 386 Ma (Appendix A1), and in the context of the model of Irish lead evolution (Figure 5.18) the data are consistent with source ages from c.390 Ma. Together, these support primary mineralisation during the Late Caledonian. Aherne et al. (1992) identified the Corvock Granite as a potential heat source for the mineralising fluids, and this has been dated to the Late Caledonian by O'Connor (1989). The Pb isotope data therefore support the theory that the Corvock Granite and/or the associated lamprophyre intrusions played an important role in the mineralisation at Cregganbaun (Aherne et al., 1992; Thompson et al., 1992).

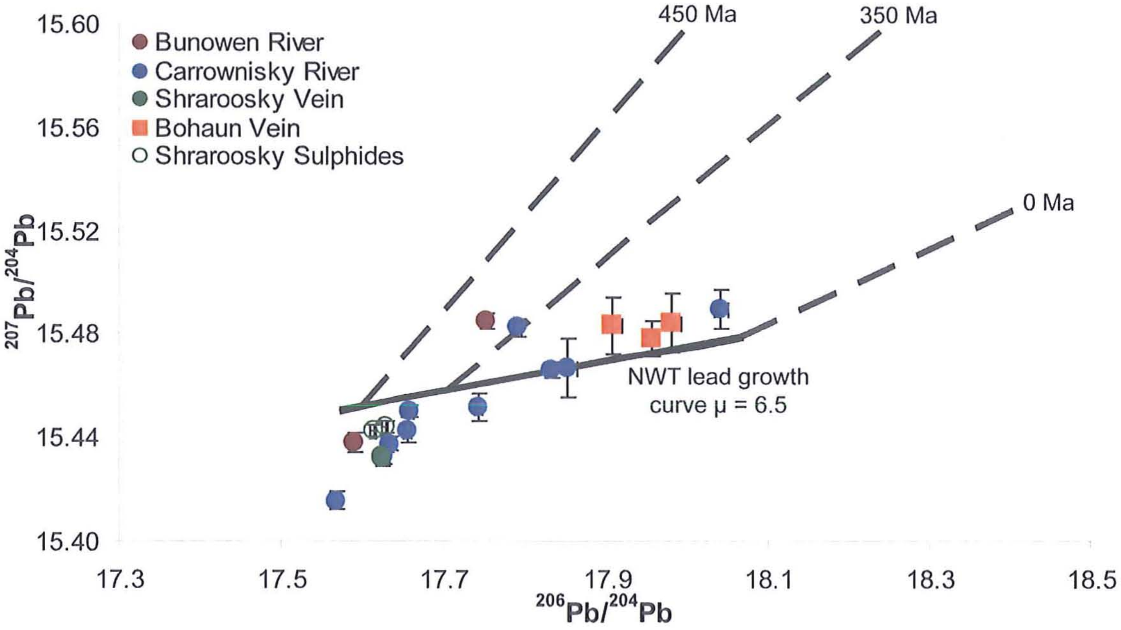


Figure 5.17: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Co. Galway-Co. Mayo gold and sulphide mineralisation by location, relative to the model of Irish lead evolution (Dixon et al., 1990). All circular data symbols relate to Cregganbaun gold mineralisation.

The Bohaun deposit (orange squares) plot along the NWT Pb evolution curve in Figure 5.18, towards the radiogenic end-member of this curve. This feature, along with the data for the Cregganbaun deposits, indicates that a second mineralising event may have occurred after the Late Caledonian. Lusty et al. (2011) proposed that the gold at Bohaun was not consistent with an orogenic style of mineralisation; instead an association with Carboniferous or later low temperature basinal brines was preferred. In figure 5.17, the Pb isotope compositions of the Bohaun gold mineralisation overlap with the field of the Irish base metal mineralisation (grey domain), indicating that fluids originating from similar sources may have been responsible for both events. Additionally, Pb model ages ranging between 298 Ma and 243 Ma (Appendix A1) further support such an association; some Irish base metal deposits have been dated to the Early Permian (Pannalal et al., 2008, Kinnaird et al., 2002). The similarities in the Pb isotope signatures of the Irish Zn-Pb deposits and the Bohaun gold deposit therefore adds support to the proposal by Lusty et al. (2011) that Carboniferous or later basinal brines could be responsible for the gold mineralisation at Bohaun. The more radiogenic samples at Cregganbaun also demonstrate a Bohaun-type isotopic signature. If Bohaun is associated with Carboniferous-Permian basinal brine fluids, then the more radiogenic Cregganbaun gold could also be explained if remobilisation by, and mixing with, these Carboniferous solutions occurred at certain locations within the Cregganbaun shear zone. No evidence for this was put forward by Aherne et al. (1992) or Thompson et al. (1992), however these studies concentrated on vein deposits. The more radiogenic gold signatures have all come from alluvial samples where the source vein is unknown, thus Bohaun style mineralisation could potentially be present in the Cregganbaun shear zone.

In summary, the diversity seen in the Pb isotope signatures of Cregganbaun and Bohaun gold mineralisation suggests different sources and ages of mineralisation. The Cregganbaun shear zone mineralisation appears to be a Late Caledonian event consistent with the age of the Corvock granite and associated lamprophyre intrusions. It inherited predominantly mantle-derived Pb, however variable isotopic ratios suggest either mixing with a more upper crustal source, or remobilisation by (and mixing with) a later more evolved fluid. The more radiogenic end-member is mainly defined by the Bohaun deposit of probable Carboniferous to Permian age. Therefore the latter scenario is currently favoured until isotopic analyses can be performed on potential source regions in the Cregganbaun area.

5.5.5 Further NWT Late Caledonian gold mineralisation

5.5.5.1 Dalradian hosted mineralisation of south-west Co. Donegal

Dalradian hosted gold mineralisation has been recorded to the north and west of the Sperrin Mountains throughout Co. Donegal (Moles and Schaffalitzky, 1992). Lead isotope data for the south-west Co. Donegal gold mineralisation (Figure 5.11, yellow pentagons) are presented in Figure 5.18 and Appendix A1. In this figure, gold from Balwoges ($n = 2$) and Lougheraherk ($n = 3$) plot between the NWT and SET Pb evolution curves, which suggest that their Pb isotope composition derived from a mixture of both NWT- and SET-related sources. The sites of sampling are associated with the Dalradian Argyll Group. Lougheraherk drains both the Port Askaig and Slieve Tooey Formations (Dalradian schist and quartzite), while Balwoges drains the contact between the Termon Formation (Dalradian schist and quartzite) and the Edergole Formation (Carboniferous conglomerate, sandstone and siltstone).

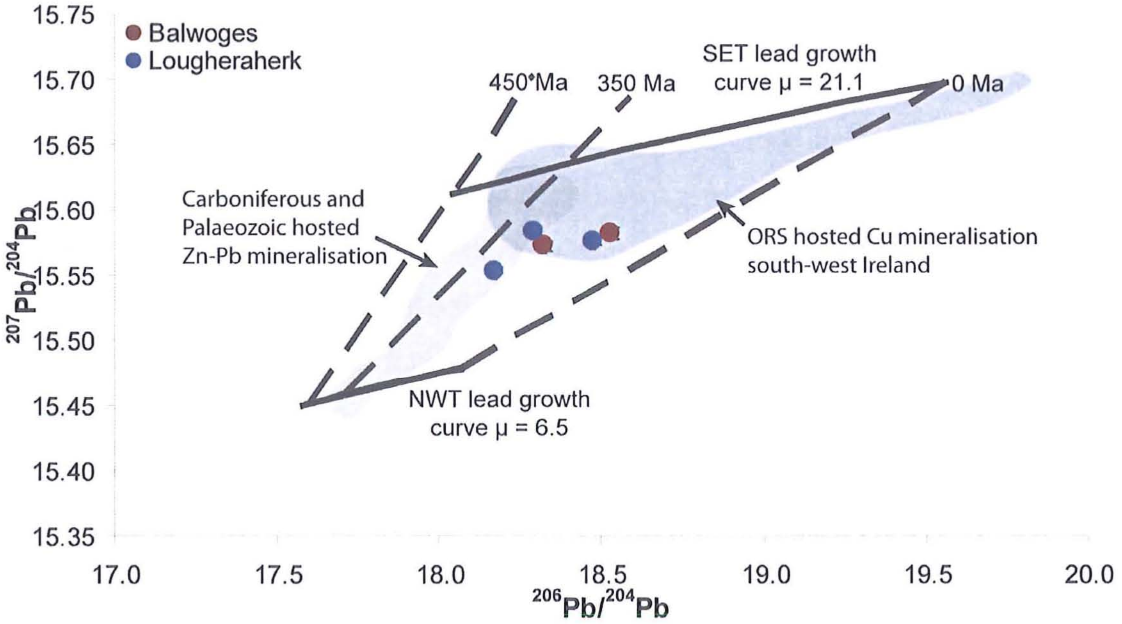


Figure 5.18: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of south-west Co. Donegal gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide fields.

Most of the south-west Co. Donegal gold deposits fall within the ORS hosted copper mineralisation field (dark blue domain in Figure 5.18) and display relatively radiogenic Pb isotope signatures typical of an association with upper crustal material. A uranium-titanite inclusion has been found in a gold grain from the site of Lougheraherk (Chapman pers. comm.) which also suggests an association with more radiogenic material, and possible links between the genesis of the Balwoges gold mineralisation and local intrusions have been highlighted based on the microchemical signature of the gold (Chapman et al., 2000a; Moles et al., in press).

The variable radiogenic signature of the ORS hosted copper mineralisation has been linked to the emplacement of S-type granites (Kinnaird et al., 2002; Everett et al., 2003), therefore the consistency between this field and the south-west Donegal deposits could be indicative of similar intrusion related mineralisation. The Donegal granites and associated intrusions have been dated to c.400 Ma (Halliday et al., 1980), and are a possible source for the mineralisation fluids. Although no Pb isotope data exists for the Donegal granites, data for similar Late Caledonian granites in the Scottish Highlands were published by Harmon et al. (1984). These authors identified a metasedimentary upper crustal input with $^{206}Pb/^{204}Pb$ = 18.1–19.2, thus an association between gold mineralisation and the Donegal granites can be considered possible.

Pb model ages (Appendix A1) suggest a source age by 240 Ma, whilst interpretation within the Irish model of lead evolution suggests a source age by c.300 Ma. However due to the variable nature of these deposits and the apparent complex mixing between NWT and SET sources in their Pb isotope signatures (Figure 5.19), these ages can only be considered as minimum ages. South-west Co. Donegal gold deposits are proximal to both Carboniferous sediments and intrusions (e.g. Gallagher and Elsdon, 1990), therefore consistency with Carboniferous to Variscan sulphide fields (both Zn-Pb and ORS hosted Cu) may favour a later genesis. However due to the small dataset, a more detailed study of mineralisation in this area could easily produce older Pb ages that would lend support to Late Caledonian mineralisation.

Interestingly south-west Co. Donegal samples have lower $^{208}Pb/^{204}Pb$ relative to $^{206}Pb/^{204}Pb$ (Appendix A1), and they plot on a different linear array to the majority of the Irish gold deposits in a $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Figure 5.30). These variations may be explained by a source depleted in Th, and/or enriched in U. If a local source region did contribute to the isotopic signature, then the inclusion of this data in the Irish model of lead evolution may not be applicable.

To summarise, the isotopic signature of south-west Co. Donegal gold deposits indicate a source age by the Variscan, and the incorporation of an upper crustal radiogenic Pb component. Whether the mineralisation resulted directly from the emplacement of Late Caledonian intrusions remains unclear. However the radiogenic nature of comparable Scottish granites, and the isotopic similarity between the south-west Co. Donegal mineralisation and the intrusion related Late Caledonian Co. Waterford gold mineralisation means this scenario is currently favoured.

5.5.5.2 Croagh Patrick , Co. Mayo

Quartzite metamorphosed to greenschist facies hosts auriferous quartz veins at Croagh Patrick (Figure 5.11 vertical yellow ellipses), north of Cregganbaun in Co. Mayo (Aherne et al., 1992). The gold is coarse grained and associated with minor sulphides and oxides; the highest concentrations of gold have been found in the A- and C-veins, whilst alluvial gold is also present in streams draining the location (Aherne et al., 1992).

A-vein samples (n = 5) and alluvial samples from Lecanvey Stream (n = 2) have similar Pb isotope compositions (Appendix A1).

In Figure 5.19 the data define a tight cluster, distinct from the local Bohaun and Cregganbaun deposits (see Figure 5.16). This highlights differences in their respective source regions, with Croagh Patrick demonstrating a more radiogenic isotopic signature consistent with a greater input of upper crustal derived Pb along with some degree of lower crustal/mantle derived Pb. Aherne et al. (1992) discussed the possibility of an ophiolitic source component, however the Pb isotope data suggest that both upper crustal and mantle material must have played a significant role. Croagh Patrick plots within the field of Irish base metal deposits (grey domain in Figure 5.19), and along the 350 Ma isochron in the model of Irish lead evolution. Pb model ages are similar (c.330 Ma; Appendix A1), suggesting a source age no younger than the Carboniferous. Croagh Patrick is however considered to be a typical orogenic gold deposit (Lusty et al., 2011), and mineralisation has been linked to the final (D_3) Caledonian deformation event (Aherne et al., 1992). This highlights the fact that consistency with Carboniferous or Variscan deposits does not necessarily reflect shared mineralisation ages.

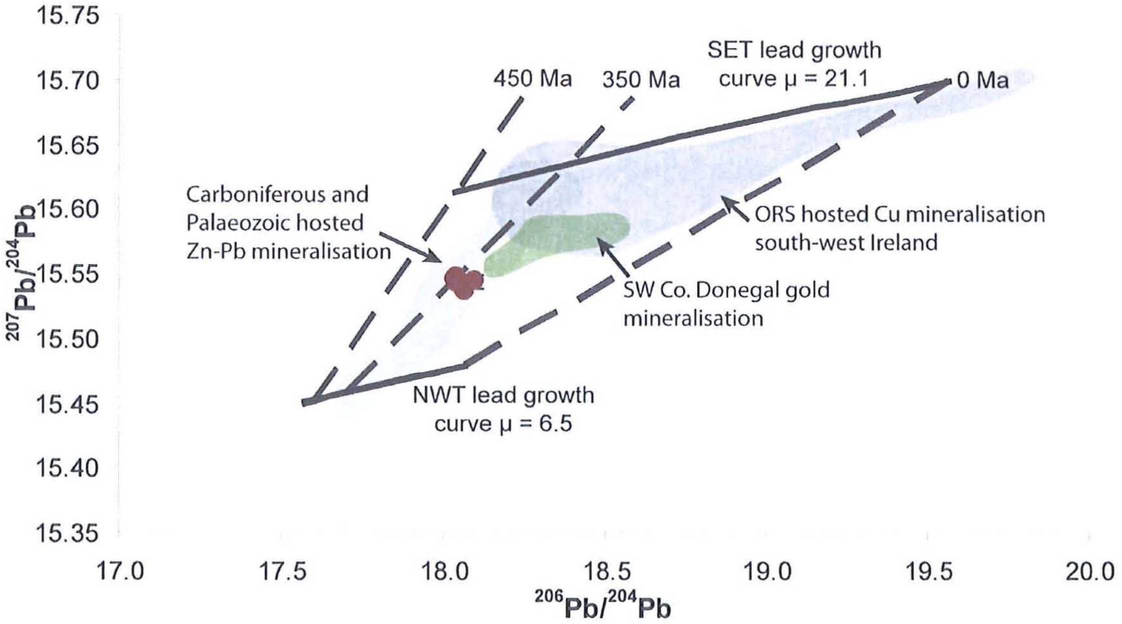


Figure 5.19: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Croagh Patrick gold mineralisation, Co. Mayo (filled red circles) relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide and gold mineralisation fields.

The isotopic signature of Croagh Patrick demonstrates affinities to the south-west Co. Donegal deposits, plotting consistent with the less radiogenic end of the data trend (green domain Figure 5.19. A further similarity is that Croagh Patrick is also characterised by lower $^{208}Pb/^{204}Pb$ relative to $^{206}Pb/^{204}Pb$, and plots with the south-west Co. Donegal deposits in Figure 5.30 to form a distinct linear array. An input from a U-enriched and/or Th-depleted source can be therefore be postulated, and if a local source region did contribute to the isotopic signature, then the inclusion of the Croagh Patrick data in the Irish model of lead evolution may also not be applicable. It was suggested that the isotopic signature of the south-west Co. Donegal deposits may relate to the emplacement of late Caledonian intrusions and an input of radiogenic upper crustal Pb. Consequently if both the Croagh Patrick and south-west Co. Donegal gold deposits resulted from related processes, Pb ages can only be considered as minimum ages. The Croagh Patrick mineralisation plots between the NWT and SET Pb evolution curves suggesting mineralisation post-dates the mixing of the two lead reservoirs. As a result, mineralisation occurred after the main Grampian collisional event, and can not pre-date the Late Caledonian.

5.5.5.3 Palaeozoic associated deposits of the Longford-Down inlier

Alluvial and bedrock gold is present in the Longford-Down inlier, NE Ireland (Figure 5.11, upright yellow rectangles). Alluvial gold has been recovered from streams in and around the western Mourne Mountains of Co. Down (Chapman et al., 2006; Warner et al., 2009, 2010b), a Tertiary granitic complex intruded into Silurian greywacke and slate between 56 Ma and 52 Ma (Gibson et al., 1987; Stevenson and Bennett, 2011). A number of gold prospects also exist to the west, such as Clontibret (Co. Monaghan); an antimony-arsenic-gold deposit is hosted in mid to Late Ordovician greywackes (Morris et al., 1986; Steed and Morris, 1986), and Clay Lake (Co. Armagh).

Alluvial gold was collected from five locations in the Mourne Mountains: the Ballincurry River ($n = 1$), the lower Leitrim River ($n = 5$), the upper Leitrim River ($n = 2$), the River Bann ($n = 3$), and the Rocky River ($n = 2$). Pb isotope compositions for these samples are presented in Figure 5.20 and Appendix A1. Due to the low levels of free gold in the mineralisation at Clontibret and Clay Lake, sampled lode deposits did not provide enough gold for analysis. Sulphides that host gold mineralisation were therefore analysed as a proxy for the isotopic signature of the gold itself. Data for arsenopyrite grains from Clontibret (n = 5) and arsenopyrite and pyrite grains from Clay Lake (n = 5) are presented in Figure 5.20 and Appendix A1.

The gold and sulphide Pb isotope signatures are consistent with each other. This suggests the Clontibret and Clay Lake sulphides are a good proxy for the associated gold mineralisation, and that they have a similar origin to the Mourne Mountains alluvial gold. On Figure 5.20 they plot between the NWT and SET Pb evolution curves, indicating Pb was derived from multiple source regions. The isotopic ratios are consistent with both the Carboniferous and Palaeozoic hosted Zn-Pb mineralisation field (grey domain in Figure 5.20), and the ORS hosted copper mineralisation field (dark blue domain in Figure 5.20).

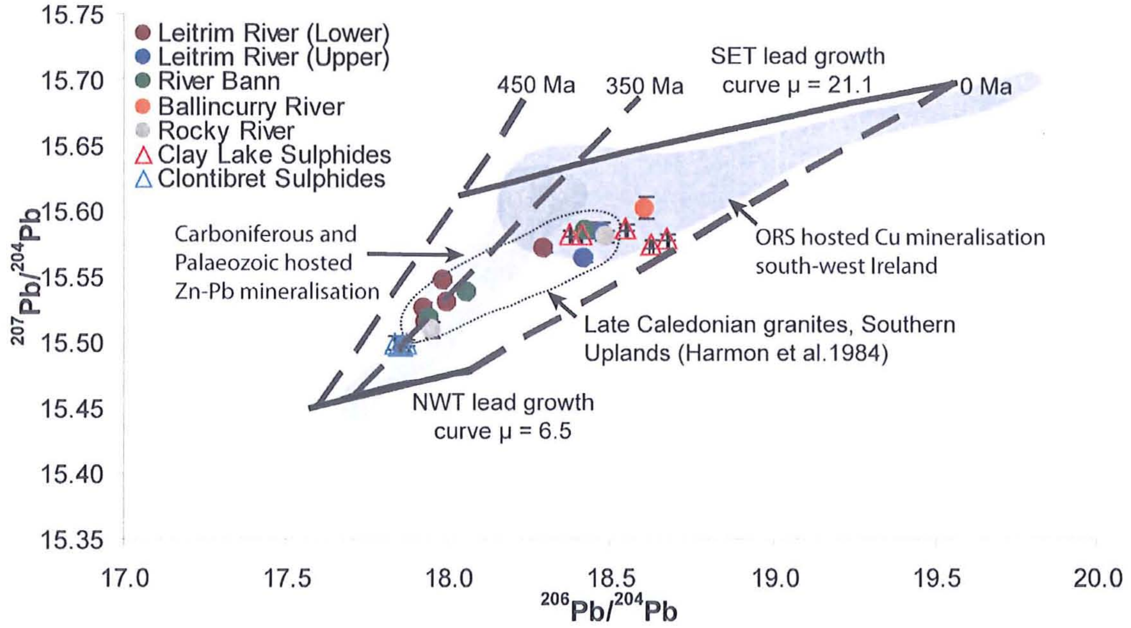


Figure 5.20: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Longford Down inlier gold and sulphide mineralisation by location relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide fields.

Those samples consistent with the Zn-Pb deposit field can be explained by a source dominated by NWT mantle derived Pb due to their depleted isotopic signature (for example the Clontibret deposit). Based on the isotopic composition of oxygen, carbon and sulphur in the ore fluids, Steed and Morris (1997) linked the Clontibret mineralisation with a deep homogenous source region and igneous processes; hornfelsed greywackes and local diorite sills were seen as evidence for larger scale concealed intrusions in the area. It was noted that the majority of British Caledonide gold deposits are found close to Caledonian granitoids and lamprophyre dyke swarms. Steed and Morris (1997) therefore proposed that magmatic activity following the subduction and closure of the Iapetus Ocean may have generated the Clontibret ore fluids, and highlighted a model of magma generation by Rock and Groves (1988) where mantle derived lamprophyric magmas induced partial melting in the crust producing both granitic magmas and gold bearing mineralising fluids. Indeed the Clontibret samples are not that dissimilar from the Cregganbaun deposits which have been linked to a similar genesis. Late Caledonian mineralisation associated with mantle derived lead if therefore possible.

The mineralisation at Clontibret post-dates the main Caledonian metamorphism and deformation (Steed and Morris, 1986). In agreement, the Clontibret samples plot on the NWT-SET mixing line consistent with a c.350 Ma source age similar to the Carboniferous Zn-Pb deposits. Carboniferous phases of mineralisation have been identified through paragenesis and fluid inclusion studies of Zn-Pb-Cu veins hosted by the Longford Down inlier (Moles et al., 1997), therefore it is possible that the Clontibret deposit is also of Carboniferous age. The mantle-like Pb isotope signature of the mineralisation is not seen to be problematic because isotopic studies (namely Sm-Nd isotopes) of Southern Uplands sediments are consistent with a basic volcanic component (O'Nions et al., 1983) and thus mantle derived Pb could have been inherited directly from the Longford Down inlier sediments. However Dixon et al. (1990) evidenced a continuous Pb isotope evolution of the Longford Down inlier sedimentary host rocks, therefore if Pb originated from the same Lower Palaeozoic host rocks for both mineralisation types, a disparity in the isotopic signature between Late Caledonian and Carboniferous mineralisation would be expected. Pb model ages range from 390 Ma to 363 Ma (Appendix A1) favouring a late Caledonian source age (mean of 375 Ma), and a K-Ar age of 360 ± 7 Ma for the stibnite phase of mineralisation at Clontibret (Halliday and Mitchell, 1983) is thought to post-date the gold mineralisation. This suggests the Pb model ages are a more accurate representation of the gold mineralisation source age than the Irish model of lead evolution. As previously discussed, Steed and Morris (1997) proposed an association with magmatic activity and concealed igneous intrusions. A basement source region beneath the Lower Palaeozoic sediments can therefore be postulated, with the consistency between the Clontibret and Carboniferous Zn-Pb mineralisation instead reflecting similar source ages.

The proposed association with Late Caledonian magmatic fluids can be considered further. Although no Pb isotope data exists for local Late Caledonian intrusions, Harmon et al. (1984) published age-corrected Pb isotope data for the Caledonian intrusions of Scotland and northern England. The authors concluded that the Late Caledonian granitoids of the Southern Uplands terrane (which equates to the Irish Longford Down inlier) define a Pb isotope array (dashed black ellipse in Figure 5.20) between two key source regions: the upper mantle or subducted oceanic crust ($^{206}Pb/^{204}Pb$ c.17.9–18.1) and Lower Palaeozoic sedimentary upper crust ($^{206}Pb/^{204}Pb$ c.18.4). The former of these two groups was linked to mantle or subducted oceanic crust source regions, and is consistent with the Clontibret signature. The granite data are age-corrected, and therefore represent the isotopic signature at the time of emplacement. Late Caledonian Pb was therefore evolved to the same degree as Carboniferous Pb, supporting the theory that similarities between Clontibret and the Carboniferous Zn-Pb deposits represent similar source ages and not similar mineralisation ages. Intrusion related genesis can therefore be postulated for the Clontibret deposit.

The Pb isotope signature of the Clay Lake gold prospect is distinct from that of Clontibret (Figure 5.20). It is consistent with the ORS hosted copper mineralisation isotopic field, which is believed to be derived from a mixture of a less radiogenic basement source (similar to that responsible for the Zn-Pb deposits) and a more radiogenic component possibly of granitic derivation (Kinnaird et al., 2002; Everett et al., 2003). Although the granitic sources linked to the copper deposits are known to have a radiogenic upper crustal signature (e.g. the S-type Leinster granite), a similar association can be proposed here. Referring again to the work of Harmon et al. (1984), the second Pb component associated with the Late Caledonian granites of the Southern Uplands was upper crustal in nature ($^{206}Pb/^{204}Pb$ c.18.4), and the importance of continental crust in the generation of Caledonian granites has previously been highlighted by Nd and Sr isotope analyses (Hamilton et al., 1980). In a similar fashion to Clontibret, the Clay Lake sulphides are also consistent with a genesis relating to Late Caledonian granites, albeit with a greater degree of crustal contamination. The Longford Down inlier consists of sediments derived from both the NWT and SET (Hutton and Murphy, 1987; Murphy, 1987), and the basement of the SET is known to be characterised by a radiogenic upper crustal Pb isotope signature. Therefore SET-derived material is a potential source for the radiogenic upper crustal Pb incorporated into the Clay Lake deposit. Alternatively, Late Caledonian mineralisation occurred once the

NWT and SET had collided, therefore the isotopic signatures could have been mixed by mineralising fluids circulating across the suture zone throughout both terranes.

Together, Clontibret and Clay Lake define the same isotopic range as the Southern Upland's Late Caledonian granites and represent mixing of mantle-derived basement and upper crustal Pb sources. As a result, an origin relating to the emplacement of Late Caledonian granites is preferred over a later Carboniferous or Variscan mineralising event. Disparities between the two gold-bearing deposits formed because Clontibret incorporated predominantly basement (mantle-derived) Pb, whilst Clay Lake incorporated a significant amount of upper crustal Pb.

The Pb isotope signature of alluvial gold mineralisation from the Mourne Mountains, Co. Down, is consistent with the field defined by the Clontibret and Clay Lake deposits and Late Caledonian granites from the Southern Uplands (Figure 5.20). It is therefore considered likely that they are the result of the same source mixing. Samples from the Leitrim River (Lower), River Bann and Rocky River are consistent with a predominantly basement-derived source (and have Pb model ages from c.380 Ma), whilst samples from the Leitrim River (Upper), Leitrim River (Lower), Rocky River and Ballincurry River are consistent with a significant input of upper crustal Pb. Moles et al. (in press) applied microchemical characterisation techniques to investigate these alluvial deposits, and in conjunction with this study identified two distinct populations. The authors concluded that the mineralisation principally corresponds to orogenic gold mineralisation found elsewhere in the Longford Down-Southern Uplands terrane. Distinct sub-populations reflected a different style of mineralisation, with possible explanations being further orogenic mineralisation formed under atypical conditions or intrusion related mineralisation. Interestingly the locations where the typical orogenic style of gold was collected broadly correspond to the locations where the less radiogenic samples were found, whilst the locations where the atypical style of mineralisation was collected broadly corresponds to the locations were the more radiogenic samples were found. It is therefore likely that the same distinct gold populations have been identified, with the less radiogenic mineralisation dominated by basement-derived Pb of orogenic origin and the more radiogenic mineralisation dominated by upper crustal Pb resulting from either atypical orogenic or intrusion related mineralisation.

Evidence from Pb isotope analysis suggests a role for Late Caledonian intrusions in both styles, however as the less radiogenic deposits are dominated by basement-derived Pb, the intrusions may have acted as a heat source mobilising disseminated metals from the basement rocks. Conversely, the more radiogenic deposits could have resulted from increased Pb input from the intrusions themselves after incorporation of crustal material. This would explain the possible intrusion related genesis highlighted by Moles et al. (in press). The radiogenic Mourne Mountains gold is more abundant in sample locations that are nearer to the Mourne granites, therefore a spatial association exists. Additionally, Moles et al. (in press) discussed the relevance of a copper-rich gold alloy present in the Mourne Mountains; copper-rich alloys identified elsewhere have had possible magmatic associations with the Balwoges deposit of Co. Donegal linked to a nearby granitic intrusion (Chapman et al., 2000a). No Pb isotope data exists for the Mourne granites, however geochemical data demonstrates that they are predominantly basaltic differentiates whilst Sr isotope analysis has highlighted minor crustal involvement (Meighan et al., 1984; Stevenson and Bennett, 2011). This probable lack of a significant upper crustal Pb input in the Mourne granites suggests that they were unlikely to have played a role in the generation of the Mourne Mountains gold, and an association with Late Caledonian intrusions is preferred. This of course does not rule out remobilisation of pre-existing gold when the Mourne granites were emplaced.

To summarise, the gold and sulphide mineralisation of the Longford Down inlier demonstrates variable Pb isotope signatures consistent with a mixed source. The two end members are 1) less radiogenic mantle derived Pb from basement sources and 2) more radiogenic upper crustal Pb. Variations between different gold-bearing deposits were the result of varying proportions between these two end member compositions. A genesis relating to the emplacement of Late Caledonian intrusions is preferred due to the consistency with the isotopic signature of Late Caledonian granites located in the Southern Uplands and the Pb model ages of the analysed samples. Although these deposits are consistent with Carboniferous to Variscan mineralisation, this is likely to be the result of similar source ages and does not relate to similar ages of mineralisation.

5.5.5.4 Palaeozoic hosted mineralisation of the central southern Irish inliers

Gold is associated with the Lower Palaeozoic inliers of central southern Ireland; for example alluvial gold has been recovered from streams draining the Galtee and the Slieve Bloom Mountains (Stanley et al., 2000; Chapman et al., 2006). Alluvial gold was collected from the Camcor River (Figure 5.11, horizontal yellow rectangle), which flows off the north-west flanks of the Slieve Bloom Mountains in Co. Offaly (n = 2). Although only two samples were analysed, their Pb isotope composition is very variable (Figure 5.21, Appendix A1). The data are consistent with the Longford Down inlier sulphide and gold data (green domain Figure 5.21), and both are associated with analogous Lower Palaeozoic geology (the Camcor River drains Silurian sediments). As a result, similar Pb sources (less radiogenic mantle derived Pb and more radiogenic upper crustal Pb) and Late Caledonian genesis can be postulated. A uranium titanite inclusion has been identified in a gold grain from this site (Chapman pers. comm.), thus supporting an association with radiogenic material.

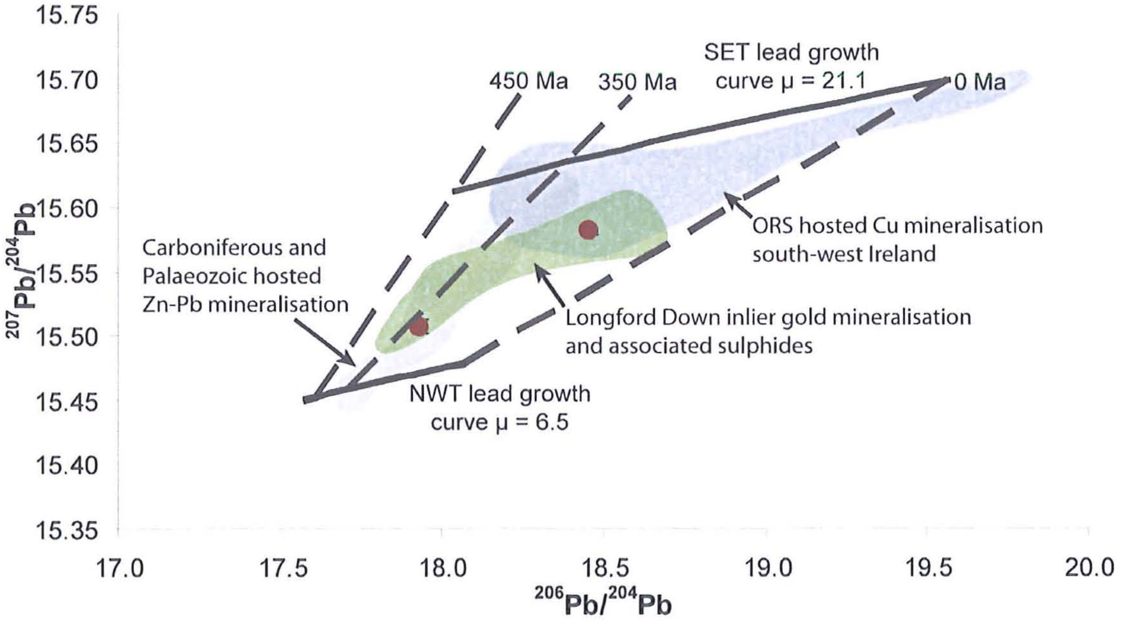


Figure 5.21: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of the Camcor River (Co. Offaly) gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide and gold mineralisation fields.

5.5.5.5 Palaeozoic hosted deposits of Co. Kildare

Gold mineralisation has been identified in Co. Kildare (Stanley et al., 2000; Chapman et al., 2006). Located to the north-west of the Leinster granite and hosted in Silurian greywackes (Carrighill Formation), the region has been the focus of vein-hosted, shear-hosted and stratabound gold mineralisation exploration after the discovery of gold nuggets in the 1990s (Minco, 2003).

Data (n = 6) for alluvial gold from the Walishtown gravel pit (Figure 5.11, yellow circle) are presented in Figure 5.22 and Appendix A1. Data plot proximal to the SET Pb evolution curve, suggesting a predominance SET-derived material in the Pb source. This is consistent with the deposit's geographical location within the SET. Similarly to the Lower Palaeozoic hosted Longford Down and Slieve Bloom mineralisation, the Walishtown samples are encompassed by both the field of the Carboniferous Irish Zn-Pb deposits (grey domain) and the field of the ORS hosted copper mineralisation of SW Ireland (dark blue domain). However they show significantly higher $^{207}Pb/^{204}Pb$, therefore a genetic relationship is not clear. Two possible explanations exist, and further work is required before either can be favoured. The first is that the deposits resulted from Late Caledonian mineralisation similar to the Longford Down and Slieve Bloom deposits, only with an upper crustal dominated rather than mantle-derived dominated source. The second is that the Walishtown mineralisation resulted from Variscan mineralisation; Pb model ages suggest mineralisation by the end of the Permian and the samples plot to the right of the 350 Ma isochron in Figure 5.22. The lack of Variscan gold mineralisation in this region may support the former.

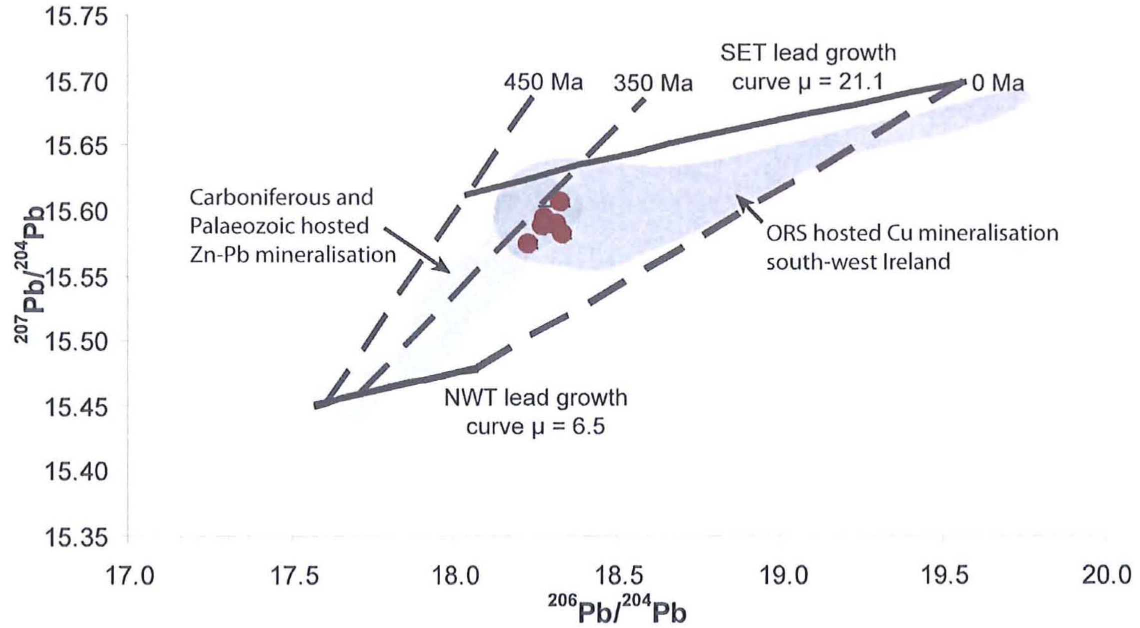


Figure 5.22: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Walishtown (Co. Kildare) gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide fields.

5.5.5.6 Dalradian hosted mineralisation of north-east Co. Donegal and Northern Sperrins: Carboniferous mineralisation of the NWT

The Pb isotope signature of Dalradian hosted gold in the Sperrin Mountains is consistent with Early Caledonian mineralisation (Section 5.5.2). Dalradian successions continue north of the Sperrin Mountains into north-east Co. Donegal, and are believed to be an attractive exploration target for orogenic gold mineralisation (Lusty et al., 2009). Alluvial gold was collected from three locations in this region: Berry Burn, the Burntollet River, and the Cabry River (Figure 5.11, yellow hexagons).

Analysis of one gold sample from the Burntollet River, seven gold samples from Berry Burn and three gold samples from the Cabry River are presented in Appendix A1 and Figure 5.23. In this figure, gold mineralisation from this region can be distinguished from that of the Sperrin Mountains (red domain) by its more radiogenic signatures. The Burntollet River sample plots proximal to the Sperrin Mountain data field indicating a major contribution from the NWT lower crustal/mantle-like reservoir, and it may have resulted from the same or a similar Early Caledonian mineralising event. This proposal is supported by a Pb model age of c.465 Ma (Appendix A1) and its proximity to the 450 Ma isochron in Figure 5.23.

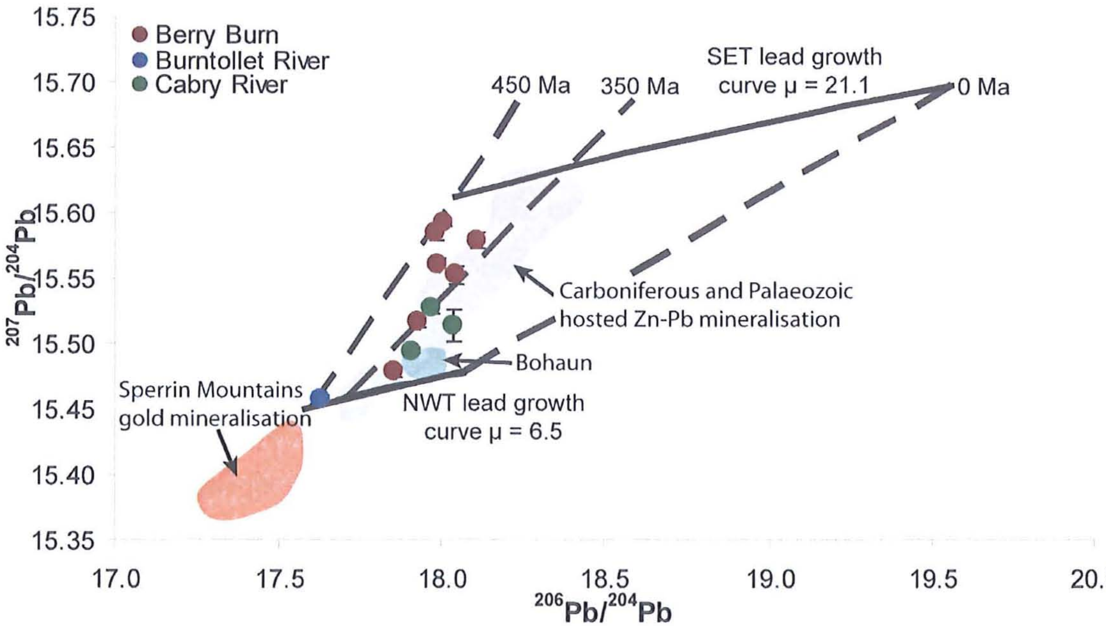


Figure 5.23: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of north-east Co. Donegal and Northern Sperrins gold mineralisation relative to the model of Irish lead evolution (Dixon et al., 1990) and relevant sulphide and gold mineralisation fields.

In contrast, the Berry Burn and Cabry River mineralisation incorporated Pb with an increasingly upper crustal signature. The samples trend from a signature with high $^{207}Pb/^{204}Pb$ proximal to the SET Pb evolution curve, to a more mantle-like signature proximal to the NWT Pb evolution curve (Figure 5.23). Interestingly, the end member composition characterised by low $^{207}Pb/^{204}Pb$ is consistent with the isotopic signature of the Bohaun deposit (light blue domain in Figure 5.23). This raises the possibility that the Berry Burn and Cabry River mineralisation results from a mixture of NWT lower crustal/mantle-derived Pb evolved to a Variscan age, and upper crustal derived Pb. All the alluvial sites in this region drain similar Dalradian psammite, pelite, semipelite, and metabasaltic geology, however it could be possible that local compositional variations are behind the radiogenic end member. This is consistent with the work of O'Keeffe (1986) who also identified upper crustal Pb sources in the far north-west of Ireland (see Section 3.5.1). As with most of the alluvial samples analysed during this investigation, the inability to relate the gold to known bedrock mineralisation of a certain age and type does hinder geological interpretations.

Two Berry Burn data points plot on the 450 Ma isochron in Figure 5.24, and have Caledonian Pb model ages (Appendix A1), suggesting that the upper crustal component was characterised by a Grampian source age. However the remaining samples have higher $^{206}Pb/^{204}Pb$ and plot close to the 350 Ma isochron in Figure 5.23, in the same field as the Irish Carboniferous Zn-Pb ore deposits (grey domain). Similarly, the mean Pb model age of the remaining Berry Burn and Cabry River samples is 341 Ma, further supporting a Carboniferous to Variscan age. Clearly there is a potential link between Carboniferous/Variscan fluids and gold mineralisation in north-east Co. Donegal and the Northern Sperrins. The reactivation of major structural features and the remobilisation of gold deposits located in the Sperrin Mountains during the Carboniferous has already been discussed (Earls et al., 1997; Parnell et al., 2000), and this appears to be the best mechanism for explaining the isotopic signature of the Berry Burn and Cabry River samples.

The data therefore suggest that Carboniferous fluids remobilised both lower crustal/mantle- and upper crustal-derived Pb and resulted in further Dalradian hosted gold mineralisation. The mixing between these two sources accounts for the variation in $^{207}Pb/^{204}Pb$ similar to that recorded in the Carboniferous and Variscan Zn-Pb deposits. It may be of interest that the economically important gold deposits of Cavanacaw and Curraghinalt are both characterised by the less radiogenic Early Caledonian isotopic signatures. Future exploration work in the Dalradian of NW Ireland may therefore want to concentrate on deposits characterised with this signature, rather than those that were apparently the result of later remobilising events.

5.6 Synthesis: the formation of Irish gold deposits inferred through lead isotope analysis

The Pb isotope signatures of Irish gold deposits are variable, and the data suggest that the Pb incorporated into Irish gold mineralisation originated from two principal sources; one 'NWT source' of mantle and/or lower continental crust origin, and one 'SET source' of upper continental crust origin (Figure 5.24). Additionally a secondary upper crustal Pb component was incorporated into some gold deposits, and Caledonian granites or associated intrusions are seen as the most likely source of this component.

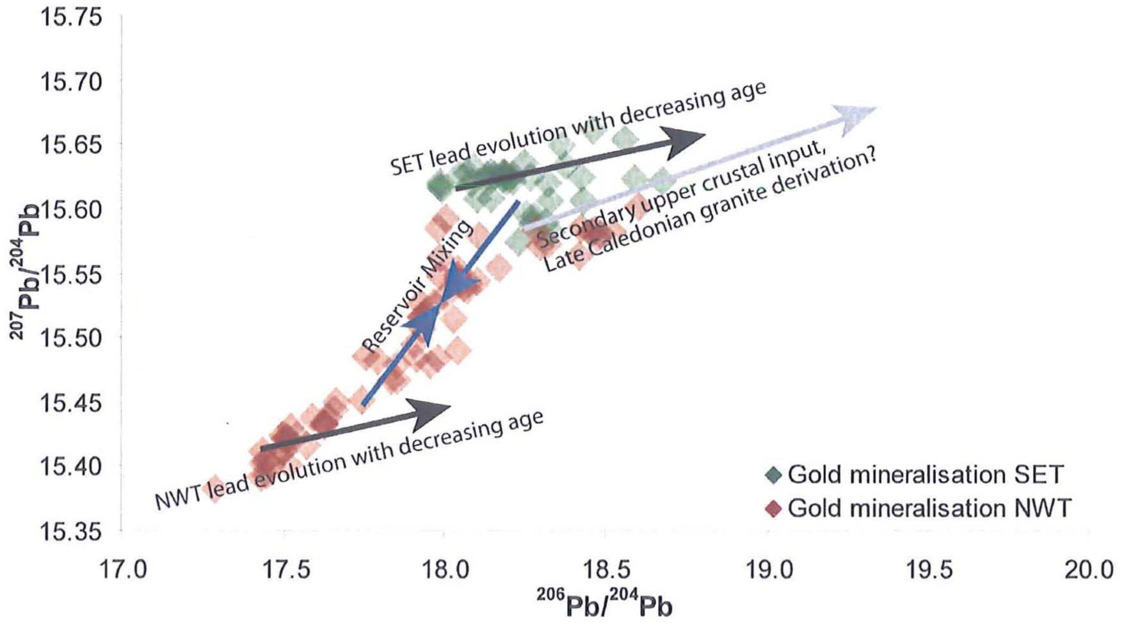


Figure 5.24: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot explaining the three principle causes of Pb isotope variation in Irish gold mineralisation. Black arrows represent radioactive decay related variation, blue arrows represents reservoir mixing, and grey arrow represents secondary upper crustal inputs (Late Caledonian granites or associated intrusions?).

On the basis of the present data, and the work of O'Keeffe (1986), LeHuray et al. (1987), Dixon et al. (1990), Kinnaird et al. (2002) and Everett et al. (2003) regarding the genesis of the extensive base metal deposits of Ireland, a model for the formation of Irish gold based on five distinct stages of geochemical/geodynamical evolution is proposed (Figures 5.25 and 5.26):

- Stage 1 (pre-Caledonian): Prior to the Caledonian orogeny, Ireland was divided by the Iapetus Ocean (Figure 5.26). Laurentia consisted of Palaeoproterozoic and younger (see Daly, 2001) less radiogenic crust, and sedimentary rocks up to Ordovician in age were formed directly from erosion of this less radiogenic basement. Avalonian crust was dominated by more radiogenic late Proterozoic rocks (minimum age of 626 ± 6 Ma; Max and Roddick, 1989) of upper crustal origin, and overlying lithologies up to Ordovician in age derived directly from these rocks. The Laurentia and the Avalonia plates therefore constitute the two principal lead reservoirs for the less radiogenic NWT, and the radiogenic SET, respectively. An additional source of less radiogenic Pb is constituted by the upper mantle, as evidenced by palaeo-volcanic arcs and ophiolitic complexes (for example the Tyrone Igneous Complex).

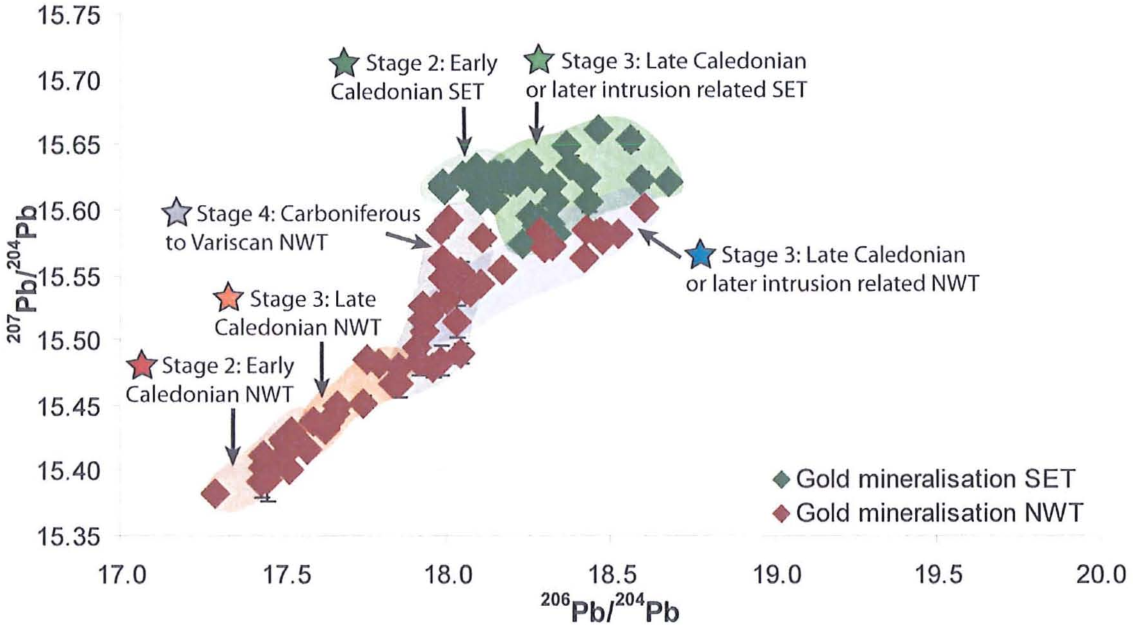


Figure 5.25: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ summarising the isotopic signatures of Irish gold mineralisation based on age and source region. Stage 1 is not represented on this plot because it is the stage prior to gold mineralisation. Stars link to Figure 5.26 and are not data points.

- Stage 2 (Early Caledonian): This stage is characterised by the dual subduction of the Iapetus oceanic crust, beneath the Laurentian crust to the north, and beneath the Avalonian crust to the south (Max et al., 1990) (Figure 5.26). In NW Ireland, gold mineralisation is located in the Sperrin Mountains of Co. Tyrone (Figures 5.25 and 5.26, red star). The Sperrin Mountain deposits typify the less radiogenic NWT end member lead reservoir that consists of Pb derived from the mantle and the lower continental crust. Primary mineralisation occurred c.470 Ma, and was contemporaneous with the formation of the Tyrone Igneous Complex. This is consistent with the Grampian phase of the Caledonian

Orogeny. The gold deposits of Co. Wicklow-Co. Wexford (Co. Kerry) define the SET end member Pb reservoir. Their isotope signatures support an Early Caledonian age of mineralisation from 470 Ma (Figures 5.25 and 5.26, dark green star), contemporaneous with the Grampian related gold deposits in the NWT. Mineralising fluids associated with the evolution of the subduction zone and related metamorphism are likely mechanisms for metal mobilisation. The distinction from the Early Caledonian NWT gold deposits is created because the source of the lead incorporated into the SET mineralisation originates in the Avalonian upper crustal basement. The sediments that host the gold mineralisation may have derived directly from this basement, and are therefore also a viable source region.

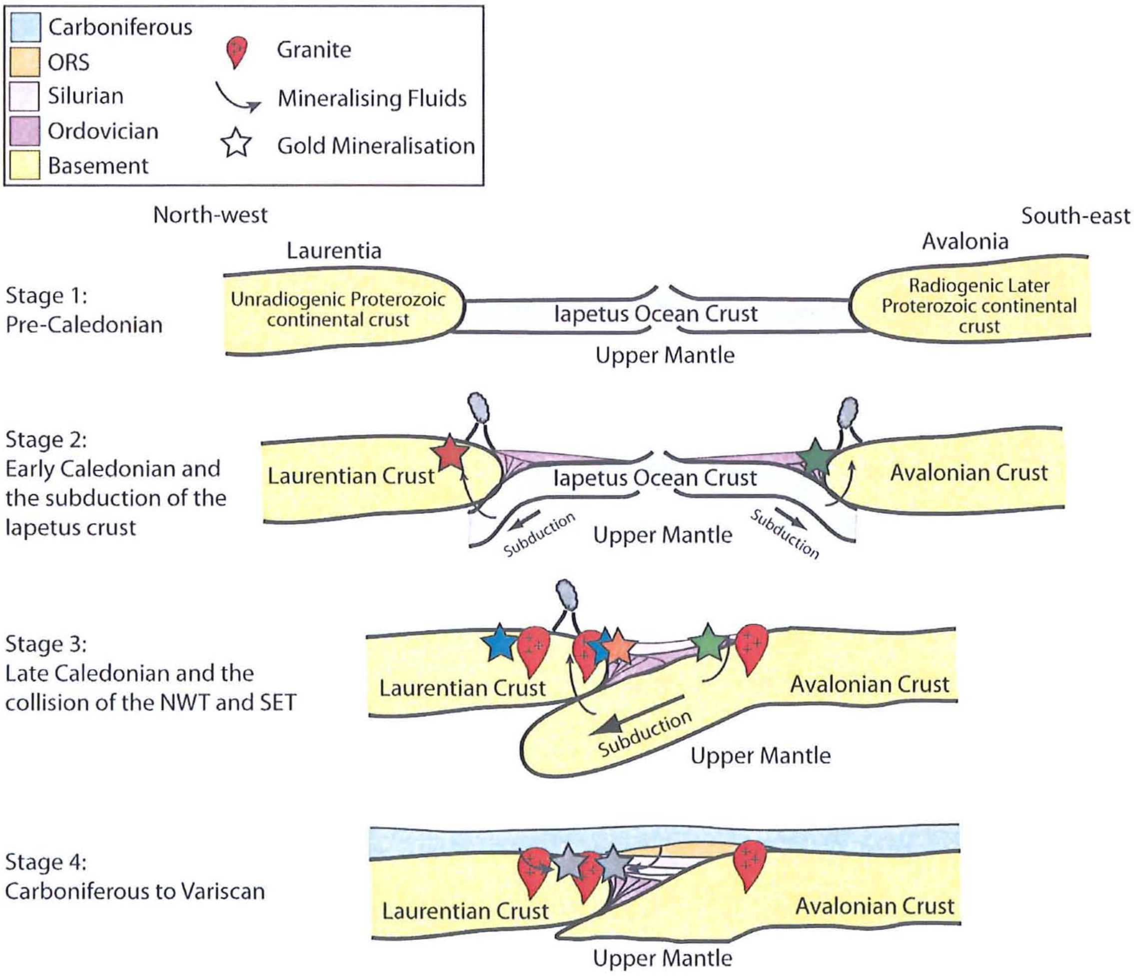


Figure 5.26: Simplified schematic diagram (not to scale) of the key stages involved in the formation of Irish gold deposits. Stars represent locations of gold mineralisation.

- Stage 3 (Late Caledonian): This stage is associated with the continental collision following the closure of the Iapetus Ocean (Figure 5.26). It is believed that this collision led to a series of successor basins that filled with Silurian sedimentary sequences (Hutton and Murphy, 1987). The sediments that filled these basins are a mixture of detritus from both the NWT and SET, therefore the Pb from the Silurian lithologies will constitute a mixture, in various proportions, between the radiogenic SET and less radiogenic NWT reservoirs. The mineralisation at Cregganbaun incorporates Pb primarily from the less radiogenic NWT reservoir (Figure 5.26, orange star), and a Late Caledonian age c.390 Ma is preferred. This supports theories that it relates to the emplacement of local granitic and/or associated lamprophyre intrusions. Significant variation in the Cregganbaun isotopic signature suggests either a) mixing with a more radiogenic Pb component, or b) that some deposits were remobilised by and mixed with more evolved fluids, for example during the Carboniferous. The NWT gold mineralisation of south-west Co. Donegal, Croagh Patrick, the Longford Down inlier and central southern Irish inliers are also likely to be associated with Stage 3; however they are distinct due to contrasting sources of Pb (Figure 5.26, blue star). The Longford-Down and central southern Irish inliers deposits represent a mixture between a mantle-derived basement source and a more radiogenic upper crustal component, with a Late Caledonian intrusion association probable. The south-west Co. Donegal and Croagh Patrick deposits are distinct due to the involvement of a source relatively depleted in Th, and are again likely to result from a mixture of more than one lead source. Of these, the south-west Co. Donegal deposits are likely to have a significant upper crustal association, and again may be linked to Late Caledonian intrusions. The variation in the $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ during this stage (Figure 5.25) primarily represents remobilisation by later Caledonian fluids associated with the emplacement of intrusions such as the Leinster granite. The gold deposits of Co. Waterford incorporate lead from the same source, and are likely to be associated primarily with the Late Caledonian (intrusion related) mineralising event (Figure 5.25, light green domain). Co. Waterford gold mineralisation can therefore be distinguished from the deposits of Co. Wicklow-Co. Wexford (Co. Kerry). The Co. Kildare deposits may be associated with Stage 3, though a later mineralisation is also possible.

- Stage 4 (Carboniferous to Variscan): Fluids relating to Carboniferous basin development resulted in mineralisation throughout Ireland (Kinnaird et al., 2002), and this was followed by the Variscan orogeny when the continents of Gondwana and Laurasia collided during the Late Carboniferous to Permian periods (Graham, 2001). These episodes of mineralisation resulted in the vast Zn-Pb and Cu-polymetallic mineral deposits of Ireland, and the gold mineralisation of north-east Co. Donegal-northern Sperrins and Bohaun. Post collision, mineralising fluids could flow through the suture zone and mobilise Pb from the basement rocks of both terranes, therefore allowing further mixing processes between the SET and NWT reservoirs (Figure 5.26, grey stars). Consequently, gold mineralisation of Silurian age or later displays isotopic signatures that are mixtures of the NWT and SET lead reservoirs (Figure 5.25, grey domain).

5.7 The characterisation of Irish gold through lead isotope analysis

Different gold bearing regions of Ireland (Figure 5.27) can therefore be characterised by their Pb isotope signatures because they incorporated Pb from more than one distinct lead reservoir to varying degrees (less radiogenic crustal and mantle derived NWT, Th-depleted crustal NWT, and radiogenic crustal derived SET, Caledonian granites), and at three principle stages of geological history: Early Caledonian, Late Caledonian, and Carboniferous/Permian.

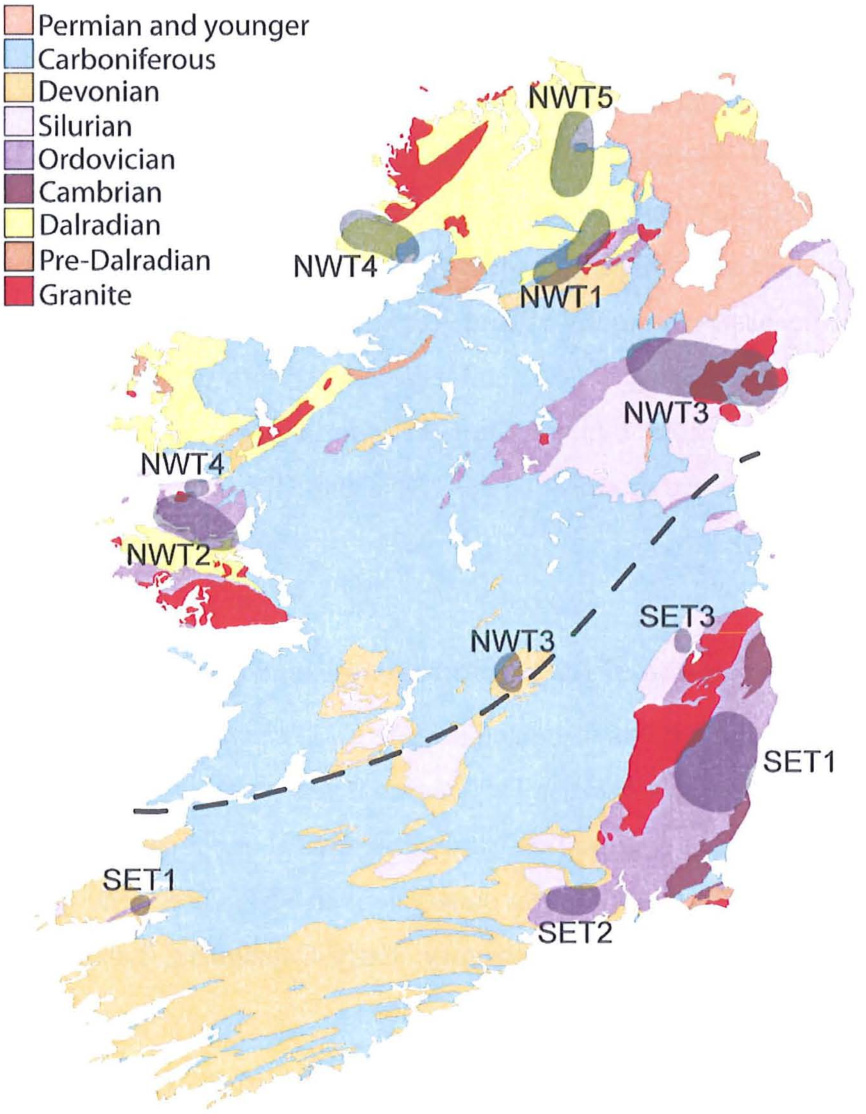


Figure 5.27: Map of gold bearing regions distinguished by lead isotope analysis. Dashed black line represents approximate trace of Iapetus suture, gold bearing regions defined in Table 5.1.

Irish gold deposits hosted by the NWT and SET are identifiable due to contrasting primary Pb sources; NWT less radiogenic crustal and mantle derived Pb and SET radiogenic crustal derived Pb. This distinction is demonstrated by Figure 5.28 which plots $^{207}Pb/^{204}Pb$ versus the sample locations (Irish National Grid northing), and clearly shows that SET gold deposits are characterised by increasingly radiogenic Pb isotope signatures.

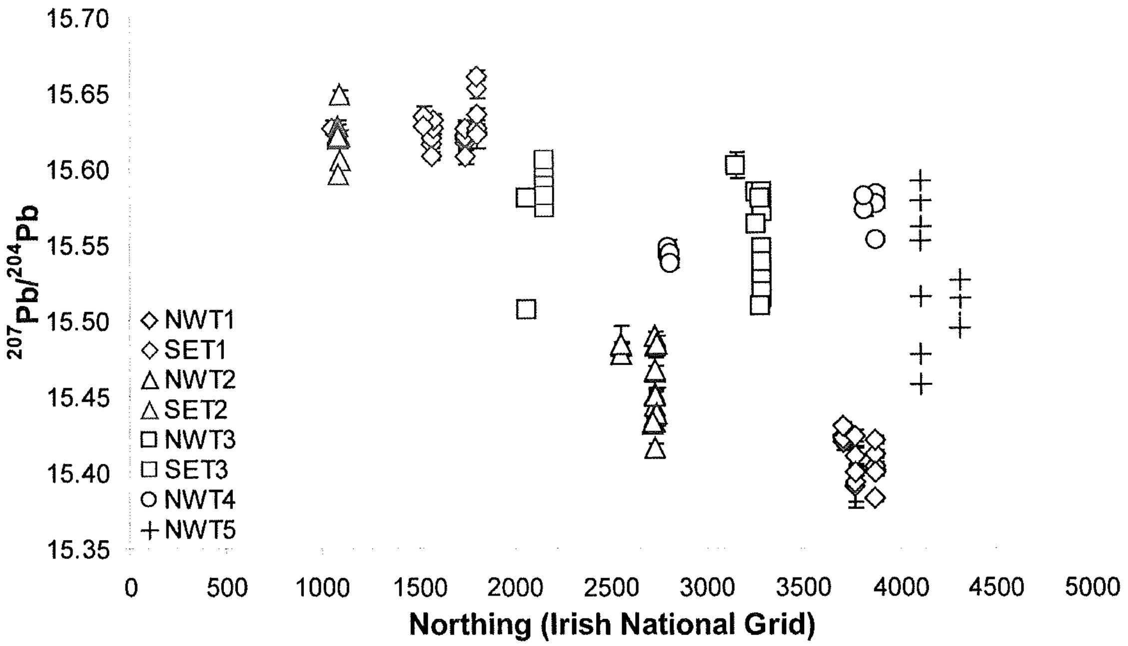


Figure 5.28: ^{207}Pb/^{204}Pb versus gold mineralisation sample location (Irish National Grid northing).

The Sperrin Mountains gold mineralisation have the most less radiogenic isotopic signatures and are distinguishable by their low ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb (NWT1 Figure 5.27 and Table 5.1), whilst Cregganbaun gold mineralisation is characterised by slightly higher ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb and variable ^{206}Pb/^{204}Pb that trends towards the Bohaun deposit (NWT2). Mineralisation from Co. Wicklow-Co. Wexford-Co. Kerry (SET1) and Co. Waterford (SET2), have the most radiogenic isotopic signatures and are particularly distinguishable by high ^{207}Pb/^{204}Pb. Co. Waterford gold can be identified from Co. Wicklow-Co. Wexford-Co. Kerry gold due to its high average ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb. Gold mineralisation from the Longford Down (NWT3) and central southern inliers define a linear array, trending from medium to high ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb. The Croagh Patrick and south-west Co. Donegal deposits (NWT4) define a similar array with comparable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, however are distinguishable due to lower ^{208}Pb/^{204}Pb relative to ^{206}Pb/^{204}Pb. Gold mineralisation of south-west Co. Donegal and the northern Sperrins (NWT5) are characterised by medium to low ^{206}Pb/^{204}Pb, medium ^{207}Pb/^{204}Pb and low ^{208}Pb/^{204}Pb, whilst the Co. Kildare gold deposit (SET3) has a tight isotopic signature with high ^{207}Pb/^{204}Pb and medium to high ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb. These gold bearing regions, as defined by Pb isotope analysis and presented in Table 5.1, can be employed by lead isotope provenance studies that aim to locate the sources of gold exploited during antiquity.

Table 5.1: Gold bearing regions and their key characteristics inferred through Pb isotope analysis. Symbols next to each region correspond to those used in Figure 5.27.

Pb Isotope Group	Mineralisation Age	Pb Reservoir	Secondary Upper Crustal Pb Input?	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
NWT1: Sperrin Mountains:	Early Caledonian	NWT	No	17.287-17.538	15.382-15.430	37.517-37.763
SET1: Co. Wicklow-Co. Wexford-Co. Kerry:	Early and Late Caledonian	SET	Yes, during the Late Caledonian	17.985-18.560	15.608-15.661	38.025-38.635
NWT2: Cregganbaun-Bohaun:	Late Caledonian and Variscan	NWT	No?	17.567-18.043	15.415-15.489	37.553-38.000
SET2: Co. Waterford:	Late Caledonian	SET/(NWT?)	Yes	18.184-18.679	15.596-15.649	38.153-38.567
SET3: Co. Kildare:	Late Caledonian or Variscan	SET/(NWT)	No?	18.233-18.337	15.574-15.606	38.070-38.217
NWT3: Longford Down and central southern inliers:	Late Caledonian	NWT/SET	Yes	17.926-18.605	15.507-15.602	37.791-38.492
NWT4: Croagh Patrick and South-west Co. Donegal:	Late Caledonian	NWT/(SET?)	Yes	18.040-18.525	15.537-15.583	37.649-38.208
NWT5: North-east Co. Donegal-Northern Sperrins:	Early Caledonian and Variscan	NWT/SET	No	17.629-18.109	15.458-15.592	37.620-38.056

In Chapter 3, it was noted that gold occurrences have been recorded in association with the copper mineralisation of south-west Ireland. Although many of these reports are of dubious accuracy, it is worth briefly considering the isotopic signature of such deposits because no gold was successfully collected for analysis from this region. The isotopic signatures of these copper deposits are plotted as a field in Figure 5.8 (blue domain). They occupy a region suggesting a mixed NWT and SET source of Carboniferous age, with a trend towards an upper crustal granitic composition when hosted by ORS lithologies. They occupy a distinct isotopic field, and therefore this style of mineralisation can also be identified using lead isotope analysis.

Figure 5.29 presents the gold bearing regions graphically on the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot. The $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ (Figure 5.30) and $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ (Figure 5.31) plots of the same data are now also introduced. It is apparent that there is good differentiation between regions on the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ graphs. When mass 204 is not included, i.e. the $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot, there is greater overlap between regions. This highlights the importance of ^{204}Pb when distinguishing different gold deposits in Ireland. The ability to differentiate between gold bearing regions is critical for the success of the following provenance study, and an understanding of why variations occur allows uncharacterised or undiscovered gold sources to be taken into account.

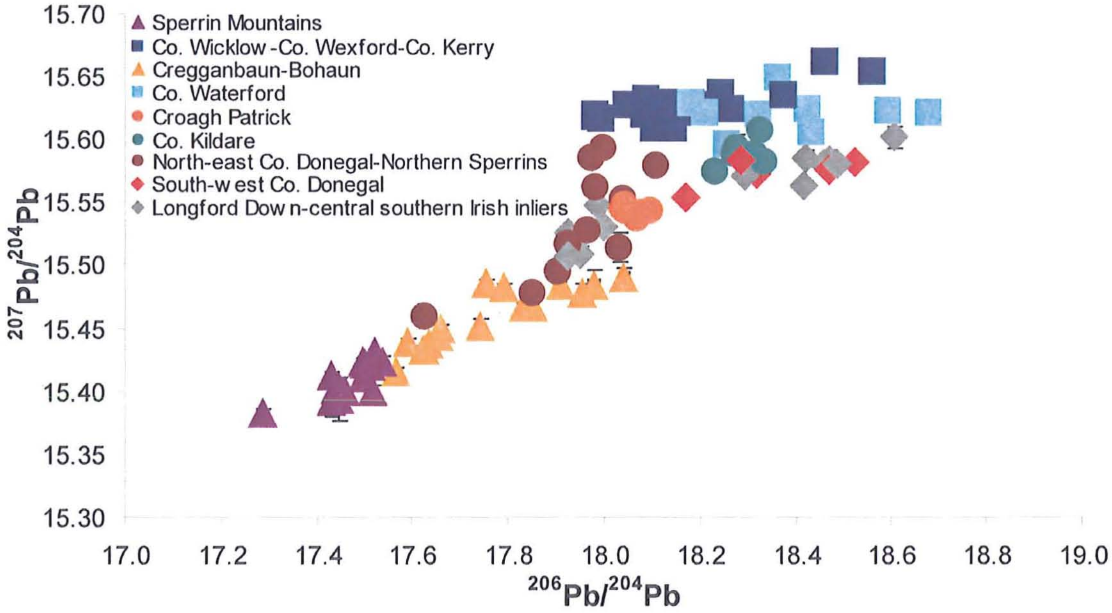


Figure 5.29: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot demonstrating the characterisation of Irish gold bearing regions using lead isotope analysis.

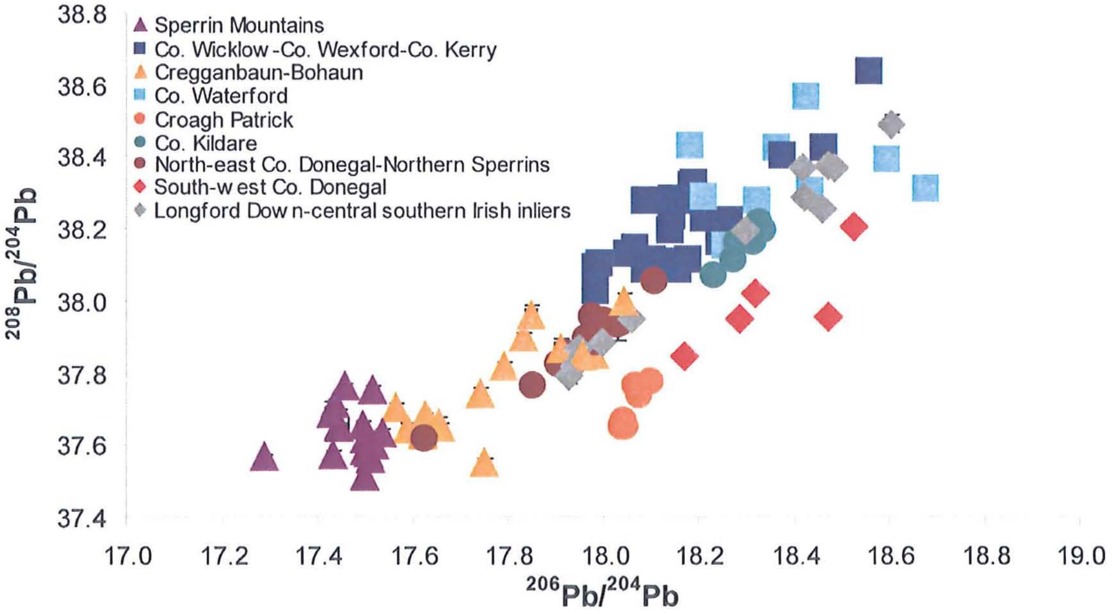


Figure 5.30: ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot demonstrating the characterisation of Irish gold bearing regions using lead isotope analysis.

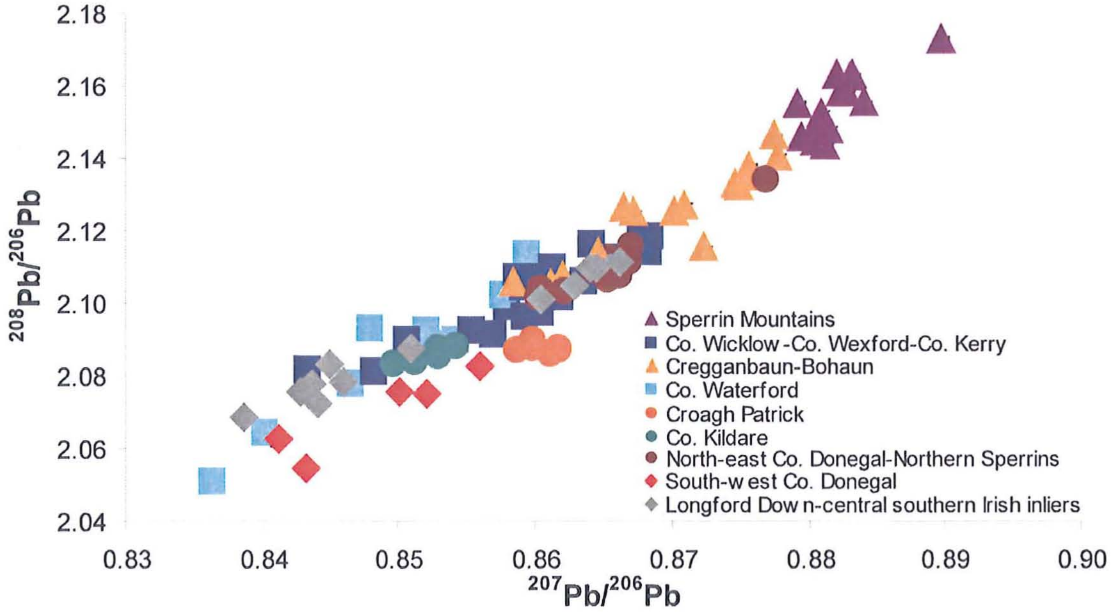


Figure 5.31: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot demonstrating the characterisation of Irish gold bearing regions using lead isotope analysis.

Chapter 6: The source of Irish Chalcolithic and Early Bronze Age gold

6.1 Synopsis

Identifying the source(s) of gold is a key research goal of Bronze Age archaeology. A significant concentration of Chalcolithic and Early Bronze Age (EBA) goldwork has been discovered in Ireland (Chapter 2), whilst this region hosts a number of gold deposits capable of supporting early goldworking industries (Chapter 3). The likelihood that Irish gold sources were exploited during the EBA is clear, and major element compositional studies have identified the Mourne Mountains of Co. Down as the most likely Irish source of EBA gold (Warner et al., 2009, 2010a, 2010b). However the desire to apply an independent analytical technique to test this hypothesis has been highlighted, with the lack of significant gold reserves in the Mourne Mountains a principle concern (Meighan, 2011). Methodologies allowing lead isotope analysis of gold through both solution and laser ablation techniques have been developed as part of this project (Chapter 4), and native deposits from all the key gold bearing regions of Ireland have been characterised for their lead isotope signatures (Chapter 5). Importantly, the ability to differentiate between deposits on a regional scale due to variations in source composition and age has been demonstrated.

Chapter 6 presents the analysis of 52 samples taken from 50 Chalcolithic and EBA Irish gold artefacts. Analytical data are first presented (Section 6.2), followed by an assessment of isotopic and major element composition heterogeneity (Section 6.3). Artefact associations and chronology (Section 6.4) and recycling/mixing (Section 6.5) are discussed, before the question of provenance is addressed (Section 6.6). In Section 6.6 three competing hypotheses are critically assessed, before the favoured theory is presented. This facilitates a discussion on the role of gold in Chalcolithic and EBA societies (Section 6.7). Isotopic data for lunulae 1881:91 and W15/R137 are published in Standish et al., 2013.

All artefact samples presented in this chapter have been donated for study by the National Museum of Ireland, Dublin. When specific artefacts are discussed, the museum accession number is provided along with the find location (when known). Samples were originally taken for compositional analysis by Hartmann (1970, 1982). In conjunction with lead isotope analysis, artefact samples were also analysed for their major element composition (copper, silver and tin) and their mineral inclusion suite. This allows direct comparison to related provenance studies.

The terms ‘single source’ and ‘multiple sources’ will be used in relation to the lead isotope signatures of the artefacts. These directly relate to the degree of characterisation achieved in the previous chapter, therefore single source refers to gold originating from one ore field (as defined by lead isotope analysis) whilst multiple sources refers to gold originating from more than one isotopic ore field (as defined by lead isotope analysis). Consequently even when the term single source is used, gold may have been exploited from more than one location within that ore field.

6.2 The composition of Chalcolithic and EBA Irish gold artefacts

6.2.1 Introduction to the EBA artefacts analysed

Fifty two Chalcolithic and EBA Irish gold artefact samples were analysed for their lead isotope signature, chemical composition, and mineral inclusion suit (Appendix B). Lead isotope analysis was initially carried out using laser ablation mass spectrometry. Due to the isobaric interference of mercury on mass 204, ^{204}Pb data lacked both accuracy and precision. Characterisation of gold deposits based on their lead isotope signature is most effective when ^{204}Pb data is available (see Section 5.7), therefore 21 samples were also analysed by solution mass spectrometry. Mercury is removed through ion exchange chromatography, therefore no significant interferences are present.

The Chalcolithic and EBA samples are from a range of artefact types: basket ornaments (n = 1), discs (n = 4), lunulae (n = 40), oval plaques (n = 5; three samples are from the same artefact), pins (n = 1) and trapezoidal plaques (n = 1). Of these, one band and two lunulae samples failed lead isotope analysis due to their low lead concentrations. Figure 6.1 details the find locations of these artefacts when recorded.

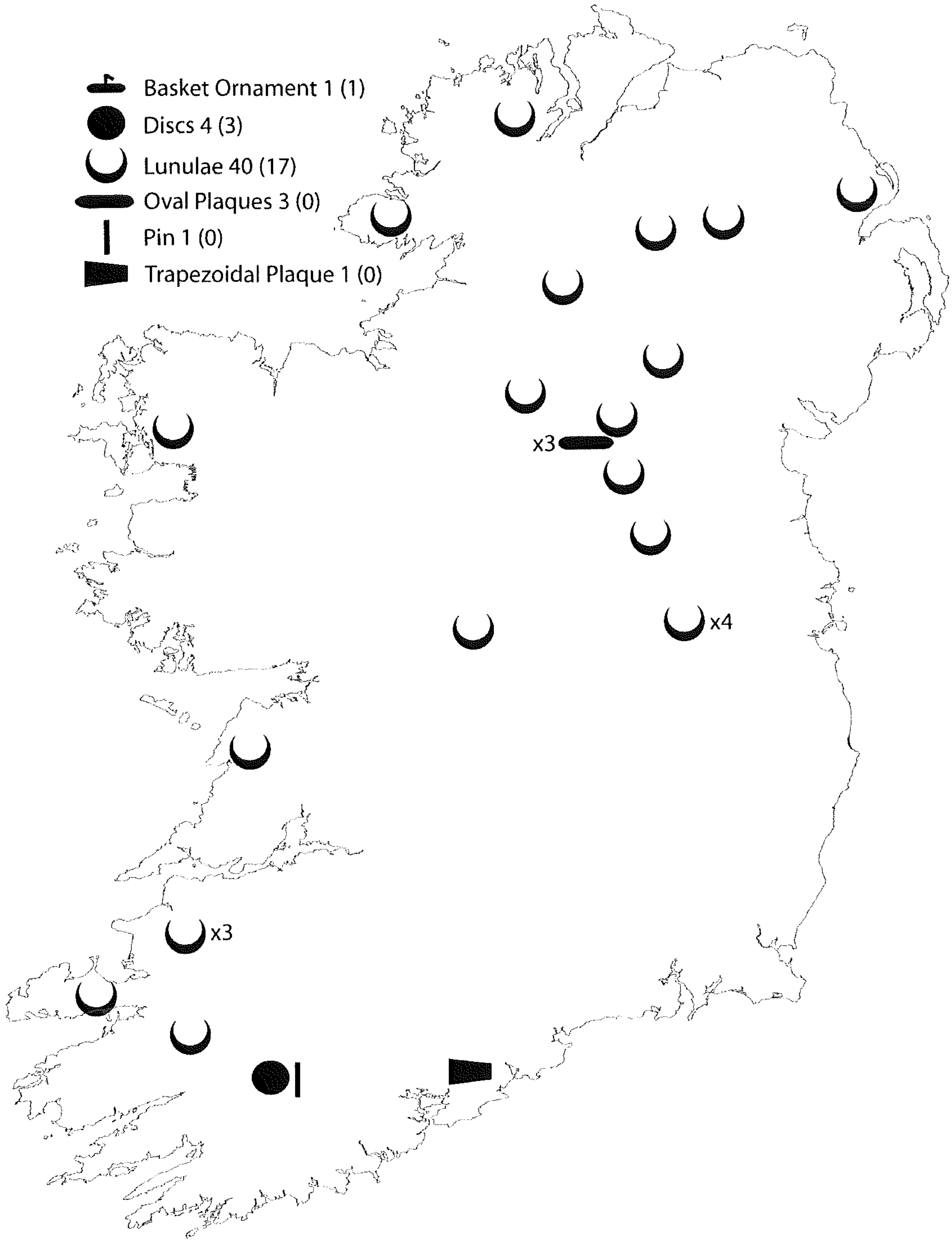


Figure 6.1: Find locations of Chalcolithic and EBA artefacts analysed in this study. Legend: numbers outside parenthesis represent total number of artefacts analysed, numbers in parentheses represents number of these with no known find location.

6.2.2 Major element compositional analysis

All artefacts were analysed for their major element composition (methodologies detailed in Section 4.4) therefore this study is directly comparable to related provenance studies (Hartmann, 1970, 1982; Chapman et al., 2006; Warner et al., 2009, 2010a, 2010b). The results of major element compositional characterisation are presented in Figure 6.2 and

Figure 6.3 (Appendices B1 and B2). Each data point (±2 S.E. of the mean of the multiple analyses, see Section 4.6) represents the average composition of three or more analyses. Where errors are not visible, they are smaller than the data symbol.

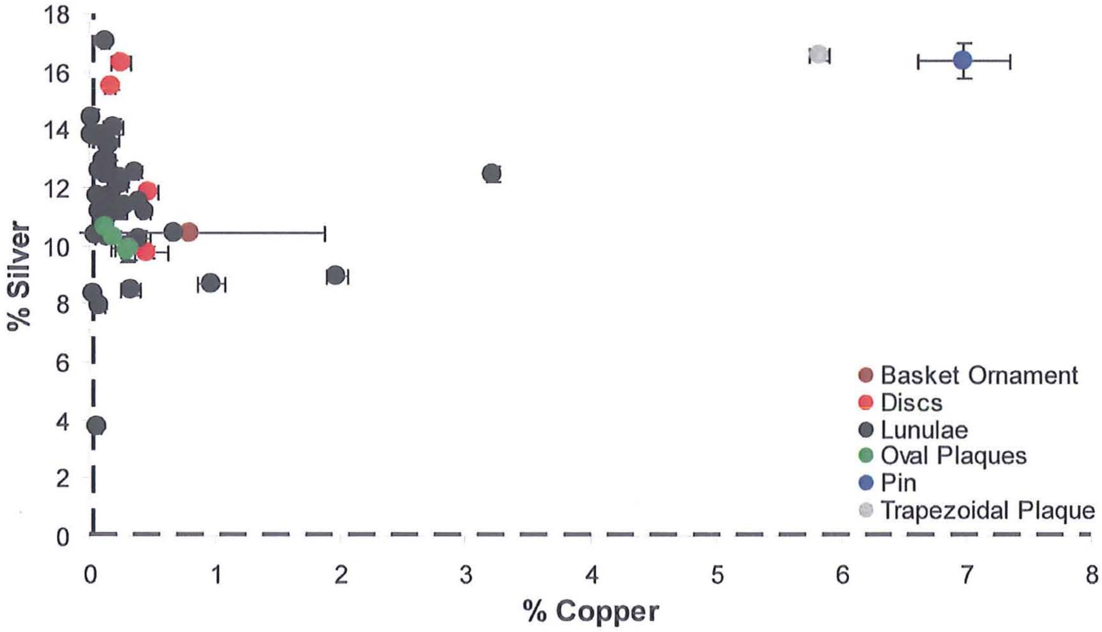


Figure 6.2: % silver versus % copper concentration of Irish Chalcolithic and EBA gold artefacts. Dashed grey lines represent analytical limits of detection.

Silver values range from 3.79% to 17.06%, with the majority of the samples forming a compositional group between 9.5% and 14.5% (n = 41). Five samples exceed this range: one lunulae (R2612), two discs (W266 and SA1913.128 from Ballyvourney, Co. Cork), the pin (SA1913.127 also from Ballyvourney), and the trapezoidal plaque (SA1913.131 from Knockane, Co. Cork). Six lunulae have silver concentrations below this range, including a lunula from Killarney (Co. Kerry; W2) which is characterised by an atypically low silver concentration of 3.79%.

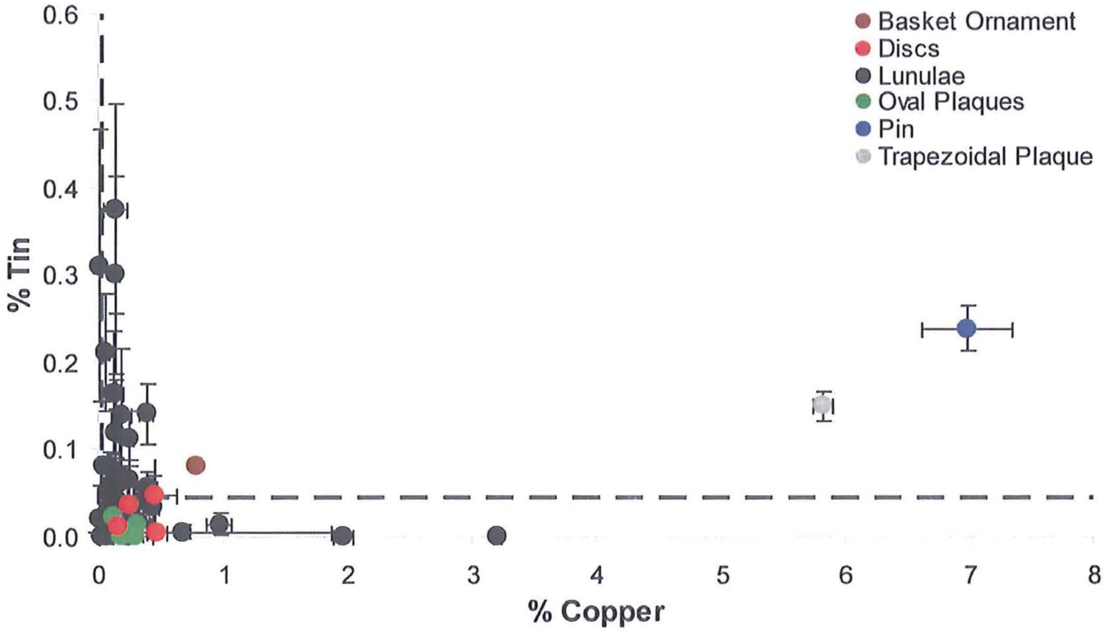


Figure 6.3: % tin versus % copper concentration of Irish Chalcolithic and EBA gold artefacts. Dashed grey lines represent analytical limits of detection.

Copper values typically range from below the limit of detection (0.029%) to 0.79% (where the limit of detection was 0.029%). There are five artefacts that exceed this range: three lunulae (1893:04 Athlone, Co. Westmeath, at 0.97%, 1997:74 Ballinagroun, Co. Kerry at 1.97% and 1884:07 Mullingar, Co. Westmeath at 3.21%), the trapezoidal plaque (SA1913.131 Knockane at 5.83%), and the pin (SA1913.127 Ballyvourney at 6.99%). Copper concentrations this high are usually interpreted as the product of deliberate alloying (Cahill, 2006; Chapman et al., 2006). If this is the case, then the silver concentrations of these potentially alloyed artefacts do not accurately represent the silver concentrations of the gold-silver alloy used for their manufacture. If the dilution due to copper addition was to be corrected for, the % silver expressed as a fraction of % gold+silver would be no more than c.1% higher than the values quoted in this chapter. As this does not significantly change the overall pattern of artefact silver concentrations, all silver is presented as % total for consistency. Tin values range from below the limit of detection (0.044%) to 0.38%.

Comparability to other provenance studies is an important issue. Hartmann (1970, 1982) was the first to investigate the chemical composition of Irish Bronze Age gold artefacts. For the majority of Irish samples, silver concentrations were estimated by either the specific gravity of the whole artefact, or by gravimetric analysis of an artefact sample, and Warner and Cahill (2011) have recently cast doubt on the accuracy of these analyses. The authors recommended that the values should be considered as qualitative only, and a relative uncertainty of 25% (1 S.D.) be applied. Conversely, the copper and tin values were considered as reliable. Figure 6.4 plots the silver, copper and tin concentrations of all the artefact samples analysed by both Hartmann and this study (Hartmann's copper and tin data has been converted from % of gold to % of total to allow direct comparison with data from this study).

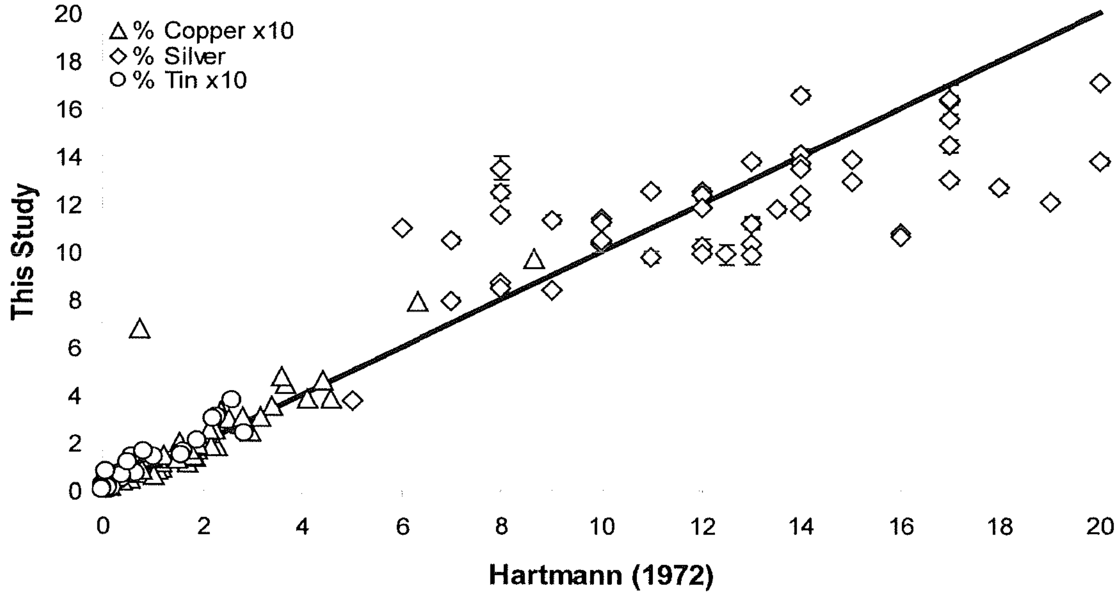


Figure 6.4: Comparative plot of the silver, copper and tin concentrations of Chalcolithic and EBA gold artefacts analysed by Hartmann (1970, 1982) and this study.

The poor correlation of the silver datasets (Slope = 0.43, R^2 = 0.432) supports the view that the data should be considered as qualitative only. However in agreement with Warner and Cahill (2011), good correlation is apparent for the copper (Slope = 1.04, R^2 = 0.992) and tin data (Slope = 1.14, R^2 = 0.8938). One sample demonstrates poor correlation for copper (this study % Cu x10 = 6.79, Hartmann % Cu x10 = 0.74), however this can be explained by its atypically variable copper composition.

Figure 6.5 compares the compositional analysis of EBA artefacts from this study with the six EBA artefact analyses using EPMA from Chapman et al. (2006). The plot highlights the excellent inter-laboratory comparability for all three elements; slopes are 0.98, 1.02, and 0.90 and R^2 values 0.933, 0.998 and 0.890 for copper, silver and tin respectively. Importantly this means that the compositional data obtained in this study is also directly comparable to the database of Irish gold deposits published by Chapman et al. (2000a, 2000b, 2006).

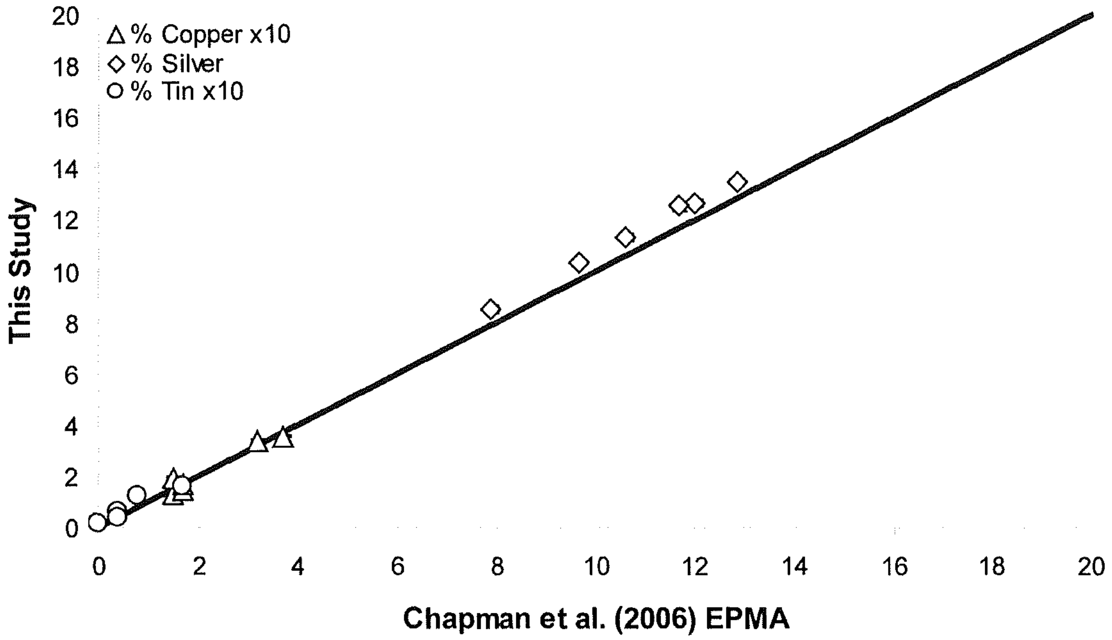


Figure 6.5: Comparative plot of the silver and copper concentrations of Chalcolithic and EBA gold artefacts analysed by Chapman et al. (2006) using EPMA and this study (also EPMA).

The majority of the artefact samples analysed by Chapman et al. (2006) were analysed by XRF. The six EBA samples analysed by using EPMA were also analysed by XRF (along with 18 chronologically later artefacts), and the offsets between the values calculated using the two techniques were used to correct all XRF analyses. For example, adjusted % Ag = % Ag XRF × 1.035 + 0.194. This equates to a correction factor of c.+5% from the XRF values. As a result, the data collected in this study is also comparable to all the compositional values of artefacts published by Chapman et al. (2006). XRF data published by Warner et al. (2009, 2010a, 2010b) did not apply this correction, therefore a small offset with the elemental data presented in this study can be expected.

6.2.3 Lead isotope analysis

The lead isotope signatures of Irish Chalcolithic and EBA gold artefacts are highly variable and are presented in Figure 6.6, Figure 6.7 and Figure 6.8 (Appendices B3 and B4). All the artefact samples were first analysed by laser ablation (methodology presented in Section 4.3). The majority underwent three analyses, however the small size of some samples restricted the number of analyses that could be performed. The data points plotted in Figure 6.6 are the results of laser ablation analysis, with each data point representing one sample. As with the compositional data, when multiple analyses were performed the data point represents the average isotopic value with errors ±2 S.E. of the mean of the multiple analyses. Twenty-one samples were analysed using solution techniques (methodology presented in Section 4.2), the results of which are presented in Figure 6.7 and Figure 6.8. Each sample was analysed once, therefore the errors are ±2 S.E. of the mean of 50 integration cycles. In all cases, if errors are not visible they are smaller than the data point. Solution and laser ablation techniques have been shown to be directly comparable in Chapter 4.

As with the compositional data, some artefacts can be identified as having atypical compositions. In reference to Figure 6.6, the majority of the artefacts form a large cluster with $^{207}Pb/^{206}Pb > 0.83$ and $^{208}Pb/^{206}Pb > 2.04$. Six lunulae (1986:15 Ross, P817, SA1928:715 Rossmore, W7, W10 and W13), two discs (P949 and W266) and an oval plaque (W75 Belville) all have isotopic ratios below these values. Out of this group, six were analysed by solution methods to collect ^{204}Pb data. They can not be distinguished with $^{207}Pb/^{204}Pb$ or $^{208}Pb/^{204}Pb$, however they are characterised by $^{206}Pb/^{204}Pb > 18.792$.

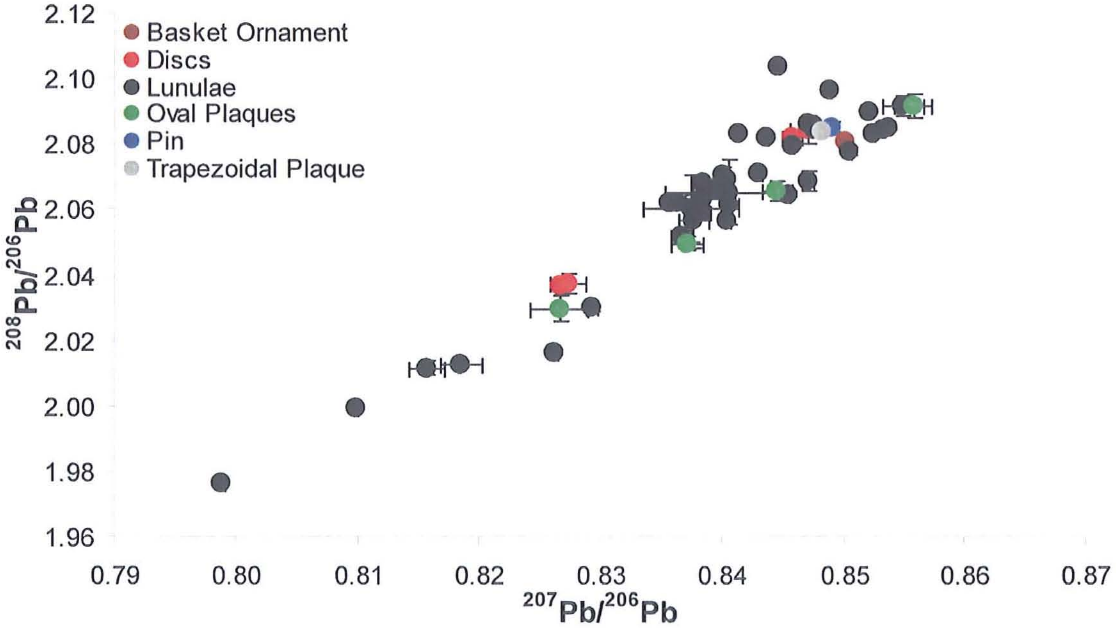


Figure 6.6: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of Chalcolithic and EBA Irish gold artefact samples.

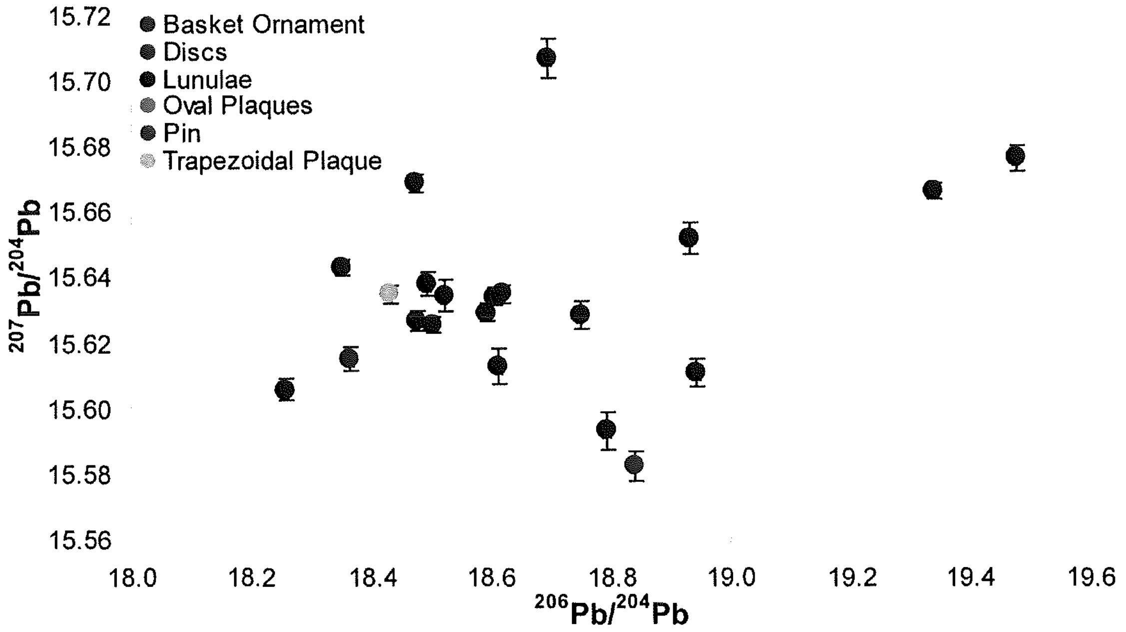


Figure 6.7: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Chalcolithic and EBA Irish gold artefact samples.

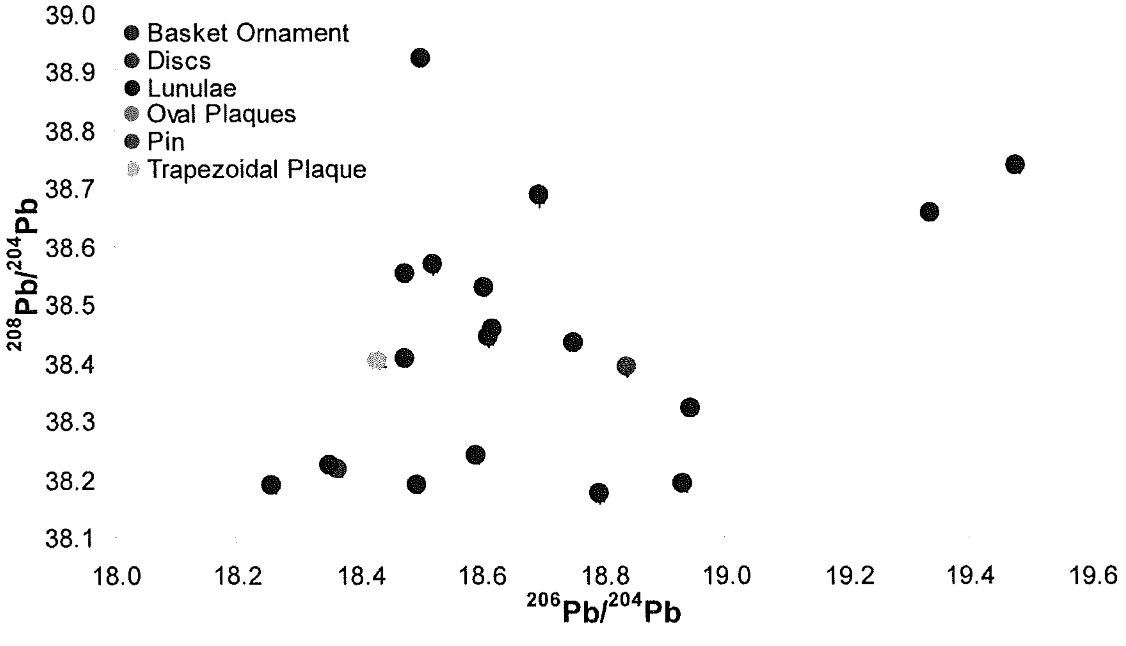


Figure 6.8: ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Chalcolithic and EBA Irish gold artefact samples.

6.2.4 Mineral inclusion suite

Natural gold grains often contain a suite of opaque mineral inclusions. These inclusions have been used in microchemical characterisation studies that aim to identify the different sources of alluvial populations, and link them to particular styles of gold mineralisation (Leake et al., 1992). This analytical technique has been employed in numerous studies of Irish gold, and has resulted in a database that covers all the principle gold bearing regions (Chapman et al., 2000a, 2000b, 2006; Moles et al., in press). The mineral inclusion suite of the artefact samples were therefore characterised using a scanning electron microscope (methodology presented in Section 4.5). By comparison with the published database of natural gold deposits, this potentially provides an extra level of characterisation when comparing the signatures of artefact and natural gold. The result of the mineral inclusion study is presented in Table 6.1 and Appendix B5.

Table 6.1: Mineral inclusions identified in Chalcolithic and EBA artefact samples per artefact type. The five lunulae and one oval plaque already characterised by Chapman et al. (2006) are not included in this table.

Inclusion type	Basket Ornament (n = 1)	Oval Plaques (n = 4)	Discs (n = 4)	Lunulae (n = 35)	Pin (n = 1)	Trapezoidal Plaque (n = 1)
AlO				1		
Ca				2		
NaClK		2		4	1	
Quartz		6	11	91	1	
Al-silicate		2		6		
AlCa-silicate				1		
AlK-silicate				2		
AlNa-silicate				1		
AlNaCl-silicate				1		
Mg-silicate				9		

The dominant mineral inclusion is quartz. Other silicate species are also present, along with further inclusion types such as a calcium only phase. This is consistent with the mineral inclusions suite identified in Chalcolithic and EBA artefacts by Chapman et al. (2006). These inclusions are typical rock forming minerals and are not characteristic of any particular type of mineralisation or geology. The inclusion suite is therefore of little use for characterising sub-groups of artefacts or linking them to specific gold sources, and will not be discussed any further.

6.3 Artefact Heterogeneity

It is clear from Figure 6.6 that the isotopic inter-artefact heterogeneity (i.e. variation between artefacts) was large during the Chalcolithic and EBA; variation is 13.9‰ on the ^{207}Pb/^{206}Pb and 13.0‰ on the ^{208}Pb/^{206}Pb (defined as standard deviation/average*1000). To quantify this, it is useful to know the typical intra-artefact heterogeneity (i.e. variation within an artefact). The artefact samples were analysed up to three times each for both isotopic and compositional characterisation, and the average variation within each sample (therefore on a millimetre scale, henceforth termed intra-sample variation) was 0.79‰ and 0.76‰ on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ respectively. Two lunulae samples are noticeable for significantly higher heterogeneity; 1881:91 has a variation of 4.1‰ and 4.4‰ and W12 has a variation of 5.4‰ and 4.3‰ on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$.

These samples were a maximum of c.2 mm in diameter, therefore the high spatial resolution could produce a false sense of intra-artefact variation. An oval plaque (a possible diadem from Co. Cavan; Figure 2.5), was discovered in four separate pieces. Three of these produced isotopic data (samples W78, W79 and W81), and are plotted with enlarged data points in Figure 6.9. The variation of the three samples (and therefore on a centimetre scale; henceforth termed intra-artefact variation) is 9.0‰ and 8.0‰ on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ respectively, a range more comparable to the inter-artefact variation rather than the typical intra-sample variation. This represents the best indication of isotopic variation within a single artefact. It should be noted that this artefact is likely to be one of the chronologically earliest artefacts analysed; it is typically included in the primary Beaker goldwork assemblage (see Section 2.3.1.2) therefore if manufacturing processes changed in subsequent periods this may not be representative of all the artefacts analysed. However two of the lunulae (W12 and 1881:91, see also Standish et al., 2013), which date to the later insular traditions, also have isotopic variation on a similar level to the diadem, therefore this is considered unlikely.

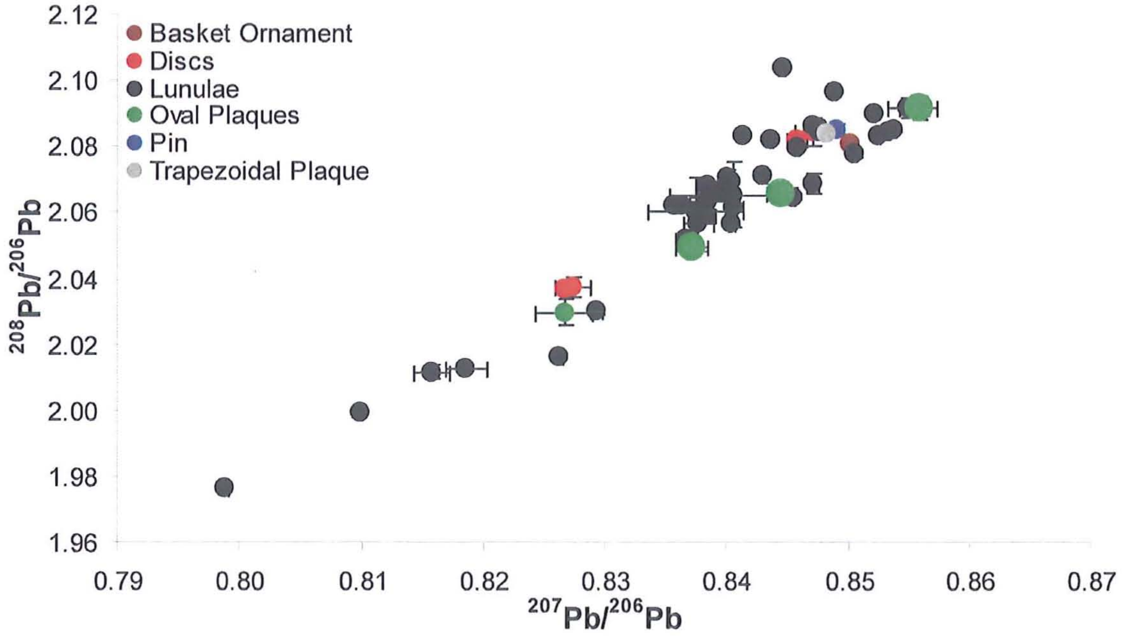


Figure 6.9: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of Chalcolithic and EBA Irish gold artefact samples. The data points representing the three analysed sections of the long Belville oval plaque have been enlarged.

The compositional inter-artefact variation is also significant (Figure 6.2 and Figure 6.3); the variation (defined as standard deviation/average*100) between the artefacts is 20.5% for silver, 232.1% for copper and 126.0% for tin. The variation for the copper is particularly high due to the four artefacts with exceptionally high copper concentrations identified previously (without these, the variation drops to 85.3%). All variations are summarised in Table 6.2. The intra-artefact and average intra-sample variations are lower by a factor of ten for both silver and copper. The variation of the tin concentrations does not conform to this pattern. The levels of variation quoted are consistent with the EPMA data from Chapman et al. (2006).

Table 6.2: Intra-sample (average), intra-artefact (based on the long oval plaque) and inter-artefact variation for Chalcolithic and EBA gold artefact copper, silver and tin concentrations, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. *represents variation when the four possible gold-copper alloy artefacts are excluded.

	% Copper	% Silver	% Tin	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Intra-sample	27.5%	1.2%	60.6%	0.79‰	0.76‰
Intra-artefact	26.2%	2.6%	186.6%	9.0‰	8.0‰
Inter-artefact	232.1% (85.3%*)	20.5%	126.0%	13.9‰	13.0‰

The silver and copper variations remain the same relative to each other on all spatial levels; the intra-artefact and intra-sample variations are a factor of ten lower than the inter-artefact variation. If the silver and copper reflect the composition of the natural alloy, their variations are likely to remain the same relative to each other at all scales. This pattern is not mirrored by the tin data where relatively similar variations remain on all spatial levels. It is generally accepted that the tin concentrations of Chalcolithic and EBA artefacts are too high to correspond to the composition of natural gold alloys, therefore tin is seen as an indication of a cassiterite bearing alluvial source (e.g. Hartmann, 1970; Warner et al., 2009). The higher variation of the tin concentrations may be a function of this providing the two minerals could not be efficiently separated from each other after co-collection (Chapman pers. comm.). The variation of the tin concentrations may therefore be further evidence for alluvial gold exploitation.

The lack of intra-sample variation in the major element composition of Chalcolithic and EBA artefacts could indicate the processing of a homogenous charge or a homogenising manufacturing process (Chapman et al., 2006). The recorded decrease in compositional variation from the inter-artefact scale may support the latter. Chalcolithic and EBA gold artefacts were created by sheet gold techniques; ingots were beaten into thin sheets before decoration was applied (Eogan, 1994), therefore presumably some degree of heating would have been required to form the initial ingot. This process could potentially homogenise the documented inter-artefact variability thus creating the homogeneity within single samples and artefacts. However experimental work by Chapman et al. (2006, p.908) demonstrated that it was difficult to produce truly homogenous gold alloys from heterogeneous melting charges (when gold underwent 'violent mixing for several seconds'). Providing these experiments accurately reproduced the technological processes used during this period then the variation within an artefact or sample may instead be indicative of the variability of natural gold source(s) and/or deliberate alloying practices (Chapman et al., 2006). Accordingly at small spatial scales the gold sources must have been compositionally homogenous (for example within a particular mineralisation vein). However if these experiments were not accurate representations, then homogenisation due to manufacturing processes is still a possible explanation. Irrespective of this, the inter-artefact variability is the best proxy for the overall compositional variation of the gold sources under exploitation, and therefore points towards heterogeneous sources.

If the compositional homogeneity on the artefact and sample scale does not reflect homogenisation due to manufacturing processes, then the same may be true for the isotopic variation. On the sample scale the lead isotope variation is low, therefore at small spatial scales the gold charge may also have been isotopically homogenous. The greater variation on the artefact scale suggests that the overall isotopic variation of the exploited gold sources was heterogeneous. This is significant because different gold deposits vary isotopically to different degrees (see Chapter 5). If the variability of the source can be characterised through the analysis of an artefact, then a further parameter for linking artefact to ore is available. By developing this argument, it is possible to say that the gold deposits exploited were homogenous on the small scale (again perhaps relating to individual mineralisation veins) yet heterogeneous on the larger scale (perhaps indicative of an ore district). This also sheds important information on the technological processes involved. The isotopic signatures (on the centimetre scale) were not systematically homogenised when natural grains of gold were transformed into workable gold ingots, perhaps indicating that sintering techniques rather than long periods of mixing in a molten state were employed. In order to explore this idea further, experimental investigations would be required.

It has been proposed that the isotopic variation within and between artefacts record the variation of the gold sources exploited for their manufacture. This hypothesis can be tested by comparing the artefact variation with the variation typically found in Irish natural gold deposits introduced in Chapter 5. Variation ranges from 0.04 to 17.3‰ (average of 5‰) and 0.09 to 12‰ (average of 4‰) on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ respectively (Figure 6.10). This range is broadly consistent with the intra-sample, intra-artefact and inter-artefact variations, and therefore supports the hypothesis that the isotopic variation within and between the artefacts could directly relate to the variation of the exploited natural gold deposits.

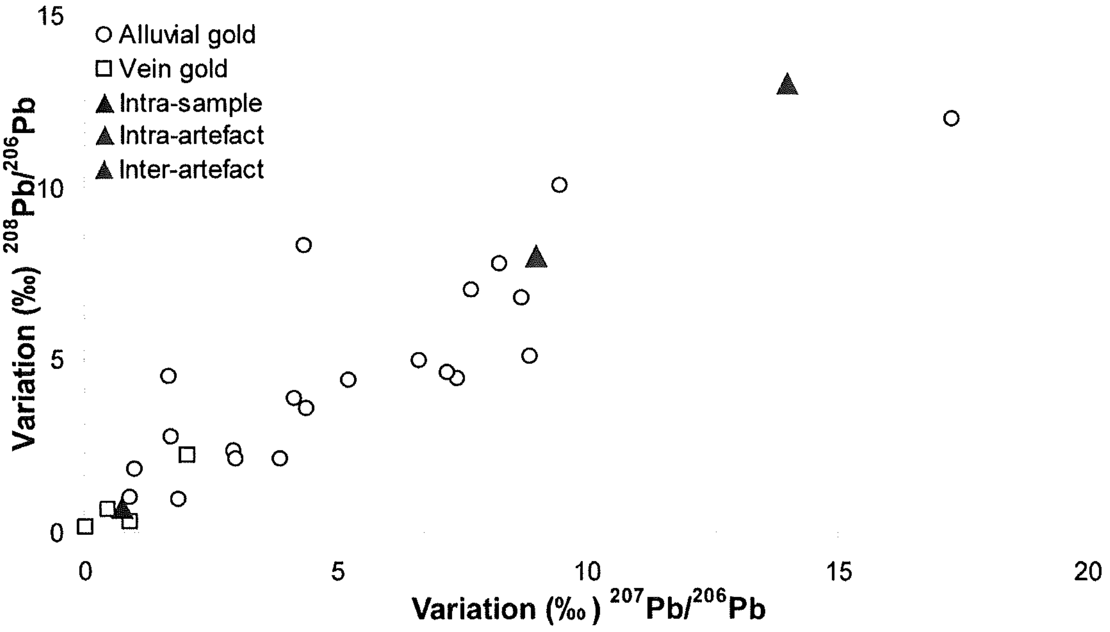


Figure 6.10: Variation ^{208}Pb/^{206}Pb versus variation ^{207}Pb/^{206}Pb of natural gold sample sites (vein and alluvial) compared to the intra-sample, intra-artefact and inter-artefact variation of Chalcolithic and EBA gold artefacts detailed in Table 6.2.

Of the Irish natural gold deposits studied, four were vein mineralisations (Figure 6.10 open black squares) whilst the remainder were alluvial deposits (Figure 6.10 open black circles). The vein deposits plot with low isotopic variation along with some alluvial deposits and the intra-sample variation. Consequently the typical variation within a single vein is low, and those alluvial deposits with similarly low variability are likely to derive from a single vein source or few but genetically related vein sources. This supports the theory that the intra-sample variation reflects derivation from highly spatially resolved sources. Conversely the higher intra-artefact and inter-artefact variation are only consistent with the more variable alluvial sources. Alluvial sources can be composite deposits of numerous vein mineralisations, therefore this variation could reflect either the exploitation of a high number of isotopically discrete vein sources, or the exploitation of larger alluvial deposits. To summarise, the variation suggests that Chalcolithic and EBA goldwork was manufactured from isotopically heterogeneous gold originating from multiple vein occurrences. It has already been argued that the high tin content of the artefacts is indicative of an alluvial source, therefore exploitation of large scale alluvial deposits is favoured.

6.4 Artefact Associations and Chronology

There are few distinguishable patterns in the isotopic and elemental composition of Chalcolithic and EBA artefacts. As has been discussed, both the major element composition and lead isotope signature of these artefacts are variable. This variation is typified by the long oval plaque discovered at Belville, Co. Cavan. When compared to the isotopic signature of other artefacts that date to the primary phase of goldworking (Figure 6.6; the other oval plaque, basket ornament, and potentially some of the discs) it is apparent that there is no clearly defined isotopic group within the overall Chalcolithic and EBA field. This is despite the compositional homogeneity of these artefacts; the two (potentially early) A-type discs along with other primary goldwork are characterised with silver concentrations between 9.77% and 11.84%; Figure 6.2).

Despite the doubts raised over the typology of Chalcolithic and EBA discs (see Chapter 2), the A- and B-type discs (Case, 1977) are compositionally distinguishable. Two A-type discs (P949 and W270) have lower silver concentrations (9.77% and 11.84% respectively) in keeping with the other primary goldwork analysed, whilst the B-type discs (SA1913:128 and W266) are characterised by higher silver concentrations (16.33% and 15.5% respectively). The pairs of discs may therefore have been manufactured from distinct charges thus supporting a chronological separation. However as with the general isotopic pattern, these groups are not distinguishable using their lead isotope signatures (the discs plot in pairs in Figure 6.6, however these to not correspond to the same pairs identifiable through elemental composition analysis). If these two groups of discs were manufactured from different charges, then the gold sources were apparently located within the same isotopic ore field.

The lunulae encompass the full isotopic and compositional range of EBA artefacts (Figure 6.6). Taylor (1980) classified the lunulae into three principle group: classical, unaccomplished, and provincial; whilst some plain forms also exist. Figure 6.11 plots the lead isotope signatures of the lunulae, and it is clear that there is no correlation between isotopic composition and lunulae type. This is consistent with Eogan's (1994) view that both classical and unaccomplished lunulae are of Irish manufacture; it would be expected that the same metal pool was used for both forms. Unfortunately no provincial lunulae were included in this study, so no consideration of their isotopic signature can be made.

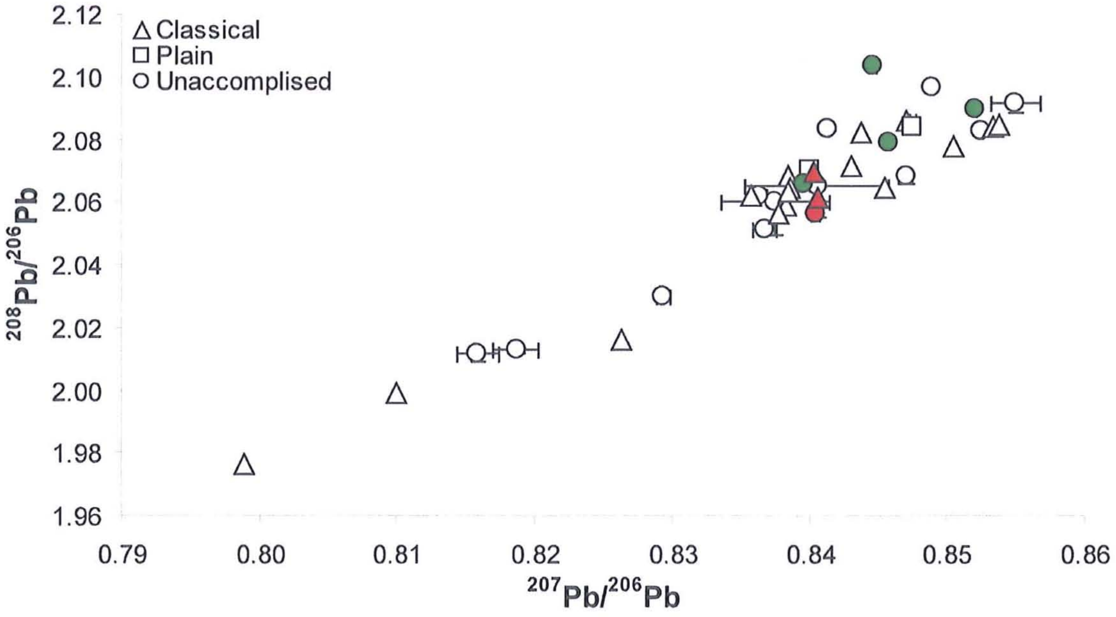


Figure 6.11: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of EBA lunulae based on lunulae type. Green symbols represent lunulae from the Dunfierth, Co. Kildare, hoard and red symbols represent lunulae from the Banemore, Co. Kerry, hoard.

Figure 6.11 also highlights the lunulae recovered from two hoards; the Dunfierth (Co. Kildare) lunulae are depicted by green symbols whilst the Banemore (Co. Kerry) lunulae are depicted by red symbols. Those from the Banemore hoard are isotopically similar, however their silver concentrations range from 7.94% to 11.71% indicating compositional variation. The Dunfierth lunulae are isotopically variable, yet based on their silver concentrations they are compositionally more homogenous (ranging from 12.46% to 13.82%). This reinforces the lack of correlation between major element composition and isotopic signature.

The lead isotope signature and silver concentration indicates compositional links between the trapezoidal Knockane plaque (SA1913.131) and the Ballyvourney pin (SA1913.127). Both are characterised by high copper that is indicative of alloying, and are likely to date from late in the EBA; parallels have been drawn between the plaque Wessex I goldwork of southern Britain (Cahill, 2006). A possible association between the alloy used to manufacture these two artefacts can therefore be proposed, and the distinct compositional signature that they define may be characteristic of later EBA artefacts in general. Despite this, it should be noted that they still plot within the Chalcolithic and EBA artefact lead isotope field and not as an external group. Cahill (2006) suggested that these artefacts represent an early stage of experimental gold-copper alloying. As a result, the tight isotopic clustering could result from the additional input of lead originating from the copper ore. However it is interesting to note that the Ballyvourney disc (with a typical copper concentration) has a similar silver concentration and isotopic signature to the supposedly alloyed Ballyvourney pin. The high copper of the pin must suggest alloying, however the fact that the isotopic signatures are so similar may indicate that the alloyed copper had a similar isotopic signature to that of the gold, i.e. the copper originated from sources characterised by similar isotopic signatures. This would explain why the two alloyed artefacts plot within the Chalcolithic and EBA isotopic field. Two lunulae (1884:07 Mullingar and 1998:74 Ballinagroun) also demonstrate elevated copper, albeit not to the same degree. Although the isotopic signatures of these two artefacts are similar to the pin and trapezoidal plaque they are distinct enough to exclude them from this group. This suggests differences in the alloy used for manufacture and thus provides a reason to exclude them from this 'late' group of artefacts.

The overriding picture generated by the Chalcolithic and EBA assemblage is that these artefacts were manufactured from a heterogeneous metal pool. Although certain groups of artefacts may demonstrate homogeneity on either their elemental composition or isotopic signature, this is rarely achieved by both at the same time. Consequently whilst it may be possible to genetically link certain artefacts together, such as the A-type discs based on silver composition or the Banemore lunulae hoard based on lead isotope signature, this is unlikely to be indicative of discrete ore sources. The majority of Chalcolithic and EBA artefacts were therefore manufactured from the same principle ore field, and no clear sequence based on composition and relating to chronological stages can be put forward.

6.5 Mixing and Recycling

6.5.1 Mixing of isotopically heterogeneous gold

Mixing metals with variable isotopic compositions has the potential to homogenise the isotopic signature of a metal pool. As discussed in Section 6.3 it is perhaps difficult to achieve complete isotopic homogenisation, however it is possible that variation would decrease if charges are in a molten state for any prolonged period of time. This could result in a disparity between ore and artefact. Similarly, repeated recycling of artefacts from a pre-existing metal pool could result in gradual homogenisation, with the new recycled isotopic signatures becoming inconsistent with contemporaneously exploited ore sources. Recycling is a practice that should always be considered in studies concerning metalwork. Due to the restricted nature of ore deposits and the effort required for procuring the raw material, recycling unwanted or obsolete objects is likely. This is especially so during the early period of metal exploitation when the metal pool would have been of limited size, and the redecoration of three Irish EBA lunulae indicates that recycling did occur in some form (Taylor, 1980). The ability to identify the composition of a recycled metal pool is therefore of vital importance to provenance studies.

The average isotopic ratio for Chalcolithic and EBA gold artefacts is 0.83942 and 2.06291 on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ respectively (mixing point a; red cross Figure 6.12). This represents a potential isotopic composition of homogenised Chalcolithic and EBA gold assuming the artefacts analysed are a good proxy for the overall variation of the gold in circulation at this time. Regarding the lunulae, approximately 50% of all known Irish examples have been analysed, therefore this can be seen as a reasonable assumption. This composition is consistent with what could be termed the principle artefact cluster for the Chalcolithic and EBA data (red domain Figure 6.12), therefore highlighting that this cluster may be the result of heterogeneous source mixing or artefact recycling. The average isotopic ratio for Chalcolithic and EBA gold artefacts excluding those that fall into this cluster is 0.83986 and 2.06326 on the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ respectively (mixing point b; filled black square Figure 6.12). This is comparable to the signature when all the artefacts are included in the calculations, therefore the composition of the cluster is not significantly biasing the data.

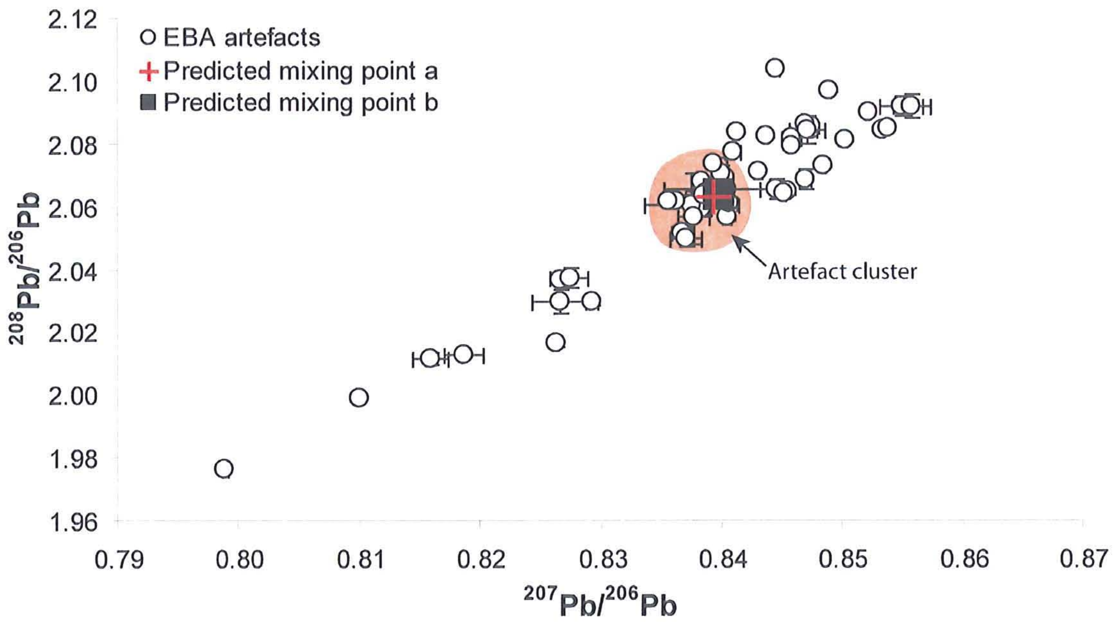


Figure 6.12: ^{208}Pb/^{206}Pb versus 207Pb/^{206}Pb plot of Chalcolithic and EBA artefacts, predicted mixing points and the data cluster representing possible mixing or recycling.

This cluster of artefacts is therefore consistent with a mixing origin, however it is not clear if this is simply a result of heterogeneous source mixing or recycling. The isotopic variation documented within the long oval plaque from Belville, Co. Cavan, and within the two lunulae samples 1881:91 and W12 suggests that homogenisation is difficult to achieve. This perhaps supports the latter because repeated recycling would have required the gold to be in a molten state on a greater number of occasions. However without experimental investigations this is somewhat difficult to prove. The theory that this cluster is the product of recycling can be explored further by modelling hypothetical recycling practices. Pairs of artefacts that do not plot within the mixing cluster have been isotopically averaged modelling what would occur if two artefacts were combined for the manufacture of a new artefact. This was repeated over five ‘mixes’ until one artefact remained, therefore resulting in a single isotopic composition. Selecting pairs of artefacts is arbitrary, and a higher number could be mixed over fewer stages. However this modelling is merely designed to provide an example for the isotopic evolution of the Chalcolithic and EBA gold metal pool if recycling occurred, and is therefore appropriate. Modelling was performed 100 times, with the results are plotted in Figure 6.13 relative to the initial isotopic signature of the Chalcolithic and EBA artefacts.

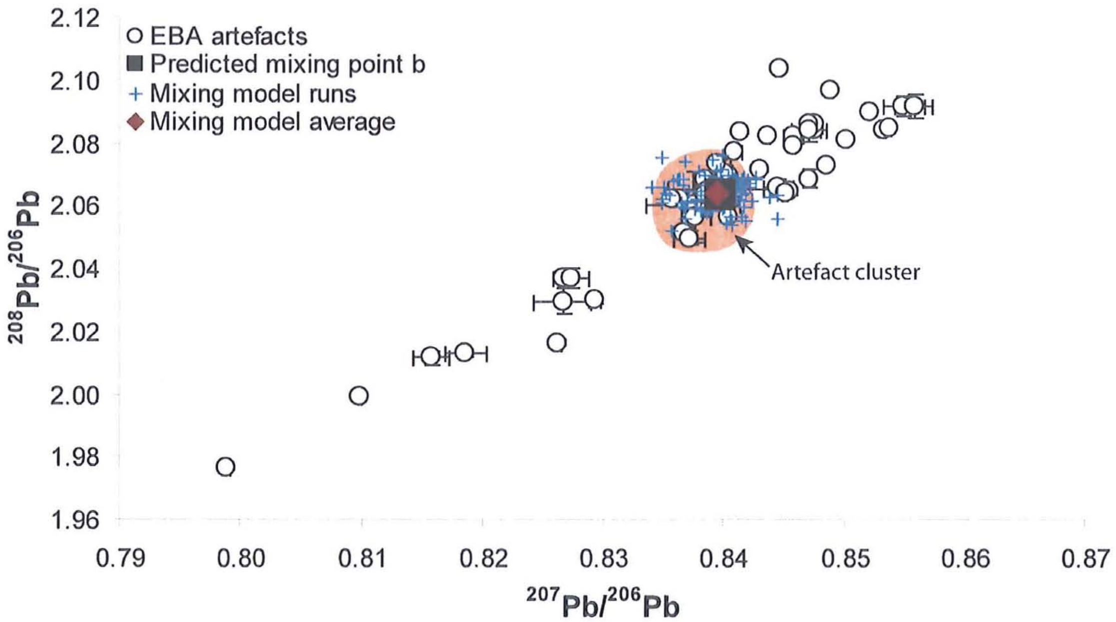


Figure 6.13: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of recycling models. The final composition of each model run is plotted, along with the average composition of the 100 runs, the predicted mixing point b from Figure 6.12, and all Chalcolithic and EBA artefacts.

The spread of final mixing compositions (blue crosses Figure 6.13) is consistent with the artefact cluster (red domain Figure 6.13), whilst the average final mixing composition (filled red diamond Figure 6.13) is consistent with the predicted mixing point (filled black square Figure 6.13). Figure 6.14 plots a histogram of the average $^{208}Pb/^{206}Pb$ compositions for each stage of the artefact recycling model. The filled black data series represents the starting composition, i.e. the composition of all the artefacts that do not fall within the cluster. The dashed black line represents the composition of the possible mixing cluster. The blue to turquoise data series represent each subsequent stage of recycling.

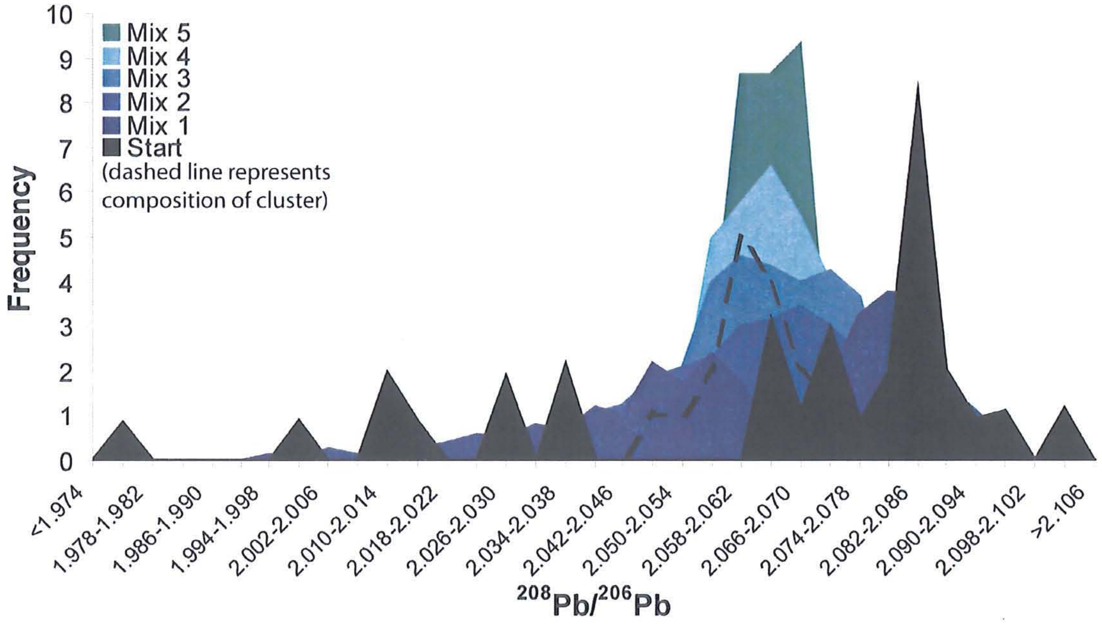


Figure 6.14: Histogram of average $^{208}Pb/^{206}Pb$ isotopic compositions for each stage of the artefact recycling model.

It is clear that the average modelling compositions are consistent with an isotopic evolution from the variation of the non-clustered Chalcolithic and EBA artefacts to that of the possible mixing cluster. The potential mixing can be further assessed by considering the elemental composition of those artefacts that plot within this cluster; in theory they should also demonstrate homogenisation. Figure 6.15 plots the silver and copper composition of the Chalcolithic and EBA artefacts, with blue crosses marking those artefacts that fall into the potential mixing cluster. The results are somewhat inconclusive, although the potentially mixed artefacts do generally fall towards the centre of the overall compositional range proximal to the average artefact composition (open black square). Further work is therefore required before the origin of the artefact cluster can be confirmed, and experimental investigations that can characterise the behaviour of the lead isotope and major element signatures during melting and mixing is a necessity. The preceding discussion does however suggest that such an origin should be considered during any attempts to link artefacts to ore deposits.

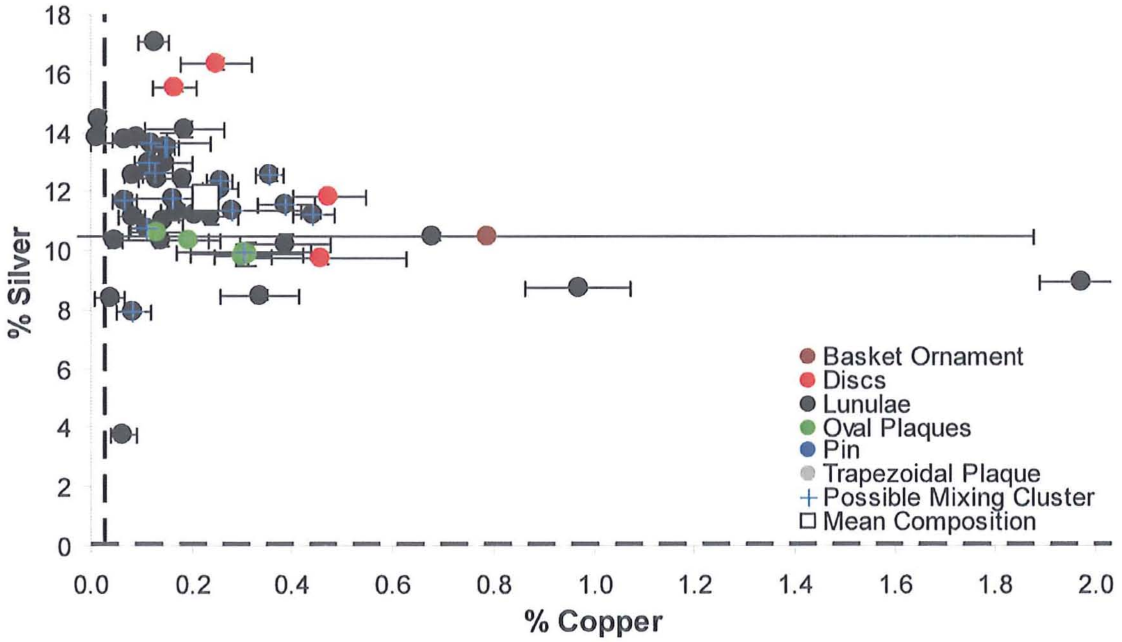


Figure 6.15: % copper versus % silver composition of Chalcolithic and EBA artefacts. Those artefacts falling in the possible mixing cluster highlighted (blue cross), and the average artefact composition plotted (open black square, excludes the copper alloyed artefacts).

6.5.2 Copper alloying in the Early Bronze Age

Four of the EBA artefacts have copper concentrations that are high for naturally occurring gold alloys (>1%), thus suggesting that copper alloying was practiced to some degree. If this was the case, the lead isotope signatures of these samples will represent a mix of the isotopic signatures of both the gold and copper sources. The artefacts in question are the Ballyvourney pin (SA1913.127), the plaque from Knockane (SA1913.131), the Ballinagroun lunula (1998:74) and the Mullingar lunula (1884:07).

It is perhaps hazardous to predict which copper sources were exploited for the manufacture of these artefacts, however it is necessary if an assessment on the probable gold source is to be made. Archaeological evidence can indicate the potential copper sources, and a subsequent correction can be applied that calculates the isotopic signature of the gold component. The ages of the artefact types in question have all previously been discussed in Section 2.3.1. Lunulae are thought to date to the EBA primarily due to a radiocarbon date of 2460-2040 cal BC for the alder box associated with the Crossdoney lunula (Cahill, 2006), and they were probably in circulation from c.2300/2200 BC for a number of centuries. Typologically both the pin and plaque have also been assigned to the EBA (Case, 1977; Cahill, 2006) although they are perhaps somewhat later than the lunulae. The plaque has been paralleled with the Wessex linear style (Cahill, 2006) which dates from c.1950 to 1750/1700 BC. The pin has been paralleled with a gold pin from Areia, Aveiro, Portugal (Cahill, 2006), therefore a more distant origin is possible. However links with Irish bone pins have also been proposed (Case, 1977) and, as the artefact has a remarkably similar major element composition and isotopic signature to the plaque, an Irish or British source is perhaps more likely.

Copper was mined from Ross Island, Co. Kerry, from c.2400 BC to c.1800 BC, and was the principle source of copper for earlier periods; an estimated 95% of Irish copper artefacts from the final Neolithic or Copper Age were made using the Ross Island 'type A' metal (Northover et al., 2001; O'Brien, 2004). As lunulae are believed to be of Irish manufacture, this represents the most probable source for the copper in the potentially alloyed lunulae, and is also a possible source for the later pin and plaque. The Mount Gabriel type mines of south-west Co. Cork rose to prominence from c.1800 BC until c.1500 BC (O'Brien, 1994, 2003) and are therefore a further potential copper source for the plaque and pin. However copper mines also went into production in Britain at this time; those at Alderley Edge, Great Orme, Parys Mountain and Cwmystwyth were all active during this period (Dutton and Fasham, 1994; Ixer and Budd, 1998), whilst Cornish copper may also have been exploited (Rohl and Needham, 1998). Clearly it is more difficult to predict the copper sources of this later period, especially as both the pin and plaque are atypical artefact forms in Ireland. Nevertheless an Irish source can perhaps be considered likely due to the proximity of their find locations to the EBA copper mines of south-west Ireland.

An attempt to calculate the lead isotope signature of the gold component used to manufacture these four artefacts has been made. This calculation required the following information: the copper concentration of each artefact (%Cu); typical lead concentrations (ppm) of gold (where gold represents the naturally occurring gold-silver alloy) and copper ($ppmPb_{Au}$ and $ppmPb_{Cu}$ respectively); the isotopic composition of the analysed artefact sample (r_{AuCu}) and the average composition of the potential copper source (r_{Cu}). The average lead concentration of all the natural gold analysed during this study was 20 ppm, with most samples falling within the range 0.5 ppm to 100 ppm. The value of 20 ppm was therefore used for the typical lead concentration of gold ($ppmPb_{Au}$). The lead concentration used for the copper input was based on the typical lead concentrations of copper/bronze artefacts contemporaneous with the goldwork in question. Regarding the EBA, the typical value was 500 ppm although this did range from <100 ppm to a few thousand ppm (Rohl and Needham, 1998; Northover et al., 2001). The first step undertaken was to calculate the percent input of lead from the copper component ($\%\mathrm{Pb}_{\mathrm{Cu}}$):

$$\%\mathrm{Pb}_{\mathrm{Cu}} = \%\mathrm{Cu} + \left(\mathrm{ppmPb}_{\mathrm{Cu}} / \left(\mathrm{ppmPb}_{\mathrm{Cu}} + \mathrm{ppmPb}_{\mathrm{Au}}\right) \bullet 100\right)/2 \qquad 6.1$$

The 2σ error for $\%\mathrm{Pb}_{\mathrm{Cu}}$ was also calculated:

$$2\mathrm{error} = \left(\left(\%\mathrm{Cu} + \%\mathrm{Cu}_{2\sigma\sigma\mathrm{erro}}\right) + \left(\mathrm{ppmPb}_{\mathrm{Cu}} / \left(\mathrm{ppmPb}_{\mathrm{Cu}} + \mathrm{ppmPb}_{\mathrm{Au}}\right) \bullet 100\right)/2\right) - \%\mathrm{Pb}_{\mathrm{Cu}} \qquad 6.2$$

where $\%\mathrm{Cu}_{2\sigma\mathrm{error}}$ is the analytical error on the copper concentration analysis. To calculate the isotopic ratio of the gold (r_{Au}), the function $f\mathrm{Cu}$ was employed. This is a representation of the lead input from the copper component and allows subsequent calculations to avoid the use of percents:

$$f\mathrm{Cu} = \%\mathrm{Pb}_{\mathrm{Cu}}/100 \qquad 6.3$$

The isotopic ratio of the gold component could then be calculated:

$$r_{Au} = r_{AuCu} - \left(r_{Cu} \bullet f\mathrm{Cu}\right) \bullet \left(1 - f\mathrm{Cu}\right)^{-1} \qquad 6.4$$

A 2σ error was also calculated for the corrected ratio:

$$\left(2\sigma_{\mathrm{rAu}}\right)^2 = \left(1/\left(1 - f\mathrm{Cu}\right) \bullet 2\sigma_{\mathrm{rAuCu}}\right)^2 + \left(f\mathrm{Cu}/\left(1 - f\mathrm{Cu}\right) \bullet 2\mathrm{s.d.}_{\mathrm{rCu}}\right)^2 + \left(\left(\mathrm{r}_{\mathrm{AuCu}} - \mathrm{r}_{\mathrm{Cu}}\right)/\left(1 - f\mathrm{Cu}\right)^2 \bullet 2\sigma_{f\mathrm{Cu}}\right)^2 \qquad 6.5$$

Error propagation was required so that all the key sources of uncertainty would be accounted for: the analytical error on the original isotopic analysis of the alloyed artefact sample $[1/(1-f\mathrm{Cu})*2\sigma_{\mathrm{rAuCu}}]^2$, the variance of the copper deposit's isotopic signature $[f\mathrm{Cu}/(1-f\mathrm{Cu})*2\mathrm{s.d.}_{\mathrm{rCu}}]^2$, and the error on the percent lead input originating from the copper component $[(\mathrm{r}_{\mathrm{AuCu}}-\mathrm{r}_{\mathrm{Cu}})/(1-f\mathrm{Cu})^2*2\sigma_{f\mathrm{Cu}}]^2$. All errors are at 2σ confidence. The typical lead concentrations of gold and copper are a further source of error but were not propagated into this calculation; variation was so great that it would result in errors too large to be of practical use. Due to the typical copper concentrations of the artefacts and the typical lead concentrations of gold and copper respectively, the input of lead from each source is generally c.50%. This does not change significantly if the lead concentrations of the gold or copper vary within the expected range. For example, an isotopic deviation of <3400 ppm on all ratios was calculated when the $ppmPb_{Cu}$ was varied from 100 ppm to 1000 ppm for the four EBA artefacts under consideration. It is therefore believed that the errors present are a fair representation of the uncertainty in these calculations, with the principle source of error originating from the isotopic variation of the copper source. As the calculation utilises the mean isotopic signature of these copper sources, and some degree of isotopic homogenisation is likely during the manufacturing process, the errors are in fact considered over representations of uncertainty. Lead isotope data for all the previously mentioned copper mines exist, therefore all could be considered as potential sources of copper when relevant (Appendix C1).

Ross Island was proposed as the most realistic copper source for the lunulae (copper mineralisation lead isotope data from Rohl, 1995; Northover et al., 2001; Kinnaird et al., 2002). The calculated signatures of their gold components are consistent with the non-alloyed lunulae data field (Figure 6.16), therefore the gold used to manufacture these two artefacts probably originated from the same source or sources as for the non-alloyed examples. It is also interesting to note that they are not consistent with the potentially mixed artefact cluster, suggesting a recycled gold origin is unlikely.

Ross Island is also a potential source for the copper component of the pin and plaque, and the corrected lead isotope signature of the gold are again consistent with the already defined Chalcolithic and EBA isotopic field (Figure 6.16). However a number of other potential copper sources existed and need to be considered. Assumed copper sources of Parys Mountain (Fletcher et al., 1993), Alderley Edge (Gale, 1990; Rohl and Needham, 1998) and Cwmystwyth (Rohl and Needham, 1998) also produced isotopic signatures for the gold that are consistent with the EBA artefact isotopic field (Figure 6.16). They are therefore considered potential sources of the copper component, and importantly the gold used to manufacture these artefacts would have come from the same source or sources as other EBA Irish gold. If any of these copper deposits were responsible for the alloyed copper, then knowing which of these mines was responsible is somewhat irrelevant. In all scenarios the calculated signature of the unalloyed gold is consistent with the non-alloyed Chalcolithic and EBA artefact field, therefore the gold originated from the same metal pool as was responsible for the non-alloyed artefacts.

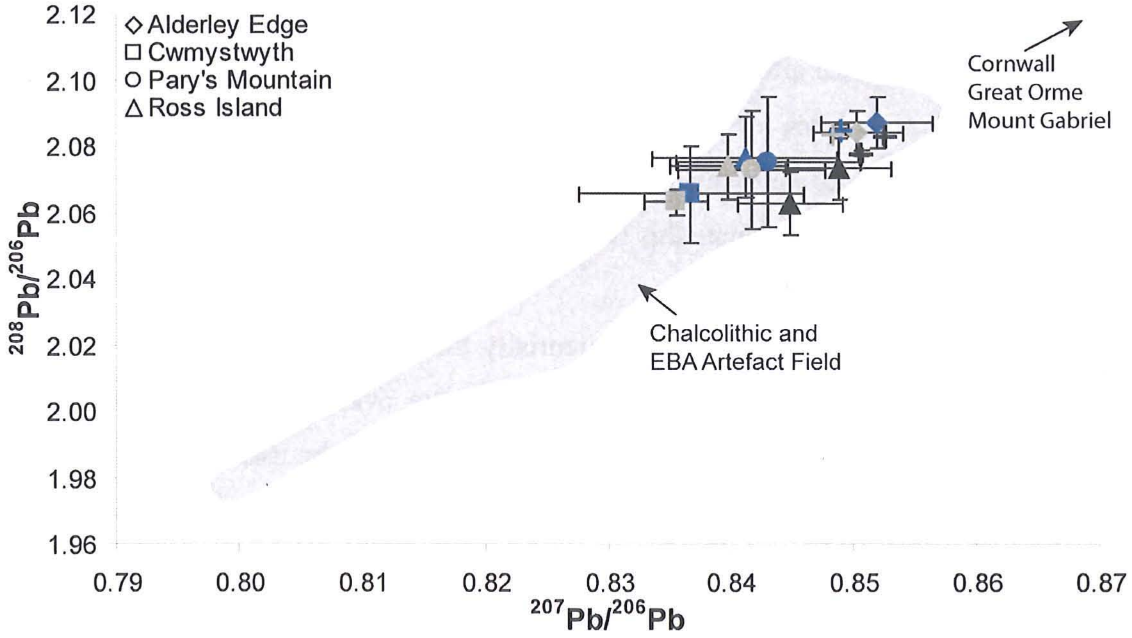


Figure 6.16: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of corrected ratios for the gold components of copper alloyed EBA artefacts based on an Alderley Edge (diamonds), Cwmystwyth (squares), Parys Mountain (circles) and Ross Island (triangles) copper source when relevant. Colours of filled symbols represent artefact type as depicted in previous graphs; black for lunulae, blue for the pin, and grey for the trapezoidal plaque. Uncorrected ratios represented by colour co-ordinated plus symbols. The Chalcolithic and EBA artefact field is represent by the grey domain, whilst the arrow labelled as Cornwall, Great Orme and Mount Gabriel indicates the location off to the top right of the graph for the corrected ratios if these deposits were the source of copper.

The copper deposits of Great Orme (Rohl and Needham, 1998), Mount Gabriel (Rohl, 1995; Kinnaird et al., 2002) and Cornwall (Rohl and Needham, 1998) are however problematic; the corrected isotopic signatures of the gold have uncertainties too large to be of use (Appendix C1). This is due to the heterogeneous lead isotope signature of these deposits. If the errors resulting from isotopic heterogeneity are discounted and the mean signature of the copper is presumed to reflect the true isotopic signature of the alloyed copper, then the radiogenic nature of the copper deposits results in less radiogenic gold signatures outside the Chalcolithic and EBA artefact field. This might suggest the exploitation of a different gold source. However regarding Mt Gabriel and

Great Orme, the calculated signatures are too less radiogenic for all Irish (and European) sources considered in this study. It is therefore perhaps unlikely that these were the sources of the alloyed copper. This of course can not be proven, and highlights the difficulties encountered when attempting to characterise the isotopic signature of alloyed artefacts. Rohl and Needham (1998) demonstrated the isotopic heterogeneity of EBA copper and bronze artefacts from any one EBA metalworking period, thus using average isotopic signatures for heterogeneous copper deposits in the above calculations may not be appropriate. Alloying is problematic for lead isotope studies, and further work may be required to eliminate this issue.

Evidence for possible mixing of gold, potentially through recycling, was presented in Section 6.5.1. A cluster of artefacts representing the average isotopic signature of Chalcolithic and EBA Irish goldwork was identified, and can be used to investigate the source of the copper components within these four alloyed artefacts. The equations detailed above (6.1 to 6.5) can be adapted by swapping all references to Cu with Au and vice versa thus allowing the calculation of the artefacts copper component, albeit based on the assumption that the gold component was isotopically consistent with this mixed gold signature. Regarding the lunulae, the calculated copper components (Figure 6.17, Appendix C1) are not consistent with any of the considered copper deposits. This suggests that they were not manufactured using gold with the signature of mixed composition, or that the copper originated from an unknown copper deposit. The former is considered more likely, and thus supports the outcome of the copper corrections applied above which calculated a gold component isotopically less radiogenic than the mixed artefact cluster.

Regarding the plaque and pin, although the calculated copper components are consistent with one end of the Ross Island copper field, they are most compatible with copper from the Cwmystwyth mine (Figure 6.17, Appendix C1). They are not consistent with any other of the considered copper deposits. The isotopic signature of the pin and plaque are therefore consistent with a) a gold component with an isotopic signature of mixed (recycled?) origin and b) copper from the Cwmystwyth copper mine. This is compatible with the later age of these two artefacts and the British associations highlighted by the typology of the plaque. Equally, the plaque and the pin could be produced from gold that is not of mixed origin or Cwmystwyth copper.

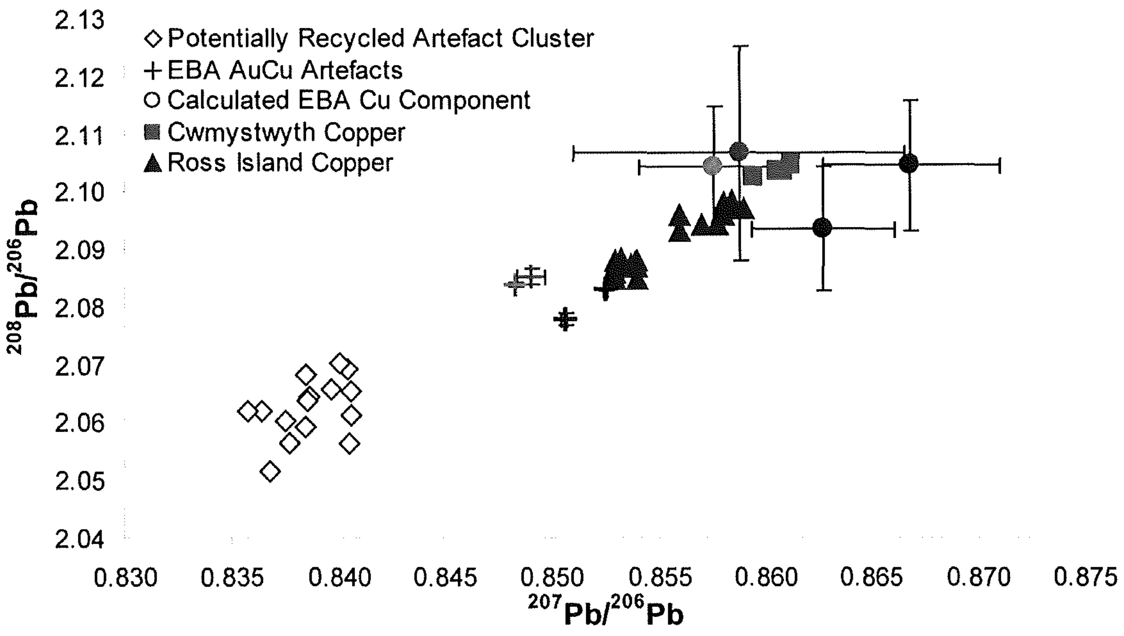


Figure 6.17: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of corrected ratios for the copper components of copper alloyed EBA artefacts assuming a gold component of mixed composition (open black diamonds). Corrected artefact ratios depicted by filled circles, uncorrected ratios depicted by plus symbols, with colours following Figure 6.6. Cwmystwyth and Ross Island copper deposits depicted by filled green squares and filled red triangles respectively.

To summarise, the two alloyed lunulae were manufactured from gold with an isotopic signature already represented in the unalloyed artefact field. It is less clear if this is true for the pin and trapezoidal plaque, however it is considered likely due to the large Chalcolithic and EBA isotopic field and the fact that the majority of the calculations place the corrected signatures within this field. To avoid confusion, all subsequent graphs will plot the uncorrected ratios for these artefacts unless otherwise stated.

6.6 The source of Chalcolithic and Early Bronze Age gold

6.6.1 Introduction

Despite evidence for possible mixing, c.65% of the artefacts are not consistent with a mixed origin and therefore may allow the identification of Chalcolithic and EBA gold sources. Before discussing possible source deposits, two questions will be explored. Firstly, the majority of the natural gold samples analysed in this study were collected from alluvial deposits. It is therefore of interest to know if the lead isotope signatures of alluvial gold grains can also characterise associated bedrock mineralisation or if modification of the isotopic ratios can occur in the alluvial/fluvial environments. Secondly, it is worth exploring how many principle ore sources were responsible for the artefact metal pool. The variability of the artefact compositions may suggest a number of key gold sources were exploited, however variable ore fields do exist thus the exploitation of one primary ore source is possible. It should be reiterated here that gold deposits within the same isotopic ore field can have indistinguishable lead isotope signatures (see Chapter 5), therefore a single gold source defined by lead isotope analysis represents gold originating from a single isotopic ore field.

Once these two questions have been explored, a discussion on the source of Chalcolithic and EBA Irish gold can proceed. This will concentrate on the principle source(s) of gold, and three hypotheses will be evaluated: the exploitation of principle gold sources located within Ireland and identified in this study through lead isotope analysis; the exploitation of principle gold sources located within Ireland and not analysed in this study; and the exploitation of principle gold sources located outside of Ireland. A brief consideration regarding the input of gold from minor sources will also be made.

6.6.2 The relationship between bedrock and alluvial gold

Gold grains liberated from bedrock mineralisation into alluvial systems can undergo chemical changes (Chapman et al., 2006) and therefore a disparity in their elemental composition can arise. The majority of the natural gold samples collected for analysis in this study were of alluvial origin, therefore if these samples are also to be used as a guide to the isotopic signature of local vein gold, it is important to check that there is no significant disparity between the two sample types. Figure 6.18 plots the isotopic composition of alluvial and vein gold from three locations: Cregganbaun, Croagh Patrick and Curraghinalt. Both sample types are consistent with each other, thus indicating there is no significant change in the isotopic signature of gold grains when exposed to fluvial systems.

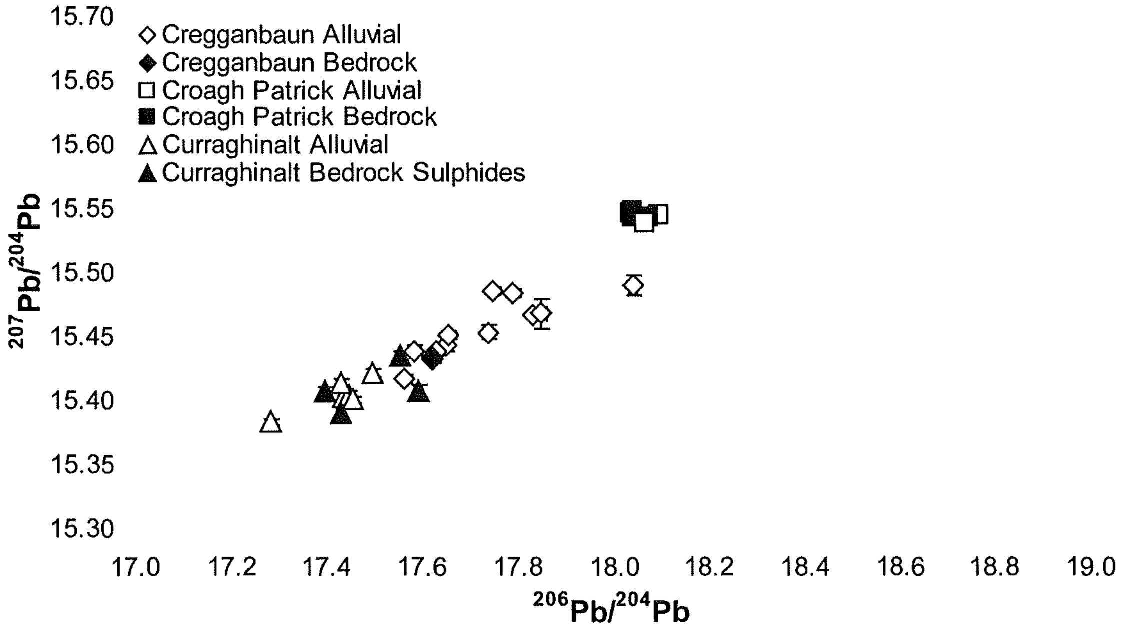


Figure 6.18: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of bedrock and alluvial gold from the same locations. All samples are gold except for those from Curraghinalt vein material which are sulphides.

6.6.3 The number of principle gold sources

A number of artefacts with atypical major element compositions were highlighted in Section 6.2.2, and when discussing the theory of a Mourne Mountains source, Warner et al. (2009) suggested that those with atypical silver concentrations may represent an input from non-Mournes sources. If multiple deposits were exploited then the isotopic signature of the Chalcolithic and EBA artefacts would represent a mix of these sources, and consequently this scenario needs to be explored before provenance can be discussed.

It is therefore of interest to see if the artefacts with atypical elemental compositions also have atypical lead isotope signatures (in this study, atypical silver defined as outside the range 9.5% to 14.5%). Unfortunately both the lunula with very low (3.79%; W2 Killarney) and the lunula with high silver (17.06%; R2612) both failed lead isotope analysis. Five lunulae have silver concentrations of 7.9% to 8.9% (1893:04 Athlone, 1919:04 West Coast Co. Mayo, R625, 1998:74 Ballinagroun, R1756 Banemore) whilst two discs (SA1913:128 Ballyvourney and W266), the pin (SA1913:127 Ballyvourney) and the trapezoidal plaque (SA1913:131 Knockane) have silver concentrations of 15.5% to 16.5% just outside the primary EBA silver concentration range. Figure 6.19 demonstrates that there is no correlation between silver concentration and isotopic signature, and the artefacts with atypical silver concentrations are not distinguishable by lead isotope analysis. This favours either compositionally heterogeneous gold sources within one principle isotopic ore field or sources from multiple ore fields characterised by the same isotopic signature. The two artefacts with more extreme silver concentrations may still have been manufactured from gold with a discrete isotopic signature.

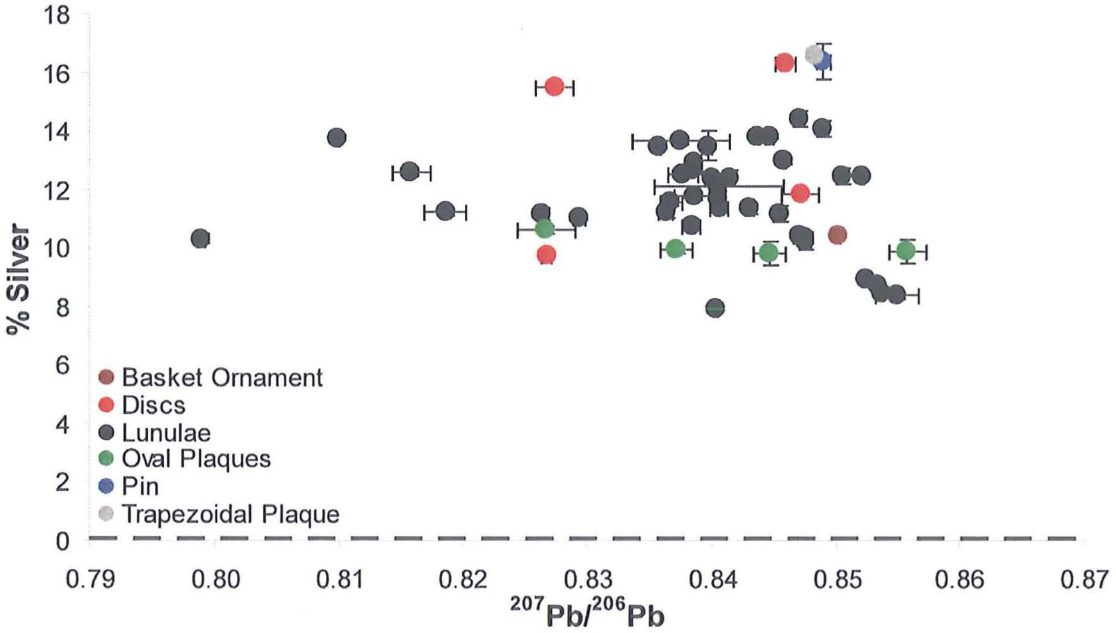


Figure 6.19: % Silver versus ^{207}Pb/^{206}Pb plot of Chalcolithic and EBA gold artefacts.

It has also been noted that some lunulae are characterised by high tin concentrations (Warner, 2004). A discontinuity at 0.08% tin was highlighted, however it was concluded that this was unlikely to indicate the presence of two distinct compositional groups. Warner et al. (2009) discussed a correlation between the silver and tin concentrations; artefacts with atypical silver (high or low) tended to demonstrate low or absent tin concentrations. The distinction in the tin is also visible in the data collected during this study, and again the break falls at c.0.08% tin (with 12 of the 52 Chalcolithic and EBA samples falling above this value). However although the high tin artefacts do have a higher average silver concentration (13.45% average for high tin artefacts compared to 11.27% average for low tin), this group does not include those artefacts with the most atypical silver concentrations (i.e. those discussed in the previous paragraph with >14.5% or <9.5% silver). It is therefore unlikely that there is a relationship between the atypical tin and silver concentrations and in agreement with Warner (2004) there is no clear evidence to suggest that the tin values represent more than one compositional group. This conclusion is supported by the isotopic data (Figure

6.20). There is no correlation between the tin concentration and lead isotope data; those artefacts with high tin are indistinguishable from those with low tin. This again favours primary exploitation of sources with the same isotopic signature.

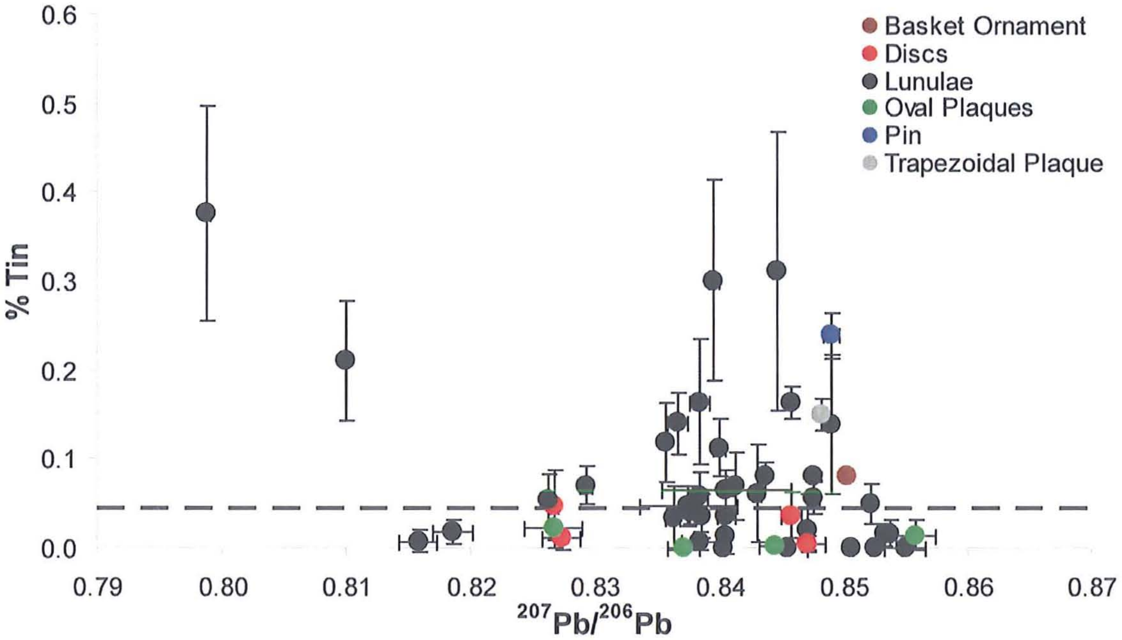


Figure 6.20: % Silver versus $^{207}Pb/^{206}Pb$ plot of Chalcolithic and EBA gold artefacts.

As discussed in Section 6.5.2, the four artefacts with copper >1% are best explained by deliberate alloying. Interestingly the lead isotope signatures of these four artefacts are indistinguishable from the remaining Chalcolithic and EBA artefacts. It has been demonstrated that if the copper components originated from Ross Island or a number of British mines, then the lead isotope signature of the gold components will not be significantly different from those of the gold-copper alloys. Therefore the gold used to manufacture the alloyed artefacts is likely to have originated from the same source(s) as the gold used to manufacture those that are unalloyed. There is no correlation between copper concentration and isotopic signature within the remaining artefacts (Figure 6.21).

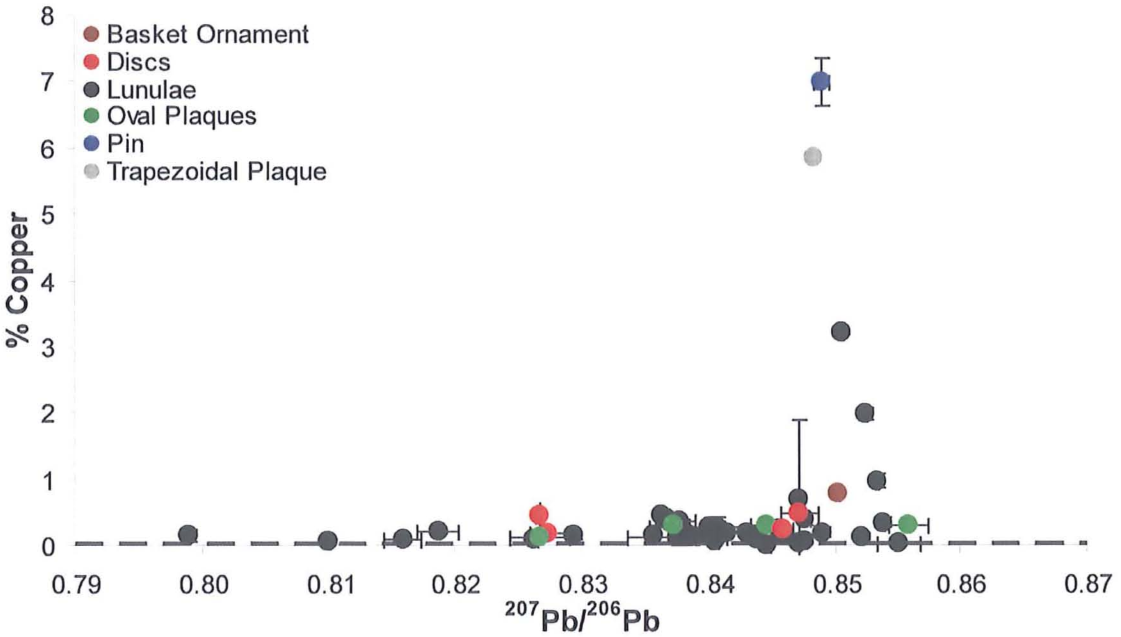


Figure 6.21: % Copper versus $^{207}Pb/^{206}Pb$ plot of Chalcolithic and EBA gold artefacts.

In summary, although the isotopic signature of the Chalcolithic and EBA artefacts demonstrates heterogeneity there is a lack of correlation with the variation of silver, copper and tin. The absence of distinct groups identifiable by both elemental and isotopic signatures favours compositionally heterogeneous gold sources within one principle isotopic ore field or sources from multiple ore fields characterised by the same isotopic signature. As with the case of all provenance studies, small inputs from discrete sources can not be ruled out. These will be discussed when relevant for individual artefacts.

6.6.4 Hypothesis 1: an Irish source of Chalcolithic and EBA gold identified through lead isotope analysis

The working hypothesis throughout this investigation was that the Irish artefacts were manufactured from gold originating from an Irish source (Chapter 2). Consequently, an Irish source of Chalcolithic and EBA gold identified through lead isotope analysis will first be considered. All artefacts have recorded $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ compositions, therefore the artefact data is initially plotted with the Irish gold mineralisation data fields using these ratios (Figure 6.22). It is clear that the majority of the Chalcolithic and EBA artefacts are consistent with an Irish source (grey domain Figure 6.22). However those with atypically radiogenic signatures first highlighted in section 6.2.3 are inconsistent with an Irish source (red domain Figure 6.22) due to low $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. Nine artefacts fall into this group: six lunulae (1986:15

Ross, P817, SA1928:715 Rossmore, W7, W10 and W13), two discs (P949 and W266) and an oval plaque (W75 Belville). Lunula W8/R135 (Dunfierth) is also inconsistent with an Irish source due to high $^{208}Pb/^{206}Pb$. Consequently there appears to be some degree of non-Irish gold in circulation during this period.

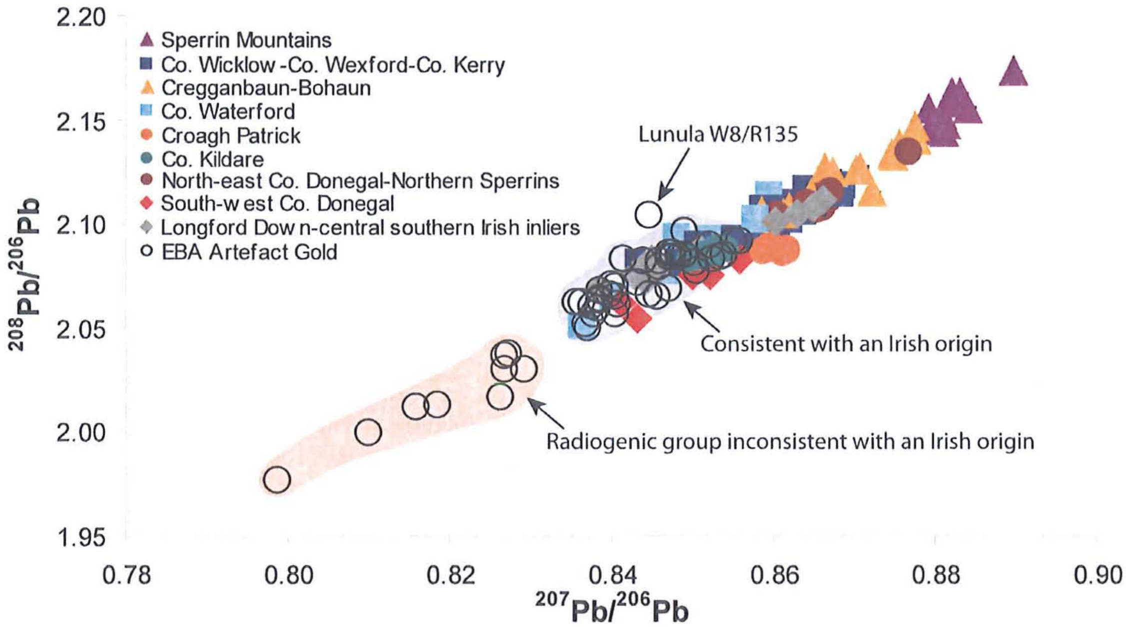


Figure 6.22: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of Chalcolithic and EBA Irish gold artefacts and Irish gold mineralisation.

The group of artefacts that are consistent with an Irish source overlie a number of different Irish ore fields based on their $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ signatures, thereby highlighting potential source regions: Co. Wicklow-Co. Wexford-Co. Kerry, Co. Waterford, Co. Kildare, south-west Donegal, and the Longford Down and central southern Irish inliers. There is no evidence for a significant gold input from the following gold bearing regions: the Sperrin Mountains (see also Standish et al., 2013), Cregganbaun-Bohaun, Croagh Patrick, or north-east Co. Donegal-northern Sperrins.

Figure 6.23 plots the $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ Chalcolithic and EBA artefacts and Irish ore deposit data. In accordance with Figure 6.22 the majority of the artefacts are consistent with an Irish source (grey domain Figure 6.23). The more radiogenic artefact group is now represented by six artefacts (red domain Figure 6.23) because a total of only 21 samples were analysed by solution MC-ICP-MS techniques for the collection of ^{204}Pb data. These artefacts are again inconsistent with an Irish source. Lunula R1756

(Banemore) is also now distinguishable from the Irish ore fields based on high $^{207}Pb/^{204}Pb$ again highlighting some degree of input from a non-Irish source.

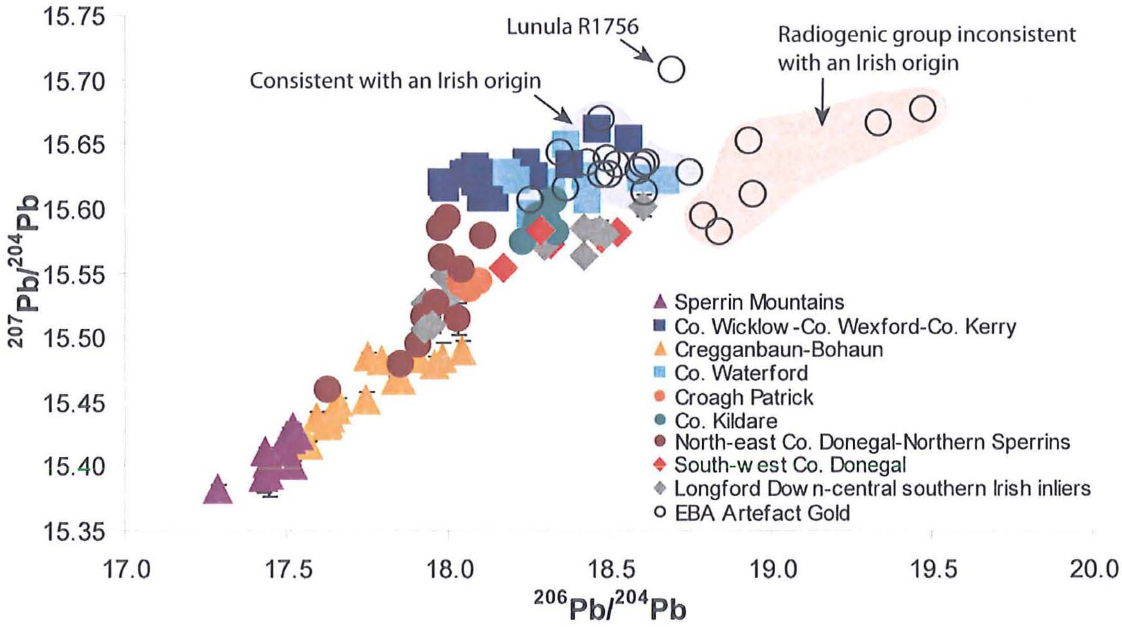


Figure 6.23: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Chalcolithic and EBA Irish gold artefacts and Irish gold mineralisation.

As detailed in Chapter 5, separation of the different gold bearing regions of Ireland is greatest when the isotope ^{204}Pb is employed. This allows the exclusion of further potential source regions; it is apparent from Figure 6.23 that there is no evidence for a significant degree of gold input from the south-west Donegal, the Longford Down-central southern Irish inliers or Co. Kildare ore fields. Those artefacts consistent with an Irish source (grey domain Figure 6.23) are only consistent with the Co. Wicklow-Co Wexford-Co. Kerry and Co. Waterford ore fields. It is important to note that because the radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are daughter isotopes of separate radioactive decay chains, artefacts and ore must be consistent on all ratios if an association is to be proposed.

Figure 6.24 plots the $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ Chalcolithic and EBA artefacts and Irish ore deposit data. This plot supports the patterns highlighted in Figure 6.22 and Figure 6.23. The majority of the artefacts are consistent with an Irish source (grey domain Figure 6.24), with the only ores fields to match on all isotopic ratios being the Co. Wicklow-Co Wexford-Co. Kerry and Co. Waterford fields. The group of radiogenic artefacts are again inconsistent with an Irish source (red domain Figure 6.24), along with lunulae W8/R135 (Dunfierth) and R1756 (Banemore).

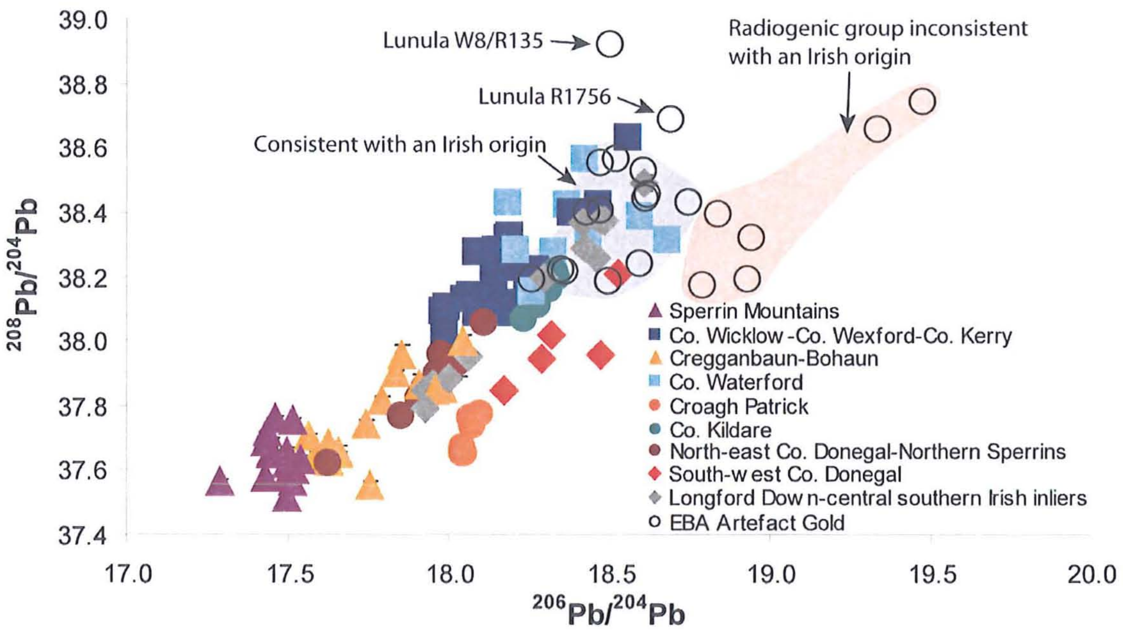


Figure 6.24: ^{208}Pb/^{204}Pb versus 206Pb/^{204}Pb plot of Chalcolithic and EBA Irish gold artefacts and Irish gold ore isotopic fields.

A group of Chalcolithic and EBA artefacts isotopically consistent with an Irish origin on all ratios has been identified (grey domain Figure 6.22, Figure 6.23, Figure 6.24). The gold deposits of Co. Wicklow-Co. Wexford-Co. Kerry and Co. Waterford have been highlighted as the most likely source region of this group of artefacts. These deposits are both located on Ireland's south-east terrane (SET), and their lead composition is dominated by SET derived lead as defined in Chapter 5. It is possible to distinguish these two fields from each other; the Co. Waterford gold deposits typically have higher ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb (Figure 6.24). This disparity relates to differences in the primary age of mineralisation; whereas the primary mineralisation of the Co. Wicklow-Co. Wexford-Co. Kerry gold deposits is consistent with an Early Caledonian source age, the primary mineralisation of the Co. Waterford deposits is consistent with a Late Caledonian source age. Consequently although they share similar lead sources, the Co. Waterford deposits incorporated lead that was on average compositionally more evolved. Some gold samples from Co. Wicklow do demonstrate more evolved isotopic signatures (which may relate to uranium and thorium rich inclusions, see Section 5.5.3), however the principle isotopic signatures of these two groups are clearly distinguishable. The artefacts are consistent with the more evolved isotopic signatures of Co. Waterford (Figure 6.23, Figure 6.24), therefore based on lead isotope analysis the gold deposits of Co. Waterford are the most likely Irish source of Chalcolithic and EBA gold.

It should also be noted that these two ore regions have the potential to account for the more radiogenic artefacts so far described as being inconsistent with Irish deposits. They have both been interpreted as having a secondary upper crustal association, and the incorporation of more radiogenic lead such as that linked to the S-type Leinster granite is possible (see Section 5.5.3). This is demonstrated by the south-west Irish Variscan copper mineralisation (see Section 3.5.2.4) which has a similar such association, and displays these more radiogenic signatures. However at present there is no data to prove this, therefore the radiogenic artefact group remains inconsistent with an Irish source.

Warner et al. (2009, 2010a, 2010b) proposed that the Mourne Mountains of Co. Down were the principle source of EBA gold. Alluvial gold from this region provided the best compositional match to the silver and copper concentrations of the artefact alloy, whilst the presence of cassiterite represented a credible explanation for the tin content present in these artefacts (which is typically too high for natural gold alloys). However the lead isotope signature of the Mourne Mountains gold is not consistent with the Chalcolithic and EBA artefacts (Figure 6.23 where the Mourne Mountain samples form part of the Longford Down inlier group). The Longford Down inlier group plots as a trend in Figure 6.22, Figure 6.23 and Figure 6.24 (grey diamonds), and this signature relates to a mixed source of lead from both the north-west terrane (NWT) and SET reservoirs, plus a further input of radiogenic upper crustal lead. The artefacts are not consistent with any source containing a significant input of NWT lead, therefore it is unlikely that the Mourne Mountains were the principle source of Chalcolithic and EBA gold.

Due to the compositional correlation with the artefacts, it is worth considering if a contribution of Mourne Mountains gold into the Chalcolithic and EBA metal pool can be identified. The more radiogenic Mourne Mountains gold samples plot proximal to the artefacts, therefore a small contribution from these grains is possible. When the elemental composition of Mourne Mountains gold is considered it is apparent that there are multiple populations of gold present (Moles et al., in press), and not all are consistent with the Chalcolithic and EBA gold artefacts. In fact the vast majority of

Mourne Mountains gold samples have copper <0.2% whilst the artefacts typically have copper 0.1% to 0.5%. As discussed in Chapter 5 (section 5.5.5.3), there is a potential relationship between the more radiogenic Mourne Mountain gold and the high copper gold (that are consistent with the artefacts). Only the Ballincurry River alluvial deposits are dominated by the high copper populations (see figure 8 of Moles et al., in press) and this is also a location where the more radiogenic lead isotope gold was recovered. However if this region was exploited even to a small degree then exploitation must have been selective, with only streams dominated by the more radiogenic/copper rich grains or only the more radiogenic/copper rich grains themselves exploited. Based on a small population, the copper rich grains are typically larger in size (Chapman pers. comm.) therefore selectivity is technically possible if recovery techniques demonstrated a size bias. However this is considered unlikely and it is doubtful that the gold inconsistent with the artefact composition would not have been exploited once gold bearing deposits were discovered in the region.

Lead isotope analysis has ruled out the Mourne Mountains as the principle source of Chalcolithic and EBA gold, therefore the elemental composition of Co. Waterford gold must also be considered. The artefacts ranged from 3.79% to 17.06% silver (with most falling between 9.5% and 14.5%), <lod (limit of detection) to 0.79% copper with the majority <0.5% (not including the potentially alloyed artefacts), and <lod to 0.38% tin. The two alluvial deposits used to characterise Co. Waterford gold, Ballybrack and Whelanbridge, were both studied by Chapman et al. (2006). Two sampling locations at Ballybrack produced mean silver compositions of 6% and 5.6% silver (medians of 5.1% and 4.9% respectively) and mean copper concentrations of 0.12% and 0.06%. Two sampling locations at Whelanbridge produced mean silver compositions of 5% and 4.9% silver (medians of 5% and 4.3% respectively) and mean copper concentrations of 0.12% and 0.06%. These are not consistent with the composition of the Chalcolithic and EBA artefact gold, with both silver and copper means falling too low. Additionally, no cassiterite was recorded in the heavy mineral fraction during fieldwork. Conversely, 80% of grains analysed from the Ballincurry River, Mourne Mountains, demonstrated copper concentrations of >0.1%, and silver ranged from c.8 to 15% (Moles et al., in press), therefore this natural gold alloy remains the best Irish match to Chalcolithic and EBA gold based on elemental analysis.

Metallurgical processes can change the composition of metals from ore to artefact. If Co. Waterford was the principle source region of Chalcolithic and EBA gold, then this requires a c.100% increase in silver relative to gold. This is considerably unlikely. The stability of silver is high; Chapman et al. (2006) demonstrated that the silver concentrations of gold melts are typically close to the mean silver content of a population of grains from the same sites. Consequently the silver concentration of the artefacts should reflect the mean silver content of the source, and it is unclear if any metallurgical processes could validate the Co. Waterford source hypothesis. Deliberate addition of silver is one such theory, however there is a lack of evidence for widespread silver exploitation during the Irish and British Chalcolithic and EBA. As a result, the assumption that silver contents reflect the source alloy is reasonable.

Chapman et al. (2006) highlighted a trend of increasing silver content in Irish lode gold from south to north, therefore making a south-eastern source appear unlikely. However there were exceptions to this trend; the Goldmines East River of Co. Wicklow demonstrated a mean silver concentration of 11.4% and mean copper concentration of 0.11%, whilst the Coolbawn River of Co. Wicklow demonstrated a mean silver concentration of 10.1% and mean copper concentration of 0.01%. The average Chalcolithic and EBA mean silver concentration from this study is 11.78% whilst the mean copper concentration is 0.23% (excluding the four potentially alloyed artefacts). Both sites therefore demonstrate appropriate silver concentrations whilst the Goldmines East River also has a mean copper concentration similar to that of the artefacts. Additionally, cassiterite present in the region (Jackson, 1979) could account for the high tin signature. There is clear potential for a Co. Wicklow source based on compositional analysis. Figure 6.25 demonstrates the compositional pattern of Irish gold discussed. The majority of the mean compositions of Irish gold deposits (filled green diamonds Figure 6.25) are not consistent with the Chalcolithic and EBA artefacts (open black circles). Regionally the artefacts are most similar to the mean compositions of gold from the Longford Down inlier which includes the Mourne Mountains sources (filled blue diamonds), however the Goldmines River East (filled red star) also proves to be a compositional match.

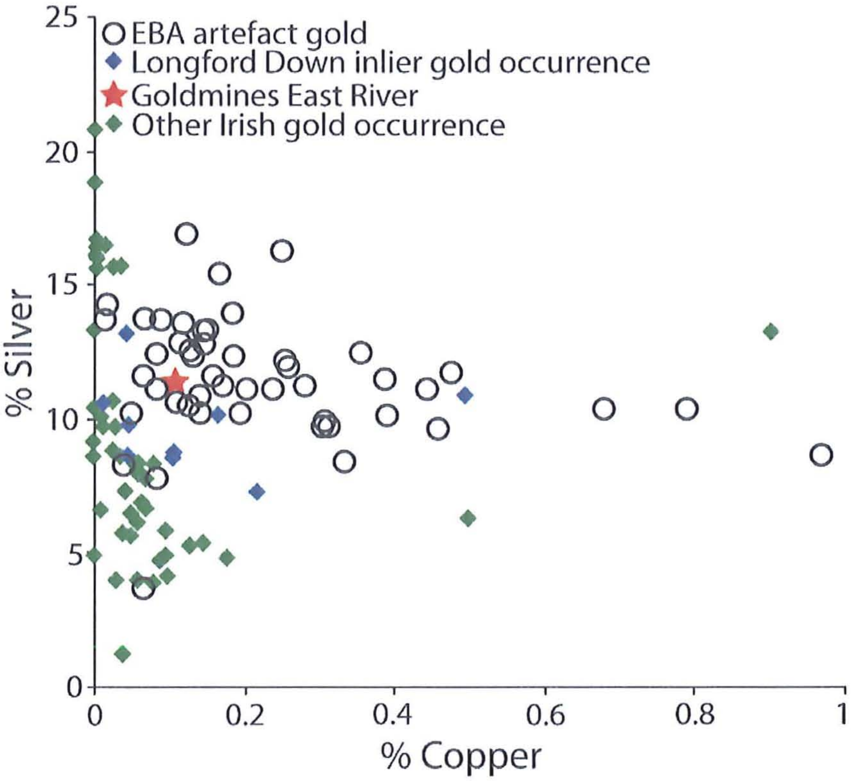


Figure 6.25: % silver versus % copper concentration of Chalcolithic and EBA gold artefacts and mean compositions for Irish gold deposits. Irish gold deposit data from Warner et al. (2009), artefact data from this study.

It is however unlikely that the Co. Wicklow gold was the principle source during the Chalcolithic and EBA. Firstly, and as discussed previously, the lead isotope signatures of Co. Wicklow gold grains are not consistent with the artefact cluster (Figure 6.24). Grains from the Goldmines East River were analysed in this study, and all (n = 8) plot in the principle Co. Wicklow-Co. Wexford-Co. Kerry cluster with lower $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$. None of the analysed samples exhibit the more radiogenic signatures seen in some Co. Wicklow deposits. The Coolbawn River was not sampled for this study, therefore it is possible that gold from this location does exhibit the more radiogenic signatures. However when the more radiogenic signatures are present in Co. Wicklow gold deposits (for example the Ow River), the majority of samples still plot within the principle Co. Wicklow cluster that is inconsistent with the Chalcolithic and EBA artefacts. The more radiogenic samples tend to plot as outliers. Furthermore, the copper content of Coolbawn River gold is not consistent with the artefacts. It is therefore unlikely that any gold deposit in the Co. Wicklow region would be characterised by a mean lead isotope signature that is consistent with the artefact cluster unless a completely new style of mineralisation is present.

Secondly, the opinion of Chapman et al. (2006) can be reiterated. If the high silver/high copper gold deposits of Co. Wicklow were exploited, then the more abundant low silver/low copper gold deposits were never exploited. This is considered unlikely; the Goldmines West River was the focus of the Wicklow gold rush of the 18th-19th centuries AD therefore if alluvial gold exploitation was occurring in the region it is difficult to believe this source was not identified also. The mean silver concentration of this rich deposit is 8.4% whilst the mean copper concentration is 0.08% (Chapman et al., 2006), and is therefore inconsistent with the gold artefacts. Similarly, it is doubtful that a currently unidentified alluvial gold deposit located in Co. Wicklow and consistent with Chalcolithic and EBA artefacts on both compositional and lead isotopic grounds was exploited during this period whilst other rich deposits (such as the Goldmines River West) were left undiscovered.

There is clearly a disparity between the compositional and lead isotope approaches. Warner et al. (2009, 2010a, 2010b) highlight the Mourne Mountains as the most likely Irish source of EBA gold and rule out the gold of south-east Ireland, especially Co. Waterford, based on gold alloy compositions. Conversely lead isotope analysis has ruled out the Mourne Mountains in favour of Co. Waterford as the most likely Irish source of Chalcolithic and EBA gold. It can therefore be stated that no Irish gold deposit analysed as part of both provenance studies is consistent with the Chalcolithic and EBA artefacts based on combined major element and lead isotope analysis.

6.6.5 Hypothesis 2: an unanalysed Irish source of Chalcolithic and EBA gold

A common critique of provenance studies is that they do not characterise every potential gold source. This is certainly the case for this investigation, there are too many known gold occurrences in Ireland let alone Europe for this to be feasible (Figure 3.3) and it is possible that some occurrences are still undiscovered. However patterns within the composition of gold deposits can be used to predict the signatures of unanalysed deposits.

The lead isotope signature of gold reflects the composition and age of the lead source. Chapter 5 interpreted the natural gold in terms of deposit genesis, and characterisation of different gold bearing regions was possible primarily because they incorporated lead from different source reservoirs (SET and NWT) to varying degrees and at different stages of geological time (early Caledonian, late Caledonian, Variscan). If the Chalcolithic and EBA artefacts are interpreted in a geological sense within the model of Irish lead evolution presented in section 5.6, they would be interpreted as deriving predominantly from the SET lead reservoir during or after the Late Caledonian with a secondary upper crustal lead contribution (for example, S-type granite); Figure 6.26.

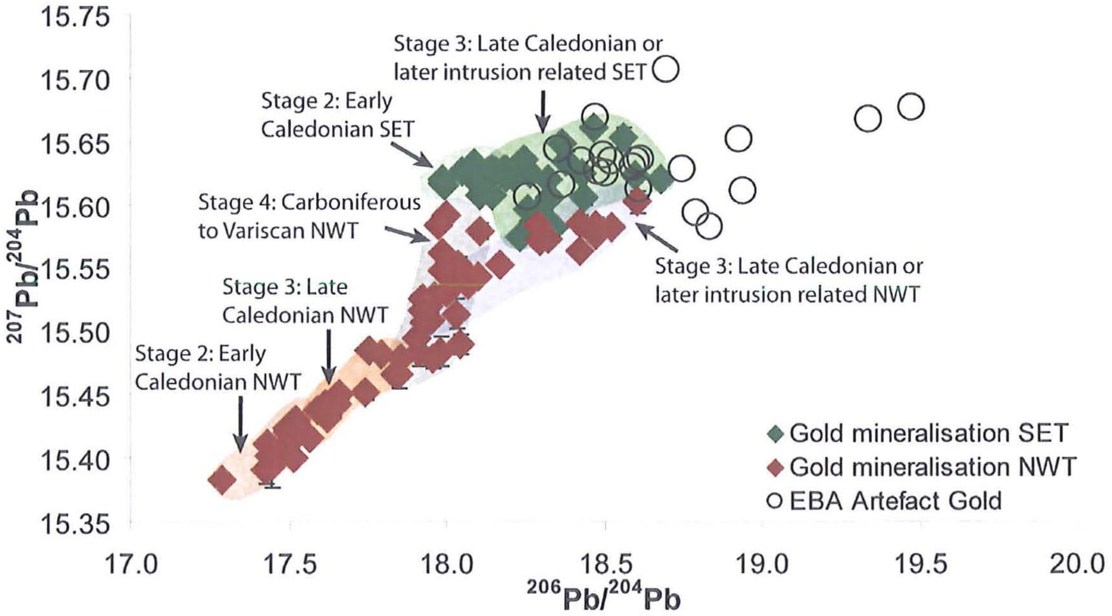


Figure 6.26: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Chalcolithic and EBA artefact gold within the model of Irish lead evolution.

This interpretation suggests it is possible to exclude Irish gold deposits of Early Caledonian age or that incorporate any significant NWT lead component, i.e. any deposit consistent with the following isotopic groups: the Sperrin Mountains, Cregganbaun-Bohaun, Croagh Patrick, north-east Co. Donegal-northern Sperrins, south-west Co. Donegal, Co. Kildare, and the Longford Down-central southern Irish inliers, Co. Wicklow-Co. Wexford-Co. Kerry. In contrast to the conclusions of Chapman et al. (2006), it appears that if Chalcolithic and EBA gold was derived from Irish sources then the sources must be located in the south of the country. Gold mineralisation hosted by the Leinster Massif in south-east Ireland is typically characterised by low silver concentrations and primary mineralisation occurred principally in the early Caledonian, therefore it is considered unlikely that undiscovered deposits consistent with the artefacts exist in this region (see discussion in previous section), especially following the amount of exploration work that has been carried over the last c.40 years. It is of course possible that gold mineralisation matching the signature of Chalcolithic and EBA artefacts both isotopically and compositionally does exist in southern Ireland, especially as widespread Variscan mineralisation is known to have been responsible for the vast copper deposits of south-west Ireland. Figure 6.27 plots the artefact gold against the Variscan copper mineralisation fields of south-west Ireland as introduced in Chapter 3. It is clear that the ORS hosted copper deposits are generally consistent with the artefact signatures. This supports an association between the artefact gold and SET Variscan mineralisation with an input of upper crustal lead; ORS hosted mineralisation has been linked to partial derivation from the S-type upper crustal Leinster granite.

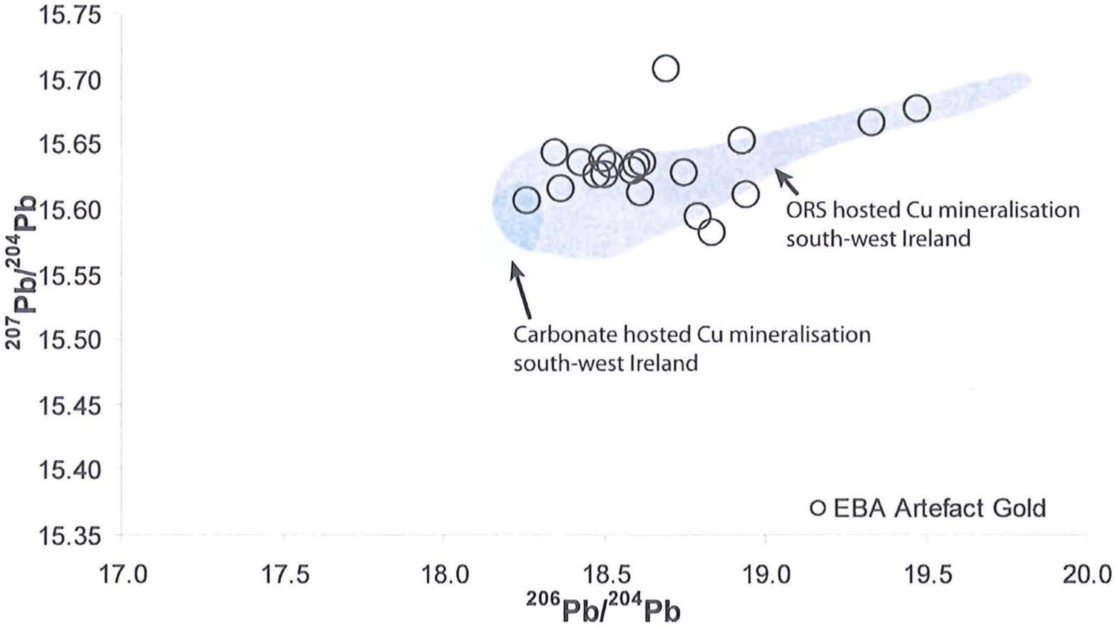


Figure 6.27: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Chalcolithic and EBA artefact gold and south-west Ireland copper mineralisation data fields.

If an unknown Irish gold deposit was exploited during the Chalcolithic and EBA, this south-western ore field is considered the best candidate. Importantly, mineralisation in this region has the potential to account for those more radiogenic artefact samples previously identified as being inconsistent with an Irish origin. Gold associated with south-west Irish copper mineralisation has been reported (McArdle et al., 1987; Stanley et al., 2000; Pracht and Sleeman, 2002), and McArdle et al. (1987) discuss the potential that the gold was leached from local palaeoplacers. This region is seen as a potential host for Witwatersrand type palaeoplacer deposits (Stanley et al., 2000), however a key requirement for this type of occurrence is a gold rich source area which has yet to be identified in the region (Stanley et al., 2000). Consequently the presence of this style of gold mineralisation remains unproven.

Many of the accounts for gold mineralisation in this area are historical mining reports of dubious accuracy (McArdle et al., 1987; Cowman and Reilly, 1988), whilst the modest grade of the gold mineralisation (for example Reilly, 1986) may suggest that these deposits were unlikely to have been able to account for the Chalcolithic and EBA goldworking traditions. Furthermore these gold occurrences are vein hosted and there are no known significant alluvial gold deposits in the region. As it is generally accepted that the high tin content of the artefact alloy is indicative of a cassiterite bearing alluvial source, this can be seen as further evidence against this hypothesis.

To summarise, no gold deposit analysed in this study is consistent with the Chalcolithic and EBA gold artefacts in both their lead isotope signature and major element composition. If an undiscovered or unanalysed Irish gold deposit was exploited, then lead isotope analysis suggests it will be of Late Caledonian or younger source age and that it predominantly incorporated lead from the SET reservoir with an input of a secondary upper crustal lead (intrusion related?). The south-west Irish Variscan ore field responsible for vast copper deposits is seen as the most likely candidate region, however based on the current evidence for Irish gold mineralisation, the presence of significant gold deposits able to support EBA goldworking industries in this area is considered unlikely.

6.6.6 Hypothesis 3: a non-Irish source of Chalcolithic and EBA gold?

6.6.6.1 European ore fields

Lead isotope analysis has highlighted a number of Chalcolithic and EBA artefacts that are inconsistent with the signatures of Irish gold deposits (red domain Figure 6.22, Figure 6.23, Figure 6.24). Whilst the majority of Chalcolithic and EBA artefacts are consistent with gold from Co. Waterford, these are not compatible with any Irish gold deposit when alloy composition is also considered. Accordingly there is now reasonable doubt that the principle gold source exploited for the manufacture of Irish Chalcolithic and EBA goldwork was located in Ireland.

The existence of non-Irish Chalcolithic and EBA gold sources has previously been hypothesised. Hartmann (1978) preferred a principle association with the gold deposits of Iberia, whilst Penhallurick (1986, 1992) argued for a Cornish origin based on the believed exploitation of gold bearing alluvial deposits during the Bronze Age and the significant tin content of Cornish gold. Additionally, Warner (2009) discussed the presence of atypical goldwork compositionally different from the principle artefact range linked to the Mourne Mountains. Chapter 2 discussed the typological origins of the artefacts in question. The distribution of the basket ornaments are centred in Britain and are considered an insular design, however the Benraw ornament provides a potential link to Iberian goldwork (Taylor, 1980) and consequently Iberian gold sources. The oval plaques have also been paralleled with Iberian goldwork although affiliations with the basket ornaments have also been postulated (Taylor, 1980), and the Ballyvourney pin is of similar form to a pin discovered in Portugal (Cahill, 2006). Gold discs are most prevalent in Ireland, yet both form and design can be paralleled with artefacts from northern Europe (Taylor, 1980; Eogan, 1994). The lunulae are generally considered to be of Irish manufacture again due to distribution, however small concentrations have also been found elsewhere including Cornwall and Brittany. Eogan (1994) highlighted possible links to artefacts from northern Europe, and proposed a continental origin whereby the provincial lunulae stimulated the development of Irish classical and unaccomplished types. The trapezoidal Knockane plaque has few parallels within Ireland, however stylistic links have been made with the Wessex linear goldwork (Cahill, 2006). Irish goldwork therefore has typological and stylistic links to a number of different areas of Europe. If these artefacts were manufactured from imported gold, the gold sources are likely to be located within these regions.

Lead isotope analysis has rarely been performed on natural gold prior to this study, therefore little published data exists. The lead isotope signatures of sulphides can act as a guide to the signatures of associated gold if formed in the same mineralisation event, therefore literature data was compared to the signature of the artefact gold in order to investigate the potential for a non-Irish source. The lead isotope composition of mineralisation in north-west (Arias et al., 1996; Neiva et al., 2008), south-west (Marcoux, 1998) and south-east (Arribas and Tosdal, 1994) Iberia is not consistent with the artefact isotopic field. This is also the case for mineralisation in both central France (Touray et al., 1989; Le Guen et al., 1992) and Brittany (Oh et al., 1989; Gloaguen et al., 2007). Figure 6.28 plots the EBA artefacts with sulphide mineralisation lead isotope data for Cornwall (Rohl and Needham, 1998), the Alps (Curti, 1987; Horner et al., 1997), the Pyrenees (Romer and Soler, 1995) and the Carpathians (Marcoux et al., 2002). The best differentiation between these fields is visible on the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot therefore only this graph is presented. Clearly some artefacts are consistent with each of these isotopic fields, however the vast majority of artefacts bear a striking resemblance to the Cornubian isotopic field.

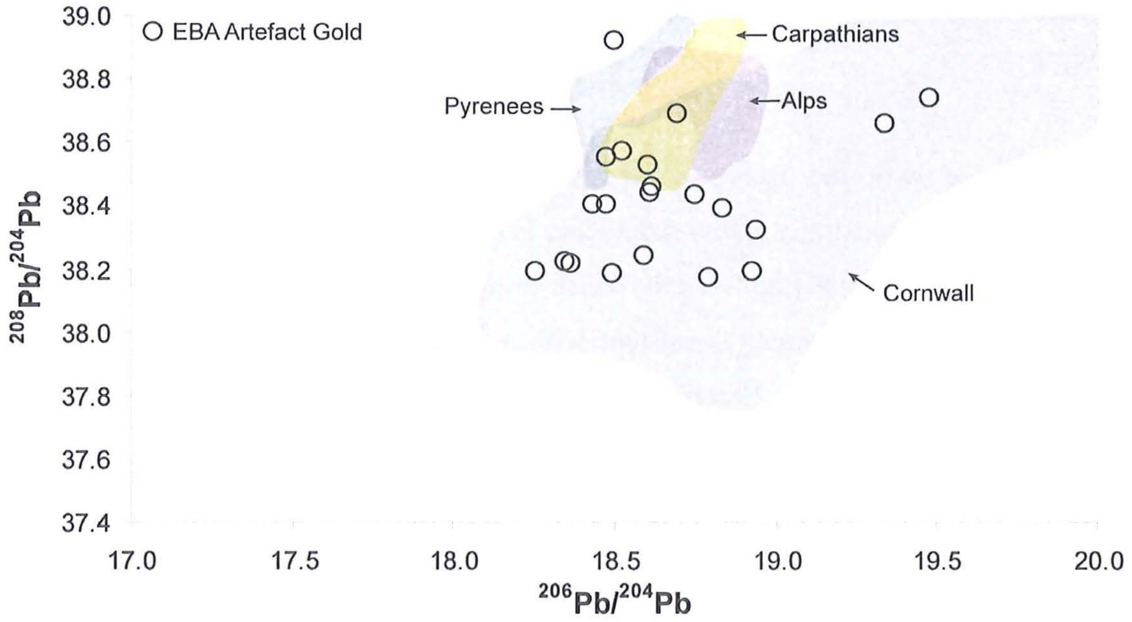


Figure 6.28: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of Chalcolithic and EBA gold artefacts and sulphide data from selected regions of Europe.

It should be noted that there are many more European mining districts that can be considered as potential sources of Chalcolithic and EBA gold, and ideally when comparing to the isotopic signature of the artefacts, data from samples of gold rather than sulphides would be used. Nevertheless the artefacts are consistent with the Cornish field, therefore a further investigation into the gold deposits of Britain is warranted.

6.6.6.2 Gold sources of Britain

Gold mineralisation is present throughout northern and western Britain (Colman and Cooper, 2000). Six alluvial deposits were sampled as a preliminary study into the lead isotopic composition of British gold (Appendix A2): Borland Glen, Perthshire, and Wanlock Water, Dumfries and Galloway (both Scotland); Afon Brynberian, Pembrokeshire (Wales); Carnon River and Crow Hill, Cornwall, and Challon's Comb, Devon (England). The samples from the two Cornish locations were donated for study by the Royal Cornwall Museum, Truro.

Figure 6.29 plots the British data along with the isotopic fields of Irish gold deposits as defined in Chapter 5. The geological structure of Britain is a continuation of the same terranes that underlay Ireland, therefore the data are directly comparable to these isotopic fields. The Iapetus suture is approximately situated below the present day political border of England and Scotland. Consequently the gold deposits located in Scotland overly the NWT basement whilst those located in England and Wales overly the SET.

In accordance with the isotopic signatures of Irish gold deposits, Scottish gold mineralisation demonstrates a less radiogenic isotopic signature typical of a significant NWT lead input, whilst English and Welsh gold deposits are characterised by more radiogenic isotopic signatures consistent with a significant SET lead input. The less radiogenic signature of the Scottish gold samples suggests that a Scottish source is unlikely, thus reaffirming an association with the SET. It is of course possible that gold mineralisation with a more radiogenic signature is present in Scotland if localised lead sources exist. However it could not be in the remit of this study to fully characterise the gold deposits of Britain.

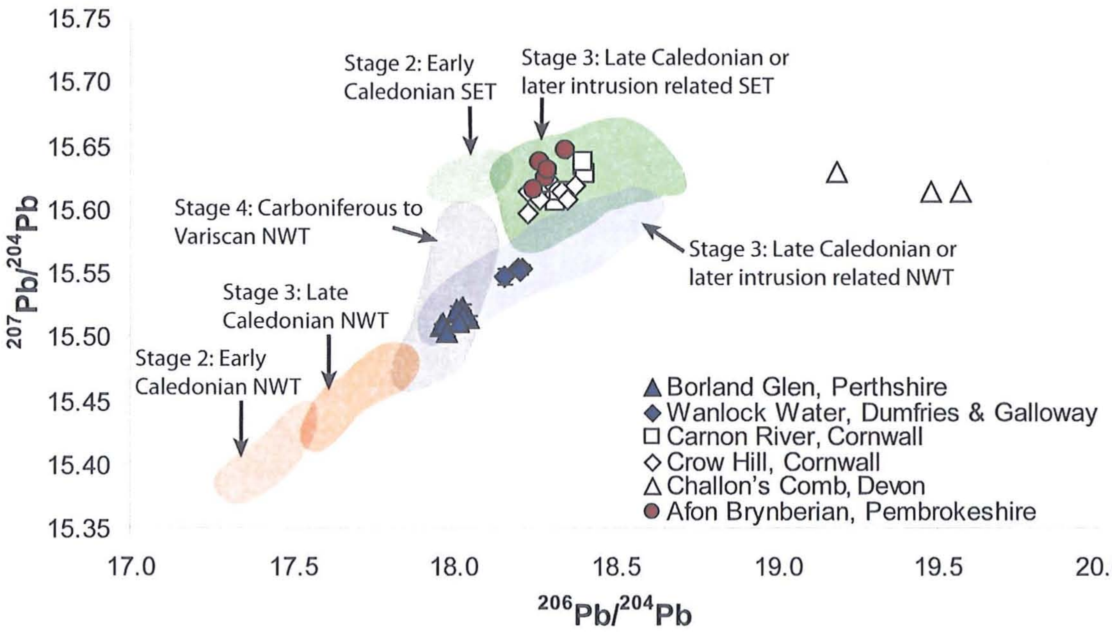


Figure 6.29: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of British gold deposits relative to the Irish gold deposit isotopic fields as detailed in Chapter 5.

A Chalcolithic and EBA gold source in the SET of Britain can therefore be hypothesised. Figure 6.30, Figure 6.31 and Figure 6.32 plot the isotopic signature of EBA artefact gold with the signatures of the Welsh and south-west English gold mineralisation along with the Cornish copper mineralisation from Rohl and Needham (1998). Note the change in axes scales from previous graphs due to the increasingly radiogenic signature of the copper mineralisation.

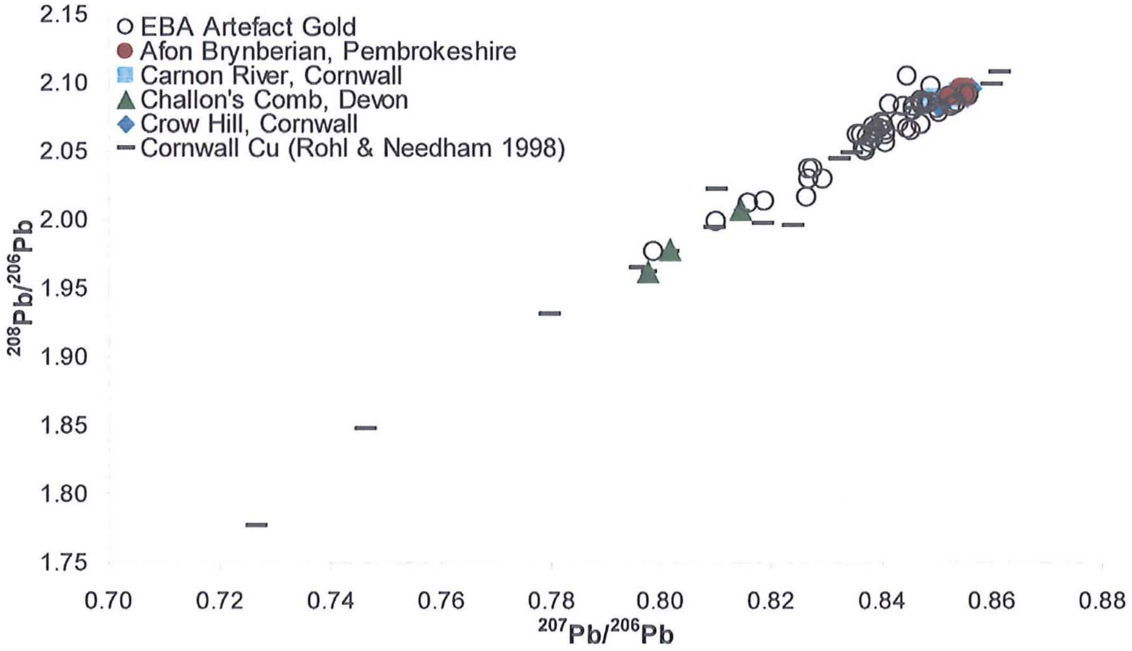


Figure 6.30: ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb plot of Chalcolithic and EBA artefact gold relative to natural gold of Wales and south-west England and Cornish copper mineralisation.

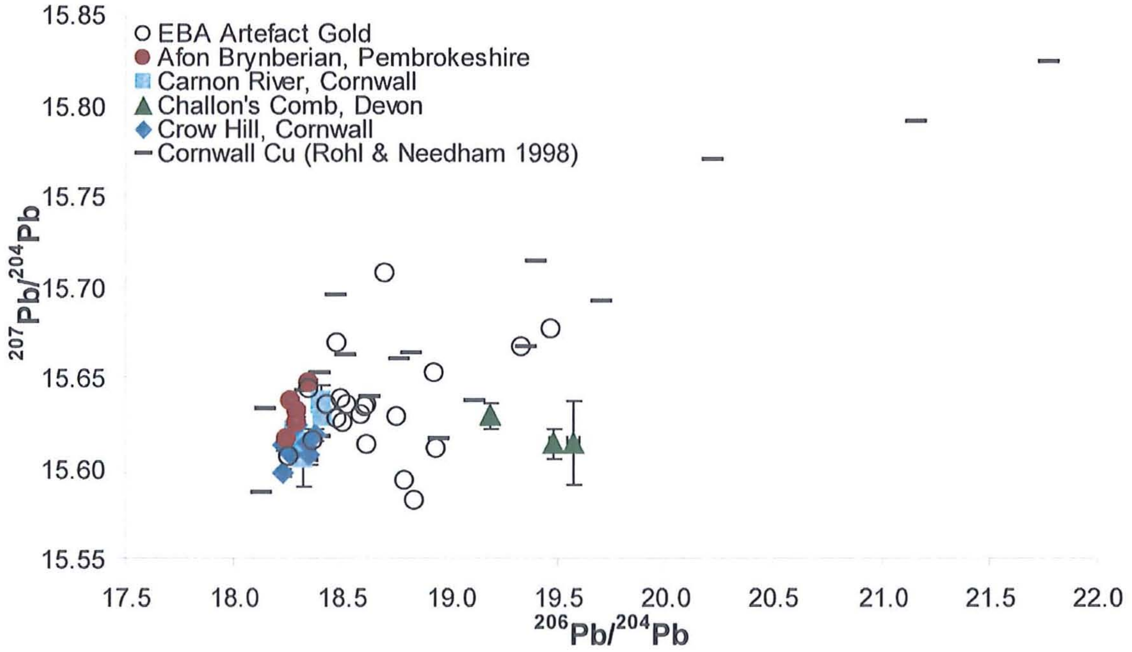


Figure 6.31: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Chalcolithic and EBA artefact gold relative to natural gold of Wales and south-west England and Cornish copper mineralisation.

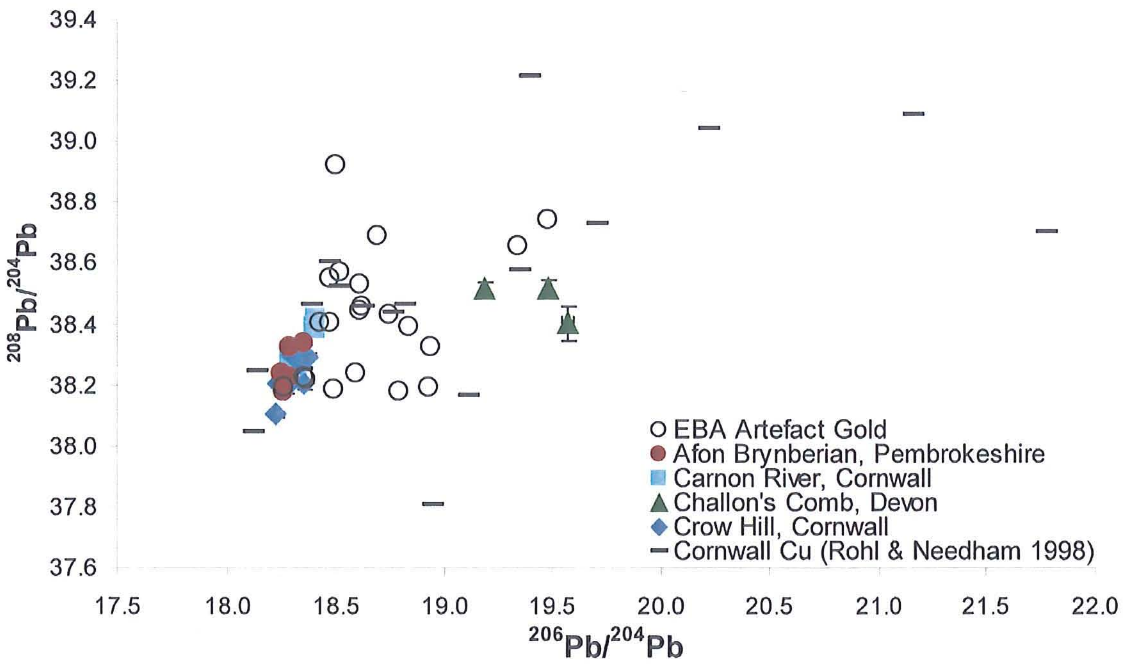


Figure 6.32: ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot of Chalcolithic and EBA artefact gold relative to natural gold of Wales and south-west England and Cornish copper mineralisation.

The alluvial gold deposits of Afon Brynberian, Carnon River and Crow Hill demonstrate a similar isotopic signature, although the Afon Brynberian is characterised by slightly higher ^{207}Pb/^{204}Pb relative to ^{206}Pb/^{204}Pb (Figure 6.31). A significant proportion of possible southern British gold sources have not been characterised, therefore it is unwise to relate specific artefacts to ore deposits. However the deposits that have been characterised are consistent with the basket ornament (W74) and a lunula (R625), along with the copper-uncorrected signatures of lunula 1998:74 (Ballinagroun) and the trapezoidal plaque (SA1913:131 Knockane) on all ratios. Furthermore, five lunulae have similar isotopic signatures (1946:392, R1755 Banemore, W1, W14, W15/R137 Dunfierth). Consistency with additional artefacts can also be postulated based on ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb, i.e. those that were not analysed by solution techniques for ^{204}Pb data. These deposits therefore represent potential sources for some of the artefacts analysed in this study, with the Cornish deposits perhaps providing the best match. Consequently the gold deposits of southern Britain are potential sources of Chalcolithic and EBA gold.

The Challon's Comb gold deposit is characterised by a distinctly more radiogenic isotopic signature. Although this deposit is not consistent with any of the artefacts, its signature indicates that gold from south-western England can demonstrate the radiogenic signature recorded in some of the EBA artefacts. It was these artefacts that were not consistent with any of the analysed Irish gold deposits, therefore south-west England is a potential source region of Chalcolithic and EBA gold even if the principle cluster of artefacts relates to an as yet unidentified Irish source.

The analysis of one Welsh gold deposit and three from south-west England confirms these regions as potential sources of Chalcolithic and EBA gold. However the small number of deposits analysed does not characterise all the possible gold sources in this region. The copper mineralisation is a compilation of data from 15 sites located across the county of Cornwall. This data therefore provides evidence for the overall isotopic field of mineralisation in south-west England, a good proxy for the overall isotopic field of gold mineralisation if a significant number of deposits were to be analysed. The field as defined by the copper data adds further support to the hypothesis of a south-western British source; all the Chalcolithic and EBA artefacts are consistent with this field except perhaps lunulae W8/R135 (Dunfierth) due to high $^{208}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$.

A principle Irish source was disputed based on the incompatibility of the lead isotope and compositional data, therefore a consideration of the composition of south-west British sources must also be made. Chapman et al. (2000a) present median silver concentrations for a number of Welsh alluvial and bedrock hosted gold occurrences. Vein gold from the Tyn Y Cornel level of the Clogau mine has a median silver concentration of 10.8%, whilst the Afon Mawdach and the Afon Wen have median concentrations of 11.7% and 10.2% respectively. Although these deposits were not analysed for their lead isotope signature, it indicates that some Welsh deposits are consistent with the silver concentrations of the Chalcolithic and EBA artefacts. The Afon Brynberian was analysed for its lead isotope signature. This river is situated in south-west Wales, in an area where gold exploration has been performed. Norton et al. (2000) identified a principle gold grain population with silver at 15% to 27% which is perhaps to high to account for the primary artefact range of 9.5% to 14.5%, whilst other populations characterised by low silver, around c.6% and <1% respectively, were also identified. Although these silver concentrations do not correspond to the artefact gold and no significant copper concentrations were recorded, alluvial cassiterite was recorded in the streams of the study region.

The gold mineralisation of south Devon where the Challon's Comb sampling site was located typically demonstrates low silver concentrations (<5%) with significant levels of palladium (up to 10%), although a population of grains with higher silver does also exist (Shepherd et al., 2005). Gold mineralisation is also present in the Crediton Trough of north Devon. In concordance with the south Devon mineralisation, silver is typically low (<5%) although some grains contain silver rich films, whilst palladium is present up to 3.1% (Cameron et al., 1994; Leake et al., 1994). Palladium was analysed as part of the EPMA artefact analysis during this study, however no artefacts contained this element above the detection limit. This element is stable during geological and metallurgical processes, and is often used in compositional provenance studies (Ehser et al., 2011). Consequently the presence of palladium in conjunction with the low silver concentrations typical of the Devon gold deposits suggest that they are not potential sources of Chalcolithic and EBA gold unless only high silver mineralisation was exploited.

Cornish gold mineralisation is poorly understood although it is known to be present in alluvial deposits that have in the past been exploited for cassiterite (Camm, 1995); it has been estimated that the tin streams of Cornwall may contain over one tonne of alluvial gold (Penhallurick, 1986). Ehser et al. (2011) examined the composition of Cornish alluvial gold when investigating the provenance of the Nebra Sky disc goldwork. The median silver values of eight alluvial populations and one vein mineralisation ranged from 3.8% to 33% highlighting the heterogeneous nature of Cornish gold deposits. Of these, Crow Hill is most consistent with the Chalcolithic and EBA artefacts analysed in this study with a median value of 12% (the median value of the artefacts investigated in this study is 11.63%). Gold from the Carnon River alluvial population analysed in this study has a median value of 5.3%. This is low for the artefacts, however the lead isotope variation of Cornish mineralisation in conjunction with the range of silver concentrations from Ehser et al. (2011) suggest there are likely to be Cornish deposits that match both parameters. The copper concentrations of these gold deposits have median values ranging from 0.0022% to 0.11%. The median copper concentration of the Chalcolithic and artefacts is 0.18% (including those that are potentially alloyed), therefore Cornish gold could potentially account for the copper concentration of the artefacts. The median tin concentrations of the Cornish gold deposits analysed by Ehser et al. (2011) ranged from 0.00078% to 0.046%. The median tin concentration of the artefacts investigated in this study is 0.039%, therefore the natural abundance of tin in Cornish gold could account for the tin concentration of the artefacts. The widespread occurrence of cassiterite in association with alluvial gold in Cornwall (Camm, 1995) also provides a mechanism for the accidental incorporation of tin into the artefact gold.

Based on the available compositional data for the gold mineralisation of Devon, it is unlikely that Chalcolithic and EBA artefact gold resulted from exploitation in this region. Likewise a number of Welsh sources are also compositionally inconsistent with the artefact gold although some could potentially provide a match. Compositional data from Ehser et al. (2011) demonstrates that Cornish deposits can match the silver, copper, and tin concentrations of these artefacts, therefore both Welsh and Cornish gold mineralisation have the potential to be both isotopically and compositionally consistent with the artefact gold. These two areas are highlighted as potential locations for the principle sources of Chalcolithic and EBA gold.

6.6.6.3 The potential for an Chalcolithic and EBA gold source in Wales or south-west England

Chalcolithic and EBA Wales and south-west England

Thus far the lead isotope signature and elemental composition of the Chalcolithic and EBA artefacts have highlighted south-west England and Wales as the potential location of the principle gold source(s) from these periods. A brief consideration of the archaeological evidence for Bronze Age activity in these regions is required before an assessment of this hypothesis can be made.

Evidence exists for Chalcolithic and EBA activity throughout Wales. This is primarily through the funerary record which includes the continued use of megalithic tombs along with the construction of round barrows, cairns, and cemetery mounds (Lynch, 2000). Settlement evidence is more limited; whilst there are a number of Beaker period occupation sites across the country, examples dating to the full EBA are rare. Upland clearance cairns with associated huts and field systems are also thought to date to this period, however dating these structures has proved problematic (Lynch, 2000).

Evidence for Chalcolithic and EBA human activity is also present in Cornwall (e.g. Christie, 1986; Pollard and Healy, 2007). As with Wales, early settlement sites are rare, however this is offset by the ritual and funerary record (Christie, 1986). Evidence for domestic occupation relies on lithic and artefact scatters, post- and stake-holes, pots and hearths (Pollard and Healy, 2007), whilst some domestic buildings have been dated to the Beaker period or EBA including examples at Gwithian, Poldowrian, Polcoverack, Trevisker and Bodmin Moor (Christie, 1986). Barrows are a significant feature of south-west England (Pollard and Healy, 2007), whilst secondary insertions of Beaker or Food Vessel pottery highlights the re-use of earlier megalithic burial monuments (Christie, 1986). Stone circles, stone rows, cup marked rocks and burnt mounds may also be found in these two regions, and also date to the Chalcolithic and EBA (Christie, 1986; Lynch, 2000).

Early Bronze Age Mining in Wales and south-west England

Wales hosts important gold deposits such as those in the Dolgethau gold belt of north Wales and at Ogofau, central Wales (Colman and Cooper, 2000). There is however no evidence to suggest that any of these were worked during the Chalcolithic or EBA. A number of Welsh copper deposits were exploited at this time, including those at Parys Mountain (Anglesey); Great Orme (north Wales); Cwmystwyth, Nantyarian, Llancynfelin and Nantyreira (central Wales) (Timberlake, 1990a, 1990b, 1992, 1994, 1995; Dutton and Fasham, 1994; Craddock, 1995; Ixer and Budd, 1998; Rohl and Needham, 1998). Evidence ranges from open cast trenching, adits, tools, tool marks, fire setting and associated charcoal, and highlights the existence of a rich mining industry in Wales during the EBA. The majority of these mines were active from c.1900 BC until c.1500 BC, although activity at Cwmystwyth began as early as c.2100 BC (Timberlake et al., 2004) and some mines including Great Orme were still in production during the MBA and LBA (Timberlake, 1994; Dutton and Fasham, 1994; Ixer and Budd, 1998). This principle period of mining therefore post-dates the age of the Chalcolithic and EBA goldwork in question; the lunulae tradition is likely to date from c.2300/2200 to 1900 BC.

Cornwall has traditionally been seen as a key source of Bronze Age tin (Shell, 1978; Penhallurick, 1986, 1997; Sheridan, 2008), however the probable exploitation of placer deposits means that direct evidence for mining is rare and often circumstantial. Copper mineralisation is also present in the region, and despite indications that Cornish copper may have been exploited (Rohl and Needham, 1998), physical evidence for this is also lacking. No clear evidence for lode mining during the Chalcolithic or EBA exists, although a MBA palstave was reportedly discovered in an open cast working containing both tin and copper ores. Penhallurick (1986, 1997) lists over 40 prehistoric artefacts that have been recovered from the tin grounds of Cornish rivers including an EBA flat axe from the Carnon Valley. Cornish tin grounds are often located at great depth with some artefacts found >10 ft below the present day surface, and they are typically sealed geological horizons with overlying sequences of gravels, silts and sands (Penhallurick, 1997). Consequently artefacts recovered from these contexts can not have filtered down from the surface and must reflect human activity during the Bronze Age (Penhallurick, 1997). The lack of archaeological records regarding the context of these finds does mean that doubt over the sealed nature of the specific tin grounds containing Bronze Age artefacts will remain. However cassiterite and tin slag has been found at the EBA site of Caerloggas Down, St Austell (Miles, 1975), thereby confirming tin processing was occurring during the EBA (albeit by Period 4/the Arreton stage late in the EBA; Rohl and Needham, 1998). All other evidence for Bronze Age processing of cassiterite in south-west England dates to the Middle or Late periods (Penhallurick, 1986), yet the evidence presented here lends support to the widespread view that Cornish tin was exploited during the EBA.

Numerous gold deposits are also present in Cornwall (Camm, 1995) and gold is typically found associated with cassiterite in the tin grounds of Cornish rivers (Penhallurick, 1986, 1997). It is well documented that over the last 500 years Cornish tinners would also collect alluvial gold to sell on to goldsmiths. In fact tinners received lower wages at certain streamworks where supplementary income was available from the collection of alluvial gold (Penhallurick, 1986, 1997). If these deposits were exploited for cassiterite during the Bronze Age, it seems inevitable that alluvial gold would also have been recovered.

Early Bronze Age goldworking in Wales and south-west England

Chalcolithic and EBA goldworking is rare in Wales. Only two artefacts date to the end of the 3rd millennium BC: the Banc Tynddol disc (dated to c.2500-2100 BC) was recovered from a grave located near to the EBA copper mine of Cwmystwyth in Ceredigion, central Wales (Timberlake et al., 2004); whilst the Llanllyfni provincial lunula was discovered in Caernarvonshire, northern Wales (Taylor, 1980; Eogan, 1994).

The only other Welsh artefact of possible EBA date is the embossed Mold Cape, a unique item recovered from a burial context in north-east Wales (Needham, 2000a, 2012b). However its age is still contested, and instead may date to the MBA (Gerloff, 2007).

Although the number of EBA gold artefacts from Cornwall is only slightly higher, the small geographic area in which they were found means that they represent a significant concentrations outside of Ireland. An overview of the Cornish EBA goldwork has been provided by Mattingly et al. (2009). Four lunulae are detailed: a classical type from St Juliot, a classical type from Penwith, and both a classical and provincial type of Harlyn Bay. These are significant because they represent the only confirmed examples of classical types to be found outside Ireland; the most accomplished and stylistic of the lunulae forms that represent the peak of Irish EBA goldworking. Furthermore there is a possibility that some of the Cornish lunulae, namely the Harlyn Bay examples, may have been deposited in funerary contexts (Mattingly et al., 2009). However it must be stated that this theory gains little support from the primary accounts of artefact discovery, thus funerary associations remain unproven. The final item of Cornish EBA goldwork is the embossed Rillaton Cup. This artefact was found in a burial context; a cist containing decayed human bone along with further grave goods including a bronze dagger and faience beads (Needham and Varndell, 2006). The cup was discovered in an important ceremonial complex by Bodmin Moor in the east of the county (Mattingly et al., 2009), and dates to c.1700 - 1500 BC (Needham, 2000a).

Discussion

Goldwork was in circulation in Wales and south-west England during the EBA. Relative to Ireland the number of artefacts was apparently much lower, however when considering the size of Cornwall, four lunulae represents a significant concentration of goldwork even by Irish standards.

Both Wales and south-west England had a rich mining industry during the EBA; Wales was an important source of copper whilst Cornwall was one of the principle sources of tin. Mining in Wales appears to have commenced by c.2100 BC with the primary output occurring after 1900 BC. This postdates the appearance of the initial Chalcolithic and EBA goldworking traditions (both the primary and lunulae phase), and there is no evidence to suggest that the country's gold deposits were ever worked in prehistory.

Conversely south-west England was apparently an important source of tin throughout the British Bronze Age from c.2200 BC. There is strong circumstantial evidence that alluvial deposits were being exploited for cassiterite at this time, and the presence of gold in association with cassiterite in many streams and rivers strongly suggests that people who exploited these deposits would also have encountered native gold. This period is contemporary with the lunulae tradition, a tradition that is well represented in Cornwall, therefore highlighting the possibility that gold was being exploited in south-west England at this time. The distributional focus of lunulae in Ireland strongly suggests that the classical and unaccomplished lunulae were of Irish manufacture, however this does not preclude an external source for the raw material.

The basket ornaments, the early discs and the oval plaques are part of the primary goldworking assemblage which began circulation during the Chalcolithic, i.e. before the exploitation of tin. The lack of a clear mining industry in Cornwall during this early period may preclude a south-west English source. However these artefacts have been dated using a limited number of radiocarbon dates and the potential that some were manufactured post-2200 BC remains (see Chapter 2, Section 2.3.1.2). Furthermore, during this early period of gold exploitation there is less disparity between Britain and Ireland in terms of the amount of gold in circulation; the distribution of basket ornaments centres on Britain. A non-Irish source is therefore less problematic than it first seems.

Lead isotope analysis suggests the principle source of Chalcolithic and EBA gold originated from an Irish/British SET source, yet no SET Irish gold deposit was consistent with the artefact gold when considering both their lead isotope signature and major element composition. Archaeological evidence indicates that metals were being exploited in Wales and south-west England during the EBA, whilst goldworking was in circulation at this time. Consequently both areas can be considered as potential locations for the principle source of EBA gold. With respect to Wales, the rarity of gold artefacts and the fact that the principle period of copper mining post dates the Chalcolithic and EBA goldworking under consideration suggests a Welsh source is less likely. Conversely evidence exists that suggests Cornish alluvial deposits were being exploited for cassiterite throughout the EBA, thus indicating the presence of a widespread mining industry. These deposits also contain native gold, therefore some degree of Cornish input into the EBA gold supply appears inevitable. Based on combined archaeological and analytical evidence, the currently favoured hypothesis is that the principle source of Irish Chalcolithic and EBA gold was located outside Ireland, with its most likely location in southern Britain.

6.6.7 Minor sources of Chalcolithic and EBA gold

The majority of the Chalcolithic and EBA artefacts are consistent with the Cornubian ore field, however one lunula (W8/R135 Dunfierth) is inconsistent due to high $^{208}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$. This may highlight an input from a secondary, comparatively minor, gold source. Continental European ore deposits can be characterised by higher $^{208}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$, however at present no known gold deposit matches the isotopic signature of this artefact sufficiently on all ratios. The closest signature is from sulphides associated with a gold-bearing skarn deposit at Vall de Ribes, central Pyrenees, Spain (Figure 6.33; sulphide data from Romer and Soler, 1995), however further analyses of gold samples from numerous European sources would be required before a named source can be linked to this artefact with any certainty.

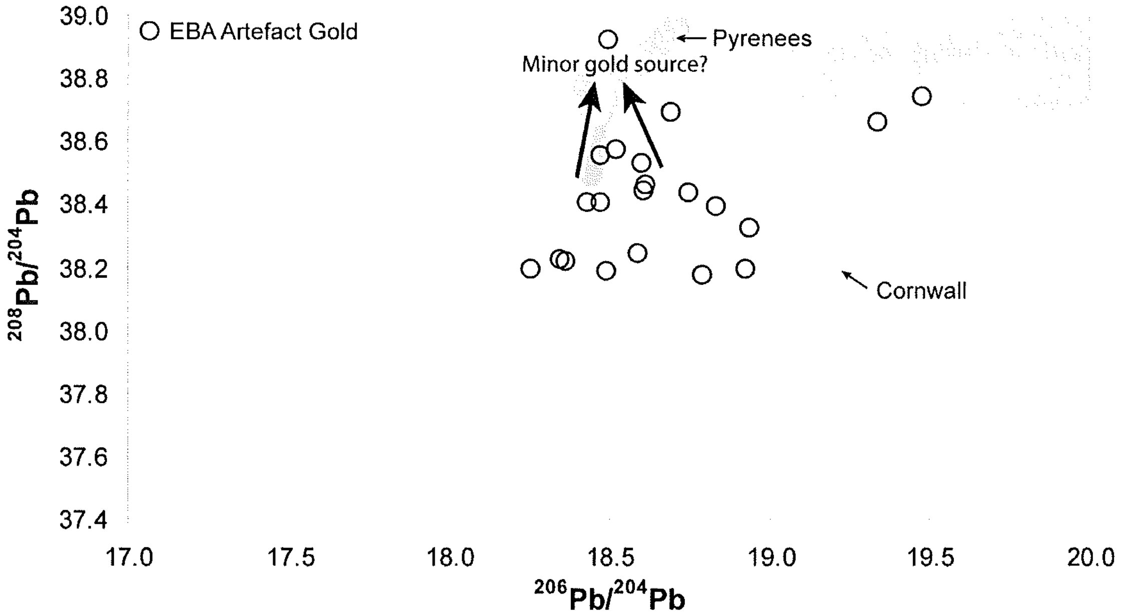


Figure 6.33: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of potential secondary gold input from a continental source. Large arrows represent potential mixing of the primary (principle cluster of artefacts) and secondary (minor) gold sources.

Irrespective of where this potential minor source was located, or even the location of any primary gold source, the mixing of gold from more than one source into the

Chalcolithic and EBA metal pool can be hypothesised. The effect on the isotopic composition of the metal pool would be a homogenisation of the signatures of the two source deposits, therefore artefacts that plot intermediately between the core signatures may reflect a mix of gold from both source regions. Full characterisation of this secondary source would be needed before its relative importance can be discussed.

6.7 Synthesis: Gold in the Chalcolithic and Early Bronze Age

Lifeways during the Chalcolithic and EBA were comparable to those in the preceding Neolithic, there is little evidence for social stratification and agricultural subsistence was the focus of daily existence. As the Bronze Age progressed, a pattern of increasing social complexity formed. There was widespread adoption of new technologies such as metalworking, an increase in specialisation, settlement hierarchies formed, and elites became visible in the archaeological record. As a result, the mechanisms behind this pattern of increasing complexity and how elites acquired and maintained their status are crucial questions within Bronze Age archaeology. A further development that occurred during the Chalcolithic period was the significant increase in the deployment of exotic materials. Controlling the procurement, circulation, deployment and transformation of material goods such as metals are all mechanisms for acquiring power (Mann, 1986; Shennan, 1993; Earle, 1997), and with the added significance of gold through its inclusion within the exotic material framework, it is clear why the ability to control this specific material would be of social importance.

Recognising the source locations is therefore key if the role gold played in Bronze Age societies is to be explored. This must begin with the first exploitation of the material, therefore any changes in procurement over time can be identified and discussed within a wider Bronze Age context. Although no specific source has been proposed outright for Irish Chalcolithic and EBA gold, current evidence suggests that a non-Irish origin is a distinct possibility. Is a non-Irish source consistent with the patterns seen in the exploitation of exotic materials during the Bronze Age? As discussed, it is not uncommon for the principle region of exotic consumption to be located some distance from the source. One of the key centres of Whitby jet deployment was in Scotland (Sheridan et al., 2002), whilst amber with a likely Baltic source (see Section 2.2.3) is preferentially found in regions away from Scandinavia (and the east coast of England) such as Wessex (Beck and Shennan, 1991). A non-Irish source of gold for Irish goldwork is therefore consistent with the wider pattern of exotic material consumption.

It is important to note that a non-Irish source does not mean Irish-centric traditions were not of local manufacture. The transportation of raw material allowing localised manufacture would mirror the pattern observed in the Baltic-Wessex amber trade by Beck and Shennan (1991).

This raises ideas relating to the control of knowledge. Ireland is host to multiple gold deposits including a number that were capable of supporting Bronze Age goldworking industries (see Chapter 3), however current evidence suggests they were not exploited. Once gold was in circulation it is reasonable to assume that exploration for new sources would have been performed, yet for some reason this did not lead to the discovery and large scale exploitation of Irish gold deposits during the Chalcolithic or EBA. Perhaps this was simply by chance, and active exploration was carried out across the region without success. Alternatively, the knowledge of how to obtain gold may have been restricted by those procuring the material elsewhere. Ireland was a major producer of copper during this early metalworking period through bedrock mining, however if as believed gold was sourced from alluvial deposits, alternate knowledge and skills would have been required for the procurement of gold. Perhaps societies in Ireland were not conscious of these, and the lack of awareness regarding where this material originated from helped enhance its exoticness leading to increased demand.

The manufacturing processes employed during the Chalcolithic and EBA did not significantly homogenise the artefact alloys, whilst the overall isotopic and compositional variation of the artefacts is indicative of the variation within and between the source deposits. The high inter-artefact variation suggests that heterogeneous sources were exploited. With the tin content of many artefacts supporting an alluvial origin, this favours the exploitation of alluvial deposits that incorporated gold from numerous vein mineralisations. This may imply relatively uncontrolled exploitation, where local streams could be accessed by anyone with the knowledge of how to extract gold from such deposits. It has already been stated that no large scale homogenising process was employed. If gold exploitation was under the control of a centralised authority, a homogenous signature may be expected if raw gold from multiple locations was processed and fabricated at a small number of locations into a centralised metal pool for controlled distribution. The fact that variation is so great suggests the opposite was true, and no centralised or controlled fabrication centres existed. The variation therefore advocates a lack of control over the procurement of Chalcolithic and EBA gold.

There is no apparent difference in the isotopic signature of the primary goldworking traditions and the supposedly later EBA traditions. This suggests the continued exploitation of deposits within the same ore field. It is interesting to note that the low silver variation of the earliest artefacts may indicate one or few sources within this ore field were exploited during the primary period of goldworking before further deposits were discovered allowing an increase in production. The potential for mixing or recycling has been discussed, and a central cluster of artefacts represents the most likely composition of gold with such an origin. This would also reflect the composition of a homogenised EBA gold metal pool if one formed during this period.

South-west England has been proposed as the most likely principle source region of Chalcolithic and EBA gold based on the current analytical data. Evidence for contemporary goldworking and mining also lends support to this theory; Cornwall hosts a significant concentration of EBA goldwork, whilst the believed exploitation of gold bearing alluvial deposits for cassiterite suggests that the exploitation of local gold is highly likely. Furthermore, Cornwall hosts the only confirmed examples of classical lunulae outside Ireland, Cornish lunulae have been found associated with non-gold artefacts, and although unproven the possibility that some of these lunulae were deposited in funerary contexts remains. These factors may endorse the view that gold fulfilled a significant, and perhaps slightly different, role in Cornish society than it did in Irish society.

The role of exotics has been discussed, with numerous past societies linking materials such as gold to supernatural and cosmological powers. Irish lunulae are typically deposited as isolated finds in uncontexted deposits (Taylor, 1980, Eogan, 1994) and evidence exists for both long term curation and prolonged life histories (Cahill, 2006), yet a lack of physical wear on many also indicates limited use (Taylor, 1980). These factors have helped to make the lunulae one of the most enigmatic artefacts of the Bronze Age, and their purpose is still debated. Communal or group ownership is preferred by Taylor (1980) and O'Brien (2004), whilst associations with celestial bodies are also possible (Cahill, 2006) thus roles within public ceremonies or customs are likely. Communal ownership and ceremonial use may help explain why local sources were not exploited during this period. Perhaps gold was not simply a commodity where increased demand resulted in the search for, and exploitation of, new sources. The exotic nature and esoteric origin may have been intrinsic in defining its role, and as a result there was neither a need nor a desire to find local sources. In conjunction with the evidence towards a non-Irish source, the depositional practices employed in Ireland can be interpreted as local traditions relating to the treatment of exotic materials. The majority of Irish Chalcolithic and EBA goldwork is found in similar contexts to the lunulae, although the trapezoidal plaque from Knockmore was reportedly found within a funerary context (Cahill, 2006). Its similarities with Wessex goldwork highlight possible links with this distant community, and perhaps can explain the differing depositional context. Clearly gold must have played a significant role within Chalcolithic and EBA Irish society.

It now seems likely that the primary consumption of pre-c.1900 BC goldwork did not correlate with where it was procured. This could be a function of higher demand from Irish societies, however if the transformation from raw material into finished artefact was occurring elsewhere, then perhaps it was this transformational process that created the meanings associated with these artefacts. The Chalcolithic and EBA gold discs are often termed ‘sun discs’ (e.g. Taylor, 1980) due to their sun-like appearance, whilst lunulae have also been associated with celestial bodies (Cahill, 2006). If these artefacts were produced as deliberate representations of cosmological bodies and were fundamental to Chalcolithic and EBA belief systems, gold transformed into celestial images may have taken on greater significance than that attributed to the raw material alone. As a consequence, shamanistic powers may have been accredited to the goldworkers who themselves would have been central to the deployment of these artefacts (resulting in the distributional focus associated with manufacture rather than raw material source region). Deliberate limiting of the number of artefacts produced would further explain why local sources were not exploited. Taylor (1980) presented evidence for the identification of individual lunulae smiths, and if the artefact form had elevated value and meaning over that of the raw gold, perhaps the smiths themselves controlled the number of artefacts under production (or alternatively production may have been administered by those who controlled access to the smiths).

Metal can represent wealth in the regions where it was procured; it is transferable into tools or ornaments and can be exchanged for other goods, whilst access to metal wealth and its resulting control could award certain degrees of power (Shennan, 1993). Deposition of goldwork in funerary contexts creates an association with the person or persons interned, therefore implying a direct relationship with the embodied wealth or power. The exact connotation of this embodied wealth is open to interpretation; it could relate to control of its procurement, exchange, transformation or associated magical/supernatural powers. Rich graves situated in the periphery of metal producing regions (for example Wessex) have been related to aspects of exchange control (Shennan, 1993), therefore if gold was procured from an undiscovered Irish source this interpretation may be preferred for the Cornish lunulae burials. However if Cornish exploitation of gold is hypothesised, an economic association through procurement can be proposed. The isotopic variation has been discussed in terms of a lack of centralised production. If this was the case, the deposition of the Cornish lunulae can be associated with persons who had some degree of control over gold exchange with the principle regions of consumption. Harding (2000) discussed notions of territoriality in the EBA, which included the control of local resources despite a lack of centralisation in life in general. It is entirely possible that the export of gold from its source region was controlled by a small number of individuals.

The Harlyn Bay and St Juliot lunulae have known find locations situated on the northern coast of Cornwall, whilst one of the possible find spots of the Penwith lunula is also on this coastline. This distribution along Irish facing coast has been seen as evidence for contacts with Ireland and the wider Atlantic fringe, and is typically seen to reflect the flow of gold into the county (Mattingly et al., 2009). Rather than an indication of simply where the lunulae were coming from, it may be indicative of an important two-way relationship and reflect close ties resulting from the trade of raw gold in the opposite direction. Interestingly the chronologically later Rillaton cup was found in the east of Cornwall, and in conjunction with the artefact form is suggestive of a shift in social connections from the Atlantic façade, to southern Britain, Wessex, and continental Europe (Mattingly et al., 2009).

Indeed the decline of the Irish lunulae tradition is consistent with the emergence of both the embossed and linear goldworking traditions of Britain, supporting theories regarding a shift in control over the Cornish gold supply from west to east. This hypothesis is supported by further evidence for increased contacts between Cornwall and southern Britain during the first half of the 2nd millennium BC; Trevisker-style pottery (a Cornish tradition that originated towards the end of the EBA) has been discovered in Wessex (and indeed further afield; Gibson et al., 1997), whilst elements of Wessex II such as Camerton-Snowshill daggers have been found in Cornwall (Christie, 1986). Although some EBA British goldwork is distinct from earlier Irish artefacts based on major element composition, many are indistinguishable. Additionally much of the British dataset relies on Hartmann's data which is of dubious accuracy, thus it is entirely possible that the same source region was exploited for the manufacture of both the Irish and British goldworking traditions. An expansion of this project is clearly required, both through the characterisation of the gold sources of southern Britain and a selection of Chalcolithic and EBA British artefacts, and would allow further investigations into these important changes in Bronze Age goldworking.

Needham (2000a) argued for the emergence of the embossed tradition in Britain at the turn of the 2nd millennium BC, and its subsequent expansion into continental Europe. A number of continental embossed gold artefacts, including the MBA Schifferstadt and Ezelsdorf gold hats/cones, are also compositionally indistinguishable from much of the Irish and British goldwork. Consequently this potential shift in the patterns of EBA gold deployment could extend further afield than Britain. In fact the gold of the Nebra Sky Disc, dating to c.1600 BC, has been linked to a Cornish source by Ehser et al. (2011). Interestingly the median silver composition of the Nebra Disc gold is 25%, significantly different to the Irish goldwork investigated in this study. However Ehser et al. (2011) also demonstrated the heterogeneous nature of Cornish gold; of the nine natural gold deposits analysed, the median silver concentrations ranged from 3.8% to 33%. Cornish gold therefore has the potential to account for the typical silver concentrations seen in the majority of Chalcolithic and EBA goldwork, and the difference between the elemental composition of different goldworking traditions is not a reason to exclude a Cornish gold source for all. The potential for a major gold source located in southern Britain that supplied gold to north-west Europe is apparent.

There is evidence for a shift in influence over the EBA gold sources from Ireland to Britain c.2000 to 1900 BC. If so, why this shift occurred is an important research question. A possible mechanism can be found in the Chalcolithic and EBA copper mines of south-west Ireland. O'Brien (2004) hypothesised about the appearance of 'lunulae lords' in south-west Ireland as hierarchies began to form in the area. The large scale exploitation of copper from the rich ore deposits at Ross Island was one of the most important sources of copper in north-west Europe during the second half of the 3rd millennium BC. Demand for copper from external regions would have accredited economic power to this region, and as the distribution of the local metal resource was controlled, exchange contacts that extended across and beyond Ireland would have formed. It could therefore be proposed that in south-west Ireland at least, economic power driven by copper exploitation aided the ability to import gold into the region. The decline of the Ross Island mine is roughly contemporaneous with the supposed end of the lunulae tradition. Did the decline of the Ross Island mine result in a loss of economic power for the region and help lead to a diminishing influence on neighbouring areas? The new Mount Gabriel type mines that came into existence by c.1700 BC represent a different approach to copper procurement, where small surface workings were exploited on a sporadic or seasonal basis (O'Brien, 2004). Perhaps this less intensive style of mining was unable to compete with other copper mines that appeared contemporaneously in Britain, and thus the economic influence of south-west Ireland diminished as it grew in areas of Britain and continental Europe. A widespread shift in exchange networks c.1900 BC may have occurred.

When the exploitation of Cornish gold is discussed, it is often assumed that it was a by-product of the tin extraction industry (Penhallurick, 1997), yet the first exploitation of gold predates the first exploitation of tin in Britain and Ireland. Goldwork from the earliest phase of production, i.e. Chalcolithic period, is indistinguishable from the later EBA artefact field, and consequently the exploitation of the same source is likely. The potential that this source was in Cornwall has been discussed, therefore raising the possibility that the alluvial deposits of this region were exploited for gold before they were exploited for cassiterite. This supports the view of Craddock and Craddock (1996) who proposed this sequence on chronological grounds. Additionally, the technicalities of discovering these two resources add further support to this theory. Alluvial gold deposits can be discovered by eye due to its tendency to form nuggets and its distinct visual appearance, whereas the dark colour of cassiterite means that its initial identification is difficult without some form of exploration work. It is therefore more logical that gold would be identified in an alluvial deposit first. The presence of cassiterite would then have become apparent during exploitation due to its occurrence in the heavy mineral fraction, and once the significance of this metal was learnt, the exploitation of gold and tin would have been possible.

Combined lead isotope and major element compositional analysis of Irish Chalcolithic and EBA artefacts has cast serious doubt for the hypothesis of a major Irish gold source. Rather than the exploitation of local gold deposits, the Irish gold manufacturing industry can be viewed within an exotic materials framework, where the raw material was imported from a distant location for transformation into enigmatic artefact forms such as the cresentic lunulae ornaments. Deposition in isolated locations unassociated with human burials or non-gold objects helps to suggest a communal and ceremonial role within society, perhaps relating to magical or supernatural properties often linked with this material by numerous societies in the past.

Variation within and between the artefacts suggests the exploitation of numerous alluvial deposits within one principle gold bearing region, and a lack of centralised control of production. Lead isotope analysis has highlighted the gold deposits of Wales and south-west England as the most likely principle source region of Chalcolithic and EBA gold. A preliminary analytical study combined with archaeological evidence suggests that of this area Cornwall is perhaps most likely to host this principle source. Although Chalcolithic and EBA goldwork is not abundant in the county it does host a significant concentration of artefacts, and there is strong evidence to suggest that Cornish alluvial deposits were being exploited for cassiterite during the EBA. The existence of gold in these deposits means that it is difficult to believe gold would not also have been exploited. The lead isotope signatures of the majority of the artefacts analysed in this study are consistent with an origin from the Cornish ore field, whilst literature data suggests that Cornish gold has the potential to also match the elemental composition of the artefacts. Consequently in agreement with Penhallurick (1986, 1997) and Craddock and Craddock (1996) the exploitation of Cornish gold is considered likely, although further investigations into the lead isotope signature and major element composition of Cornish gold is required before a full assessment can be made.

Chapter 7: Irish Goldwork of the Middle and Late Bronze Age

7.1 Synopsis

As the EBA came to a close, an apparent hiatus in Irish goldworking began. Significant production did not return to the region until the Early Bishopsland metalworking phase (c.1400 BC to 1300/1250 BC) of the MBA. The gold alloy used to manufacture these artefacts has been termed mba1 or B-gold (Warner, 2004; Warner and Cahill, in press), and was used to produce new artefact forms such as bar and 3-flanged torcs through innovative manufacturing techniques including bar-working. Henceforth lowercase mba or lba denotes alloy groups whereas uppercase denotes chronological periods. A number of these artefact forms were still under production during the Late Bishopsland metalworking phase (c.1300/1250 BC to 1150 BC). These were complimented by new forms including 4-flanged torcs as local goldworking industries advanced. Gold alloy mba2 (F-gold) was used to manufacture artefacts dating to this metalworking phase (Warner, 2004; Warner and Cahill, in press). Whilst there is little evidence for goldworking at the beginning of the LBA, Irish goldworking traditions peaked during the Dowris-A metalworking phase (c.950 BC to 800/750 BC) when gold alloy lba (G-gold) was employed (Warner, 2004; Warner and Cahill, in press). This period witnessed a diversification in the range of artefact forms under production and the quantity of gold in circulation was it its greatest.

Critical to gaining a full understanding of gold exploitation throughout the Bronze Age is the need to recognise the changing patterns of gold procurement. Chapter 6 raised serious doubt over the exploitation of an Irish EBA gold source, and instead highlighted south-west England or Wales as potential source regions. Chapter 7 presents preliminary data from the analysis of Irish MBA and LBA gold artefacts. The study of artefacts from these later periods is more complex due to widespread, deliberate, alloying of copper with gold, alongside the increased potential for mixing gold from multiple sources and presumed higher rates of recycling. These factors, along with the small number of samples analysed, prevents detailed discussions on the gold sources exploited. Instead, the aim of this chapter is to assess the application of lead isotope analysis to studying artefacts from these later periods.

Seventeen artefacts dating from the MBA and LBA have been analysed for their lead isotope signature and major element composition. The analytical data are presented in

Section 7.2, before sample heterogeneity is discussed (Section 7.3). Section 7.4 assesses how a lead isotope investigation into these alloyed artefacts could proceed. This includes preliminary attempts to correct the analysed isotopic signature for the input of copper derived lead, and a brief consideration on the sources of MBA and LBA Irish gold. Section 7.5 draws all the data together to assess the potential of a full lead isotope provenance study of later prehistoric goldwork, before some broad conclusions are drawn in Section 7.6. One Iron Age artefact was also analysed (Appendix B), however as it is inadvisable to base conclusions on a single analysis, it will not be discussed any further.

7.2 The lead isotope and major element compositional signature of Irish MBA and LBA goldwork

7.2.1 Introduction to the artefacts analysed

Seventeen MBA and LBA artefacts were analysed for their lead isotope signature and major element composition. These artefacts were all previously analysed by Chapman et al. (2006) for their major element composition and mineral inclusion suite, therefore their alloy groupings are already known. Major element analysis was performed to determine inter-study comparability, however it was not deemed necessary to repeat characterisation of the mineral inclusion suite.

Two artefacts are composed of Early Bishopsland mba1 gold alloy (a ribbed ring and a 3-flanged torc), five are composed of alloy mba2 which is typically assigned to the later Bishopsland metalworking phase (three penannular rings, a bar torc and a wire bound torc), and ten are composed of Dowris-A lba gold alloy (five bracelets, two sleeve fasteners, a neck ring, a large ring and a bulla). Six of these artefacts are housed at the Ulster Museum, Belfast (accession numbers beginning with the letter A) whilst the rest are housed at the National Museum of Ireland, Dublin. One LBA artefact failed to produce isotopic data due to low lead concentration (W175 neck ring). Figure 7.1 presents the find locations of these artefacts when known.

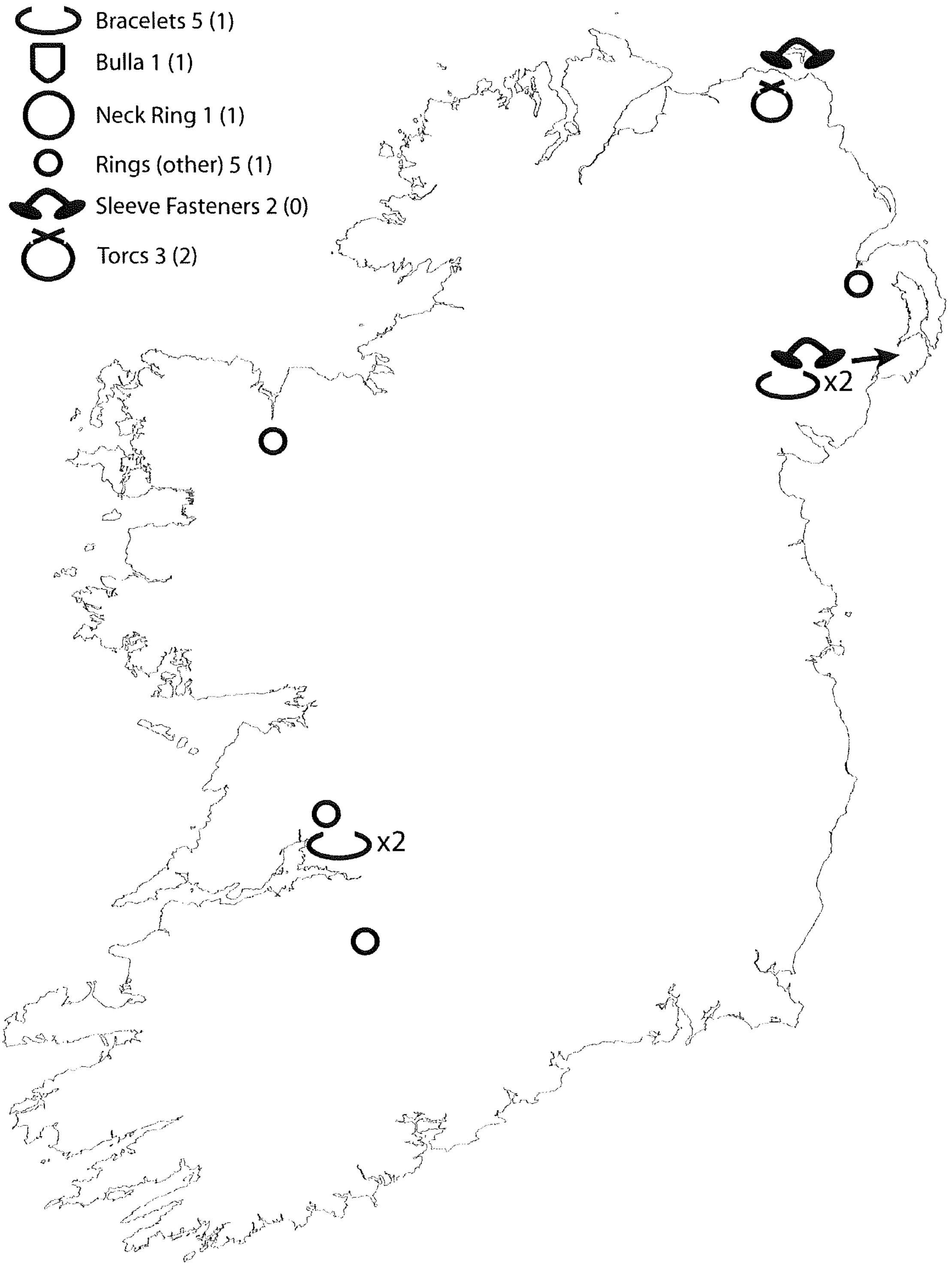


Figure 7.1: Find locations of MBA and LBA artefacts analysed in this study. Legend: numbers outside parenthesis represent total number of artefacts analysed, numbers in parentheses represents number of these with no known find location.

7.2.2 Major element compositional analysis

A number of recent publications have dealt with the compositional analysis of Irish Middle and Late Bronze Age gold artefacts (Warner, 1993, 2004; Chapman et al., 2006), and it is not the intension of this study to re-interpret these data. Major element composition analysis was performed so that the new lead isotope data could be discussed in conjunction with the overall compositional patterns visible in these artefact assemblages. The results are presented in Figure 7.2 and Figure 7.3 (Appendices B1 and B2). Each data point represents the average composition of three analyses, ±2 S.E of the mean of the multiple analyses (see Section 4.6). Throughout this chapter, silver concentrations have been adjusted from percent of total to percent of gold plus silver. This accounts for dilution of the original gold-silver alloy by copper alloying.

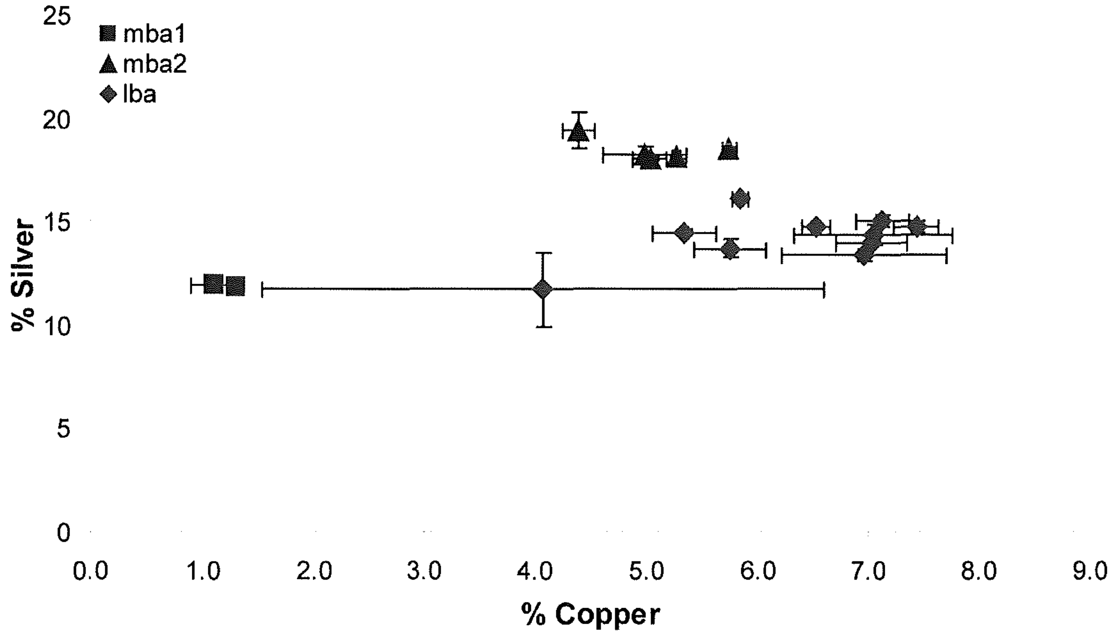


Figure 7.2: % silver versus % copper concentration of Irish MBA and LBA gold artefacts. Dashed grey lines represent analytical limits of detection.

In agreement with previous compositional studies (Hartmann, 1970, 1982; Warner, 1993, 2004; Chapman et al., 2006), the three alloy groups can be distinguished using the silver, copper and tin concentrations. The two mba1 artefacts have (adjusted) silver concentrations of 11.95% and 11.81%, copper concentrations of 1.12% and 1.3%, and tin concentrations of 0.16% and 0.46% respectively. These are consistent with other artefacts in Warner's (1993, 2004) B-gold compositional group although 0.46% tin is perhaps a little high. The mba2 artefacts are characterised by (adjusted) silver concentrations ranging from 18.04% to 19.39% (mean of 18.46%), copper concentrations between 4.39% and 5.74% (mean of 5.09%) and tin concentrations of 0.24% to 0.35% (mean of 0.29%) respectively. These are consistent with the composition of Warner's (1993, 2004) F-gold. The lba artefacts are characterised by (adjusted) silver concentrations ranging from 11.69% to 16.10% (mean of 14.20%), copper concentrations of 4.06% to 7.44% (mean of 6.31%) and tin concentrations between 0.03% and 0.23% (mean of 0.13%) respectively. These are consistent with the composition of Warner's (1993, 2004) G-gold. As demonstrated in chapter 6, the EMPA analyses are in agreement with those of Chapman et al. (2006) on the same samples.

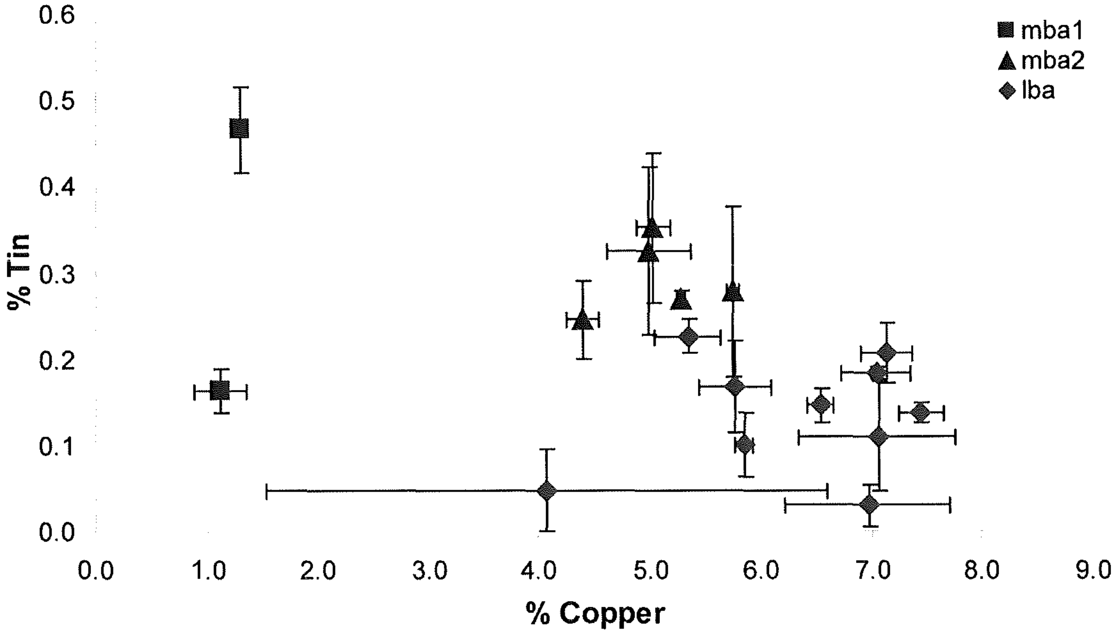


Figure 7.3: % tin versus % copper concentration of Irish MBA and LBA gold artefacts. Dashed grey lines represent analytical limits of detection.

7.2.3 Lead isotope analysis

The lead isotope signatures of Irish MBA and LBA artefacts are presented in Figure 7.4, Figure 7.5 and Figure 7.6 (Appendices B3 and B4). Samples were analysed by laser ablation only. Figure 7.4 plots the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ for all artefacts, however due to the isobaric interference of mercury only 11 artefacts could be characterised for their ^{204}Pb ($^{204}Pb+Hg/^{202}Hg$ is >1). Of these, the analytical errors on seven samples were too large (defined as >0.05 on the $^{206}Pb/^{204}Pb$) to be of use based on the typical isotopic variation between different isotopic ore fields (as discussed in Chapter 5). Therefore ^{204}Pb data was successfully collected for a total of four artefacts (Figure 7.5 and Figure 7.6). These include examples from each of the three gold alloy groups under consideration. When more than one analysis was possible on a sample, the data presented in this chapter are the means ±2 S.E. of the mean of the multiple analyses. If only one analysis was possible, errors are ±2 S.E. of the mean of the ≤140 integration cycles.

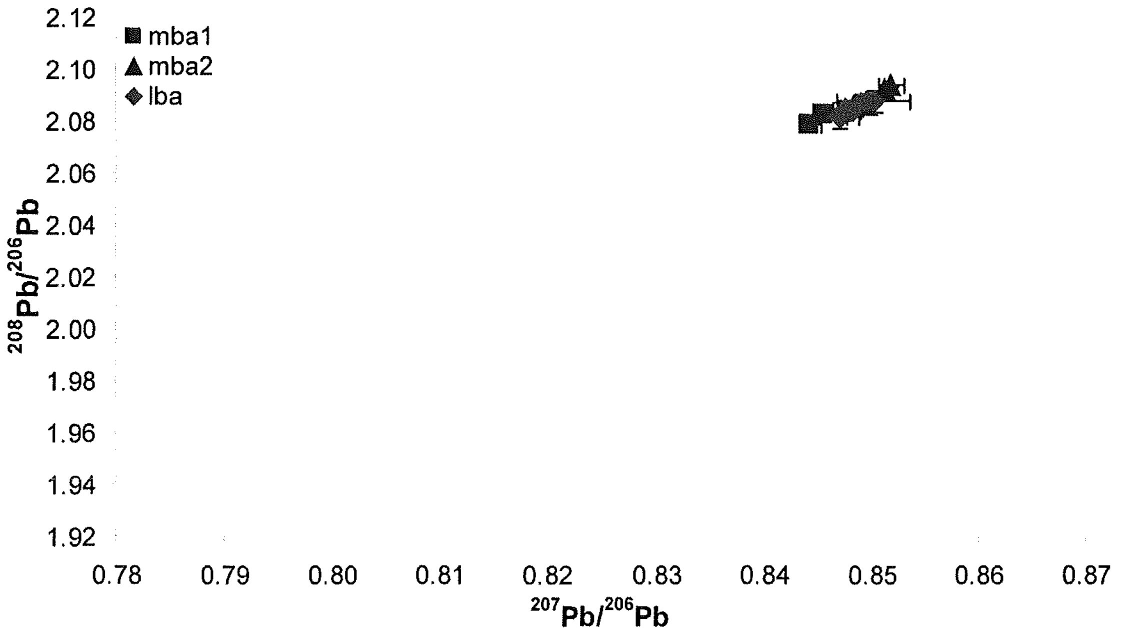


Figure 7.4: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of MBA and LBA Irish gold artefact samples.

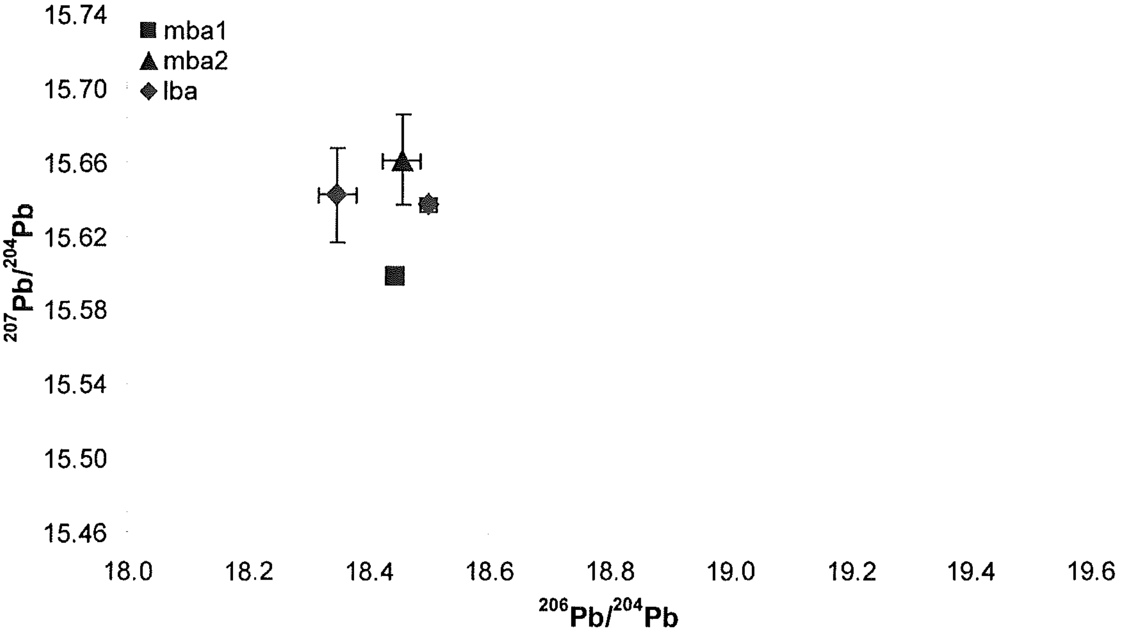


Figure 7.5: $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of MBA and LBA Irish gold artefact samples.

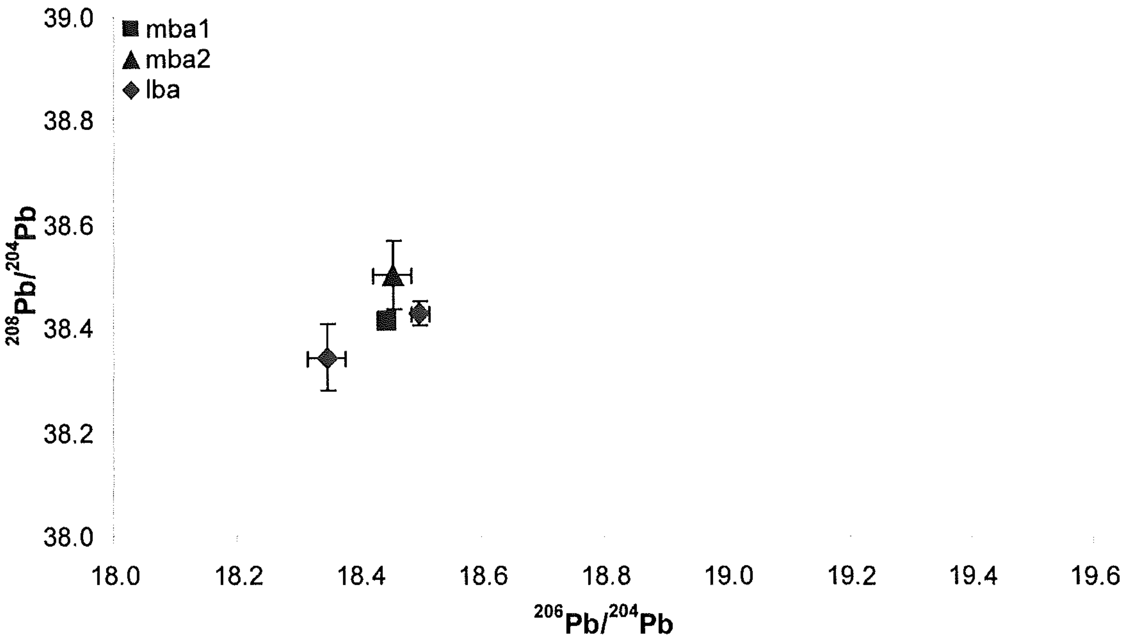


Figure 7.6: $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot of MBA and LBA Irish gold artefact samples.

The MBA and LBA artefacts are characterised by a similar isotopic signature. All fall between 0.84438 and 0.85198 on the $^{207}Pb/^{206}Pb$ and between 2.07833 and 2.09367 $^{208}Pb/^{206}Pb$ respectively. Within this field, artefacts belonging to each alloy group also plot in tight clusters. The two mba1 artefacts have lower $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, relative to the mba2 and lba artefacts which are effectively indistinguishable from each other. Regarding the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, mba1 artefacts typically have lower $^{207}Pb/^{204}Pb$ than the mba2 and lba artefacts. However due to the low number of samples with ^{204}Pb data these patterns should be viewed with some caution, and with larger sample numbers all three chronological groups may become indistinguishable.

7.3 Artefact heterogeneity

The isotopic inter-artefact variation for the Middle and Late Bronze Age assemblages are significantly lower than that seen in earlier goldwork (Table 7.1). Compared to 13.9‰ on the 207Pb/206Pb in the EBA, variation is a factor of ten lower at 1.1‰ for mba1 (n = 2), 1.9‰ for mba2 (n = 5), and 1.3‰ for lba (n = 9).

Table 7.1: Inter-artefact variability by goldworking assemblage. *represents variation when the four possible EBA gold-copper alloy artefacts are excluded.

	% Copper	% Silver	% Tin	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
EBA	232.1% (85.3%*)	20.5%	126.0%	13.9‰	13.0‰
mba1	11.0%	1.2%	68.2%	1.1‰	1.5‰
mba2	9.7%	3.3%	14.8%	1.9‰	1.9‰
lba	16.7%	7.8%	47.9%	1.3‰	1.1‰

The mean intra-sample variation on the $^{207}Pb/^{206}Pb$ averages 0.09‰ for mba1, 0.15‰ for mba2, and 0.65‰ for lba. These are comparable to 0.79‰ for the EBA artefacts (Table 7.2). The maximum intra-sample variation documented in any of these later artefacts is 1.6‰ for an lba artefact.

Table 7.2: Mean intra-sample variation by goldworking assemblage.

	% Copper	% Silver	% Tin	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
EBA	27.5%	1.2%	60.6%	0.79‰	0.76‰
mba1	10.7%	2.0%	11.3%	0.09‰	0.35‰
mba2	6.5%	4.2%	30.8%	0.15‰	0.08‰
lba	53.9%	13.7%	87.4%	0.65‰	0.56‰

The compositional inter-artefact variation by goldworking assemblage ranges from 1.2% to 7.8% for silver, 9.7% to 16.7% for copper and 14.8% to 68.2% for tin respectively (Table 7.1). In agreement with the isotopic variation, this is noticeably lower than that documented between the EBA artefacts. The mean compositional intra-sample variations for the later goldworking assemblages range from 2.0% to 13.7% for silver, 6.5% to 53.9% for copper and 11.3% to 87.4% for tin respectively. Intra-sample variation can therefore be considered consistent with that documented within the EBA samples. This contrasts with Chapman et al. (2006) who documented greater internal variation of silver and copper in LBA artefacts. This may relate to the lower number of analyses performed per sample in this study.

It must again be stressed that the low number of artefacts analysed from each goldworking assemblage prevents an in-depth discussion, and more artefacts need to be studied to fully characterise both their compositional signature and variation. However based on the current data, there is a clear pattern in both the elemental and isotopic variation. Relative to EBA goldwork, inter-artefact variation is significantly lower (generally by a factor of 10) in MBA and LBA assemblages. The significant drop in inter-artefact variation may suggest a greater control over the circulating gold metal pool.

Chapter 6 concluded that the inter-artefact variation of EBA artefacts reflected the variation of the ore sources under exploitation. If this is still the case, it suggests a shift to a rich, homogenous, source of gold. Whereas the large variation of EBA artefacts has been interpreted as the exploitation of numerous alluvial deposits throughout a compositionally and isotopically variable ore district, the tight clustering in the MBA and LBA would indicate the exploitation of a more homogenous source such as a large bedrock deposit. Primary exploitation of a single large source of gold throughout the MBA and LBA would facilitate greater control over its distribution.

However goldworking technologies had developed since the EBA traditions. The MBA witnessed the introduction of casting techniques, therefore there is greater potential for the homogenisation of alloys; gold would have been in a molten state for longer periods of time during fabrication. The likelihood that the technological processes employed in these later periods could have created a homogenised metal pool is far higher. If the low variability was a product of fabrication rather than the exploitation of a single source, the creation of a homogenous metal pool still suggests a greater degree of control. Rather than control over the gold source (which may still have occurred), it is suggestive of control over the gold supply where small numbers of individuals transformed raw gold into workable ingot form before distribution at centralised production centres. High levels of recycling may also help to create a homogenous signature, however if this signature was derived from a number of sources with distinct isotopic signatures, some samples should represent unmixed compositions. It is therefore likely that MBA and LBA gold was under a greater degree of control, due to either the exploitation of a low number of sources (potentially even a single deposit) or control of the gold supply and its initial transformation from raw material into workable ingot form.

7.4 The isotopic signature of Irish gold in later prehistory

7.4.1 Copper alloying in the MBA and LBA

The elevated copper concentrations of MBA and LBA goldwork are indicative of copper alloying (Warner, 2004; Chapman et al., 2006). This is particularly problematic for lead isotope analysis because the isotopic signature is a product of both the gold and copper sources. The typical copper concentrations of these alloys and the typical lead concentrations of copper and gold respectively suggest approximately 50% of the lead within each artefact is derived from the gold source. Consequently if the isotopic signature of the copper can be characterised with some degree of certainty, corrections can be applied that deduce the isotopic signature of the gold component.

Archaeological evidence for copper exploitation can indicate which deposits were in production at the time of artefact manufacture. This type of evidence was applied in Chapter 6 when discussing four alloyed EBA artefacts; there is widespread evidence for EBA copper exploitation at a number of mines across Ireland (and Britain). Consequently, copper alloying corrections for artefacts dating to earlier stages of the EBA, i.e. the lunulae period, are seen as being reasonably accurate because of the high probability of where copper component was procured (Ross Island). However this certainty decreases in later stages of the EBA as more deposits went into production. Current dating evidence suggests the majority of Irish and British copper mines went out of production towards the end of the EBA. Regarding Ireland, the main phase of exploitation at Ross Island had already ceased c.1800 BC (Northover et al., 2001; O'Brien, 2004), whilst primary exploitation of the Mt Gabriel type deposits dates between c.1800 and 1500 BC (O'Brien, 1994, 2003). The exploitation of Great Orme continued through to the LBA (Dutton and Fasham, 1994), however there is no direct archaeological evidence for the exploitation of any other Irish or British copper source during this period (Ixer and Budd, 1998). Thus when discussing later prehistoric artefacts a new problem arises; it is less clear through archaeological evidence which deposits could have been responsible for the copper alloyed into Irish goldwork.

Without good evidence for which copper sources were being worked at the time of artefact manufacture, mathematical corrections for the input of copper derived lead are extremely difficult. However a second line of evidence exists: the lead isotope signature of contemporary copper or bronze artefacts. The signature of such artefacts indicates the composition of the copper pool during each metalworking phase, with the added benefit that any homogenisation that occurred during fabrication will be taken into account. Unfortunately no widespread database of later Irish metalwork exists, however the signature of contemporary British metalwork has been characterised (Rohl and Needham, 1998). A number of the Irish gold artefact forms are likely to be the product of Irish industries (Eogan, 1994), and there is no guarantee that British and Irish copper/bronzework are characterised by the same lead isotope signature. If a detailed study into the source of MBA and LBA gold is to be attempted, the first step must be to isotopically characterise the copper that was in circulation throughout Ireland at this time. However at present, this British database provides the best proxy for the lead isotope signature of copper alloyed in MBA and LBA Irish goldwork.

The lead isotope signature of British copper/bronzework is heterogeneous. The $^{207}Pb/^{206}Pb$ isotopic variation is 7.9‰ for Taunton metalwork, 6.9‰ for Penard metalwork and 3.7‰ for Ewart metalwork (based on data from Rohl and Needham, 1998). This provides a further hurdle to overcome because if the Irish metal pool is similarly heterogeneous, the signature of the alloyed copper may be consistent with any part of this field. As with the copper corrections applied in Chapter 6, this variability can be taken into account during error propagation. However large variations such as these result in greater uncertainties that may be too large for realistic discussions on the gold source. An interesting aspect of the MBA and LBA Irish goldwork is the very low inter-artefact variability (a maximum variation of 1.9‰ seen between those dating to the LBA). This could be coincidental due to the low number of artefacts analysed in this study, or alternatively may reflect that isotopically homogenous gold and copper sources or metal pools were exploited. Presumably similar fabrication processes were employed for gold and copper working (i.e. melting and casting), therefore homogenisation due to processing techniques would be of a similar level in both industries.

The small number of artefacts analysed from these later assemblages prevents an in depth discussion on the sources of Irish gold in later prehistory, whilst the issue of copper alloying adds further complications and corrections must be applied to negate the isotopic signature of the copper component. In order to apply these corrections accurately the Irish copper pool should first be characterised, however at present data only exist for neighbouring British copper and bronze assemblages. Although the Irish metal pool may have been isotopically distinct, this British data has been used to apply copper corrections to the Irish goldwork because it is currently the best proxy available. As there is no evidence for the exploitation of Irish copper deposits during the MBA and LBA it is likely that at least some copper was entering the country from external sources. Combined with the apparent high isotopic variation of the British copper pool, it is also likely that the isotopic signatures used for the copper components in the following calculations will not be significantly different from the true. As a result, the following discussion is seen as a relatively good starting point for a lead isotope study of later Prehistoric Irish goldwork, at least until the Irish copper pool can be fully characterised. The isotopic signature of both copper and bronzework can be used for these corrections because the signature of bronze primarily reflects that of the copper component. Only small quantities of lead are introduced with the tin thus the isotopic signature of the copper is not significantly altered (Rohl and Needham, 1998).

Each compositional goldworking assemblage will be discussed separately in the following section. The artefact forms are attributed to each assemblage based on their major element composition, however when this is inconsistent with archaeological evidence further considerations will be made. Corrections follow the equations set out in Section 6.5.1. The variation (two standard deviations) of the British metalwork assemblages are propagated into the error calculations, and it is this variation that is the greatest cause of the resulting errors and consequently the greatest obstacle to interpretive discussions.

7.4.2 The lead isotope signature of later prehistoric Irish gold

7.4.2.1 Gold alloy mba1

Irish mba1 goldwork is contemporary with the Taunton metalworking phase of Britain. The lead isotope signature of Taunton bronze/copper artefacts (open black symbols Figure 7.7) from England and Wales define a linear array that could be interpreted as a mix of two principle metal compositions (Rohl and Needham, 1998). However when combined with the impurity patterns of these metals, Rohl and Needham (1998) concluded that there was little interaction between these two groups and the data actually represent two independent metal pools. These two metal groups (defined using elemental impurities and lead isotope signatures) were termed IMP-LI 12 (open black squares Figure 7.7) and IMP-LI 13 (open black circles Figure 7.7). IMP-LI 12 is characterised by a more radiogenic lead isotope signature (^{207}Pb/^{206}Pb = 0.847-0.852, ^{208}Pb/^{206}Pb = 2.079-2.095), whilst IMP-LI 13 is characterised by a less radiogenic lead isotope signature.

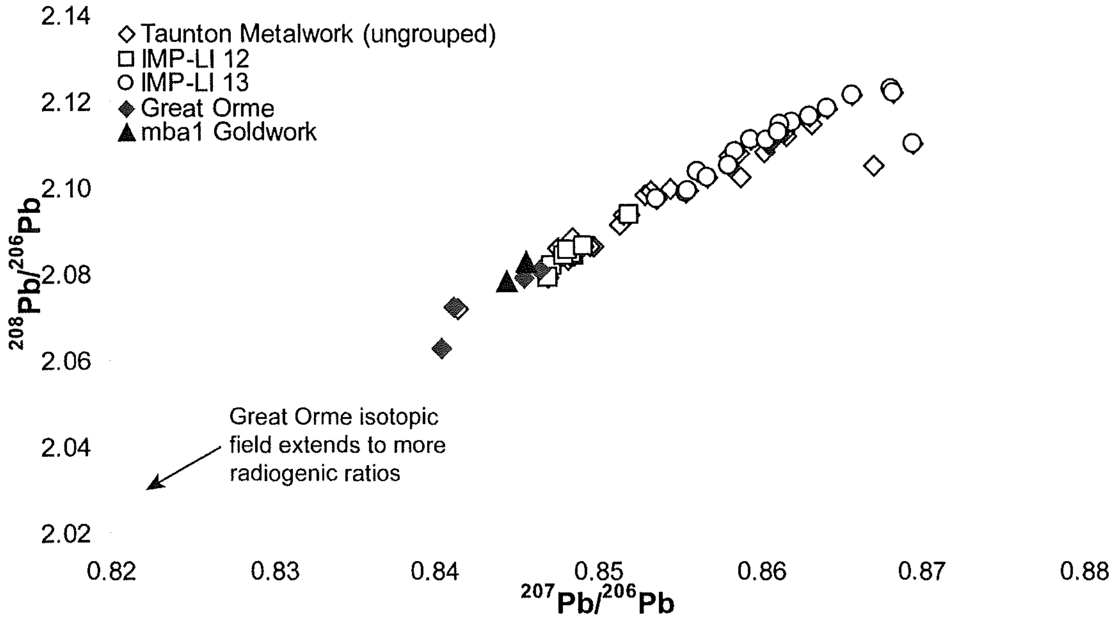


Figure 7.7: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of Taunton metalwork (IMP-LI 12 = open black squares, IMP-LI 13 = open black circles, ungrouped = open black diamonds) from Rohl and Needham (1998) and mba1 goldwork (filled black triangles) analysed in this study. Great Orme copper mineralisation (filled blue diamonds) is also plotted (data from Rohl and Needham, 1998).

The geographic distribution of these two metal groups adds further support to the idea that they represent separate metal pools; IMP-LI 12 artefacts have been found in the north and west of the study region, whilst IMP-LI 13 artefacts have been found in southern Britain only (as far west as Devon). The less radiogenic end of IMP-LI 13 is inconsistent with English and Welsh copper ores, and combined with the southerly distribution a continental origin was proposed. Tight impurity patterns indicated the metal pool had undergone significant mixing, and the variable lead isotope signatures lead the authors to suggest more than one continental source were responsible. IMP-LI 12 is consistent with an English or Welsh origin, and it was proposed that it represents continued exploitation of the same source that was responsible for an earlier compositional metal group (part of the Acton metalworking assemblage); the composition of metal originating from the same location can change over time as different deposits were exploited (Rohl and Needham, 1998). Great Orme (closed blue diamonds Figure 7.7) was seen as the most likely source deposit, a theory that is supported by archaeological evidence that dates the continued exploitation of this source into this period (Dutton and Fasham, 1994). The geographic position of Ireland would suggest that out of these two metal groups, IMP-LI 12 is more likely to have been consumed by local metalworking industries.

There are a number of possible sources for the copper alloyed in mba1 goldwork. An input from Ross Island and/or the Mt Gabriel type mines (through recycling) must be considered, whilst the composition of the British IMP-LI 12 metal group highlights Great Orme as a further potential source. It is interesting to note that the isotopic variation of IMP-LI 12 is significantly lower than that of the Great Orme copper mineralisation (1.1‰ compared to 46.8‰ based on data from Rohl and Needham, 1998), therefore if an association between the two is correct, significant homogenisation has occurred during fabrication with a bias towards the less radiogenic end of the Great Orme isotopic field. If the copper alloyed with mba1 goldwork underwent similar homogenisation, then using the signature of the metal pool rather than the ore deposit would significantly reduce the uncertainty on the corrected isotopic ratios thus aiding data interpretation.

The two analysed mba1 gold artefacts are also plotted in Figure 7.7. It is apparent that they are characterised by similar isotopic signatures to the Taunton metalwork, and plot at one end of the Taunton isotopic field. If this British metalwork is an accurate representation of the Irish copper supply, then it suggests that the gold and copper originated from isotopically similar ore fields. Copper corrections were applied to the mba1 artefact data (as set out in section 6.5.1), with the signature of IMP-LI 12 used as a proxy for the composition of the copper component. The corrected ratios (Appendix C2), currently the best indication of the signature of mba1 gold, are presented in Figure 7.8. They plot within the EBA artefact isotopic field and are therefore consistent with exploitation of the same gold source. This is in agreement with the view of Warner (2004) and Chapman et al. (2006) who reached the same conclusion based on the similarities in the silver concentrations of EBA and mba1 artefacts. The proximity of the two corrected artefacts to the possible EBA mixing cluster also suggests continued use of the same EBA source or sources (potentially through recycling). If there was a significant input from new isotopically distinct gold sources then the mean artefact signature would shift away from this field.

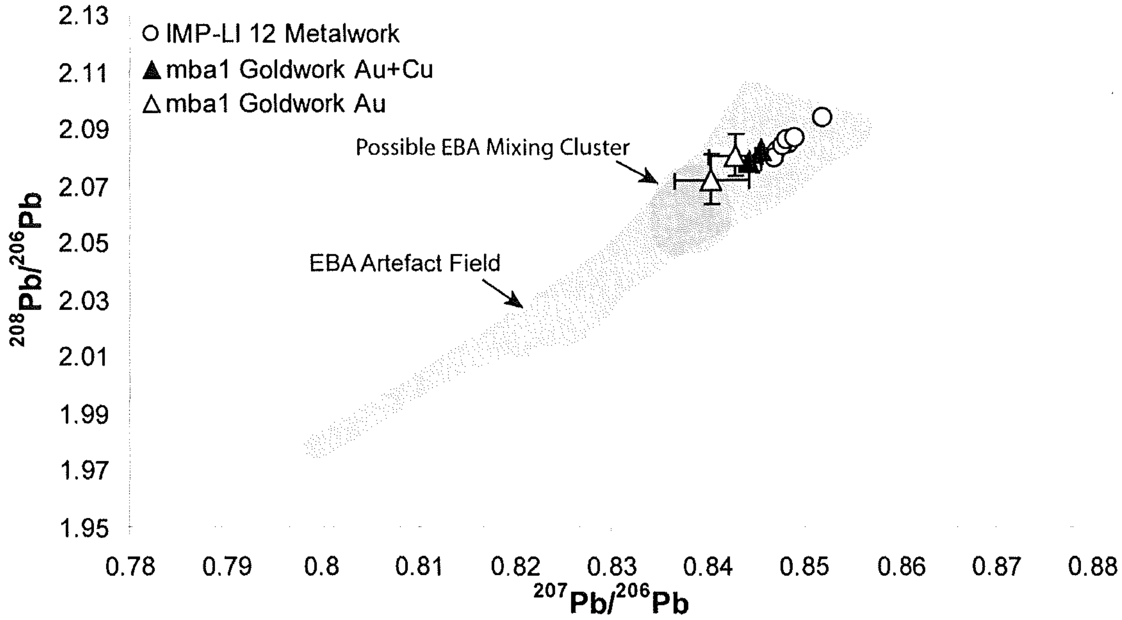


Figure 7.8: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of copper corrected mba1 Irish goldwork (open black triangles). Corrections used IMP-LI 12 Taunton metalwork (open black circle, data from (Rohl and Needham, 1998) as a proxy for the signature of the copper component. The uncorrected mba1 ratios are also plotted (filled black triangles) along with the isotopic field of EBA Irish artefacts and the possible EBA mixing cluster.

Due to the similarities between the isotopic signatures of the uncorrected mba1 artefacts and the EBA copper alloyed goldwork, it is also possible to say that Ross Island copper would result in the mba1 gold plotting in a similar location within the EBA artefact field. Regarding Mt Gabriel, the high isotopic variation of the deposit would result in large errors with limited use to provenance studies. If Mt Gabriel copper was still in circulation at this time, characterising the metal pool would clearly be advantageous.

One of the mba1 artefacts analysed was a flange-twisted torc (R1680, Co. Down). The geographical distribution of this artefact type is focussed on Britain, with significant numbers also found in Ireland (Waddell, 1998). Although Eogan (1994) sees continental stimulation for the MBA Irish and British traditions, it would appear that this external influence resulted in the exploitation of more local gold deposits to supply local goldworking traditions. It should be stressed that interpretations based on two artefacts are preliminary in the extreme, however it is possible to state that these two artefacts are consistent with continued exploitation of the EBA gold source and there is no evidence for a significant shift in the pattern of gold procurement.

7.4.2.2 Gold alloy mba2

The only evidence for copper exploitation in Britain or Ireland contemporary with mba2 Irish goldwork comes from the Great Orme (Dutton and Fasham, 1994; for a summary of radiocarbon dates see Ixer and Budd, 1998). This is contemporary with the Penard metalworking phase of Britain (open black circles Figure 7.9), which is characterised by a similar lead isotope signature to that of the preceding Taunton phase (grey domain Figure 7.9; Rohl and Needham, 1998).

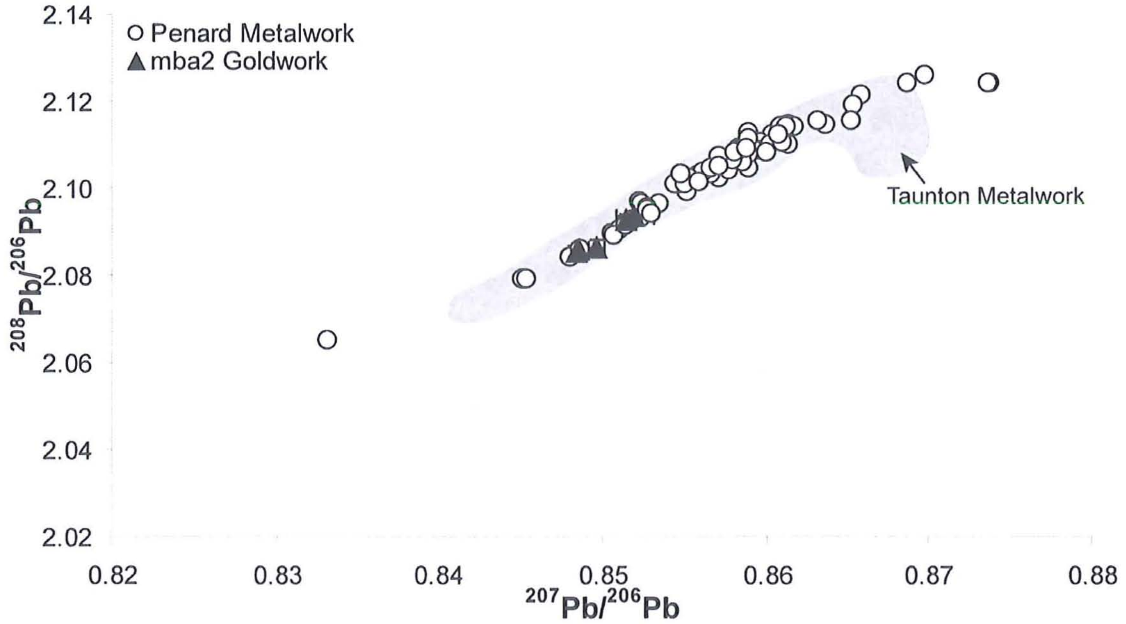


Figure 7.9: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of Penard metalwork (open black circle) from Rohl and Needham (1998) and mba2 goldwork (filled black triangles) analysed in this study. Grey domain represents isotopic signature of preceding Taunton metalwork.

Rohl and Needham (1998) defined metal group IMP-LI 14, characterised by a variable lead isotope signature ($^{207}Pb/^{206}Pb = 0.848$-$0.866$, $^{208}Pb/^{206}Pb = 2.085$-$2.122$). It was suggested that this was a modified version of IMP-LI 13. The difference from the earlier metal group was attributed to possible further influxes of continental copper (the less radiogenic end of the isotopic field), however fresh supplies or inherited stock would also be required to account for those artefacts that are consistent with British deposits (the more radiogenic end of the data field). North-west England was identified as a potential source region (deposits such as Alderley Edge, or those in the Pennines or the Isle of Man), whilst Great Orme is clearly a potential source based on the archaeological dating evidence.

IMP-LI 15 was recognised through the analysis of late Penard swords. Its lead isotope signature falls within the field of IMP-LI 14 ($^{207}Pb/^{206}Pb$ = 0.852-0.862, $^{208}Pb/^{206}Pb$ = 2.092-2.112), yet it is distinguishable by its impurity composition (Rohl and Needham, 1998). This metal is also characterised by an increase in its lead concentration (up to 1%), which may reflect deliberate alloying. If this is the case, further complications would be added to attempts to calculate the signature of the gold component as the lead isotope signature would primarily reflect the lead source. Which copper sources were responsible for these metals is not clear. Rohl and Needham (1998) discussed the potential for an Alpine origin, however this was found to be inconsistent with some impurity patterns. The potential for a more local origin, such as central Wales, was also highlighted.

In a similar fashion to the mba1 artefacts, mba2 goldwork plot at the less radiogenic end of the copper/bronzework field (filled black triangles Figure 7.9 and Figure 7.10). Similar deductions can therefore be made; the gold and copper are likely to have originated from isotopically similar ore fields. Figure 7.10 plots copper corrected isotopic ratios (Appendix C2) for the mba2 artefacts (open black triangles), where the signature of Penard metalwork was used as a proxy for the copper component of the artefacts.

Although the uncertainties on these correction are now much larger (due to the large isotopic variation of Penard metalwork), the corrected ratios are again consistent with the EBA artefact fields and are indistinguishable from the copper corrected mba1 goldwork. This suggests that the gold deposits exploited during the later Bishopsland phase remained in the same isotopic ore field, an interesting development considering the compositional difference between the mba1 and mba2 goldwork. Due to the deliberate addition of copper (and potentially tin) silver is the only major element that can be used to help distinguish between different alloys during this period, and mba2 goldwork is characterised by significantly higher silver concentrations. In this study, the mean silver concentration increased from 11.7% in mba1 goldwork to 17.5% in mba2 goldwork, and this is consistent other compositional studies that investigated far greater numbers of artefacts (Warner, 2004; Warner and Cahill, in press). Assuming this silver does not reflect deliberate alloying, the documented increase is seen to represent the exploitation of a new silver rich source (Warner, 2004; Chapman et al., 2006). Isotopic data therefore suggests that this new silver rich deposit was located within the same ore field. Based on the current data, there is again no evidence for a significant shift in the location of the principle Bronze Age gold sources.

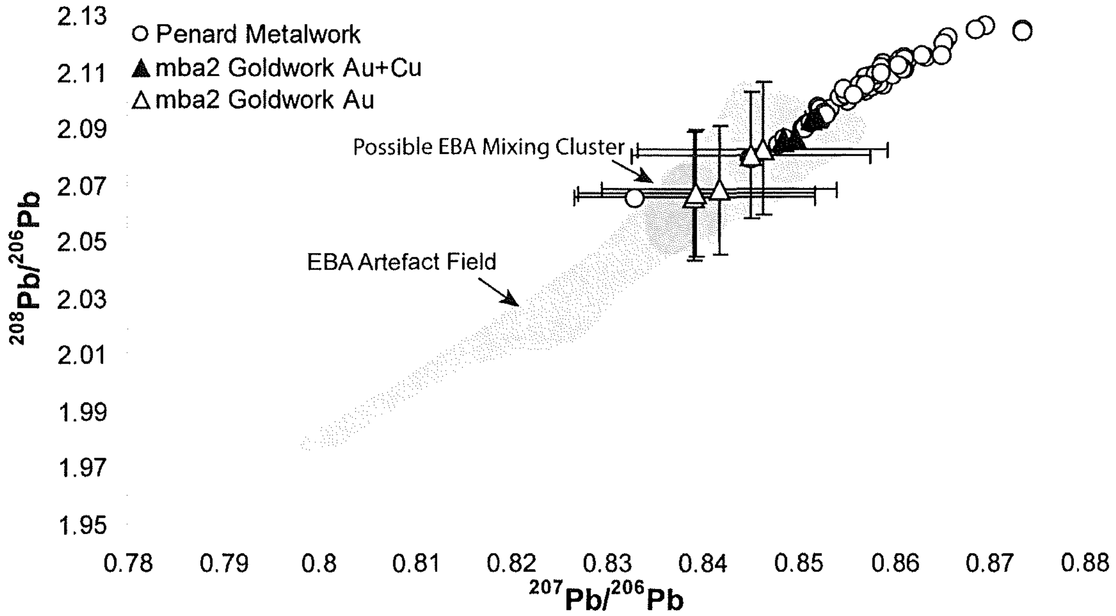


Figure 7.10: $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ plot of copper corrected mba2 Irish goldwork (open black triangles). Corrections used Penard metalwork (open black circle, data from (Rohl and Needham, 1998) as a proxy for the signature of the copper component. The uncorrected MBA2 ratios are also plotted (filled black triangles) along with the isotopic field of EBA Irish artefacts and the possible EBA mixing cluster.

7.5.2.3 Gold alloy lba

The Irish lba goldworking tradition is contemporary with the Ewart metalworking assemblage of Britain. Copper and bronzework from this assemblage demonstrates a variable compositional signature (open black circles Figure 7.11) and a number of metal groups were identified by Rohl and Needham (1998); IMP-LI 19, 20, 21, 22a, 22b, and 22c. IMP-LI 19 is inconsistent with an English or Welsh source, and was linked to the Middle Rhine region, whilst an association between IMP-LI 21 and the Alderley Edge copper deposits was also discussed.

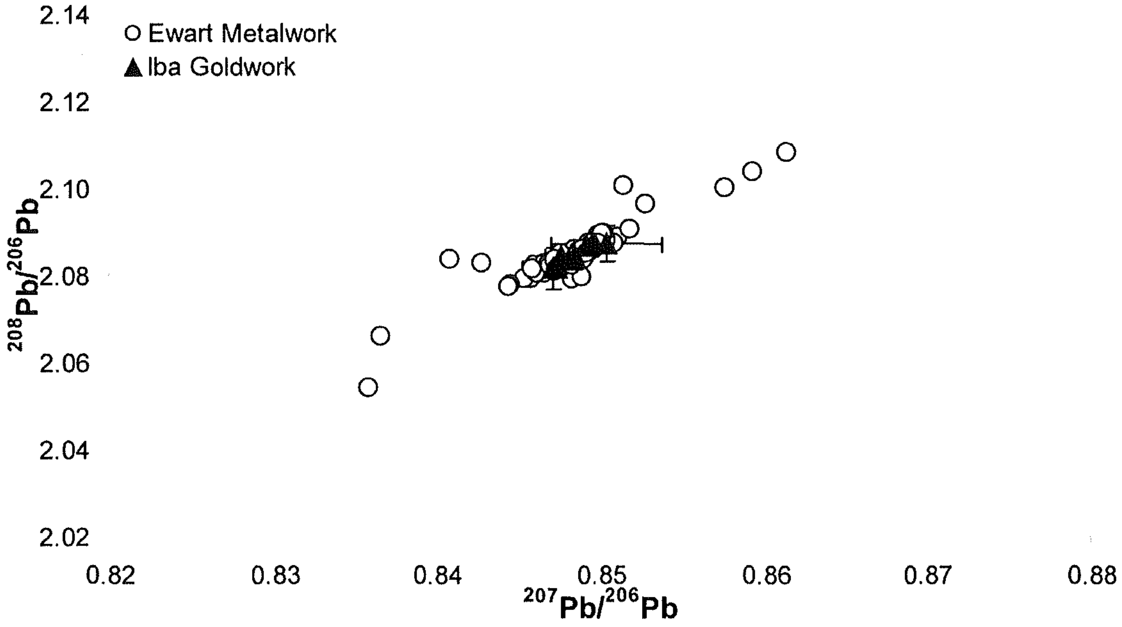


Figure 7.11: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of Ewart metalwork (open black circle) from Rohl and Needham (1998) and lba goldwork (filled black triangles) analysed in this study.

The isotopic signature of the Ewart assemblage is complicated. Numerous sources, both local and continental, contributed to the copper supply along with significant inputs from the pre-existing metal pool. Furthermore, a number of bronze artefacts demonstrate deliberate addition of lead (Rohl and Needham, 1998) thus making them poor indicators for the signature of copper. The isotopic signatures of lba Irish goldwork plot as a cluster, supporting Warner's (2004) view that the artefacts represent one industry. The (uncorrected) ratios are consistent with the main cluster of Ewart metalwork, therefore the potential that this reflects the practise of alloying lead must be considered. However this can be discounted based on the lead intensities during laser ablation analysis; the mean voltage on ^{208}Pb for the lba artefacts was 0.15 V compared to 0.16 V for EBA artefacts, 0.17 V for mba1 artefacts and 0.21 V for mba2 artefacts. As the leaded Ewart copper/bronzework is isotopically consistent with the unleaded varieties, the entire isotopic field was again used to apply copper corrections to the lba goldwork data (Figure 7.12).

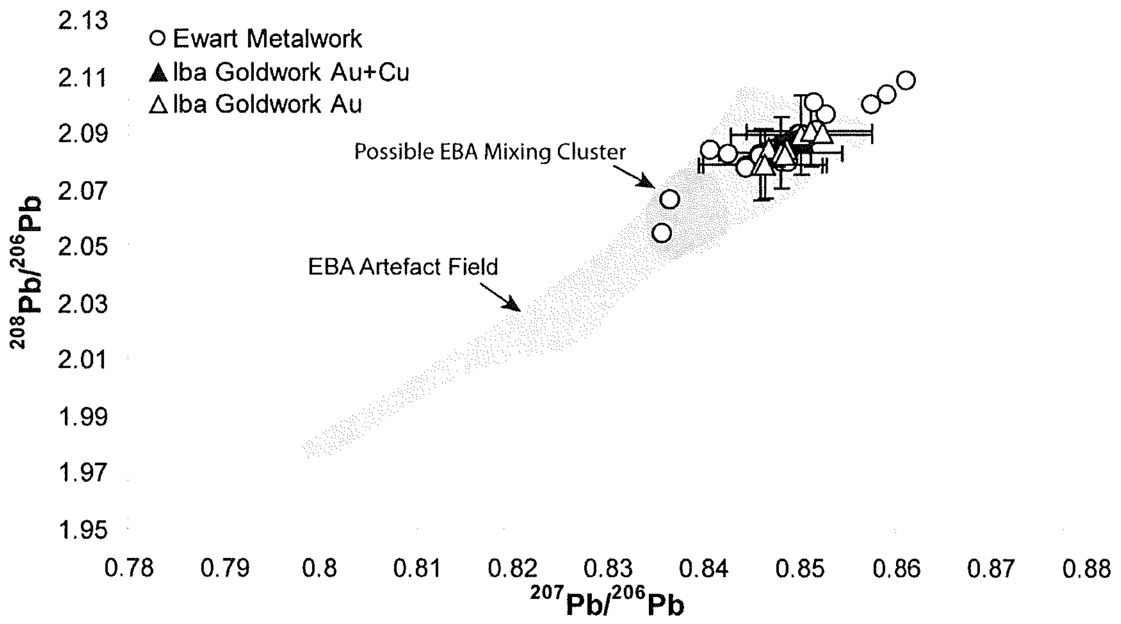


Figure 7.12: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot of copper corrected lba Irish goldwork (open black triangles). Corrections used Ewart metalwork (open black circle, data from (Rohl and Needham, 1998) as a proxy for the signature of the copper component. The uncorrected lba ratios are also plotted (filled black triangles) along with the isotopic field of EBA Irish artefacts and the possible EBA mixing cluster.

Due to the similarity between the Ewart metalwork (open black circles Figure 7.12) and the uncorrected lba goldwork (filled black triangles Figure 7.12), the corrected ratios (open black triangles, Figure 7.12, Appendix C2) do not significantly change. As with previous assemblages, they are consistent with the less radiogenic end of the EBA artefact field suggesting either the same ore field or a new yet isotopically similar ore field was under exploitation. With the analysis of ten lba artefacts, it is noticeable that the mean isotopic signature has shifted towards the less radiogenic end of the EBA artefact field. This is likely to indicate some degree of input from new gold sources. If all the lba gold originated from the same source exploited during the EBA, the mean lba artefact signature should be consistent with the mean EBA artefact signature. On the contrary, all the artefacts occupy the less radiogenic end of the EBA field therefore significant inputs from less radiogenic sources can be postulated.

When interpreting the less radiogenic signature of certain copper/bronze artefacts, Rohl and Needham (1998) often discussed inputs from continental sources. Although this may also be the case for the lba goldwork, a different explanation can also be presented; the exploitation of a gold source that incorporated lead from the north-west terrane

(NWT) of Britain or Ireland. As Chapter 5 demonstrated, gold deposits situated in the NWT, i.e. located in the north of Ireland such as those in the Sperrin Mountains or Co. Mayo, exhibit less radiogenic isotopic signatures. Exploitation of Irish (or Scottish) gold deposits is therefore a possibility. Incidentally, Chapman et al. (2006) demonstrated that both the Sperrin Mountains and Co. Mayo contain gold deposits that are consistent with the silver composition of lba artefacts, and also hypothesised the exploitation of a gold source located in the north of Ireland during the LBA. Numerous lba gold artefact types are either unique to Ireland with no clear typological forerunners suggesting insular development, or have an Irish-centric distribution (Eogan, 1994; Waddell, 1998). This highlights the presence of important goldworking industries, and the exploitation of a new, local, gold source is conceivable.

Goldwork discovered in two hoards near Downpatrick, Co. Down, have recently been discussed by Warner and Cahill (in press). One of these hoards (hoard 1) contained eleven LBA bracelets accompanied by a neck-ring of probable Iberian origin. This neck-ring and one of the bracelets are incomplete. The core composition of the Irish style bracelets matches that typical for other Irish lba goldwork, however the surface of a number of these artefacts displayed a different compositional signature altogether. This surface composition matched that of the possible Iberian imports, therefore deliberate coating of recycled (non-Irish) goldwork was favoured. Warner and Cahill (in press) prefer an MBA date for the neck-ring and although this age is not universally accepted, its incomplete form and composition suggests it was being recycled for the manufacture of new artefacts. Two of the Irish style bracelets were analysed in this study (AD1.2 and AD1.5). According to Warner and Cahill (in press), AD1.5 consists of a lba metal core with a surface of the recycled alloy, whilst AD1.2 consists of the recycled alloy at both surface and sub surface level. The elemental composition of the two samples analysed in this study are consistent with other lba Irish goldwork, and this is in agreement with data collected by Chapman et al. (2006). It is unclear where on the artefacts these samples were taken from, but as they underwent polishing prior to analysis, they are most likely to represent the composition of the artefact cores. It can therefore be said that the core composition of bracelet AD1.2 is also of lba composition (Warner pers. comm.). This fits with the isotopic analysis; both bracelets are consistent with the other Irish lba goldwork. If either sample was manufactured from recycled Iberian gold, an isotopic signature distinct from other Irish LBA goldwork might be expected.

Three penannular rings were analysed in this study (A210.1913 Belfast, 1929.1302 Kilmallock, 1935.879 Ballina). This artefact form is problematic because they are compositionally consistent with mba2 goldwork, however they are traditionally dated to the lba goldworking tradition (Warner, 2004). In this discussion they were included with other mba2 artefacts of similar composition, however isotopic analysis highlights that these two groups are indistinguishable before copper corrections are applied (Figure 7.4). If these artefacts do in fact date to the LBA, then their apparently distinct silver compositions could represent the exploitation of multiple gold deposits located within the same ore field. Chapter 6 discussed the heterogeneous nature of the Cornish ore field; the median silver concentrations of eight alluvial populations and one vein mineralisation ranged from 3.8% to 33% (Ehser et al., 2011). Therefore it is possible that gold deposits located geographically close to each other can have very different elemental compositions. As a result, the penannular rings could be the product of an LBA high silver source. Although there is a lack of goldworking between the Late Bishopsland (mba2) and the Dowris-A (lba) traditions, it is possible that the two merged together during the Roscommon period (see Section 2.3.1.5). Continued exploitation of the same high silver source from the Late Bishopsland phase is therefore a possibility. After copper corrections are applied, artefacts from the two compositional groups plot consistent with the less radiogenic end of the EBA artefact field. By correcting the penannular rings with Ewart rather than Penard metalwork, the corrected signatures would not significantly change. Exploitation of the same isotopic ore field during both the mba2 and lba periods of production is likely.

7.5 A lead isotope investigation of later prehistoric gold sources?

This preliminary study into the lead isotope signature or MBA and LBA Irish gold artefacts can not result in the level of discussion achieved for EBA goldwork. The practice of alloying with copper is a constant issue, and corrections for lead introduced into the artefact alloys with this copper component are a necessity. The lack of archaeological evidence for the exploitation of local copper deposits during later prehistory means that the source of the alloyed copper is unclear. This prevents corrections using isotopic data from specific copper deposits as applied in Chapter 6. The signature of contemporary copper/bronzework is therefore the best means of characterising the copper component of these artefacts because it indicates the composition of the copper in circulation. This takes into account any homogenisation that may have occurred during the processing of copper or bronze; both homogenisation of a single variable deposit and of multiple discreet deposits. At present there is no lead isotope database of Irish MBA or LBA copper/bronze artefacts. Isotopically characterising such material is an essential first step before an in depth lead isotope study of later prehistoric Irish goldwork can be attempted.

Even with a fully characterised Irish copper pool, success is not guaranteed. If this pool demonstrates high variation (such as the Penard metalwork discussed above), the copper component of any single gold artefact may be consistent with any part of this field. As a result, the variation must be taken into account during error propagation. Large variations within the copper supply may make attempts at correcting the analysed artefact signatures meaningless; there is no use in a corrected ratio with errors so large that the gold component could have originated from any deposit. However the above attempts indicate that the variation should be homogenous enough to allow the identification of broader patterns. Consequently, it is likely that conclusions regarding the procurement of gold would be possible. It should also be stressed that copper corrections must be applied with care. The likely production regions of particular artefact types must be taken into account; it would be inappropriate to use the signature of copper pools from one region to correct for alloying if the artefacts in question were manufactured elsewhere.

Characterising artefacts isotopically can still inform on the patterns of gold consumption even if copper corrections are not feasible. Information regarding the circulation of metal pools, the degree of supply control and the technological processes employed may all be obtainable. As a result, a more in depth study of later prehistoric artefacts does have potential, although admittedly this would be far greater if corrections for copper alloying are deemed possible. Future advances in analytical techniques may also aid this line of research.

7.6 Gold exploitation in the Middle and Late Bronze Age

Chapter 6 presented data that cast doubt over the exploitation of an EBA Irish gold source, with south-west England and Wales highlighted as potential source regions. The major element composition of Irish and British EBA artefacts are indistinguishable, thus it is likely that the same sources of gold were exploited for the manufacture of all. The key British goldworking traditions of the EBA (Wessex linear, Scottish hilt band and embossed) are chronologically later than those in Ireland, therefore a potential shift in influence over the principle EBA gold sources was discussed. It was also hypothesised that EBA gold procurement was relatively uncontrolled, with an absence of centralised production centres and the gold supply originating from numerous alluvial deposits in a large ore district. As the Irish EBA goldworking traditions came to a close, a hiatus in production ensued. British goldworking such as the Wessex linear and Scottish hilt band traditions were never as large as the Irish lunulae tradition in terms of artefact numbers and weight of gold used, whilst EBA embossed goldworking produced few artefacts albeit from significant quantities of gold. If the recovery pattern of EBA goldwork is representative of the numbers in circulation throughout the period, then it suggests a general reduction in goldworking towards the end of the EBA.

Significant goldworking traditions did not return to Ireland until the Early Bishopsland phase of the MBA. The limited dataset produced here suggests that Irish MBA and LBA goldwork are characterised by similar lead isotope signatures. Artefacts manufactured from mba2 and lba gold alloys are indistinguishable from each other, whilst those consisting of mba1 alloy are characterised by slightly lower ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb and ^{207}Pb/^{204}Pb. Each gold alloy group (typically seen to reflect chronological stages) demonstrate low inter-artefact variability. This suggests increased control over the deployment and circulation of gold relative to the EBA, either through the exploitation of a rich homogenous gold deposit or greater control over the gold supply; if multiple sources were responsible, fabrication of raw material into transferable form must have been centralised to create such homogeneity in the metal stock.

It therefore appears that relatively uncontrolled EBA gold exploitation and a late EBA decline in gold production were followed by the growth of centralised goldworking industries during the MBA. This mirrors the patterns of copper exploitation elsewhere in Europe (Shennan, 1993; Chapman, 2008). The commodification of metal and intensification of goods exchange are seen as critical aspects of increasingly complex Bronze Age societies (Kristiansen and Larsson, 2005) and control over economic resources is a potential source of power (Mann, 1986) for the elites that appeared during this period. The significant differences in gold procurement and control identified between the EBA and MBA goldworking traditions could therefore help to explain the increasingly stratified societies that began to emerge towards the end of the Bronze Age. As these new social structures formed, the role gold played in society may have changed. Whereas Irish goldwork of the EBA was dominated by the lunulae with their possible ceremonial purpose, the MBA witnessed the appearance of a more diverse range of artefacts better suited to personal adornment. This could be evidence for a shift from gold as an expression of the supernatural, to gold as an expression of personal status, and thus this material became a commodity that could be controlled for achieving economic wealth.

Attempts to apply copper alloy corrections to the isotopic signatures of these gold-copper alloys have been made, however efforts were problematic because the isotopic signature of the Irish copper supply is poorly constrained. The signature of contemporary British copper/bronze work is currently the best proxy for the signature of the alloyed copper, therefore corrections were applied using data published by Rohl and Needham (1998). Although this is clearly not satisfactory it does allow a preliminary assessment of the signature of later prehistoric Irish gold, and it is unlikely that the Irish copper pool was significantly different to the British. As stated previously, if a full study of later artefacts is to be carried out then the signature of contemporary Irish copper must first be characterised.

Artefacts that date to the Early Bishopsland phase were manufactured using gold alloy mba1 (B-gold). Two analysed mba1 artefacts have been corrected for their copper component using the isotopic signature of IMP-LI 12 (Taunton) metalwork. They plot within the EBA artefact field and proximal to the possible EBA artefact mixing cluster. In conjunction with their major element composition they are consistent with the exploitation of the same EBA gold source. This would suggest a further realignment in the trade and exchange of this apparently major gold source with a return to supplying Irish industries, and there is as yet no evidence for a significant input from a new ore field.

The Irish goldworking industry continued to grow during the Late Bishopsland phase of the MBA, and goldwork was dominated by alloy mba2 (F-gold). Artefacts of this composition were copper corrected using the signature of Penard metalwork, and the corrected ratios are also consistent with the EBA artefact field (although large errors restrict more detailed discussions regarding where in this field they plot). Compositional data suggests a switch to a new high silver gold source (mean silver concentration of 17.47%), however it would appear that a significant source of this alloy must have remained in the same isotopic ore field or coincidentally be located in a new ore field characterised by the same isotopic signature. It should be remembered that some EBA artefacts contained up to 17.06% silver, therefore natural gold comparable to the mba2 alloy had already been exploited. There is some question as to whether the penannular rings should really be corrected using Penard metalwork due to their possible LBA date, however this would not change the overall pattern of the remaining mba2 artefacts.

Irish Bronze Age goldworking peaked during the Dowris-A phase of the LBA. Artefacts dating to this period (lba alloy composition) were copper corrected using Ewart metalwork and are again consistent with the EBA artefact field suggesting some degree of input from the same source as previous periods. However with ten artefacts analysed, a significant shift in the mean isotopic composition is apparent. The isotopic mean of the lba artefacts has moved away from that of the EBA artefact domain towards a less radiogenic composition, suggesting a significant input of gold originating from a different isotopic ore field had entered the Irish gold supply. Continental deposits may have been responsible, however sources in the NWT of Ireland or Scotland is another explanation. Chapman et al. (2006) also proposed an LBA gold source in the north of Ireland, and with the high number of gold artefacts in both Britain and Ireland during the MBA and LBA suggesting sufficient amounts of raw material was available to support local goldworking industries (Eogan, 1994), this is considered a plausible theory. Of course a more in depth study is required to develop this theory further, however if true this change in gold procurement could finally reflect the depletion of a major Bronze Age gold source. The exploitation of new sources is consistent with a shift in the role of gold towards expressions of personal status; new sources were actively sought, and increased demand lead to the control of procurement and/or deployment as a source of power.

Current evidence therefore suggests the continued exploitation of gold deposits within the same isotopic ore field throughout the entire Bronze Age. Whilst compositional data indicates the predominance of different gold deposits at different stages throughout this period (resulting in the alloy groups previously discussed), their isotopic similarities imply they were located within the same region. The earliest evidence for a significant shift in gold procurement is currently visible in the lba assemblage through the input from a less radiogenic gold deposit, however this interpretation is liable to change if larger numbers of artefacts were to be analysed in a full study of these assemblages.

What is clear is the apparent long lasting significance of the ore field responsible for the EBA goldworking industries. After its focus shifted away from Ireland during the middle of the EBA, it apparently returned to supply new Irish goldworking industries to some degree throughout the MBA and LBA.

Archaeological evidence for the expansion of Irish goldworking industries during the MBA and LBA is clear. These periods witnessed a major diversification in artefact forms and an increase in the amount of gold in circulation; widespread consumption indicates that it must have remained a prized possession. The larger quantity of gold in circulation suggests that the accessibility of this material should have been greater, thus diminishing its exotic quality. Although the apparent increase in its control could have helped to negate this effect, it is likely that the changes in how the material was procured and distributed would have led to new connotations and a transformed role in society. Current isotopic data for MBA and LBA Irish goldwork is insufficient for a true understanding of the procurement of gold in later prehistory. However the discussion presented here suggests that an in depth lead isotope investigation combined with pre-existing compositional studies could help to shed more light on the patterns of gold exploitation in later prehistory.

Chapter 8: Conclusions and Future Work

8.1 Conclusions

Recognising the source locations of Bronze Age exotic materials is crucial for understanding the controls of their procurement, trade and exchange, and could help to explain the increasingly complex societies that formed during this period. Significant quantities of Bronze Age gold artefacts have been discovered in Ireland, however the procurement of the raw material exploited by these industries is poorly understood. Recent investigations studying the elemental composition of Irish goldwork have highlighted the Mourne Mountains of Northern Ireland as the most likely Irish source of Irish EBA gold (Warner et al., 2009, 2010a, 2010b), yet doubts over the capability of these deposits to account for the quantity of gold consumed by this goldworking industry remain (Meighan, 2011). Consequently, the development and application of a new analytical technique independent from elemental characterisation to investigate the source of Irish Bronze Age gold was desired, and the first lead isotope provenance study of Chalcolithic and Bronze Age gold has been performed.

New methodologies permitting the analysis of lead isotopes in gold using solution and laser ablation multi-collector inductively-coupled plasma mass-spectrometry were developed (Chapter 4). Solution analysis followed the isolation of lead using a two-stage ion exchange chromatography methodology, and repeat analyses of gold reference materials achieved an external precision of <150 ppm for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb and <250 ppm for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb. Laser ablation analyses yielded an external precision of <600 ppm for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb. The external precision for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb is significantly lower at <1640 ppm when ^{204}(Pb+Hg)/^{202}Hg is >1 due to the low abundance of ^{204}Pb and the isobaric interference of mercury (Hg).

An essential aspect of any provenance study is a compositional database of possible ore sources and an understanding of the degree to which different source deposits or regions can be distinguished. With the focus of this study on Irish goldwork and the perceived likelihood of an Irish source, the creation of a database of Irish gold deposits was required. Consequently, Chapter 5 presented lead isotope data for 109 gold samples originating from 31 Irish gold deposits. The lead isotopic signature of Irish gold is variable, and gold deposits can be distinguished on a regional scale. An understanding of what created these variations was achieved, therefore allowing un-analysed Irish gold deposits to be taken into account.

Two principle sources of lead were incorporated into Irish gold mineralisation: a less radiogenic source of mantle and lower continental crustal derivation located within the north-west terrane, and a radiogenic upper continental crust source located within the south-west terrane. Localised minor sources are also inferred, whilst an additional upper crustal lead was incorporated into a number of gold deposits and is thought to relate to Late Caledonian intrusives. Gold deposits can therefore be distinguished on a regional scale because they mineralised at different stages of geological time (Early Caledonian, Late Caledonian, and Variscan), and incorporated lead from the aforementioned reservoirs to varying degrees.

Fifty-two samples from 50 Chalcolithic and EBA gold artefacts were characterised for their lead isotope signature, major element composition, and mineral inclusion suite (Chapter 6). The majority of the Chalcolithic and EBA artefacts have lead isotope signatures consistent with an Irish source, with the deposits of Co. Waterford providing the only satisfactory correlation. These gold deposits are however inconsistent with the major element composition of the artefact alloys; silver and copper concentrations are too low and a lack of cassiterite in the panned heavy mineral fractions results in the tin concentration of the artefacts remaining unexplained. As a result, no analysed Irish gold deposit is consistent with the Chalcolithic and EBA artefacts when both the lead isotope signature and major element composition are considered.

The potential that an undiscovered or unanalysed Irish source was exploited was also considered. When the artefacts are interpreted as geological samples, their lead isotope signature allows a source with a significant NWT lead input or Early Caledonian age to be ruled out. The signatures suggests the exploitation of SET hosted gold deposits characterised by Late Caledonian or younger source ages, along with a further input of radiogenic upper crustal lead potentially related to intrusives. This in essence requires a source in southern Ireland. The majority of gold deposits hosted by the Leinster Massif of south-east Ireland have an Early Caledonian primary source age and are typically characterised by low silver concentrations, therefore the Chalcolithic and EBA sources are unlikely to be located in this region unless a novel style of gold mineralisation is present. Old Red Sandstone (ORS) hosted Variscan copper mineralisation of south-west

Ireland is characterised by a lead isotope signature that is generally consistent with the Chalcolithic and EBA artefact field; lead is primarily sourced from the SET lead reservoir whilst an additional radiogenic upper crustal input inherited from the S-type granites of Leinster was also incorporated. The ORS hosted Variscan ore field of south-west Ireland is therefore the most likely location for a Chalcolithic or EBA Irish gold source. However this is considered unlikely based on current evidence for gold mineralisation in the region. Gold mineralisation is rare and of limited significance, whilst no noteworthy alluvial sources with associated cassiterite are known. Consequently until further evidence for significant gold mineralisation in this region is found, this hypothesis is considered doubtful.

The inability to identify a gold source in Ireland that is consistent with the artefacts for both their isotopic and elemental compositions meant that a non-Irish source had to be considered. A number of European mining regions were explored based on archaeological associations with the Chalcolithic and EBA goldwork. The lead isotope signature of copper sulphides from south-west Britain provided the best match to the artefact signatures, in fact the Cornish ore field was consistent with all but one of the gold artefacts. This highlighted Britain as a potential source region, and subsequently a preliminary study of six British gold deposits was performed. As would be expected, two Scottish gold deposits are consistent with a significant NWT lead source; the Iapetus suture runs approximately below the present day political boundary of England and Scotland. This suggests the Chalcolithic and EBA gold source is unlikely to be located in Scotland. One gold deposit from Wales and three from south-west England were consistent with a SET origin, and subsequently are also consistent with the artefact gold. The SET of Britain is therefore considered to be the most likely source region of Chalcolithic and EBA gold outside of Ireland.

Based on the presently available data, the gold sources of south-west England appear to have the most potential. Chalcolithic and EBA goldwork is rare in Wales, especially during the earlier period (i.e. contemporary with the primary goldwork and lunulae traditions). Additionally there is no current evidence to suggest that Welsh mineral deposits containing gold were ever exploited during the Bronze Age, and the principle period of the Welsh Bronze Age copper mining industry did not begin until c.1900 BC. Conversely the four Cornish lunulae represent a significant concentration of EBA goldwork, and Cornish tin deposits were exploited throughout the Bronze Age. Many of these alluvial deposits are known to contain gold, therefore the simultaneous exploitation of gold and tin appears likely. In fact it is more difficult to explain how some degree of Cornish gold did not enter the Chalcolithic and EBA metal pool. Combined with the consistency with Cornubian copper mineralisation lead isotope field, and the signatures of the three south-western gold deposits analysed in this study, the potential that the principle source of Chalcolithic and EBA gold was located in south-west England is clear. This is further supported by the compositional range of Cornish gold as presented by Ehser et al. (2011). Only lunulae W8/R135 is inconsistent with the current Cornubian field, and at present it does not match with the isotopic signatures of any gold bearing region data sets considered in this study.

Thus the currently favoured hypothesis is that the principle source of Irish Chalcolithic and EBA gold lies outside Ireland, with its most likely location in southern Britain. This conclusion is consistent with the wider patterns of exotic material consumption that existed during the Chalcolithic and EBA. Foreign sources were often preferred over local ones, as has been demonstrated in studies regarding amber and jet (Beck and Shennan, 1991, Sheridan et al., 2002). Numerous societies associate exotic materials, in particularly gold, with supernatural and cosmological powers. Irish lunulae are typically deposited as isolated finds in uncontexted deposits (Taylor, 1980, Eogan, 1994) and evidence exists for both long term curation and prolonged life histories (Cahill, 2006). Roles within communal ceremonies or customs can therefore be deemed likely, with the depositional practices interpreted as local traditions relating to the treatment of exotic materials. This may help explain why local sources were not exploited. The exotic nature and esoteric origin of gold may have been inherent in defining its role, and perhaps there was neither a need nor a desire to find local, exploitable, sources.

Ideas relating to the control of knowledge can also be raised. Ireland is host to multiple gold deposits including a number that were capable of supporting Bronze Age goldworking industries, however current evidence suggests they were not exploited. Perhaps those who procured the material elsewhere restricted the knowledge of how to obtain gold in its native state for economic gain. Alternatively the transformation of raw gold into artefact form may have created the perceived value of these artefacts, and the smiths themselves may have restricted the knowledge of how to procure this material thus allowing control of this important transformational process. Furthermore, smiths could have limited the production of these artefacts, meaning local sources were never required.

In the regions where it was procured, metal can represent wealth because it is transferable into tools or ornaments and can be exchanged for other goods, whilst the ability to control this wealth could award certain degrees of power (Shennan, 1993). However the isotopic variation of Chalcolithic and EBA goldwork advocates a lack of control over gold procurement. It favours the exploitation of numerous deposits within a single gold bearing region, and the absence of centralised fabrication centres. It may also be suggestive of some level of gold mixing, potentially through artefact recycling. Nevertheless, its widespread deployment in Ireland means that controlling its export may have been possible. If the exploitation of Cornish gold is hypothesised, an economic association through the control of gold deployment can be proposed. This would contrast with the apparent supernatural worth attributed to this material in Ireland, where gold lacked the value that would require the exploitation of local sources and instead resulted in the production of a narrow range of artefact forms that were deposited in an established manner. Irrespective of meaning, the use of Cornish gold for Irish goldworking industries would suggest important ties across the Irish Sea.

Irish and British EBA goldwork is generally indistinguishable based on major element composition, therefore derivation from the same source is possible. Considering the current preference for a Cornish EBA gold source, this can be considered even more likely. The decline of the Irish lunulae tradition is consistent with the emergence of the embossed and linear goldworking traditions of Britain (c.2000 to 1900 BC), therefore a shift in the deployment of gold from west to east can be postulated. This may relate to changes in the control of these deposits, or shifts in the relative demand for gold from different regions. A number of continental embossed gold artefacts, including the MBA Schifferstadt and Ezelsdorf hats/cones, are also compositionally consistent with the Irish goldwork, whilst the gold incorporated into the EBA Nebra Disc has recently been linked to a Cornish source (Ehser et al., 2011). The potential that Cornwall was host to a major Chalcolithic and Bronze Age gold source that supplied industries across north and west Europe is clear.

With the decline of the Irish lunulae tradition, an apparent hiatus in Irish goldworking began. Significant goldworking traditions did not return to Ireland until the Early

Bishopsland phase of the MBA, and this was followed by expansions in goldworking industries during the Late Bishopsland and LBA. A preliminary study of this later prehistoric goldwork was performed (Chapter 7). The widespread practice of alloying gold with copper during these periods is problematic for lead isotope analysis. Calculations that correct for the input of copper derived lead can be performed, however for this to be successful the isotopic signature of the copper component needs to be characterised, and it is advantageous if this component is as homogenous as possible. It is currently unclear which copper deposits were exploited for Irish metalworking industries during the Middle and Late Bronze Ages. Additionally a comprehensive database of Irish copper or bronzework does not exist for these periods. It is therefore not possible to perform such corrections with a great degree of certainty. Before an in depth study of later prehistoric goldwork is performed, Irish copper and bronzework must be characterised for its lead isotope signature.

Nevertheless, copper corrections were applied to the MBA and LBA data, along with the analysis of a single Iron Age artefact, in order to draw some preliminary conclusions. The corrections utilised the isotopic composition of contemporaneous British copper and bronzework. This is not ideal, but currently provides the best proxy for the composition of copper that was in circulation in Ireland during these periods. Each gold alloy group (typically seen to reflect chronological stages) demonstrate low variability. This suggests increased control over the deployment and circulation of gold relative to the EBA; either through the exploitation of a single rich homogenous gold deposit, or through the existence of centralised fabrication centres.

Recycling and mixing were undoubtedly important features of these later goldworking traditions, therefore the corrected isotopic data should be indicative of the circulating metal pool rather than a specific gold deposit. With this in mind, the corrected isotopic data suggest reuse of the same EBA metal stock, and/or the continued exploitation of gold deposits located in the same isotopic ore field exploited during the EBA. The earliest evidence for a significant shift in gold procurement is currently visible in the LBA assemblage through the input from less radiogenic gold deposits. This may represent influxes of continental gold, however an alternative interpretation is that gold deposits hosted by the north-west terrane of Ireland or Scotland were now under exploitation. Obviously this interpretation is liable to change if significant numbers of artefacts were to be analysed. What is clear is the potential long lasting significance of the ore field responsible for the EBA goldworking industries. After its focus shifted away from Ireland c.1900 BC, it apparently returned to supply new Irish goldworking industries throughout the MBA and LBA.

The MBA and LBA witnessed major expansions in the goldworking industries of Ireland. There was a diversification in the range of artefact forms produced and the techniques used to manufacture them, alongside a significant increase in the amount of gold in circulation. The accessibility of this material was therefore apparently greater during these later periods, thus negating its exotic quality, and the changes in how gold was procured and distributed would have led to new meanings and a transformed role in society. An apparent increase in the control of the gold supply could have helped to sustain the value of gold, however it is likely that this value was increasingly linked to expressions of personal status. Consequently gold would have become a commodity that could have been controlled for economic advantage, an idea consistent with the exploitation of new, rich, gold sources. Current isotopic data for later prehistoric Irish goldwork is insufficient for a true understanding of its procurement, however an in depth lead isotope investigation combined with pre-existing compositional studies does have the potential to help recognise the patterns of gold exploitation throughout the course of the Bronze Age.

8.2 Future Work

Further work to develop the analytical techniques employed during this study would be of great benefit to future investigations. The ability to accurately and precisely analyse ^{204}Pb using laser ablation MC-ICP-MS is of great significance because it removes the need for solution analysis and therefore dissolution of artefact samples. At present the low abundance of ^{204}Pb and the isobaric interference of mercury mean this is rarely possible, and when it is, the data typically have large analytical errors. However it has been demonstrated in Chapter 5 that gold deposits are best differentiated with isotopic ratios using this mass. Experimentation with new methods of applying mercury corrections and laser ablation systems to improve signal intensities could provide analytical advances that would be of great importance to lead isotope provenance studies.

Further consideration should also be made to the behaviour of isotopic ratios in metals that undergo fabrication, and in particular the degree to which homogenisation can occur at different spatial scales. Laser ablation lead isotope analysis allows artefacts to be studied at greater resolution than previously possible, yet despite this no published study has achieved an understanding of isotopic variation at such scales. Solution work requires the dissolution of samples greater than c.2 mg. As a result only one sample is typically analysed per artefact and this usually gives the impression of homogeneity. Analysis of a gold diadem presented in Chapter 6 has highlighted isotopic heterogeneity within a single artefact, yet without experimental studies the significance of this can only be hypothesised. As a result, investigations into the behaviour of lead isotopes in metals that undergo different degrees of heating are seen as an important aspect of future studies. Can a heterogeneous ore deposit be successfully homogenised during fabrication, or does the isotopic variation of an artefact always reflect the variation of the original melt and at which spatial scales? Answering these questions could provide important information regarding the isotopic variation of exploited ore deposits and the technological processes employed during fabrication, whilst it may also help to quantify the degree of artefact recycling that occurred during these periods.

The principle aim of this study was to investigate the source of Chalcolithic and EBA Irish gold, and there is great scope for expanding this study both geographically and temporally in order to gain an understanding of gold procurement throughout prehistoric Europe. Serious doubt has been cast on the hypothesis of an Irish Chalcolithic and EBA gold source. The lead isotope signature of the early artefact assemblages favours an origin in southern Britain, and Cornwall is currently considered the most likely source region. The next step of this research must be to test this hypothesis. Two Cornish gold deposits have been analysed to date, however the county is host to numerous and the mineralisation is compositionally complex. A full investigation that characterises the lead isotope signature and major elemental composition of a significant number of Cornish gold deposits must be performed, allowing a critical assessment of the Cornish source hypothesis. If a British source can be discounted, the potential for an undiscovered Irish gold source will become more likely. Chapter 6 also began to consider the archaeology of south-west England and Wales, and if new analytical data does corroborate the hypothesis of a southern British source, an in depth evaluation of the archaeological evidence for Bronze Age occupation and metalworking should be made. Although it is considered that a Cornish gold source is feasible during the EBA, this may be more problematic for the Chalcolithic. No gold artefacts have been found in

Cornwall from the primary Beaker tradition, and there is little evidence for the working of gold-bearing alluvial deposits during this period.

In conjunction with the analysis of Cornish gold, other deposits from southern Britain should also be investigated due to their likely association with radiogenic south-east terrane upper crustal lead. Although the composition of Devonshire gold is typically high in palladium and therefore is not consistent with the artefacts, analysis of a number of deposits would be preferable thus allowing the region to be ruled out with a greater degree of certainty. It is considered likely that a number of Welsh deposits will be isotopically consistent with the artefacts, therefore a significant number of these should also be fully characterised and discussed. Additionally, analysis of a set of Scottish gold deposits would be of benefit. Although a Scottish source is considered unlikely due to associations with the NWT, localised sources of more radiogenic lead may be present and it would help complete a comprehensive database of British gold deposits.

With this shift in focus to British gold deposits, attention should also move to British gold artefacts. Examples of British found lunulae, in particularly the provincial type, should be characterised for their lead isotope signature allowing comparisons to the Irish examples. The analysis of primary Beaker, Scottish hilt band, Wessex linear, and embossed artefacts will also allow a greater understanding of gold procurement during the EBA. Combining lead isotope and major element analysis, two independent techniques, allows for more robust conclusions. Therefore any future analytical programmes should also include the characterisation of major element compositions where relevant; artefacts whose composition was characterised by Hartmann (1970, 1982) will need to undergo re-analysis due to the apparent inaccuracy of certain data.

It has been suggested that the later EBA traditions may reflect a shift in the deployment of gold away from Ireland, therefore it is necessary to see if these later British artefacts were indeed manufactured from the same gold supply. Only then will discussions be able to turn to the reasons behind the patterns of gold deployment. It was suggested in Chapter 6 that changes in the procurement of copper c.2000 to 1900 BC may have had an effect on the movement of gold into Ireland. This is just one possible reason, and if it can be proven that such a shift in gold deployment did occur, the potential mechanisms behind this can be fully investigated. The inclusion of primary Beaker goldwork will also allow a consideration of the origins of goldworking in Britain and Ireland, and perhaps the identification of early imported gold.

Due to the suspicion of a British gold source, the obvious progression of this study is to move into this geographic region by studying of both natural gold deposits and local artefacts. However there are also both typological and compositional links that warrant the investigation of continental artefacts from this period, such as the Irish style lunulae found along the Atlantic façade, and the Nebra Sky Disc of Germany. This thesis has demonstrated the great potential of lead isotope analysis to studies of Bronze Age goldwork, and there is great capacity for extending this study into continental Europe to artefacts that have never before been characterised for their lead isotope signature. It is important that whenever artefacts from a new geographic region are analysed, local sources are also characterised thus allowing the consideration of local derivation.

The widespread alloying of gold with copper is problematic for Irish artefacts dating from later periods, and before a full investigation of these artefacts can be performed, contemporary copper or bronzework must first be characterised isotopically. If this metal pool is deemed sufficiently homogenous for the application of copper alloying corrections, then these artefacts can also be investigated. However even if identifying sources is problematic, information regarding the circulation of metal pools should become apparent. It can be noted that not all later artefacts were alloyed with copper, and a number of the continental MBA embossed gold artefacts are consistent compositionally with those from earlier periods. Therefore the option to extend this investigation into later periods does exist for certain regions without the need for complex mathematical corrections.

The study of British gold is seen as critical in order to understand the procurement of Bronze Age gold in general, and this must be the next step if this line of research is to be continued. However the analytical techniques employed here have great scope for wider investigations of early goldwork from Europe and indeed any geographic region, whilst the potential for expanding this research into other temporal periods is also clear. Performing such research will allow a greater understanding of European Bronze Age gold procurement, and will allow investigations into the more theoretical lines of research that aim to understand the reasons behind changing patterns of gold deployment. A true appreciation of the role that gold played in different prehistoric societies is therefore an achievable aim.

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Appendix A: Solution MC-ICP-MS Lead Isotope Analysis of Gold Mineralisation

A1: Irish gold mineralisation

Location	County	Easting[a]	Northing[a]	$^{206}Pb/^{204}Pb$	2 S.E.	$^{207}Pb/^{204}Pb$	2 S.E.	$^{208}Pb/^{204}Pb$	2 S.E.	$^{207}Pb/^{206}Pb$	2 S.E.	$^{208}Pb/^{206}Pb$	2 S.E.	Pb Age (Ma)[b]
Attagh Burn	Tyrone	2567	3865	17.437	0.003	15.401	0.003	37.718	0.008	0.8832	0.0001	2.1630	0.0003	500
Attagh Burn	Tyrone	2567	3865	17.287	0.003	15.382	0.002	37.567	0.008	0.8898	0.0001	2.1731	0.0003	584
Attagh Burn	Tyrone	2567	3865	17.447	0.004	15.403	0.004	37.653	0.011	0.8829	0.0001	2.1581	0.0004	496
Ballincurry	Down	3216	3157	18.605	0.009	15.602	0.009	38.492	0.025	0.8386	0.0001	2.0689	0.0005	15
Ballybrack	Waterford	2434	1079	18.184	0.004	15.628	0.004	38.427	0.012	0.8594	0.0001	2.1133	0.0004	388
Ballybrack	Waterford	2434	1079	18.324	0.005	15.619	0.004	38.275	0.014	0.8524	0.0001	2.0889	0.0004	265
Ballybrack	Waterford	2434	1079	18.595	0.006	15.623	0.006	38.390	0.020	0.8402	0.0001	2.0646	0.0005	68
Ballybrack	Waterford	2434	1079	18.425	0.005	15.624	0.004	38.567	0.012	0.8480	0.0001	2.0932	0.0003	200
Ballybrack	Waterford	2434	1079	18.211	0.005	15.621	0.004	38.285	0.010	0.8577	0.0001	2.1023	0.0003	352
Ballybrack	Waterford	2434	1079	18.257	0.005	15.596	0.004	38.153	0.011	0.8542	0.0001	2.0897	0.0003	266
Ballykale	Wexford	3159	1565	17.994	0.004	15.616	0.003	38.104	0.009	0.8678	0.0001	2.1176	0.0003	502
Balwoges	Donegal	1764	3819	18.320	0.004	15.572	0.004	38.022	0.011	0.8500	0.0001	2.0755	0.0004	170
Balwoges	Donegal	1764	3819	18.525	0.005	15.582	0.004	38.208	0.012	0.8411	0.0005	2.0626	0.0013	33
Berry Burn	Londonderry	2473	4110	17.853	0.004	15.478	0.003	37.767	0.011	0.8670	0.0001	2.1154	0.0004	332
Berry Burn	Londonderry	2473	4110	17.985	0.005	15.561	0.003	37.886	0.009	0.8653	0.0001	2.1066	0.0003	405
Berry Burn	Londonderry	2473	4110	17.926	0.007	15.516	0.004	37.851	0.010	0.8656	0.0002	2.1116	0.0005	359
Berry Burn	Londonderry	2473	4110	18.040	0.008	15.552	0.007	37.938	0.019	0.8621	0.0001	2.1030	0.0003	342
Berry Burn	Londonderry	2473	4110	17.977	0.006	15.584	0.005	37.956	0.014	0.8669	0.0001	2.1114	0.0003	460
Berry Burn	Londonderry	2473	4110	18.109	0.006	15.579	0.006	38.056	0.017	0.8603	0.0001	2.1015	0.0004	331
Berry Burn	Londonderry	2473	4110	18.002	0.004	15.592	0.003	37.945	0.009	0.8661	0.0001	2.1078	0.0003	345
Bohaun	Galway	1006	2557	17.909	0.012	15.483	0.011	37.866	0.029	0.8645	0.0001	2.1143	0.0004	298

Bohaun	Galway	1006	2557	17.957	0.007	15.478	0.007	37.845	0.021	0.8620	0.0001	2.1076	0.0006	250
Bohaun	Galway	1006	2557	17.981	0.012	15.484	0.011	37.855	0.029	0.8611	0.0002	2.1052	0.0006	243
Boley	Wexford	3069	1562	17.985	0.003	15.620	0.002	38.094	0.008	0.8685	0.0001	2.1182	0.0003	518
Boley	Wexford	3069	1562	18.105	0.003	15.608	0.002	38.112	0.007	0.8621	0.0001	2.1051	0.0003	407
Bunowen River	Mayo	8640	2743	17.589	0.004	15.438	0.004	37.646	0.013	0.8777	0.0002	2.1403	0.0005	456
Bunowen River	Mayo	8640	2743	17.752	0.004	15.485	0.003	37.553	0.010	0.8723	0.0001	2.1154	0.0004	426
Burntollet River	Londonderry	2502	4107	17.629	0.004	15.458	0.003	37.620	0.008	0.8769	0.0001	2.1340	0.0003	451
Cabry River	Donegal	2514	4314	18.031	0.010	15.514	0.012	37.932	0.040	0.8604	0.0003	2.1037	0.0012	268
Cabry River	Donegal	2514	4314	17.965	0.004	15.527	0.004	37.896	0.012	0.8642	0.0001	2.1094	0.0004	346
Cabry River	Donegal	2514	4314	17.906	0.004	15.494	0.002	37.825	0.008	0.8653	0.0001	2.1124	0.0003	331
Camcor River	Offaly	2201	2062	17.928	0.005	15.507	0.006	37.791	0.018	0.8650	0.0002	2.1079	0.0006	334
Camcor River	Offaly	2201	2062	18.459	0.003	15.581	0.002	38.257	0.008	0.8441	0.0001	2.0725	0.0003	80
Carrownisky River	Mayo	0830	2725	17.625	0.004	15.432	0.003	37.681	0.008	0.8756	0.0001	2.1379	0.0003	416
Carrownisky River	Mayo	0830	2725	17.793	0.004	15.482	0.003	37.820	0.010	0.8701	0.0001	2.1256	0.0003	389
Carrownisky River	Mayo	0830	2725	17.743	0.005	15.452	0.005	37.741	0.017	0.8708	0.0002	2.1271	0.0006	363
Carrownisky River	Mayo	0830	2725	17.655	0.005	15.443	0.005	37.660	0.016	0.8747	0.0002	2.1331	0.0005	415
Carrownisky River	Mayo	0830	2725	17.634	0.004	15.437	0.003	37.668	0.008	0.8754	0.0001	2.1361	0.0003	420
Carrownisky River	Mayo	0830	2725	17.834	0.004	15.466	0.003	37.902	0.009	0.8672	0.0001	2.1253	0.0003	321
Carrownisky River	Mayo	0830	2725	17.851	0.012	15.467	0.011	37.959	0.028	0.8664	0.0001	2.1264	0.0003	308
Carrownisky River	Mayo	0830	2725	18.043	0.009	15.489	0.008	38.000	0.019	0.8585	0.0001	2.1061	0.0003	207
Carrownisky River	Mayo	0830	2725	17.659	0.004	15.450	0.003	37.651	0.008	0.8749	0.0001	2.1322	0.0003	427
Carrownisky River	Mayo	0830	2725	17.567	0.004	15.415	0.004	37.705	0.010	0.8775	0.0001	2.1464	0.0003	427
Cavanacaw	Tyrone	2404	3701	17.497	0.004	15.423	0.002	37.586	0.008	0.8815	0.0001	2.1481	0.0004	498
Cavanacaw	Tyrone	2404	3701	17.513	0.004	15.420	0.004	37.563	0.011	0.8805	0.0001	2.1449	0.0004	479
Cavanacaw	Tyrone	2404	3701	17.509	0.009	15.422	0.008	37.578	0.022	0.8808	0.0001	2.1463	0.0004	486
Cavanacaw	Tyrone	2404	3701	17.519	0.004	15.430	0.003	37.604	0.008	0.8808	0.0001	2.1465	0.0003	495

Cavanacaw FeS_2	Tyrone	2404	3701	17.525	0.004	15.434	0.003	37.619	0.009	0.8807	0.0001	2.1466	0.0003	498
Cavanacaw FeS_2	Tyrone	2404	3701	17.507	0.004	15.428	0.003	37.643	0.009	0.8812	0.0001	2.1502	0.0003	499
Cavanacaw FeS_2	Tyrone	2404	3701	17.526	0.004	15.436	0.003	37.616	0.008	0.8807	0.0001	2.1463	0.0003	501
Cavanacaw PbS	Tyrone	2404	3701	17.534	0.004	15.432	0.004	37.598	0.014	0.8801	0.0002	2.1444	0.0006	488
Cavanacaw PbS	Tyrone	2404	3701	17.538	0.003	15.435	0.002	37.601	0.008	0.8801	0.0001	2.1440	0.0004	490
Cavanacaw PbS	Tyrone	2404	3701	17.480	0.004	15.422	0.003	37.632	0.010	0.8822	0.0001	2.1529	0.0004	509
Cavanacaw PbS	Tyrone	2404	3701	17.572	0.008	15.440	0.009	37.594	0.031	0.8787	0.0002	2.1394	0.0009	474
Clay Lake AsFeS	Armagh	2817	3357	18.548	0.004	15.587	0.002	38.012	0.007	0.8404	0.0001	2.0494	0.0003	26
Clay Lake AsFeS	Armagh	2817	3357	18.624	0.004	15.575	0.003	38.040	0.009	0.8362	0.0001	2.0425	0.0003	n/a
Clay Lake AsFeS	Armagh	2817	3357	18.674	0.004	15.579	0.003	38.029	0.008	0.8343	0.0001	2.0365	0.0003	n/a
Clay Lake FeS_2	Armagh	2817	3357	18.409	0.004	15.582	0.003	38.069	0.009	0.8465	0.0001	2.0680	0.0003	122
Clay Lake FeS_2	Armagh	2817	3357	18.376	0.003	15.582	0.002	38.064	0.007	0.8479	0.0001	2.0714	0.0003	147
Clontibret AsFeS	Monaghan	2755	3301	17.837	0.005	15.499	0.005	37.712	0.015	0.8689	0.0001	2.1143	0.0004	390
Clontibret AsFeS	Monaghan	2755	3301	17.845	0.006	15.497	0.006	37.721	0.016	0.8684	0.0001	2.1138	0.0004	378
Clontibret AsFeS	Monaghan	2755	3301	17.856	0.003	15.499	0.002	37.776	0.007	0.8680	0.0001	2.1157	0.0003	375
Clontibret AsFeS	Monaghan	2755	3301	17.857	0.003	15.498	0.002	37.736	0.007	0.8679	0.0001	2.1133	0.0003	371
Clontibret AsFeS	Monaghan	2755	3301	17.870	0.003	15.499	0.002	37.765	0.008	0.8673	0.0001	2.1133	0.0003	363
Croagh Patrick	Mayo	0896	2804	18.044	0.004	15.542	0.004	37.653	0.013	0.8613	0.0001	2.0867	0.0004	317
Croagh Patrick	Mayo	0896	2804	18.076	0.004	15.542	0.003	37.736	0.010	0.8598	0.0001	2.0876	0.0004	291
Croagh Patrick	Mayo	0896	2804	18.048	0.004	15.543	0.003	37.651	0.010	0.8612	0.0001	2.0861	0.0004	315
Croagh Patrick	Mayo	0896	2804	18.040	0.004	15.545	0.004	37.649	0.012	0.8617	0.0001	2.0869	0.0004	327
Croagh Patrick	Mayo	0896	2804	18.044	0.005	15.547	0.005	37.668	0.016	0.8616	0.0001	2.0876	0.0005	329
Curraghinalt AsFeS	Tyrone	2623	3858	17.557	0.004	15.434	0.003	37.638	0.008	0.8791	0.0001	2.1437	0.0003	474
Curraghinalt AsFeS	Tyrone	2623	3858	17.399	0.003	15.407	0.002	37.552	0.008	0.8855	0.0001	2.1583	0.0004	543
Curraghinalt Burn	Tyrone	2571	3866	17.432	0.004	15.412	0.003	37.575	0.009	0.8841	0.0001	2.1555	0.0003	527
Curraghinalt Burn	Tyrone	2571	3866	17.458	0.004	15.400	0.003	37.763	0.008	0.8821	0.0001	2.1631	0.0003	480

Curraghinalt Burn	Tyrone	2571	3866	17.499	0.004	15.421	0.003	37.517	0.010	0.8812	0.0001	2.1439	0.0004	492
Curraghinalt FeS_2	Tyrone	2623	3858	17.431	0.008	15.389	0.007	37.762	0.017	0.8828	0.0001	2.1663	0.0003	479
Curraghinalt FeS_2	Tyrone	2623	3858	17.596	0.007	15.406	0.005	37.996	0.014	0.8755	0.0001	2.1594	0.0003	384
Gibbett Hill	Wexford	2961	1575	18.189	0.005	15.627	0.005	38.280	0.014	0.8591	0.0001	2.1046	0.0004	381
Gibbett Hill	Wexford	2961	1575	18.088	0.004	15.632	0.004	38.277	0.012	0.8642	0.0001	2.1161	0.0004	465
Glencurry Burn[c]	Tyrone	2502	3767	17.499	0.007	15.411	0.007	37.620	0.017	0.8807	0.0001	2.1499	0.0003	470
Glencurry Burn[c]	Tyrone	2502	3767	17.429	0.013	15.391	0.012	37.691	0.030	0.8831	0.0001	2.1625	0.0003	486
Glencurry Burn[c]	Tyrone	2502	3767	17.446	0.019	15.393	0.017	37.657	0.045	0.8823	0.0001	2.1585	0.0004	476
Glencurry Burn[c]	Tyrone	2502	3767	17.495	0.005	15.411	0.005	37.655	0.013	0.8809	0.0001	2.1524	0.0004	474
Glencurry Burn[c]	Tyrone	2502	3767	17.517	0.004	15.400	0.003	37.754	0.010	0.8792	0.0001	2.1554	0.0003	435
Glencurry Burn[c]	Tyrone	2502	3767	17.538	0.005	15.424	0.003	37.635	0.011	0.8794	0.0002	2.1460	0.0006	467
Goldmines East River[c]	Wicklow	3180	1745	17.985	0.005	15.617	0.005	38.025	0.016	0.8684	0.0001	2.1143	0.0004	513
Goldmines East River[c]	Wicklow	3180	1745	18.087	0.004	15.619	0.003	38.087	0.011	0.8636	0.0001	2.1058	0.0004	442
Goldmines East River[c]	Wicklow	3180	1745	18.212	0.005	15.626	0.004	38.229	0.013	0.8580	0.0001	2.0992	0.0003	362
Goldmines East River[c]	Wicklow	3180	1745	18.141	0.004	15.622	0.002	38.194	0.008	0.8611	0.0001	2.1054	0.0003	408
Goldmines East River[c]	Wicklow	3180	1745	18.147	0.005	15.608	0.006	38.234	0.018	0.8601	0.0002	2.1070	0.0006	423
Goldmines East River[c]	Wicklow	3180	1745	18.131	0.005	15.626	0.005	38.106	0.018	0.8619	0.0002	2.1018	0.0006	367
Goldmines East River[c]	Wicklow	3180	1745	18.192	0.004	15.621	0.003	38.326	0.011	0.8587	0.0001	2.1068	0.0004	384
Goldmines East River[c]	Wicklow	3180	1745	18.187	0.004	15.627	0.002	38.322	0.008	0.8593	0.0001	2.1072	0.0003	384
Knockmore	Kerry	666	1046	18.069	0.005	15.627	0.004	38.144	0.015	0.8648	0.0001	2.1111	0.0005	470
Lecanvey Stream	Mayo	0890	2815	18.100	0.003	15.543	0.002	37.773	0.008	0.8587	0.0001	2.0870	0.0004	277
Lecanvey Stream	Mayo	0890	2815	18.069	0.004	15.537	0.003	37.763	0.009	0.8598	0.0001	2.0899	0.0003	287
Leitrim River (Lower)	Down	3218	3285	17.999	0.004	15.531	0.003	37.887	0.009	0.8628	0.0001	2.1049	0.0003	329
Leitrim River (Lower)	Down	3218	3285	17.928	0.004	15.515	0.003	37.824	0.009	0.8654	0.0001	2.1097	0.0003	351
Leitrim River (Lower)	Down	3218	3285	17.987	0.004	15.548	0.003	37.944	0.009	0.8644	0.0001	2.1095	0.0003	374
Leitrim River (Lower)	Down	3218	3285	18.297	0.004	15.571	0.003	38.198	0.008	0.8510	0.0001	2.0876	0.0003	185

Leitrim River (Lower)	Down	3218	3285	17.926	0.005	15.526	0.004	37.845	0.012	0.8661	0.0001	2.1112	0.0003	377
Leitrim River (Upper)	Down	3215	3259	18.420	0.004	15.563	0.003	38.370	0.009	0.8449	0.0001	2.0831	0.0003	72
Leitrim River (Upper)	Down	3215	3259	18.471	0.006	15.584	0.007	38.378	0.022	0.8437	0.0002	2.0778	0.0006	78
Lougheraherk	Donegal	1592	3882	18.171	0.003	15.553	0.002	37.847	0.007	0.8559	0.0001	2.0828	0.0003	243
Lougheraherk	Donegal	1592	3882	18.288	0.004	15.583	0.003	37.947	0.010	0.8521	0.0001	2.0750	0.0004	218
Lougheraherk	Donegal	1592	3882	18.473	0.004	15.576	0.003	37.958	0.009	0.8432	0.0001	2.0548	0.0003	59
Millshoge	Wexford	3065	1520	18.378	0.008	15.634	0.007	38.402	0.018	0.8507	0.0001	2.0895	0.0003	255
Millshoge	Wexford	3065	1520	18.146	0.004	15.628	0.003	38.280	0.008	0.8612	0.0001	2.1096	0.0003	416
Ow River	Wicklow	3111	1800	18.560	0.006	15.653	0.007	38.635	0.023	0.8433	0.0002	2.0816	0.0007	157
Ow River	Wicklow	3111	1800	18.267	0.003	15.624	0.002	38.220	0.008	0.8553	0.0001	2.0923	0.0003	317
Ow River	Wicklow	3111	1800	18.050	0.004	15.626	0.003	38.128	0.010	0.8657	0.0001	2.1124	0.0004	482
Ow River	Wicklow	3111	1800	18.160	0.005	15.626	0.005	38.086	0.015	0.8605	0.0001	2.0973	0.0004	402
Ow River	Wicklow	3111	1800	18.181	0.010	15.623	0.009	38.115	0.024	0.8593	0.0002	2.0964	0.0005	379
Ow River	Wicklow	3111	1800	18.464	0.004	15.661	0.003	38.424	0.012	0.8482	0.0001	2.0811	0.0004	246
Ow River	Wicklow	3111	1800	18.246	0.005	15.635	0.004	38.163	0.012	0.8569	0.0001	2.0915	0.0003	356
River Bann	Down	3220	3290	18.424	0.006	15.585	0.006	38.287	0.021	0.8459	0.0002	2.0782	0.0006	116
River Bann	Down	3220	3290	17.941	0.004	15.519	0.003	37.821	0.009	0.8650	0.0001	2.1081	0.0005	349
River Bann	Down	3220	3290	18.061	0.003	15.538	0.002	37.949	0.008	0.8603	0.0001	2.1012	0.0003	297
Rocky River	Down	3234	3277	18.486	0.005	15.580	0.004	38.372	0.013	0.8428	0.0001	2.0757	0.0004	58
Rocky River	Down	3234	3277	17.949	0.006	15.509	0.006	37.867	0.019	0.8641	0.0001	2.1097	0.0005	322
Shraroosky	Mayo	0797	2715	17.623	0.004	15.432	0.003	37.632	0.008	0.8756	0.0002	2.1354	0.0004	417
Shraroosky	Mayo	0797	2715	17.623	0.003	15.432	0.002	37.627	0.007	0.8757	0.0001	2.1351	0.0003	418
Shraroosky PbS	Mayo	0797	2715	17.613	0.003	15.442	0.002	37.664	0.007	0.8767	0.0001	2.1384	0.0003	446
Shraroosky PbS	Mayo	0797	2715	17.628	0.004	15.444	0.003	37.672	0.008	0.8761	0.0001	2.1371	0.0003	438
Walishtown	Kildare	2940	2156	18.329	0.003	15.606	0.002	38.217	0.007	0.8514	0.0001	2.0851	0.0003	234
Walishtown	Kildare	2940	2156	18.233	0.004	15.574	0.003	38.070	0.009	0.8542	0.0001	2.0880	0.0003	240

Walishtown	Kildare	2940	2156	18.280	0.012	15.593	0.010	38.161	0.025	0.8530	0.0001	2.0875	0.0003	244
Walishtown	Kildare	2940	2156	18.314	0.003	15.588	0.002	38.162	0.007	0.8512	0.0001	2.0838	0.0003	210
Walishtown	Kildare	2940	2156	18.276	0.004	15.588	0.003	38.114	0.009	0.8529	0.0001	2.0855	0.0004	236
Walishtown	Kildare	2940	2156	18.337	0.004	15.582	0.003	38.197	0.008	0.8497	0.0001	2.0830	0.0003	177
Whelanbridge	Waterford	2513	1088	18.366	0.004	15.649	0.003	38.425	0.009	0.8520	0.0001	2.0922	0.0003	293
Whelanbridge	Waterford	2513	1088	18.679	0.004	15.621	0.004	38.312	0.013	0.8362	0.0001	2.0511	0.0005	0
Whelanbridge	Waterford	2513	1088	18.435	0.008	15.606	0.007	38.305	0.018	0.8465	0.0001	2.0778	0.0003	153

Notes: Errors ± 2 standard errors of the mean of 50 integration cycles. [a]British National Grid, [b]Pb model ages based on Stacey and Kramers (1975), [c]Standish et al., 2013.

A2: British gold mineralisation

Location	County	Easting[a]	Northing[a]	^{206}Pb/^{204}Pb	2 S.E.	^{207}Pb/^{204}Pb	2 S.E.	^{208}Pb/^{204}Pb	2 S.E.	^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.	Pb Age (Ma)[b]
Afon Brynberian	Pembrokeshire	2117	2362	18.349	0.003	15.646	0.002	38.339	0.007	0.8527	0.0001	2.0894	0.0003	301
Afon Brynberian	Pembrokeshire	2117	2362	18.289	0.006	15.625	0.006	38.324	0.016	0.8544	0.0001	2.0955	0.0004	303
Afon Brynberian	Pembrokeshire	2117	2362	18.265	0.003	15.637	0.003	38.178	0.008	0.8561	0.0001	2.0902	0.0003	345
Afon Brynberian	Pembrokeshire	2117	2362	18.249	0.004	15.615	0.003	38.241	0.008	0.8557	0.0001	2.0955	0.0003	313
Afon Brynberian	Pembrokeshire	2117	2362	18.289	0.004	15.631	0.003	38.225	0.010	0.8546	0.0001	2.0901	0.0004	314
Borland Glen	Perthshire	2992	7055	18.025	0.004	15.520	0.003	37.723	0.009	0.8610	0.0001	2.0928	0.0003	285
Borland Glen	Perthshire	2992	7055	17.964	0.003	15.508	0.002	37.682	0.007	0.8633	0.0001	2.0976	0.0003	308
Borland Glen	Perthshire	2992	7055	18.008	0.004	15.519	0.002	37.714	0.008	0.8618	0.0001	2.0944	0.0003	297
Borland Glen	Perthshire	2992	7055	18.027	0.004	15.521	0.004	37.728	0.010	0.8610	0.0001	2.0929	0.0003	287
Borland Glen	Perthshire	2992	7055	18.046	0.004	15.514	0.002	37.723	0.007	0.8597	0.0001	2.0904	0.0004	257
Borland Glen	Perthshire	2992	7055	17.965	0.004	15.509	0.003	37.686	0.008	0.8633	0.0001	2.0977	0.0003	309
Borland Glen	Perthshire	2992	7055	18.008	0.004	15.520	0.003	37.719	0.008	0.8618	0.0001	2.0946	0.0003	299
Borland Glen	Perthshire	2992	7055	17.978	0.005	15.504	0.004	37.690	0.012	0.8624	0.0001	2.0965	0.0003	289
Borland Glen	Perthshire	2992	7055	18.027	0.005	15.516	0.005	37.719	0.014	0.8607	0.0001	2.0924	0.0005	276
Borland Glen	Perthshire	2992	7055	18.016	0.006	15.511	0.006	37.694	0.017	0.8610	0.0001	2.0923	0.0005	274
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.317	0.013	15.605	0.016	38.256	0.052	0.8520	0.0003	2.0886	0.0014	242
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.400	0.009	15.634	0.011	38.393	0.036	0.8497	0.0002	2.0866	0.0010	239
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.410	0.004	15.627	0.003	38.384	0.010	0.8489	0.0001	2.0850	0.0003	219
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.316	0.005	15.613	0.004	38.262	0.012	0.8524	0.0001	2.0890	0.0004	258
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.286	0.005	15.620	0.005	38.279	0.015	0.8542	0.0001	2.0933	0.0004	294
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.326	0.007	15.614	0.006	38.266	0.016	0.8520	0.0001	2.0881	0.0004	252
Carnon River	Cornwall	Ref: RCM 801.853[c]		18.404	0.004	15.637	0.004	38.419	0.011	0.8496	0.0001	2.0876	0.0004	241
Challon's Comb	Devon	2678	0483	19.478	0.010	15.613	0.008	38.520	0.023	0.8016	0.0001	1.9776	0.0004	n/a

Challon's Comb	Devon	2678	0483	19.187	0.007	15.629	0.007	38.516	0.022	0.8146	0.0001	2.0074	0.0006	n/a
Challon's Comb	Devon	2678	0483	19.573	0.028	15.614	0.023	38.403	0.057	0.7977	0.0002	1.9620	0.0005	n/a
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.231	0.005	15.613	0.004	38.203	0.012	0.8564	0.0001	2.0955	0.0004	321
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.336	0.004	15.614	0.003	38.268	0.009	0.8515	0.0001	2.0871	0.0003	244
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.375	0.004	15.618	0.003	38.292	0.010	0.8500	0.0001	2.0839	0.0004	225
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.350	0.006	15.607	0.005	38.203	0.016	0.8505	0.0001	2.0819	0.0004	220
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.269	0.006	15.608	0.006	38.191	0.018	0.8543	0.0001	2.0905	0.0005	282
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.228	0.003	15.597	0.003	38.102	0.008	0.8557	0.0001	2.0903	0.0003	292
Crow Hill	Cornwall	Ref: RCM 801.6372[c]		18.293	0.004	15.623	0.002	38.296	0.008	0.8540	0.0001	2.0935	0.0003	296
Wanlock Water	Dumfries & Galloway	2849	6155	18.154	0.006	15.547	0.006	38.042	0.019	0.8563	0.0001	2.0955	0.0005	242
Wanlock Water	Dumfries & Galloway	2849	6155	18.197	0.004	15.553	0.003	38.096	0.010	0.8547	0.0001	2.0935	0.0004	224
Wanlock Water	Dumfries & Galloway	2849	6155	18.213	0.003	15.554	0.002	38.113	0.007	0.8540	0.0001	2.0927	0.0003	214
Wanlock Water	Dumfries & Galloway	2849	6155	18.209	0.003	15.551	0.002	38.104	0.008	0.8541	0.0001	2.0926	0.0004	212

Notes: Errors ± 2 standard errors of the mean of 50 integration cycles. [a]British National Grid, [b]Pb model ages based on Stacey and Kramers (1975), [c]reference number for samples obtained from Royal Cornish Museum, Truro.

Appendix B: Major Element Composition, Lead Isotope Signature and Mineral Inclusion Suite of Irish Prehistoric Goldwork

B1: Major element composition of Irish prehistoric goldwork (mean data)

Accession No.	Artefact	Find Location	County	Ag %	2 S.E.	Sn %	2 S.E.	Cu %	2 S.E.
Chalcolithic and Early Bronze Age									
1877:52	Lunula	Carrowduff	Clare	14.07	0.27	0.14	0.08	0.18	0.08
1881:90	Lunula	n/a	n/a	10.75	0.11	0.06	0.03	0.11	0.03
1881:91	Lunula	n/a	n/a	13.66	0.12	0.05	0.02	0.12	0.12
1884:07	Lunula	Mullingar	Westmeath	12.48	0.27	0.00	0.00	3.21	0.03
1884:494	Lunula	Crossdoney	Cavan	11.20	0.15	0.03	0.04	0.44	0.04
1884:495	Lunula	Trillick	Tyrone	12.66	0.17	0.16	0.07	0.13	0.04
1889:20	Lunula	Trentagh	Donegal	10.23	0.30	0.06	0.02	0.39	0.09
1893:04	Lunula	Athlone	Westmeath	8.71	0.06	0.01	0.01	0.97	0.10
1896:15	Lunula	Ross	Westmeath	11.17	0.19	0.05	0.03	0.08	0.03
1900:50	Lunula	Tremoge	Tyrone	13.48	0.08	0.12	0.04	0.15	0.02
1909:04	Lunula	West Coast	Mayo	8.49	0.17	0.02	0.02	0.33	0.08
1909:06	Lunula	Naran	Donegal	10.36	0.19	0.08	0.00	0.05	0.01
1909:07	Lunula	Rosgarron	Derry	11.55	0.12	0.14	0.03	0.39	0.06
1910:45	Lunula	Bawnboy	Cavan	11.34	0.17	0.06	0.05	0.17	0.01
1946:392	Lunula	n/a	n/a	13.80	0.15	0.08	0.02	0.09	0.01
1998:74	Lunula	Ballinagroun	Kerry	8.94	0.06	0.00	0.00	1.97	0.08
P817	Lunula	n/a	n/a	11.01	0.07	0.07	0.02	0.14	0.04
P949	Disc	n/a	Roscommon	9.77	0.20	0.05	0.04	0.46	0.17
R1755	Lunula	Banemore	Kerry	11.71	0.17	0.01	0.02	0.07	0.02
R1756	Lunula	Banemore	Kerry	7.94	0.11	0.00	0.00	0.08	0.03

R1757	Lunula	Banemore	Kerry	11.38	0.09	0.04	0.02	0.28	0.14
R2612	Lunula	n/a	n/a	17.06	0.08	0.01	0.01	0.12	0.03
R4023	Lunula	n/a	n/a	12.95	0.05	0.04	0.02	0.11	0.01
R4024	Lunula	Island Magee	Antrim	12.54	0.19	0.04	0.01	0.36	0.03
R625	Lunula	n/a	n/a	8.37	0.09	0.00	0.00	0.04	0.03
SA1913:127	Pin	Ballyvourney	Cork	16.38	0.63	0.24	0.03	6.99	0.36
SA1913:128	Disc	Ballyvourney	Cork	16.33	0.18	0.04	0.03	0.25	0.07
SA1913:131	Trapezoidal Plaque	Knockane	Cork	16.57	0.16	0.15	0.02	5.83	0.08
SA1928:715	Lunula	Rossmore Park	Monaghan	13.77	0.13	0.21	0.07	0.07	0.02
W1	Lunula	n/a	n/a	11.17	0.26	0.00	0.00	0.24	0.05
W2	Lunula	Killarney	Kerry	3.79	0.05	0.01	0.01	0.07	0.02
W3	Lunula	n/a	n/a	12.40	0.26	0.07	0.04	0.18	0.01
W4/R136	Lunula	Dunfierth	Kildare	12.46	0.07	0.05	0.02	0.13	0.04
W5	Lunula	n/a	n/a	11.75	0.14	0.01	0.01	0.16	0.08
W6	Lunula	n/a	n/a	10.45	0.14	0.00	0.00	0.68	1.20
W7	Lunula	n/a	n/a	11.22	0.11	0.02	0.01	0.20	0.03
W8/R135	Lunula	Dunfierth	Kildare	13.82	0.07	0.31	0.16	0.01	0.01
W9/R138	Lunula	Dunfierth	Kildare	13.48	0.51	0.30	0.11	0.15	0.03
W10	Lunula	n/a	Galway	10.32	0.15	0.38	0.12	0.14	0.09
W11	Lunula	n/a	n/a	14.43	0.29	0.02	0.04	0.02	0.00
W12	Lunula	n/a	n/a	12.11	0.11	0.06	0.02	0.26	0.04
W13	Lunula	n/a	n/a	12.57	0.15	0.01	0.01	0.08	0.02
W14	Lunula	n/a	n/a	12.37	0.04	0.11	0.03	0.26	0.03
W15/R137	Lunula	Dunfierth	Kildare	12.97	0.11	0.16	0.02	0.14	0.06
W74[a]	Basket Ornament	n/a	n/a	10.45	0.13	0.08	0.04	0.79	0.03
W75	Oval Plaque	Belville	Cavan	10.63	0.11	0.02	0.02	0.13	0.05

W76	Oval Plaque	Belville	Cavan	10.34	0.05	0.00	0.00	0.19	0.06
W78[b]	Oval Plaque	Belville	Cavan	9.83	0.39	0.00	0.00	0.30	0.06
W79[b]	Oval Plaque	Belville	Cavan	9.94	0.14	0.00	0.00	0.30	0.13
W81[b]	Oval Plaque	Belville	Cavan	9.89	0.41	0.01	0.02	0.31	0.11
W266	Disc	n/a	n/a	15.50	0.13	0.01	0.01	0.17	0.04
W270	Disc	n/a	n/a	11.84	0.06	0.00	0.01	0.47	0.07
Middle Bronze Age mba1									
A1910:673[c]	Ribbed Ring	n/a	n/a	11.80	0.37	0.16	0.02	1.12	0.23
R1680	Flanged Torc	n/a	Down	11.60	0.15	0.46	0.05	1.30	0.06
Middle Bronze Age mba2									
1878:03	Bar Torc	Giants Causeway	Antrim	17.40	0.06	0.28	0.10	5.74	0.06
1929.1302	Penannular Ring	Kilmallock	Limerick	18.49	0.90	0.24	0.05	4.39	0.15
1935:879	Penannular Ring	Ballina	Mayo	17.07	0.08	0.35	0.09	5.03	0.15
A210.1913c	Penannular Ring	Belfast	Antrim	17.24	0.36	0.32	0.10	4.99	0.38
W174	Wire Bound Torc	n/a	Galway	17.14	0.08	0.27	0.01	5.28	0.03
Late Bronze Age lba									
1904:02	Bracelet	Mooghaun	Clare	12.95	0.12	0.18	0.01	7.03	0.32
1918:355	Bulla	River Bann	n/a	15.14	0.22	0.10	0.04	5.85	0.08
1941:1154	Bracelet	Lissandrone	Mayo	11.21	1.78	0.05	0.05	4.06	2.53
A7532c	Sleeve Fastener	Ballinagard	Antrim	13.60	0.27	0.14	0.01	7.44	0.21
A7533c	Sleeve Fastener	Ballyculter	Down	13.91	0.29	0.21	0.04	7.13	0.24
AD1.2c	Bracelet	Downpatrick	Down	13.66	0.15	0.23	0.02	5.34	0.29
AD1.5c	Bracelet	Downpatrick	Down	12.89	0.45	0.17	0.05	5.76	0.32
W27	Large Ring	Mooghaun	Clare	13.32	0.53	0.11	0.06	7.05	0.72

W117	Bracelet	Mooghaun	Clare	13.72	0.11	0.15	0.02	6.53	0.12
W175	Neck Ring	Mooghaun	Clare	12.43	0.34	0.03	0.02	6.96	0.75
Iron Age									
1888:14	Ribbon Torc	Lissandrone	Mayo	21.02	0.13	0.05	0.02	3.35	0.14

Notes: Errors ± 2 standard errors of the mean of ≥3 analyses. [a]sample analysed by Eric Condliffe (School of Earth Sciences, University of Leeds), [b]all samples from the same artefact, [c]samples donated for study by the Ulster Museum, Belfast (all others donated for study by National Museum of Ireland, Dublin).

Appendix B2: Major element composition of Irish prehistoric goldwork (all data)

Accession No.	Artefact	Find Location	County	Ag %	Sn %	Cu %
Chalcolithic and Early Bronze Age						
1877:52	Lunula	Carrowduff	Clare	13.83	0.06	0.11
				14.10	0.16	0.20
				14.29	0.19	0.24
NMI1881:90	Lunula	n/a	n/a	10.64	0.03	0.10
				10.81	0.08	0.14
				10.80	0.06	0.09
1881:91	Lunula	n/a	n/a	13.78	0.05	0.19
				13.60	0.06	0.16
				13.60	0.03	0.00
1884:07	Lunula	Mullingar	Westmeath	12.73	0.00	3.19
				12.27	0.00	3.24
				12.45	0.00	3.21
1884:494	Lunula	Crossdoney	Cavan	11.19	0.00	0.49
				11.34	0.04	0.43
				11.07	0.06	0.42
1884:495	Lunula	Trillick	Tyrone	12.61	0.20	0.16
				12.54	0.09	0.12
				12.82	0.20	0.10
1889:20	Lunula	Trentagh	Donegal	9.99	0.04	0.40
				10.50	0.07	0.46
				10.19	0.06	0.30
1893:04	Lunula	Athlone	Westmeath	8.67	0.01	0.90
				8.69	0.03	1.07
				8.77	0.01	0.93
1896:15	Lunula	Ross	Westmeath	10.99	0.04	0.06
				11.22	0.03	0.08
				11.29	0.08	0.10
1900:50	Lunula	Tremoge	Tyrone	13.54	0.12	0.16
				13.50	0.08	0.13
				13.40	0.16	0.15
1909:04	Lunula	West Coast	Mayo	8.66	0.00	0.28
				8.41	0.03	0.41
				8.40	0.02	0.31
1909:06	Lunula	Naran	Donegal	10.21	0.08	0.04
				10.32	0.08	0.04
				10.54	0.08	0.06
1909:07	Lunula	Rosgarron	Derry	11.67	0.12	0.36
				11.51	0.18	0.44
				11.48	0.13	0.36
1910:45	Lunula	Bawnboy	Cavan	11.51	0.01	0.16

				11.26	0.11	0.17
				11.25	0.06	0.18
1946:392	Lunula	n/a	n/a	13.74	0.07	0.09
				13.95	0.09	0.10
				13.71	0.08	0.08
1998:74	Lunula	Ballinagroun	Kerry	8.89	0.00	1.96
				8.99	0.00	1.91
				8.95	0.00	2.05
P817	Lunula	n/a	n/a	10.94	0.09	0.16
				11.04	0.06	0.16
				11.06	0.06	0.10
P949	Disc	n/a	Roscommon	9.65	0.07	0.31
				9.69	0.01	0.46
				9.97	0.06	0.61
R625	Lunula	n/a	n/a	8.28	0.00	0.02
				8.42	0.00	0.07
				8.41	0.00	0.02
R1755	Lunula	Banemore	Kerry	11.54	0.00	0.05
				11.75	0.03	0.06
				11.83	0.01	0.09
R1756	Lunula	Banemore	Kerry	7.90	0.00	0.08
				8.05	0.00	0.06
				7.87	0.00	0.12
R1757	Lunula	Banemore	Kerry	11.34	0.03	0.19
				11.33	0.02	0.24
				11.48	0.06	0.42
R2612	Lunula	n/a	n/a	17.02	0.01	0.12
				17.14	0.01	0.10
				17.01	0.00	0.15
R4023	Lunula	n/a	n/a	12.95	0.01	0.10
				12.91	0.04	0.11
				13.00	0.05	0.12
R4024	Lunula	Island Magee	Antrim	12.46	0.05	0.33
				12.43	0.05	0.37
				12.73	0.03	0.36
SA1913:127	Pin	Ballyvourney	Cork	16.07	0.26	7.20
				16.05	0.22	7.13
				17.00	0.23	6.63
SA1913:128	Disc	Ballyvourney	Cork	16.15	0.06	0.23
				16.38	0.01	0.32
				16.45	0.04	0.20
SA1913:131	Trapezoidal Plaque	Knockane	Cork	16.69	0.13	5.75
				16.42	0.16	5.88
				16.62	0.15	5.85
SA1928:715	Lunula	Rossmore Park	Monaghan	13.89	0.20	0.05

				13.68	0.16	0.06
				13.74	0.28	0.09
W1	Lunula	n/a	n/a	11.26	0.00	0.23
				10.91	0.00	0.19
				11.33	0.00	0.28
W2	Lunula	Killarney	Kerry	3.76	0.02	0.06
				3.76	0.00	0.09
				3.84	0.00	0.04
W3	Lunula	n/a	n/a	12.65	0.06	0.19
				12.22	0.11	0.18
				12.34	0.04	0.18
W4/R136	Lunula	Dunfierth	Kildare	12.39	0.06	0.16
				12.50	0.06	0.10
				12.48	0.03	0.13
W5	Lunula	n/a	n/a	11.84	0.02	0.12
				11.80	0.00	0.24
				11.61	0.00	0.12
W6	Lunula	n/a	n/a	10.32	0.00	1.88
				10.50	0.01	0.06
				10.54	0.00	0.10
W7	Lunula	n/a	n/a	11.23	0.00	0.18
				11.12	0.02	0.23
				11.31	0.03	0.21
W8/R135	Lunula	Dunfierth	Kildare	13.77	0.29	0.02
				13.79	0.45	0.01
				13.89	0.19	0.00
W9/R138	Lunula	Dunfierth	Kildare	13.61	0.19	0.14
				13.85	0.37	0.17
				12.99	0.34	0.14
W10	Lunula	n/a	Galway	10.32	0.27	0.07
				10.18	0.38	0.13
				10.45	0.48	0.23
W11	Lunula	n/a	n/a	14.46	0.00	0.02
				14.17	0.00	0.01
				14.66	0.06	0.02
W12	Lunula	n/a	n/a	12.04	0.05	0.26
				12.07	0.06	0.22
				12.22	0.09	0.28
W13	Lunula	n/a	n/a	12.43	0.02	0.07
				12.62	0.00	0.08
				12.68	0.00	0.10
W14	Lunula	n/a	n/a	12.34	0.14	0.24
				12.36	0.09	0.24
				12.41	0.11	0.28
W15/R137	Lunula	Dunfierth	Kildare	12.92	0.15	0.09

				13.09	0.18	0.18
				12.92	0.16	0.16
W74[a]	Basket Ornament	n/a	n/a	10.39	0.08	0.83
				10.13	0.11	0.79
				10.32	0.12	0.81
				10.56	0.09	0.75
				10.37	0.00	0.73
				10.90	0.07	0.72
				10.56	0.20	0.75
				10.37	0.00	0.86
				10.35	0.03	0.83
				10.51	0.10	0.84
W75	Oval Plaque	Belville	Cavan	10.57	0.04	0.13
				10.58	0.01	0.08
				10.74	0.02	0.17
W76	Oval Plaque	Belville	Cavan	10.29	0.00	0.15
				10.38	0.00	0.17
				10.36	0.00	0.26
W78[b]	Oval Plaque	Belville	Cavan	9.45	0.00	0.29
				9.94	0.01	0.36
				10.10	0.00	0.26
W79[b]	Oval Plaque	Belville	Cavan	9.83	0.00	0.20
				10.06	0.00	0.29
				9.92	0.00	0.43
W81[b]	Oval Plaque	Belville	Cavan	10.07	0.00	0.23
				10.12	0.03	0.42
				9.48	0.01	0.28
W266	Disc	n/a	n/a	15.63	0.02	0.21
				15.41	0.01	0.15
				15.46	0.00	0.14
W270	Disc	n/a	n/a	11.90	0.00	0.47
				11.79	0.01	0.41
				11.83	0.00	0.54
Middle Bronze Age mba1						
A1910:673[c]	Ribbed Ring	n/a	n/a	12.05	0.16	1.02
				11.91	0.14	0.99
				11.43	0.18	1.34
R1680	Flanged Torc	n/a	Down	11.49	0.44	1.31
				11.75	0.43	1.25
				11.58	0.51	1.35
Middle Bronze Age mba2						
1878:03	Bar Torc	Giants Causeway	Antrim	17.45	0.33	5.72
				17.40	0.33	5.80
				17.34	0.18	5.70
1929.1302	Penannular Ring	Kilmallock	Limerick	19.34	0.29	4.49

				18.30	0.23	4.42
				17.82	0.22	4.25
1935:879	Penannular Ring	Ballina	Mayo	17.09	0.27	4.90
				16.99	0.42	5.04
				17.13	0.37	5.15
A210.1913[c]	Penannular Ring	Belfast	Antrim	17.17	0.37	5.20
				16.97	0.37	5.15
				17.58	0.23	4.62
W174	Wire Bound Torc	n/a	Galway	15.71	0.31	5.26
				16.88	0.31	5.26
				17.17	0.24	5.27
				17.24	0.21	5.10
				17.27	0.27	5.06
				16.97	0.23	5.13
				16.96	0.26	5.22
				17.36	0.28	5.24
				17.39	0.27	5.24
				17.19	0.29	5.24
				17.15	0.26	5.29
				17.34	0.25	5.30
				17.27	0.23	5.31
				17.31	0.26	5.32
				17.13	0.29	5.30
				16.97	0.24	5.37
				17.05	0.26	5.38
				17.08	0.33	5.42
				17.16	0.29	5.45
				17.19	0.29	5.44
				17.16	0.31	5.42
				17.07	0.27	5.37
				17.25	0.30	5.36
				17.30	0.31	5.31
				17.33	0.23	5.25
				17.15	0.26	5.25
				17.46	0.34	5.27
				17.26	0.29	5.28
				17.40	0.27	5.23
				17.26	0.30	5.16
				17.36	0.22	5.05
				17.51	0.23	5.20
				17.28	0.23	5.21
				17.36	0.27	5.63
				17.11	0.28	5.33
				17.22	0.24	5.33
				16.08	0.25	5.20
				17.08	0.25	5.38

				17.09	0.29	5.28
				17.34	0.21	5.17
				17.23	0.24	5.14
				17.33	0.26	5.17
				17.05	0.27	5.18
				17.23	0.31	5.27
				17.00	0.26	5.29
				17.12	0.30	5.30
				16.96	0.26	5.23
				16.78	0.31	5.77
				17.23	0.27	5.21
				17.14	0.29	5.20
				17.09	0.27	5.18
Late Bronze Age lba						
1904:02	Bracelet	Mooghaun	Clare	13.01	0.19	7.21
				13.02	0.18	7.17
				12.83	0.18	6.71
1918:355	Bulla	River Bann	n/a	15.35	0.14	5.80
				14.99	0.08	5.92
				15.09	0.08	5.81
1941:1154	Bracelet	Lissandrone	Mayo	12.96	0.06	6.42
				10.06	0.08	3.67
				10.61	0.00	2.09
A7532[c]	Sleeve Fastener	Ballinagard	Antrim	13.76	0.15	7.27
				13.72	0.13	7.42
				13.33	0.14	7.63
A7533[c]	Sleeve Fastener	Ballyculter	Down	14.02	0.20	7.04
				14.09	0.24	6.97
				13.63	0.18	7.36
AD1.2[c]	Bracelet	Downpatrick	Down	13.75	0.22	5.05
				13.73	0.24	5.44
				13.51	0.21	5.52
AD1.5[c]	Bracelet	Downpatrick	Down	13.13	0.15	5.72
				12.44	0.13	5.50
				13.08	0.22	6.05
W27	Large Ring	Mooghaun	Clare	13.78	0.12	6.85
				13.31	0.05	6.55
				12.86	0.16	7.74
W117	Bracelet	Mooghaun	Clare	13.76	0.16	6.51
				13.79	0.13	6.44
				13.60	0.15	6.64
W175	Neck Ring	Mooghaun	Clare	12.71	0.01	6.25
				12.46	0.03	7.12
				12.13	0.05	7.52
Iron Age						

1888:14	Ribbon Torc	Lissandrone	Mayo	21.11	0.03	3.38
				20.89	0.06	3.46
				21.05	0.05	3.22

Notes: [a]sample analysed by Eric Condliffe (School of Earth Sciences, University of Leeds), [b]all samples from the same artefact, [c]samples donated for study by the Ulster Museum, Belfast (all others donated for study by National Museum of Ireland, Dublin).

B3: Lead isotope signature of Irish prehistoric goldwork (mean data)

Accession No.	Artefact	Find Location	County	^{206}Pb/^{204}Pb	2 S.E.	^{207}Pb/^{204}Pb	2 S.E.	^{208}Pb/^{204}Pb	2 S.E.	^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
Chalcolithic and Early Bronze Age													
1877:52	Lunula	Carrowduff	Clare							0.8490	0.0001	2.0966	0.0002
1881:90	Lunula	n/a	n/a							0.8384	0.0007	2.0591	0.0016
1881:91	Lunula	n/a	n/a	18.750	0.005	15.628	0.004	38.431	0.013	0.8375	0.0039	2.0602	0.0105
1884:07	Lunula	Mullingar	Westmeath							0.8506	0.0002	2.0778	0.0011
1884:494	Lunula	Crossdoney	Cavan							0.8363	0.0006	2.0619	0.0017
1884:495	Lunula	Trillick	Tyrone							0.8384	0.0008	2.0681	0.0007
1889:20	Lunula	Trentagh	Donegal							0.8476	0.0005	2.0842	0.0015
1893:04	Lunula	Athlone	Westmeath							0.8534	0.0001	2.0842	0.0002
1896:15	Lunula	Ross	Westmeath	18.931	0.005	15.652	0.005	38.193	0.015	0.8263	0.0002	2.0163	0.0010
1900:50	Lunula	Tremoge	Tyrone							0.8357	0.0002	2.0619	0.0005
1909:04	Lunula	West Coast	Mayo							0.8538	0.0001	2.0849	0.0002
1909:06	Lunula	Naran	Donegal	18.474	0.004	15.668	0.003	38.553	0.009	0.8476	0.0002	2.0858	0.0003
1909:07	Lunula	Rosgarron	Derry							0.8367	0.0009	2.0515	0.0018
1910:45	Lunula	Bawnboy	Cavan							0.8431	0.0003	2.0712	0.0003
1946:392	Lunula	n/a	n/a	18.522	0.005	15.634	0.005	38.567	0.015	0.8438	0.0001	2.0822	0.0002
1998:74	Lunula	Ballinagroun	Kerry	18.350	0.004	15.643	0.002	38.222	0.008	0.8525	0.0001	2.0830	0.0001
P817	Lunula	n/a	n/a	18.793	0.006	15.593	0.006	38.175	0.017	0.8293	0.0005	2.0298	0.0011
P949	Disc	n/a	Roscommon	18.839	0.006	15.582	0.005	38.391	0.015	0.8267	0.0003	2.0366	0.0007
R1755	Lunula	Banemore	Kerry	18.593	0.004	15.629	0.003	38.240	0.010	0.8405	0.0003	2.0564	0.0003
R1756	Lunula	Banemore	Kerry	18.696	0.006	15.707	0.006	38.687	0.019	0.8404	0.0001	2.0693	0.0004
R1757	Lunula	Banemore	Kerry							0.8406	0.0007	2.0613	0.0011
R2612	Lunula	n/a	n/a										

R4023	Lunula	n/a	n/a	18.613	0.006	15.613	0.005	38.442	0.017	0.8387	0.0002	2.0643	0.0009
R4024	Lunula	Island Magee	Antrim							0.8377	0.0013	2.0563	0.0083
R625	Lunula	n/a	n/a	18.258	0.004	15.606	0.003	38.188	0.009	0.8550	0.0017	2.0917	0.0032
SA1913:127	Pin	Ballyvourney	Cork							0.8490	0.0006	2.0852	0.0014
SA1913:128	Disc	Ballyvourney	Cork							0.8459	0.0008	2.0820	0.0012
SA1913:131	Trapezoidal Plaque	Knockane	Cork	18.430	0.004	15.635	0.003	38.402	0.009	0.8483	0.0000	2.0838	0.0004
SA1928:715	Lunula	Rossmore Park	Monaghan	19.338	0.003	15.666	0.003	38.655	0.008	0.8100	0.0001	1.9991	0.0001
W1	Lunula	n/a	n/a	18.494	0.004	15.638	0.003	38.187	0.012	0.8455	0.0002	2.0646	0.0010
W2	Lunula	Killarney	Kerry										
W3	Lunula	n/a	n/a							0.8414	0.0001	2.0834	0.0003
W4/R136	Lunula	Dunfierth	Kildare							0.8522	0.0001	2.0900	0.0002
W5	Lunula	n/a	n/a							0.8385	0.0015	2.0635	0.0035
W6	Lunula	n/a	n/a							0.8471	0.0005	2.0687	0.0030
W7	Lunula	n/a	n/a	18.943	0.005	15.611	0.004	38.322	0.011	0.8187	0.0017	2.0128	0.0009
W8/R135	Lunula	Dunfierth	Kildare	18.502	0.003	15.625	0.003	38.922	0.009	0.8446	0.0003	2.1037	0.0001
W9/R138	Lunula	Dunfierth	Kildare	18.619	0.004	15.635	0.003	38.457	0.009	0.8397	0.0004	2.0658	0.0007
W10	Lunula	n/a	Galway	19.477	0.005	15.676	0.004	38.740	0.011	0.7989	0.0003	1.9765	0.0005
W11	Lunula	n/a	n/a							0.8471	0.0002	2.0863	0.0017
W12	Lunula	n/a	n/a							0.8406	0.0052	2.0653	0.0102
W13	Lunula	n/a	n/a							0.8159	0.0015	2.0115	0.0021
W14	Lunula	n/a	n/a	18.605	0.003	15.634	0.002	38.527	0.008	0.8401	0.0005	2.0703	0.0025
W15/R137	Lunula	Dunfierth	Kildare	18.475	0.004	15.626	0.003	38.405	0.010	0.8459	0.0001	2.0793	0.0002
W74[a]	Basket Ornament	n/a	n/a	18.365	0.005	15.615	0.004	38.216	0.010	0.8503	0.0001	2.0810	0.0003
W75	Oval Plaque	Belville	Cavan							0.8267	0.0024	2.0296	0.0039
W76	Oval Plaque	Belville	Cavan										
W78[b]	Oval Plaque	Belville	Cavan							0.8446	0.0013	2.0655	0.0030

W79[b]	Oval Plaque	Belville	Cavan							0.8371	0.0013	2.0497	0.0022
W81[b]	Oval Plaque	Belville	Cavan							0.8559	0.0016	2.0915	0.0038
W266	Disc	n/a	n/a							0.8274	0.0015	2.0371	0.0031
W270	Disc	n/a	n/a							0.8471	0.0015	2.0844	0.0042
Middle Bronze Age mba1													
A1910:673[c]	Ribbed Ring	n/a	n/a							0.8444	0.0011	2.0783	0.0019
R1680	Flanged Torc	n/a	Down	18.445	0.001	15.598	0.002	38.414	0.011	0.8456	0.0001	2.0826	0.0002
Middle Bronze Age mba2													
1878:03	Bar Torc	Giants Causeway	Antrim							0.8514	0.0003	2.0927	0.0003
1929.1302	Penannular Ring	Kilmallock	Limerick							0.8497	0.0005	2.0865	0.0019
1935:879	Penannular Ring	Ballina	Mayo							0.8484	0.0005	2.0854	0.0014
A210.1913c	Penannular Ring	Belfast	Antrim							0.8520	0.0012	2.0937	0.0005
W174	Wire Bound Torc	n/a	Galway	18.455	0.031	15.661	0.025	38.502	0.066	0.8486	0.0001	2.0861	0.0002
Late Bronze Age lba													
1904:02	Bracelet	Mooghaun	Clare							0.8484	0.0003	2.0844	0.0001
1918:355	Bulla	River Bann	n/a							0.8496	0.0008	2.0875	0.0019
1941:1154	Bracelet	Lissandrone	Mayo	18.500	0.014	15.637	0.004	38.427	0.023	0.8471	0.0019	2.0818	0.0048
A7532c	Sleeve Fastener	Ballinagard	Antrim							0.8492	0.0008	2.0868	0.0017
A7533c	Sleeve Fastener	Ballyculter	Down							0.8476	0.0010	2.0844	0.0024
AD1.2c	Bracelet	Downpatrick	Down							0.8483	0.0008	2.0835	0.0019
AD1.5c	Bracelet	Downpatrick	Down	18.347	0.031	15.642	0.026	38.343	0.063	0.8503	0.0034	2.0874	0.0042
W27	Large Ring	Mooghaun	Clare							0.8481	0.0001	2.0838	0.0000
W117	Bracelet	Mooghaun	Clare							0.8473	0.0005	2.0818	0.0015
W175	Neck Ring	Mooghaun	Clare										
Iron Age													
1888:14	Ribbon Torc	Lissandrone	Mayo	18.911	0.039	15.639	0.001	38.476	0.004	0.8262	0.0003	2.0326	0.0007

Notes: ^{206}Pb/^{204}Pb, ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb collected by solution MC-ICP-MS, errors ± 2 standard errors of the mean of 50 integration cycles. ^{207}Pb/^{206}Pb and ^{208}Pb^{206}Pb data collecteed by laser ablation MC-CP-MS, errors usually ± 2 standard errors of the mean of 3 analyses, when sample size restricted the number of analyses errors are ± 2 standard errors of the mean of 2 analyses or ± 2 standard errors of the mean of 180 integration cycles. [a]W74 all data collected by solution MC-ICP-MS, [b]all samples from the same artefact, [c]samples donated for study by the Ulster Museum, Belfast (all others donated for study by National Museum of Ireland, Dublin).

B4: Lead isotope signature of Irish prehistoric goldwork (all data)

Accession No.	Artefact	Find Location	County	$^{206}Pb/^{204}Pb$	2 S.E.	$^{207}Pb/^{204}Pb$	2 S.E.	$^{208}Pb/^{204}Pb$	2 S.E.	$^{207}Pb/^{206}Pb$	2 S.E.	$^{208}Pb/^{206}Pb$	2 S.E.
Chalcolithic and Early Bronze Age													
1877:52	Lunula	Carrowduff	Clare							0.8489	0.0003	2.0966	0.0006
										0.8491	0.0002	2.0968	0.0004
										0.8490	0.0002	2.0965	0.0004
NMI1881:90	Lunula	n/a	n/a							0.8378	0.0004	2.0578	0.0007
										0.8390	0.0005	2.0605	0.0012
										0.8384	0.0004	2.0590	0.0008
1881:91[c]	Lunula	n/a	n/a							0.8393	0.0004	2.0655	0.0011
										0.8397	0.0012	2.0654	0.0031
										0.8336	0.0003	2.0497	0.0006
1884:07	Lunula	Mullingar	Westmeath							0.8508	0.0003	2.0793	0.0007
										0.8506	0.0002	2.0778	0.0004
										0.8504	0.0001	2.0769	0.0004
										0.8505	0.0002	2.0772	0.0004
1884:494	Lunula	Crossdoney	Cavan							0.8364	0.0005	2.0617	0.0008
										0.8358	0.0007	2.0605	0.0010
										0.8368	0.0005	2.0634	0.0010
1884:495	Lunula	Trillick	Tyrone							0.8389	0.0005	2.0688	0.0008
										0.8387	0.0006	2.0678	0.0013
										0.8376	0.0009	2.0678	0.0014
1889:20	Lunula	Trentagh	Donegal							0.8476	0.0003	2.0842	0.0005
1893:04	Lunula	Athlone	Westmeath	18.314	0.024	15.631	0.020	38.169	0.049	0.8534	0.0001	2.0842	0.0002
				18.312	0.024	15.628	0.021	38.161	0.052	0.8533	0.0001	2.0840	0.0002

				18.322	0.020	15.637	0.018	38.184	0.044	0.8535	0.0001	2.0842	0.0002
1896:15	Lunula	Ross	Westmeath							0.8266	0.0002	2.0179	0.0005
										0.8262	0.0001	2.0159	0.0003
										0.8261	0.0001	2.0159	0.0002
										0.8262	0.0002	2.0157	0.0004
1900:50	Lunula	Tremoge	Tyrone							0.8358	0.0006	2.0623	0.0013
										0.8355	0.0003	2.0619	0.0006
										0.8358	0.0004	2.0614	0.0009
1909:04	Lunula	West Coast	Mayo	18.331	0.040	15.649	0.034	38.265	0.082	0.8539	0.0001	2.0850	0.0002
				18.359	0.034	15.672	0.029	38.314	0.071	0.8538	0.0001	2.0848	0.0002
1909:06	Lunula	Naran	Donegal							0.8478	0.0005	2.0856	0.0008
										0.8475	0.0011	2.0861	0.0017
										0.8475	0.0005	2.0857	0.0007
1909:07	Lunula	Rosgarron	Derry							0.8370	0.0002	2.0520	0.0004
										0.8373	0.0002	2.0527	0.0004
										0.8359	0.0002	2.0497	0.0005
1910:45	Lunula	Bawnboy	Cavan							0.8429	0.0002	2.0710	0.0005
										0.8433	0.0003	2.0714	0.0006
1946:392	Lunula	n/a	n/a							0.8438	0.0002	2.0821	0.0002
										0.8438	0.0001	2.0823	0.0003
										0.8437	0.0001	2.0821	0.0003
1998:74	Lunula	Ballinagroun	Kerry							0.8526	0.0001	2.0832	0.0003
				18.358	0.038	15.648	0.031	38.236	0.076	0.8524	0.0002	2.0830	0.0004
				18.361	0.032	15.652	0.029	38.245	0.070	0.8525	0.0002	2.0829	0.0005
P817	Lunula	n/a	n/a							0.8290	0.0001	2.0291	0.0003
										0.8292	0.0002	2.0293	0.0003

										0.8298	0.0001	2.0308	0.0003
P949	Disc	n/a	Roscommon							0.8268	0.0002	2.0364	0.0006
										0.8264	0.0003	2.0361	0.0005
										0.8270	0.0002	2.0373	0.0004
R625	Lunula	n/a	n/a							0.8533	0.0004	2.0885	0.0007
										0.8557	0.0004	2.0935	0.0008
										0.8561	0.0003	2.0931	0.0006
R1755	Lunula	Banemore	Kerry							0.8402	0.0002	2.0562	0.0004
										0.8406	0.0002	2.0564	0.0004
										0.8406	0.0002	2.0567	0.0005
R1756	Lunula	Banemore	Kerry							0.8405	0.0002	2.0689	0.0004
										0.8403	0.0002	2.0696	0.0004
										0.8403	0.0002	2.0696	0.0004
R1757	Lunula	Banemore	Kerry							0.8411	0.0005	2.0621	0.0008
										0.8399	0.0004	2.0617	0.0008
										0.8408	0.0005	2.0602	0.0009
R2612	Lunula	n/a	n/a										
R4023	Lunula	n/a	n/a							0.8388	0.0005	2.0639	0.0010
										0.8387	0.0005	2.0639	0.0011
										0.8384	0.0005	2.0652	0.0010
R4024	Lunula	Island Magee	Antrim							0.8384	0.0033	2.0605	0.0065
										0.8371	0.0033	2.0522	0.0057
SA1913:127	Pin	Ballyvourney	Cork	18.405	0.040	15.631	0.033	38.394	0.082	0.8496	0.0003	2.0866	0.0004
				18.392	0.024	15.617	0.020	38.340	0.049	0.8487	0.0001	2.0842	0.0002
				18.401	0.038	15.615	0.032	38.360	0.080	0.8487	0.0001	2.0848	0.0003
SA1913:128	Disc	Ballyvourney	Cork							0.8467	0.0003	2.0831	0.0006

										0.8455	0.0006	2.0811	0.0013
										0.8455	0.0003	2.0818	0.0006
SA1913:131	Trapezoidal Plaque	Knockane	Cork							0.8483	0.0002	2.0839	0.0008
										0.8482	0.0003	2.0834	0.0007
										0.8483	0.0003	2.0839	0.0008
SA1928:715	Lunula	Rossmore Park	Monaghan	19.346	0.016	15.670	0.013	38.676	0.036	0.8100	0.0001	1.9992	0.0003
				19.347	0.016	15.671	0.013	38.676	0.034	0.8100	0.0001	1.9991	0.0002
				19.340	0.014	15.664	0.012	38.658	0.030	0.8100	0.0001	1.9991	0.0001
W1	Lunula	n/a	n/a	18.476	0.024	15.627	0.020	38.167	0.048	0.8458	0.0001	2.0659	0.0002
										0.8455	0.0003	2.0641	0.0013
				18.470	0.034	15.614	0.031	38.125	0.082	0.8453	0.0002	2.0638	0.0012
				18.455	0.026	15.603	0.022	38.099	0.054	0.8455	0.0001	2.0645	0.0002
W2	Lunula	Killarney	Kerry										
W3	Lunula	n/a	n/a							0.8413	0.0002	2.0836	0.0005
										0.8414	0.0003	2.0831	0.0005
										0.8415	0.0003	2.0834	0.0005
W4/R136	Lunula	Dunfierth	Kildare							0.8522	0.0001	2.0901	0.0004
										0.8522	0.0001	2.0901	0.0002
				18.303	0.033	15.595	0.029	38.246	0.070	0.8521	0.0001	2.0898	0.0003
W5	Lunula	n/a	n/a							0.8371	0.0009	2.0608	0.0018
										0.8394	0.0011	2.0630	0.0024
										0.8391	0.0012	2.0668	0.0023
W6	Lunula	n/a	n/a							0.8466	0.0008	2.0685	0.0018
										0.8473	0.0006	2.0662	0.0013
										0.8474	0.0006	2.0713	0.0012
W7	Lunula	n/a	n/a							0.8176	0.0008	2.0136	0.0015

										0.8203	0.0007	2.0127	0.0013
										0.8180	0.0007	2.0121	0.0011
W8/R135	Lunula	Dunfierth	Kildare							0.8447	0.0001	2.1036	0.0002
				18.509	0.035	15.631	0.029	38.928	0.073	0.8444	0.0001	2.1037	0.0002
										0.8449	0.0001	2.1038	0.0002
W9/R138	Lunula	Dunfierth	Kildare							0.8400	0.0004	2.0662	0.0008
										0.8396	0.0004	2.0660	0.0008
										0.8393	0.0005	2.0651	0.0009
W10	Lunula	n/a	Galway							0.7992	0.0003	1.9770	0.0005
										0.7988	0.0002	1.9762	0.0006
										0.7987	0.0003	1.9763	0.0006
W11	Lunula	n/a	n/a							0.8472	0.0002	2.0866	0.0004
										0.8469	0.0005	2.0847	0.0007
										0.8471	0.0002	2.0875	0.0004
W12	Lunula	n/a	n/a							0.8457	0.0007	2.0750	0.0016
										0.8383	0.0002	2.0579	0.0004
										0.8376	0.0002	2.0630	0.0005
W13	Lunula	n/a	n/a							0.8161	0.0009	2.0095	0.0019
										0.8145	0.0011	2.0130	0.0019
										0.8170	0.0009	2.0120	0.0015
W14	Lunula	n/a	n/a							0.8405	0.0004	2.0720	0.0008
										0.8401	0.0004	2.0710	0.0009
										0.8396	0.0005	2.0679	0.0010
W15/R137[c]	Lunula	Dunfierth	Kildare	18.457	0.030	15.611	0.026	38.375	0.064	0.8458	0.0003	2.0793	0.0009
				18.479	0.038	15.630	0.032	38.423	0.081	0.8458	0.0001	2.0791	0.0004
				18.458	0.054	15.615	0.046	38.382	0.113	0.8460	0.0001	2.0795	0.0003

W75	Oval Plaque	Belville	Cavan							0.8267	0.0024	2.0296	0.0039
W76	Oval Plaque	Belville	Cavan										
W78[a]	Oval Plaque	Belville	Cavan							0.8446	0.0012	2.0655	0.0027
W79[a]	Oval Plaque	Belville	Cavan							0.8383	0.0008	2.0519	0.0015
										0.8361	0.0009	2.0487	0.0016
										0.8371	0.0010	2.0484	0.0018
W81[a]	Oval Plaque	Belville	Cavan							0.8559	0.0015	2.0915	0.0035
W266	Disc	n/a	n/a							0.8274	0.0015	2.0371	0.0028
W270	Disc	n/a	n/a							0.8473	0.0006	2.0838	0.0014
										0.8458	0.0006	2.0810	0.0014
										0.8483	0.0002	2.0883	0.0004
Middle Bronze Age mba1													
A1910:673[b]	Ribbed Ring	n/a	n/a							0.8438	0.0004	2.0774	0.0007
										0.8449	0.0004	2.0793	0.0006
R1680	Flanged Torc	n/a	Down	18.447	0.045	15.601	0.038	38.423	0.095	0.8457	0.0001	2.0827	0.0002
				18.447	0.023	15.599	0.020	38.414	0.049	0.8456	0.0001	2.0825	0.0003
Middle Bronze Age mba2													
1878:03	Bar Torc	Giants Causeway	Antrim							0.8513	0.0002	2.0928	0.0004
										0.8515	0.0002	2.0926	0.0003
1929.1302	Penannular Ring	Kilmallock	Limerick							0.8497	0.0003	2.0865	0.0012
1935:879	Penannular Ring	Ballina	Mayo							0.8484	0.0002	2.0854	0.0004
										0.8486	0.0012	2.0894	0.0139
A210.1913[b]	Penannular Ring	Belfast	Antrim							0.8514	0.0019	2.0934	0.0036
										0.8526	0.0011	2.0939	0.0019
W174	Wire Bound Torc	n/a	Galway	18.441	0.054	15.651	0.046	38.473	0.113	0.8485	0.0001	2.0860	0.0003
				18.473	0.051	15.675	0.043	38.540	0.107	0.8486	0.0001	2.0862	0.0002

Late Bronze Age lba													
1904:02	Bracelet	Mooghaun	Clare							0.8483	0.0001	2.0843	0.0002
										0.8486	0.0002	2.0844	0.0002
1918:355	Bulla	River Bann	n/a							0.8496	0.0007	2.0875	0.0013
1941:1154	Bracelet	Lissandrone	Mayo							0.8462	0.0002	2.0794	0.0005
				18.509	0.046	15.636	0.040	38.443	0.098	0.8481	0.0001	2.0842	0.0003
A7532[b]	Sleeve Fastener	Ballinagard	Antrim							0.8492	0.0006	2.0868	0.0010
A7533[b]	Sleeve Fastener	Ballyculter	Down							0.8471	0.0014	2.0832	0.0024
										0.8481	0.0005	2.0855	0.0011
AD1.2[b]	Bracelet	Downpatrick	Down							0.8483	0.0007	2.0835	0.0014
AD1.5[b]	Bracelet	Downpatrick	Down	18.349	0.031	15.643	0.026	38.347	0.063	0.8520	0.0002	2.0894	0.0003
										0.8486	0.0002	2.0853	0.0003
W27	Large Ring	Mooghaun	Clare							0.8481	0.0002	2.0838	0.0004
										0.8482	0.0008	2.0838	0.0013
W117	Bracelet	Mooghaun	Clare							0.8473	0.0002	2.0818	0.0005
W175	Neck Ring	Mooghaun	Clare										
Iron Age													
1888:14	Ribbon Torc	Lissandrone	Mayo	18.936	0.035	15.643	0.029	38.488	0.072	0.8260	0.0001	2.0323	0.0003
										0.8264	0.0001	2.0329	0.0004

Notes: Errors ± 2 standard errors of the mean of ≤140 integration cycles. ^{204}Pb only presented when ^{204}(Pb+Hg)/^{202}Hg is >1. [a]all samples from the same artefact, [b]samples donated for study by the Ulster Museum, Belfast (all others donated for study by National Museum of Ireland, Dublin). [c]Standish et al., 2013.

B5: Mineral inclusion suites of Irish Chalcolithic and Early Bronze Age goldwork

Accession No.	Artefact	Find Location	County	Quartz	Al-silicate	AlCa-silicate	AlK-silicate	AlNa-silicate	AlNaCl-silicate	Mg-silicate	Calcium	NaClK
1877:52	Lunula	Carrowduff	Clare	3			1			1		
1881:90	Lunula	n/a	n/a	4								
1881:91	Lunula	n/a	n/a	3						1		
1884:07	Lunula	Mullingar	Westmeath	1		1				1		
1884:494	Lunula	Crossdoney	Cavan	2								
1884:495	Lunula	Trillick	Tyrone									
1889:20	Lunula	Trentagh	Donegal	3								
1893:04	Lunula	Athlone	Westmeath	2								
1896:15	Lunula	Ross	Westmeath	3								
1900:50	Lunula	Tremoge	Tyrone									
1909:04	Lunula	West Coast	Mayo									
1909:06	Lunula	Naran	Donegal	2								
1909:07	Lunula	Rosgarron	Derry	2								
1910:45	Lunula	Bawnboy	Cavan									
1946:392	Lunula	n/a	n/a	1						1		
1998:74	Lunula	Ballinagroun	Kerry	1								
P817	Lunula	n/a	n/a	2	1					1		
P949	Disc	n/a	Roscommon									
R1755	Lunula	Banemore	Kerry									
R1756	Lunula	Banemore	Kerry	4								
R1757	Lunula	Banemore	Kerry	1								
R2612	Lunula	n/a	n/a	2			1				1	
R4023	Lunula	n/a	n/a	3								

R4024	Lunula	Island Magee	Antrim									
R625	Lunula	n/a	n/a									2
SA1913:127	Pin	Ballyvourney	Cork									
SA1913:128	Disc	Ballyvourney	Cork									
SA1913:131	Trapezoidal Plaque	Knockane	Cork									
SA1928:715	Lunula	Rossmore Park	Monaghan	3								1
W1	Lunula	n/a	n/a	4								
W2	Lunula	Killarney	Kerry	4								
W3	Lunula	n/a	n/a	2					1			
W4/R136	Lunula	Dunfierth	Kildare	3						1	1	
W5	Lunula	n/a	n/a	2								
W6	Lunula	n/a	n/a	3						2		
W7	Lunula	n/a	n/a	6	1					2		
W8/R135	Lunula	Dunfierth	Kildare	6	3							
W9/R138	Lunula	Dunfierth	Kildare	3	1							
W10	Lunula	n/a	Galway	1								
W11	Lunula	n/a	n/a	5								
W12	Lunula	n/a	n/a	5				1				
W13	Lunula	n/a	n/a	3								
W14	Lunula	n/a	n/a	1								1
W15/R137	Lunula	Dunfierth	Kildare	1								
W74[a]	Basket Earring	n/a	n/a	-	-	-	-	-	-	-	-	-
W75	Oval Plaque	Belville	Cavan									
W76	Oval Plaque	Belville	Cavan									
W78[b]	Oval Plaque	Belville	Cavan									
W79[b]	Oval Plaque	Belville	Cavan									

W81[b]	Oval Plaque	Belville	Cavan
W266	Disc	n/a	n/a
W270	Disc	n/a	n/a

Notes: [a]sample not characterised for mineral inclusion suite, [b]all samples from the same artefact.

Appendix C: Copper Alloy Corrected Artefact Lead Isotope Signatures

C1: Early Bronze Age Goldwork

Calculated signatures of gold components assuming origins of copper:

Corrected with Alderley Edge copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.855	0.003	2.072	0.007
1998:74	Lunula	0.858	0.004	2.083	0.006
SA1913:127	Pin	0.852	0.004	2.087	0.008
SA1913:131	Trapezoidal Plaque	0.850	0.004	2.084	0.007

Corrected with Cornwall copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.878	0.075	2.133	0.178
1998:74	Lunula	0.881	0.073	2.142	0.174
SA1913:127	Pin	0.877	0.083	2.153	0.198
SA1913:131	Trapezoidal Plaque	0.875	0.079	2.148	0.188

Corrected with Cwmystwyth copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.841	0.002	2.052	0.003
1998:74	Lunula	0.845	0.002	2.063	0.004
SA1913:127	Pin	0.837	0.009	2.066	0.015
SA1913:131	Trapezoidal Plaque	0.836	0.003	2.063	0.004

Corrected with Great Orme copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.894	0.075	2.172	0.184
1998:74	Lunula	0.897	0.073	2.180	0.181
SA1913:127	Pin	0.895	0.087	2.195	0.214
SA1913:131	Trapezoidal Plaque	0.892	0.079	2.189	0.195

Corrected with Mt Gabriel copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.907	0.083	2.171	0.132
1998:74	Lunula	0.909	0.082	2.179	0.130
SA1913:127	Pin	0.908	0.100	2.193	0.162
SA1913:131	Trapezoidal Plaque	0.905	0.088	2.188	0.140

Corrected with Parys Mountain copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.847	0.006	2.061	0.017
1998:74	Lunula	0.850	0.006	2.072	0.017
SA1913:127	Pin	0.843	0.008	2.075	0.020
SA1913:131	Trapezoidal Plaque	0.842	0.006	2.073	0.018

Corrected with Ross Island copper component		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.845	0.004	2.063	0.010
1998:74	Lunula	0.849	0.004	2.073	0.009
SA1913:127	Pin	0.841	0.007	2.077	0.012
SA1913:131	Trapezoidal Plaque	0.840	0.005	2.074	0.010

Calculated signatures of copper components assuming 'mixed' gold origin:

Corrected with 'mixed' gold origin		^{207}Pb/^{206}Pb	2 S.E.	^{208}Pb/^{206}Pb	2 S.E.
1884:07	Lunula	0.863	0.003	2.093	0.011
1998:74	Lunula	0.867	0.004	2.105	0.011

SA1913:127	Pin	0.859	0.008	2.107	0.019
SA1913:131	Trapezoidal Plaque	0.858	0.003	2.104	0.010

Notes: see text of Chapter 6 for details.

C2: Later Prehistoric Goldwork

Calculated signatures of gold components:

mba1 corrected with IMP-LI 12 metalwork		$^{207}Pb/^{206}Pb$	2 S.E.	$^{208}Pb/^{206}Pb$	2 S.E.
1910:673	Ribbed Ring	0.840	0.004	2.072	0.009
R1680	Flanged Torc	0.843	0.003	2.081	0.007
mba2 corrected with Penard metalwork		$^{207}Pb/^{206}Pb$	2 S.E.	$^{208}Pb/^{206}Pb$	2 S.E.
A210.1913	Penannular Ring	0.846	0.013	2.083	0.024
1878:03	Bar Torc	0.845	0.012	2.080	0.022
1929.1302	Penannular Ring	0.842	0.012	2.068	0.023
1935:879	Ring Money	0.839	0.013	2.066	0.023
W174	Wire Bound Torc	0.839	0.012	2.067	0.022
lba corrected with Ewart metalwork		$^{207}Pb/^{206}Pb$	2 S.E.	$^{208}Pb/^{206}Pb$	2 S.E.
1904:02	Bracelet	0.849	0.007	2.084	0.013
1918:355	Bulla	0.851	0.007	2.091	0.013
1941:1154	Bracelet	0.846	0.009	2.079	0.020
A7532	Sleeve Fastener	0.850	0.007	2.089	0.013
A7533	Sleeve Fastener	0.847	0.007	2.084	0.014
AD1.2	Bracelet	0.848	0.007	2.083	0.013
AD1.5	Bracelet	0.853	0.010	2.090	0.015
W27	Large Ring	0.848	0.007	2.083	0.013
W117	Bracelet	0.846	0.007	2.079	0.013
W175	Neck Ring				

Notes: see text of Chapter 7 for details.