Standish et al., 2014. Chemical Geology **378**–**379**, 40–51.

Cite as: Standish, C.D., Dhuime, B., Chapman, R.J., Hawkesworth, C.J. and Pike, A.W.G., 2014. The genesis of gold mineralisation hosted by orogenic belts: A lead isotope investigation of Irish gold deposits. Chemical Geology **378–379**, 40–51.

Doi: 10.1016/j.chemgeo.2014.04.012.

The genesis of gold mineralisation hosted by orogenic belts: a lead isotope investigation of Irish gold deposits

C. D. Standish[a,*], B. Dhuime[a], R. J. Chapman[b], C. J. Hawkesworth[c], and A. W. G. Pike[d]

[a]School of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK.
[b]School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK.
[c]Department of Earth Sciences, University of St Andrews, St Andrews, KY16 9AL, UK.
[d]Department of Archaeology, University of Southampton, Southampton, SO17 1BF, UK.
*corresponding author, current address: Department of Archaeology, University of Southampton, Southampton, SO17 1BF, UK. Tel.: + 44 (0)23 80592235. Email: C.D.Standish@soton.ac.uk.

Abstract

Lead isotope analyses have been performed on 109 gold and 23 sulphide samples from 34 Irish gold occurrences, including 27 placers, and used to shed light on the sources of mineralising fluids and metals associated with gold mineralisation hosted by orogenic belts. The Pb isotope ratios of lode and placer gold range from $^{206}Pb/^{204}Pb$ = 17.287–18.679, $^{207}Pb/^{204}Pb$ = 15.382–15.661, and $^{208}Pb/^{204}Pb$ = 37.517–38.635, consistent with the Pb isotopic data on previously reported Irish sulphide mineralisation. There is no evidence that gold mineralisation is associated with distinctive source regions, and it appears to have been derived from similar sources to those responsible for the widespread sulphide mineralisation in Ireland. It is inferred that the principal controls on the Au mineralisation are structural and not related to the distribution of Au in their source rocks. The range of Pb isotope ratios favours the interaction of multiple source reservoirs predominantly during the Caledonian Orogeny (c.475–380 Ma). Underlying basement was the primary control on two key sources of Pb. Gold occurrences located to the south-east of the Iapetus Suture are characterised by Pb compositions that derive predominantly from the Late Proterozoic crustal basement or overlying Lower Palaeozoic sediments, whilst those located north-west of the Iapetus Suture are characterised by less radiogenic Pb signatures derived predominantly from Late Proterozoic or older crustal basement. A third source, relatively enriched in radiogenic Pb, also played a role in the formation of a number of Irish gold occurrences, and may have been associated with syn- to post-orogenic intrusives. Magmatic processes may therefore have played an important role in the formation of some gold occurrences located in orogenic settings.

Keywords

Lead isotopes; gold; orogenic belts; lode; placer; Ireland.

1. INTRODUCTION

Gold mineralisation hosted by low grade metamorphic facies, often in proximity to syn- to post-orogenic intrusives, and located within collisional orogenic belts, is commonly referred to as ‘orogenic’ (e.g. Goldfarb et al., 2005; Groves et al., 2003). Such deposits are globally important mineral resources, however their classification has proved problematic because a number of uncertainties regarding their genesis remain. These include the source(s) of the ore fluids and metals and the role of granitoid magmas which are commonly encountered within this tectonic environment (Goldfarb et al., 2005; Groves et al., 2003). Both ‘intrusion related gold’ (e.g. Goldfarb et al., 2005) and gold derived from the porphyry epithermal environment (e.g. Seedorf et al., 2005; Simmonds et al., 2005) can also contribute to the overall gold inventory of an orogenic belt. This study primarily focuses on ‘orogenic’ gold but acknowledges that different fluids may have varying influence at different localities.

Tomkins (2013) identified metamorphic rocks and felsic-intermediate magmas as the two possible sources of gold-bearing fluids. Metamorphic rocks are usually seen as the most likely of the two (Goldfarb et al., 2005; Phillips and Powell, 2010), and the presence of ethane (C_2H_6) in fluid inclusions within orogenic gold mineralisation led Gaboury (2013) to highlight the potential of deeply buried carbonaceous-pyritic metasedimentary rocks. However Yardley and Cleverley (2013) recently questioned the role of metamorphic fluids in orogenic mineralisation on the grounds that fluid release is slow and yet mineralisation forms very quickly. These authors proposed that magmatic fluids may be more important in the formation of orogenic gold than previously recognised. In addition, they suggested that periods of rapid uplift may generate the requisite conditions for orogenic gold formation in instances where there was no magmatic activity.

The lead isotope signature of an ore mineral reflects the composition and age of the geological source(s) of the lead, and acts as a proxy for the source(s) of the principal ore constituents. Lead isotope analysis is frequently used in studies of gold mineralisation worldwide, however most investigations rely on analyses of sulphide minerals associated with vein gold mineralisation (e.g. Arias et al., 1996; Curti, 1987) and only a few studies included analyses of gold particles (Eugster et al., 1995; Kamenov et al., 2013; Pettke and Frei, 1996). Recent development of an accurate and reproducible procedure for lead isotope analysis on gold now allows this technique to be widely applied directly to both vein gold and to placer deposits, and provides a more rigorous approach to the study of gold (Standish et al., 2013). A lead isotope study of placer and lode gold grain populations using this new technique therefore has the potential to provide new perspectives on the sources of ore fluids and metals involved in gold mineralisation hosted by orogenic belts.

Numerous (>100) gold occurrences are present in Ireland (Maclaren, 1903; McArdle et al., 1987; Stanley et al., 2000), the majority of which can be classified as orogenic based on their tectonic settings (e.g. Chapman et al., 2000a; Stanley et al., 2000). Furthermore, most available information (e.g. Wilkinson and Johnston, 1996) is consistent with emplacement of mineralisation by ‘typical’ CO_2-rich and Cl-poor orogenic fluids which generate gold rich and base metal poor mineralisation (Ridley and Diamond, 2000). A large-scale lead isotope study of Irish gold mineralisation therefore provides an excellent opportunity to better understand the genesis of orogenic gold.

Lead isotope analysis has rarely been performed on gold or gold-bearing mineralisation in Ireland, although O’Keeffe (1986) and Parnell et al. (2000)

performed analyses on associated sulphides from the Clontibret and Cavanacaw deposits respectively and Standish et al. (2013) presented data for two Irish placer occurrences. A number of notable studies have employed the technique to investigate other Irish mineral deposits, principally Lower Palaeozoic hosted Early Caledonian massive sulphide mineralisation and Palaeozoic hosted Carboniferous and Variscan Pb-Zn and Cu mineralisation (e.g. Boast et al., 1981; Caulfield et al., 1986; Dixon et al., 1990; Everett et al., 2003; Kinnaird et al., 2002; LeHuray et al., 1987; O'Keeffe, 1986). This wealth of Pb isotope data provides a valuable dataset that can be used to help interpret the isotopic signature of placer gold from different localities.

This paper presents the first large-scale Pb isotope study performed directly on gold mineralisation. The data relate to 34 Irish gold deposits, the majority of which are consistent with the tectonic setting of orogenic gold. This is followed by a discussion focusing on the key sources of Pb associated with Irish gold mineralisation, and the role of syn- to post-orogenic intrusive magmatic rocks.

2. GEOLOGICAL SETTING

2.1. The geology of Ireland

The geology of Ireland (Fig. 1) reflects a long and complex history. In the context of this study, the main formations can be summarised as Precambrian, Lower Palaeozoic, Upper Palaeozoic and post-Variscan.

2.1.1. Precambrian basement

The Precambrian basement of Ireland can be simplified to two distinct units: the north-west terrane (NWT) and south-east terrane (SET). The NWT (Laurentian) is formed of Dalradian (Neoproterozoic) and pre-Dalradian (Lewisian and Grenvillian) lithologies and may be further divided into the Grampian, the Midland Valley, the Southern Uplands and the Mayo (sub) terranes (Fig. 1), whilst the SET (Avalonian) is formed of Late Proterozoic rocks (Daly, 2001; Max and Long, 1985). The NWT and SET were brought together as the Iapetus Ocean closed during the Caledonian Orogeny, c.475 Ma to c.380 Ma (Chew and Stillman, 2009; Holdsworth et al., 2000). At present the Iapetus Suture (solid black line Fig. 1) runs approximately from the Shannon estuary in the south-west to Balbriggan on the east coast (Todd et al., 1991).

2.1.2. Lower Palaeozoic

Cambrian, Ordovician and Silurian rocks overlie the Precambrian basement across much of Ireland. They are exposed in four key regions: the Longford Down Inlier of the Southern Uplands terrane (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 (greywackes, mudstones, shales, siltstones and sandstones) with interbedded basic and mafic volcanics (Aherne et al., 1992; Max et al., 1990; Morris, 1987; Stillman and Williams, 1978; Thompson et al., 1992). These units were affected by Caledonian deformation and metamorphism, the peak of which occurred c.470 Ma, and were the result of a series of collisions between Iapetus crust and associated island arcs, and the Laurentian and Avalonian continents. The Grampian Orogeny (c.470 Ma), an early phase of the Caledonian Orogeny, specifically refers to the collision between an oceanic island arc and the margin of the Laurentian continent (Chew et al., 2010; Cooper et al., 2011; Fettes et al., 1985; Powell and Phillips, 1985). A suite of syn- to post-orogenic intrusions associated with the Grampian Orogeny (dating to c.475–460 Ma) are located in the north and west of

Ireland, and includes the Tyrone Igneous Complex plutons and the Oughterard Granite of Connemara (Chew and Stillman, 2009).

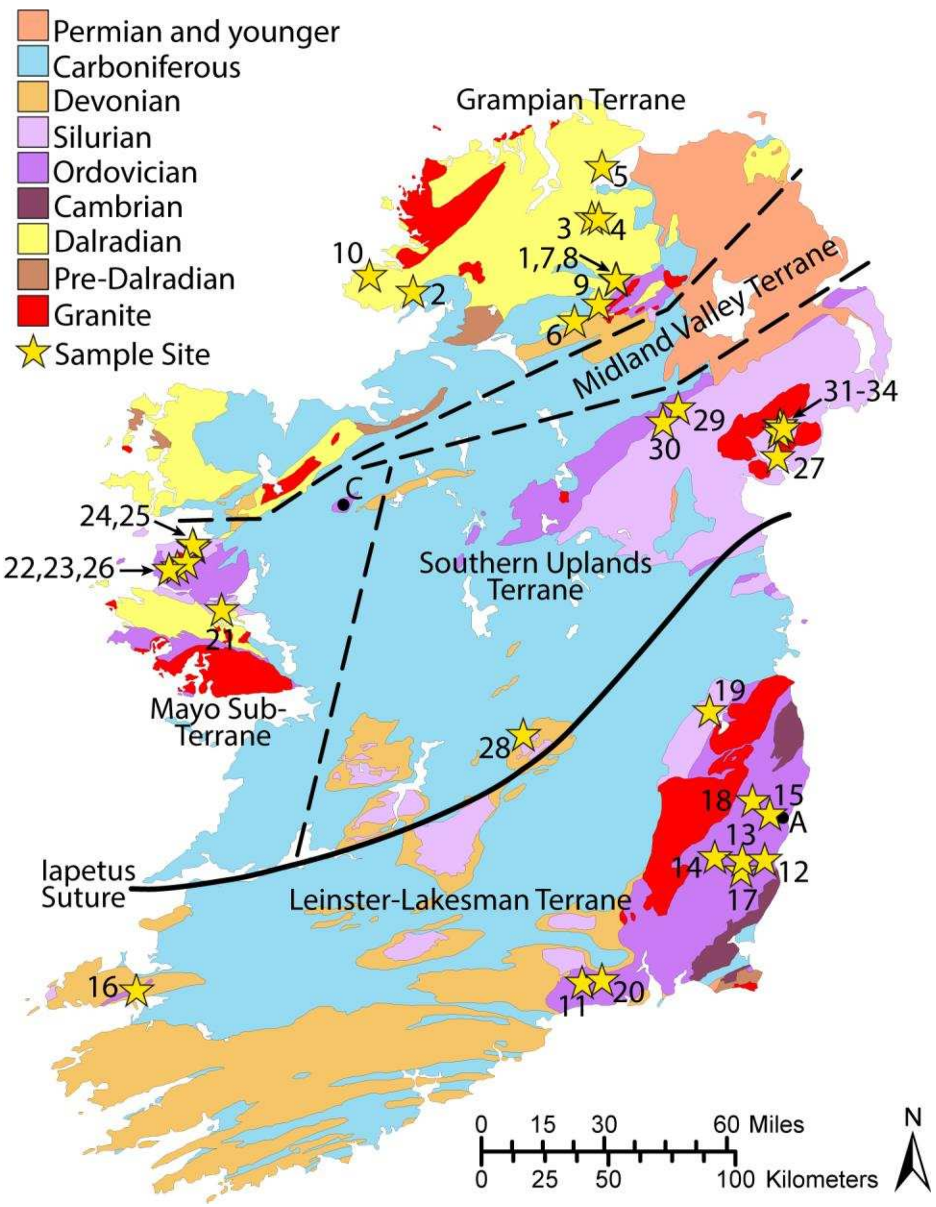

Fig. 1. Simplified geological map of Ireland (based on the Geological Survey of Ireland's 1:500,000 bedrock series map). Sampling locations referred to in this study are plotted as numbered stars (see supplementary data table for correlating location details, key sampling sites/regions discussed in the text are: 2 Balwoges, 6 Cavanacaw, 7 Curraghinalt, 21 Bohaun, 22/23/26 Cregganbaun, 24 Croagh Patrick and 30 Clontibret). Letters represent locations of other mineral deposits discussed in the text (A = Avoca, C = Charlestown). Solid black line represents the approximate trace of the Iapetus Suture, to the south of which lies the south-east terrane (SET) and to the north of which lies the north-west terrane (NWT).

2.1.3. Upper Palaeozoic

Devonian sediments are primarily found in the Munster Basin of south-west Ireland, although sequences are also exposed further north. Terrestrial Old Red Sandstone (ORS) facies dominate with placer and fluvial sequences, whilst marine facies began to develop by the late Upper Devonian (Clayton et al., 1980; MacCarthy, 1990). Syn- to post-orogenic intrusions (for example, the Donegal, Leinster, Newry and Corvock granites) associated with the final closure of the Iapetus Ocean and the late stages of the Caledonian Orogeny (also known as the Acadian Orogeny) were emplaced during the Silurian and Early Devonian, c.430–380 Ma (Chew and Stillman, 2009; Halliday et al., 1980; Murphy, 1987; O'Connor, 1975, 1989; O'Connor and Brück, 1978;). The late Upper Devonian marine transgression continued into the Lower Carboniferous when shale and siltstone deposits from the Lower Tournasian were overlain by thick limestone sequences that host important Pb-Zn deposits (Banks et al., 2002; LeHuray et al., 1987; Wilkinson, 2003). Metamorphism and mineralisation associated with Late Devonian to Carboniferous crustal extension ceased with the onset of the Variscan Orogeny (Kinnaird et al., 2002; Meere, 1995). 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, c.320–270 Ma (Graham, 2001).

2.1.4. Post-Variscan

Post-Variscan rocks are relatively rare in Ireland. Permian, Triassic, Jurassic and Cretaceous sequences are found in north-east Ireland’s Rathlin Trough and Lough Neagh-Larne Basin (McCann, 1988, 1990; Naylor, 1992), whilst Permo-Triassic lithologies have been recorded in Co. Cavan (Kingscourt Graben) and the Wexford Outlier; Jurassic sediments have been identified in the Cloyne Syncline of Co. Cork; and Upper Cretaceous lithologies are present in Co. Kerry (Ballydeenlea Outlier; Naylor, 1992). Tertiary igneous complexes relating to the rifting of North America and Eurasia and the opening of the Atlantic Ocean are present in north-east Ireland (Jolley and Bell, 2002; Stevenson and Bennett, 2011). The vast basaltic lavas of Co. Antrim date to this period (Lyle, 1980; Lyle and Preston, 1993), whilst the Mourne granites of Co. Down were also emplaced at this time (McCormick et al., 1993; Stevenson and Bennett, 2011).

2.2. Gold mineralisation in Ireland

Gold mineralisation is present throughout the Dalradian and Lower Palaeozoic metasedimentary sequences of Ireland (e.g. McArdle et al., 1987; Stanley et al., 2000). A proliferation of exploration activity in the 1980’s resulted in the discovery of several important lode gold occurrences (Table 1.1). Cavanacaw (Earls et al., 1996) has been actively mined, and exploration is at an advanced stage at Curraghinalt (Clifford et al., 1992; Hennessey et al., 2012). Alongside deposit scale studies of other regionally important discoveries, such as Croagh Patrick (Aherne et al., 1992; Wilkinson and Johnston, 1996) and Cregganbaun (Thompson et al., 1992), all have indicated orogenic style mineralisation. However Lusty et al. (2011) suggest a role for low temperature Cl-rich basinal brine-type fluids for the mineralisation at Bohaun (Co. Galway), similar to those invoked for the final phases of mineralisation at Curraghinalt (Parnell et al., 2000) and red-bed Au-Pd mineralisation.

Despite advances in gold exploration leading to better exploration targets in some areas, many Irish gold localities are small placers, or simply records of gold grains recorded during routine stream sediment sampling (McArdle et al., 1987). Chapman et al. (2000a, 2000b, 2006) re-sampled some of these to generate a regional overview of Irish gold mineralisation. Alloy and mineral inclusion signatures of placer gold populations were compared with those from some Irish lode localities and gold compositional data worldwide. The large majority of placer gold signatures (simple binary Au-Ag alloy ± Hg, together with a sulphide-sulpharsenide association) were strongly suggestive of an orogenic source (Table 1.2).

However, in a few localities markedly different signatures were recorded, which Chapman et al. (2000a) ascribed to a different source style of mineralisation. Such deposits have also been included in this study to provide comparative data for other styles of gold mineralisation. A gold alloy characterised by relative high levels of Cu and containing Cu sulphide inclusions from Balwoges, Co. Donegal is most likely related to a local porphyry stock. The occasional presence of Te- bearing minerals as inclusions at localities in Wexford and Wicklow was cited as evidence of a magmatic influence (Chapman et al., 2006), however subsequent regional scale studies in the Yukon Canada have shown that the presence of some Te-bearing minerals as inclusions (including Bi-Te) is not diagnostic of a magmatic association (Chapman et al., 2010, 2011). Nevertheless, the strong Bi-Te signature in placer gold at Curraghinalt is consistent with a magmatic influence which accords with the conclusions from previous studies (Earls et al., 1997; Parnell et al., 2000), and this association most likely relates to the source rocks involved.

Table 1. Principle Irish lode gold occurrences and regions of placer gold

1.1. Principle Irish lode gold occurrences				
Terrane	Locality	Mineralisation type	Reserves or grades of samples (where known)	References
Grampian (Sperrin Mountains)	Cavanacaw	Quartz sulphide veins in Dalradian metasediments	Measured: 20,772 oz Indicated: 121,761 oz Inferred: 295,599 oz	Earls et al. (1996), Cliff and Wolfenden (1992), Phelps and Mawson (2013)
	Curraghinalt	Quartz sulphide veins in Dalradian metasediments	Measured: 0.02 mt @ 21.51 g/t gold (10,000 oz) Indicated: 1.11 mt grading 12.84 g/t gold (460,000 oz) Inferred: 5.45 mt grading 12.74 g/t gold (2,230,000 oz)	Clifford et al. (1992), Boyce et al. (1997), Earls et al. (1997), Hennessey et al. (2012)
Mayo Sub-Terrane	Bohaun	Quartz vein hosted, stockworks, and breccias		Lusty et al. (2011)
	Cregganbaun	Quartz vein hosted, in Ordovician volcano-sedimentary sequence		Thompson et al. (1992)
	Croagh Patrick	Quartz vein hosted, in Silurian quartzites	250,000 T at 10g/t	Aherne et al. (1992), Wilkinson and Johnston (1996)
Southern Uplands	Clontibret	High grade lodes, low grade stockwork	Indicated: 259,956 oz Inferred: 341,148 oz	Morris et al. (1986), Smith et al. (2003), Chapman et al. (2000a) Conroy Gold and Natural Resources (2012)
1.2. Regions of Irish placer gold (not including those associated with the above in situ occurrences)				
Terrane	Region	Mineralisation style[a]	Comments	References
Grampian	Co. Donegal	Orogenic & intrusion related	Minor placer gold	Chapman et al. (2000a; 2000b)
Leinster-Lakesman	Co. Carlow	Orogenic	Very minor placer gold	McArdle et al. (1987), Chapman et al. (2006)
	Co. Dublin	Orogenic	Very minor placer gold	McArdle et al. (1987), Chapman et al. (2006)
	Co. Kerry	Orogenic	Very minor placer gold	Chapman et al. (2006)
	Co. Kildare		Float/minor placer gold	Chapman et al. (2006)
	Co. Tipperary	Orogenic	Very minor placer gold	McArdle et al. (1987), Chapman et al. (2006)
	Co. Waterford		Minor placer gold	Chapman et al. (2006)
	Co. Wexford	Orogenic	Minor placer gold , occasional gold in float	McArdle et al. (1987), O'Connor and Gallagher, (1994), Chapman et al. (2006)
	Co. Wicklow	Orogenic	Historic producer of placer gold	Calvert (1853), Kinahan (1882; 1883), Maclaren (1903), McArdle and Warren (1987), Chapman et al. (2006)

2.3. Lead isotope ratios; a global and regional perspective

There have been numerous attempts to model the global evolution of Pb isotope ratios and the evolution of Pb in key geochemical reservoirs (e.g. Cumming and Richards, 1975; Kramers and Tolstikhin, 1997; Stacey and Kramers, 1975; Zartman and Doe, 1981). Such models are relevant to studies of ore deposits, for example in linking mineralisation to geochemical source regions or in some cases providing them with a broad chronology. However they have a somewhat restricted application in regional Pb isotope studies because they cannot readily take into account localised mixing of material from different geochemical reservoirs.

Previous Pb isotope studies on Irish mineral deposits (Boast et al., 1981; Caulfield et al., 1986; Dixon et al., 1990; Everett et al., 2003; Kinnaird et al., 2002; LeHuray et al., 1987; O'Keeffe, 1986) have resulted in a wealth of Pb isotope data (Fig. 2).

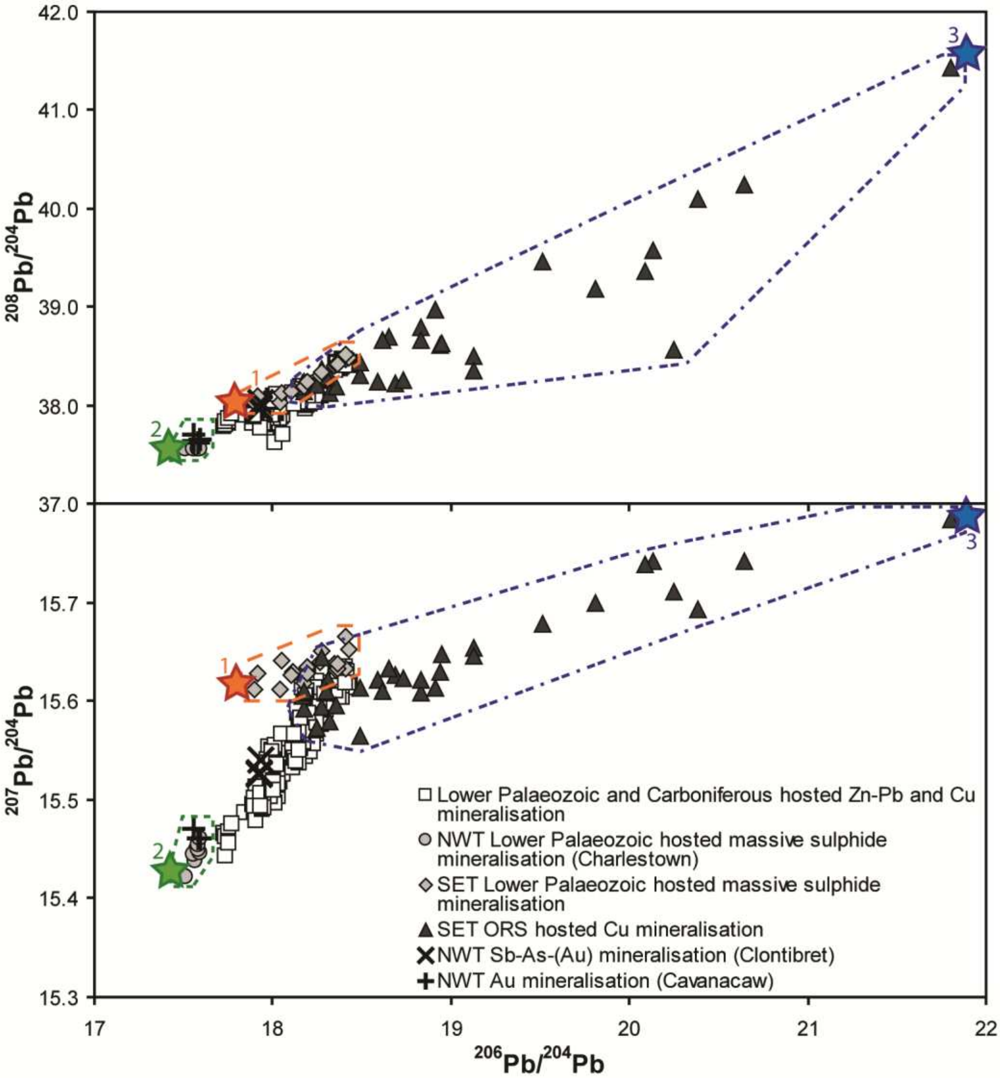

Fig. 2. Published Pb isotope data for Irish mineral deposits, with the approximate isotopic compositions of the three principal Pb sources incorporated into Irish mineralisation defined by dashed lines (stars represent approximate end-member compositions). Data from Boast et al., 1981; Boast, 1983; Caulfield et al., 1986; O'Keeffe, 1986; LeHuray et al., 1987; Dixon et al., 1990; Parnell et al., 2000; Kinnaird et al., 2002; Everett et al., 2003.

They demonstrated how two principal sources of Pb, distinct in their isotopic signatures, were incorporated into ore deposits dating from the Early Caledonian. These sources have a geographic association and are linked to Ireland's underlying basement terranes (i.e. the NWT and SET). Their isotopic compositions were characterised through the analysis of Early Caledonian arc-hosted massive sulphide deposits. Those located overlying the SET (e.g. Avoca, Fig. 1) inherited more radiogenic Pb ultimately derived from the Later Proterozoic crustal basement (henceforth termed 'source 1') whilst those overlying the NWT (Charlestown, Fig. 1) inherited relatively less radiogenic Pb (‘source 2’) from a mantle and/or U- and Th-depleted crustal source (Dixon et al., 1990; LeHuray et al., 1987; O'Keeffe, 1986). Data for Early Caledonian gold bearing mineralisation at Cavanacaw (NWT) is consistent with NWT arc-hosted massive sulphide mineralisation suggesting that a similar arc source was also responsible (Parnell et al., 2000).

Sedimentological and petrological evidence suggests that Silurian (or later) lithologies could be formed from both SET- and NWT-derived material (Hutton and Murphy, 1987; Morris, 1987). This allowed Late Caledonian (such as Clontibret) and younger mineral deposits to inherit Pb derived from both geochemical reservoirs (O'Keeffe, 1986), and resulted in a mixing array between the SET and NWT sources as defined, for example, by Irish Lower Palaeozoic and Carboniferous-hosted Zn-Pb deposits (O'Keeffe, 1986). Indeed the majority of Irish mineral deposits can be explained by variable mixing of these two principal Pb sources.

The isotope ratios of ORS-hosted Cu mineralisation (south-west Ireland) define a trend to a more radiogenic isotopic composition (Fig. 2). This radiogenic component is not present in carbonate-hosted Cu mineralisation from the same region, and so Kinnaird et al. (2002) attributed this trend to mixing between a basement Pb source and a more radiogenic component (‘source 3’) that may have been mobilised from the ORS lithologies but is ultimately derived from granitic intrusives. This hypothesis gained support from Everett et al. (2003) who demonstrated that the Pb isotope signature of the ORS is principally controlled by radiogenic Caledonian granite detritus, and that the mineralogy of the ORS and the presence of igneous clasts are consistent with a granitic input.

3. MATERIALS AND METHODS

3.1. Sampling

Gold mineralisation was sampled from all the key gold bearing regions of Ireland, with the locations of sample sites summarised in Fig. 1. Placer gold was collected through specialised field techniques described by Leake et al. (1997). Specimens of gold-bearing veins and lodes were crushed using a jaw crusher before the heavy mineral fractions were isolated using a Wilfley® concentrating table. Gold grains and sulphide minerals were isolated by handpicking under a microscope.

3.2. Analytical techniques

Lead isotope analyses were performed on gold grains and sulphide minerals. Samples, usually between 2 and 10 mg in weight, were first cleaned by ultrasonication in acetone followed by 2M HCl. Gold samples, which typically have an estimated average Pb content of c.20 ppm, were dissolved in aqua regia, and Pb was separated following the two-stage ion exchange chromatography presented in Standish et al. (2013). Sulphide minerals were dissolved in 7M HNO_3 and Pb was isolated following classic HBr ion exchange techniques (Strelow, 1978; Strelow and Toerien, 1966) and the procedures published by Darling et al. (2010).

Lead isotope composition was determined on a Thermo Fisher Scientific Neptune MC-ICP-MS at the Bristol Isotope Group, School of Earth Sciences, University of Bristol. Sample introduction as a solution employed a Cetac Aridus desolvating unit, and typical operating conditions are outlined in Standish et al. (2013). Standards and samples were both analysed at concentrations of 20 ppb. Instrumental mass bias was corrected by sample-standard bracketing, with NIST SRM981 (and the isotopic composition published by Baker et al., 2004) employed as the bracketing standard.

NIST SRM982 was used as a consistency standard (n = 131, 18 month period) and yielded averages of 36.7480 ± 80, 17.1648 ± 34 and 36.7545 ± 86 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ respectively (uncertainties are 2 standard deviations in the last decimal place). Gold reference materials RAuGP3 (34.1 ± 0.5 ppm Pb) and RAuGP5 (129 ± 4 ppm Pb) from SPEX CertiPrep Ltd (Standish et al., 2013) were processed through ion exchange chromatography and analysed for their Pb isotope composition over an 18 month period. Typical internal precisions are <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 $^{208}Pb/^{206}Pb$ (2 relative standard errors of the mean of the 50 cycles comprising one analysis). External reproducibility of these analyses are <250 ppm for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) and <150 ppm for $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ (two relative standard deviations of the mean). Procedural blanks ranged from 20 to 114 pg Pb, and averaged 57 pg Pb.

4. RESULTS

Lead isotope data of 109 gold and 23 sulphide samples from 34 Irish gold occurrences show a large variation, 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 $^{208}Pb/^{204}Pb$ (Fig. 3 and supplementary data). Samples are divided into two key datasets based on their geographic locations relative to the approximate trace of the Iapetus Suture (Fig. 1): south-east terrane (SET) and north-west terrane (NWT). SET deposits (diamonds, Fig. 3) are distinguished from NWT deposits (circles, Fig. 3) by higher $^{208}Pb/^{204}Pb$ and higher and less variable $^{207}Pb/^{204}Pb$. Data for lode gold mineralisation (grey symbols, Fig. 3) and associated sulphides (black symbols, Fig. 3) are consistent with the range of previously published sulphide data from numerous different mineralisation types and styles.

5. DISCUSSION

The Pb isotope analyses of Au shed light on: (i) the sources of Pb incorporated into Au, and whether or not the Pb in Au is derived from similar sources to that in sulphide mineralisation, but also ii) the extent to which placer deposits are representative of known lode occurrences, and/or provide new evidence for presently unknown lode mineralisation, and (iii) the nature and evolution of the sub-surface crust that was sampled by the fluids responsible for the mineralisation.

The Pb isotope ratios from the placer gold samples (open symbols, Fig. 3) overlap closely with the published ranges of Pb isotopes in sulphides and in the lode gold mineralisation presented in this study (the slopes through the lode and placer mineralisation fields in Fig. 3 differ due to the absence of SET lode mineralisation samples in this study). The isotopic signature of placer gold is therefore seen to reflect that of the hypogene source rather than chemical changes that occurred in the supergene, as argued in a recent study of placer gold from Arizona (Kamenov et al., 2013). It is concluded that placer gold inherited Pb from sources similar to those for the lode gold and sulphide mineralisation, and both lode and placer gold mineralisation are compatible with the same broad story of Pb isotope evolution for Ireland. There is no evidence that Au mineralisation was associated with isotopically distinctive source regions, and it is inferred that the primary controls on the Au mineralisation are structural rather than relating to the distribution of Au in their source rocks. Structural controls are thought to play an important role in the formation of orogenic gold deposits worldwide (e.g. Goldfarb et al., 2005).

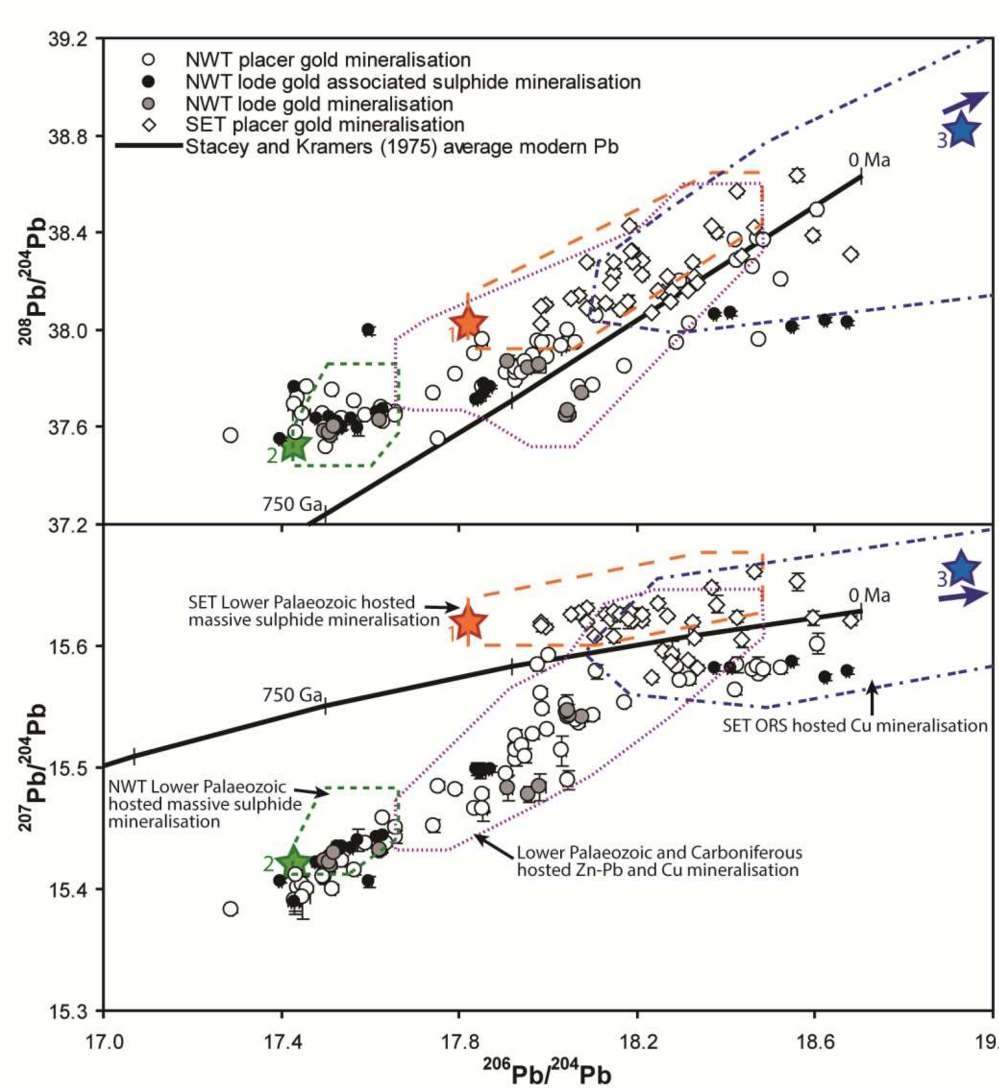

Fig. 3. Lead isotope composition of Irish gold mineralisation and associated sulphides relative to Stacey and Kramers (1975) Pb evolution curve (tick marks represent 250 Ma intervals) and key Irish sulphide data fields presented in Fig. 2.

In regions where significant lode gold mineralisation has been identified, the Pb isotope signatures of placer deposits appear to be representative of the lode mineralisation. The data highlight that the strategy of targeting placer deposits has successfully sampled the full range of gold mineralisation Pb isotope signatures present in Ireland, and in-depth isotopic studies of placer gold are likely to provide a true reflection of lode mineralisation in a study region even when direct sampling of lode gold remains difficult.

5.1. The principal sources of Pb incorporated into Irish gold mineralisation

The range of Pb isotope signatures present in Irish gold mineralisation can be explained by the interaction of material from the geochemical reservoirs invoked for Irish sulphide mineralisation: 1) a more radiogenic SET source (high $^{207}Pb/^{204}Pb$, medium $^{206}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$), 2) a less radiogenic NWT source (low $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$), and 3) locally a third source characterised by high $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ (Fig. 4).

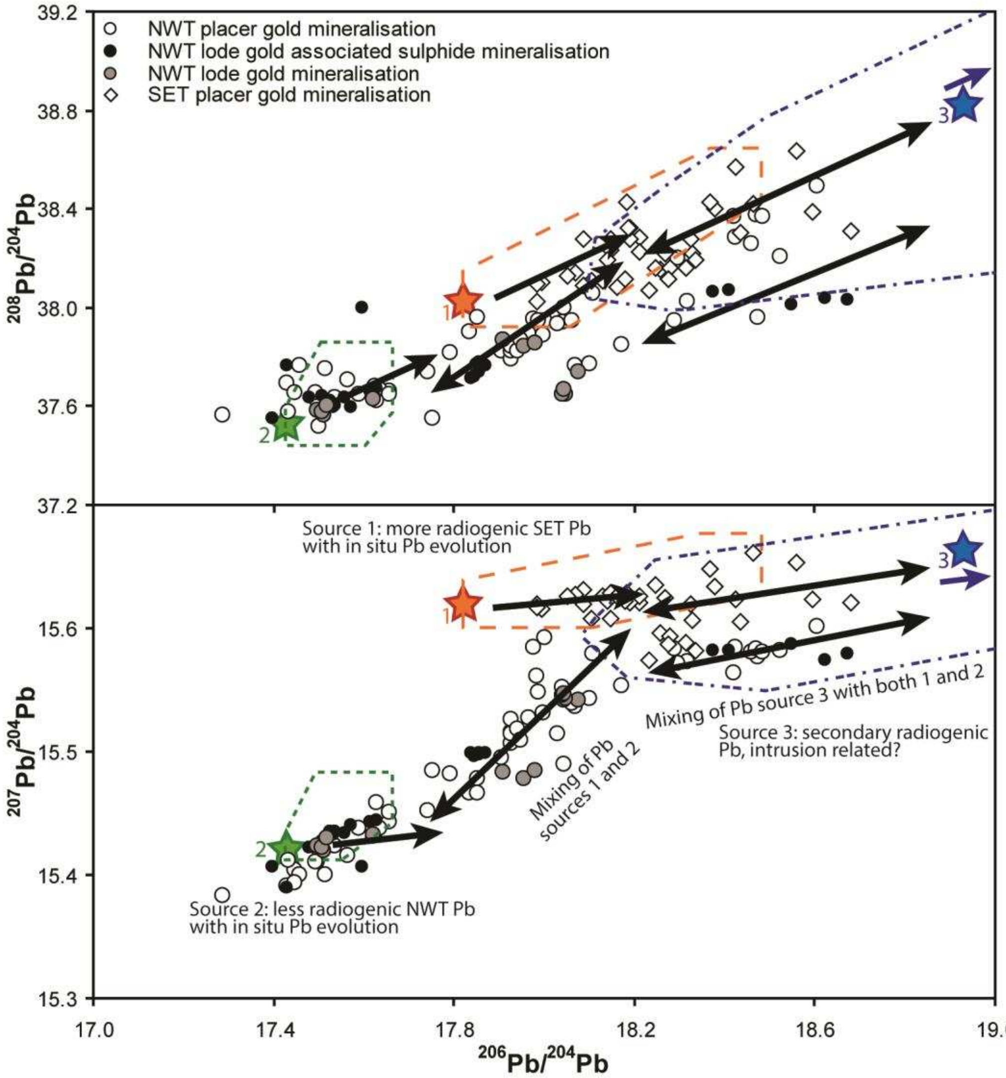

Fig. 4. The principal Pb sources incorporated into Irish gold mineralisation and the key mechanisms behind the isotopic variation.

The majority of SET data is consistent with Pb evolved from a single source characterised by higher $^{238}U/^{204}Pb$ (μ) and $^{232}Th/^{204}Pb$ values relative to Stacey and Kramers (1975) average modern Pb (source 1). The pre-Caledonian SET basement consists of Late Proterozoic crustal rocks, and it is generally accepted that this basement, or associated Lower Palaeozoic lithologies, are the most likely source region of SET mineralisation (Dixon et al., 1990; LeHuray et al., 1987; O'Keeffe, 1986).

NWT deposits are characterised by variable isotope ratios that cannot be explained by the evolution of a single source with a range of μ or $^{232}Th/^{204}Pb$, and plot between the Stacey and Kramers (1975) growth curve for average modern Pb and a less radiogenic composition on the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 3). This suggests contributions of Pb from different source reservoirs, one of more radiogenic/high μ material similar to the SET crustal reservoir (source 1) and another with a less radiogenic/low μ source (source 2) which has been attributed to mantle-derived oceanic volcanic rocks and to U- and Th-depleted crustal basement (Fig. 4). In contrast to the SET, the Grampian/Lewisian NWT basement is characterised by unradiogenic Pb isotope signatures (e.g. Blaxland et al., 1979; Marcantonio et al., 1988; Whitehouse, 1993; Whitehouse and Moorbath, 1986) that are typically less radiogenic than most Irish gold mineralisation. This basement has a Nd model age of ~2.6 Ga (see section 5.2), and so we infer that the NWT end-member is dominated by crustal, rather than upper mantle source rocks, and that its Pb isotope ratios evolved since crust formation at 2.6 Ga. Sedimentological and petrological evidence suggests that Silurian (or later) lithologies could be formed from both SET- and NWT-derived material (Hutton and Murphy, 1987; Morris, 1987). This offers a possible mechanism for the introduction of more radiogenic Pb into NWT mineralisation. The key known lode gold occurrences of economic importance (i.e. Curraghinalt, Cavanacaw, see Table 1) are characterised by Pb that derives predominantly from crust relatively depleted in U and Th, and this may indicate that the NWT is a superior exploration target, in particular those NWT gold occurrences dominated by source 2 Pb isotope signatures.

Crustal rocks are seen to be the principal sources of Pb both north and south of the Iapetus Suture, and with most gold occurrences hosted by Dalradian or Lower Palaeozoic metasedimentary sequences, this may lend support to theories surrounding metamorphic rocks as the key sources of orogenic gold mineralisation. Similarities between the isotopic signatures of Early Caledonian massive sulphide mineralisation and those gold occurrences dominated by sources 1 and 2 raises the possibility that pre-existing mineralisation hosted by these crustal sources could have been remobilised by, and incorporated into, orogenic mineralisation.

The SET mineralisation has variable $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ relative to $^{207}Pb/^{204}Pb$, and evolution following Pb growth curves may imply that this variation is primarily the result of Pb evolution from a source with variable μ and $^{232}Th/^{204}Pb$. However the total variation cannot be explained by in situ post crystallisation Pb growth based on the typical U/Pb and Th/Pb ratios of gold (<1, e.g. Eugster et al., 1995; Pettke and Frei, 1996). This could relate to the presence of U- and/or Th-rich mineral inclusions not seen in gold during handpicking. However a preferred explanation is that this variation resulted from contributions from more radiogenic crustal Pb sources similar to that involved with ORS-hosted copper mineralisation and characterised by high $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ (source 3). This source may also be associated with the most radiogenic NWT samples (Fig. 4), and Kinnaird et al. (2002) favoured a link with detritus derived from Caledonian granitic intrusives. As a result, a magmatic associated Pb contribution may be inferred and this will be discussed in more detail in sections 5.4 and 5.6.

5.2. The ages of Pb in the mineralisation source rocks

The distribution of Pb-Pb model ages calculated for samples using the two-stage model of Stacey and Kramers (1975) is presented in Fig. 5, with data also available in the supplementary material (for an overview of Pb-Pb systematics see Faure and Mensing, 2005). The Pb model ages are variable and range from 584 Ma to the present-day (1.5 % are <0 Ma, and have Pb isotope ratios that plot to the right of the geochron) suggesting a significant input of anomalous, radiogenic Pb. Nevertheless, the principal peak in ages is centred on the Caledonian Orogeny, indicating sources that were at least remobilised in the Caledonian (Fig. 5).

As discussed above, two key sources of Pb are identified, one in the SET and one in the NWT and termed source 1 and source 2 respectively. The remaining Pb isotope compositions reflect mixing processes, either during erosion and sedimentation, or in response to magmatic processes (Fig. 4). The implication is that the Pb isotope ratios within the restricted fields for sources 1 and 2 (grey bars in Fig. 5) will yield more meaningful Pb model ages, and they are largely in the range 550–350 Ma. Thus they are broadly consistent with sources that were developed in the lead up to and during the Caledonian Orogeny, for example the gold mineralisation from the Sperrin Mountains (median Pb-Pb model age = 487 Ma) and the Shraroosky vein occurrence (median Pb-Pb model age = 428 Ma) in Cregganbaun (both NWT), and placer gold mineralisation from Co. Wicklow, Co. Wexford and Co. Kerry (median Pb-Pb model age = 402 Ma). These source ages are similar to the Caledonian mineralisation ages previously proposed for gold in these regions (Aherne et al., 1992; Ixer et al., 1990; Milner and McArdle, 1992; Parnell et al., 2000; Rice et al., 2013), highlighting that the Pb in sources 1 and 2 was at least remobilised shortly before the time of mineralisation.

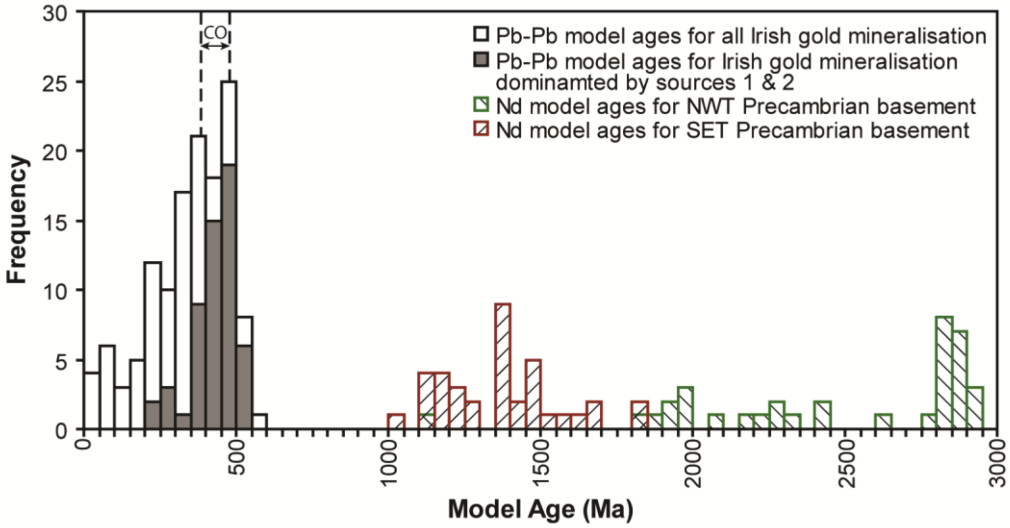

Fig. 5. Distribution of model ages for a) Pb sources incorporated into Irish gold mineralisation (Pb-Pb model ages based on the two-stage Pb evolution model of Stacey and Kramers, 1975) with a particular focus on those deposits dominated by Pb from sources 1 and 2 (excludes those that are < 0 Ma), and b) SET and NWT Precambrian basement (Nd model ages suggesting earliest time of crustal extrication, see text for references). The approximate time of the Caledonian Orogeny (CO) is also highlighted.

The Pb-Pb model ages contrast with Nd model ages for Precambrian crust both north and south of the Iapetus Suture (Fig. 5). The average Nd model ages for NWT and SET basement are 2580 Ma (Hamilton et al., 1979; Marcantonio et al., 1988; O'Nions et al., 1983; Whitehouse, 1988) and 1380 Ma (Davies et al., 1985; Murphy et al., 2000; Thorogood, 1990; Thorpe et al., 1984) respectively, and so the Pb-Pb model ages significantly post-date the generation of the crust in these areas. We infer that the processes of SET and NWT crust formation in the early and mid-Proterozoic were characterised by slightly different degrees of U/Pb fractionation, responsible for the different Pb isotope ratios of sources 1 and 2 (Fig. 3). Remobilisation of these sources in the lead up to, and during the Caledonian orogeny, in turn resulted in the Pb model ages observed in Fig. 5. The Nd model ages highlight that the SET and NWT crust, which are both sources of metals that contributed to Irish gold mineralisation, were derived from the mantle at different times, ~1.4 Ga and ~2.6 Ga respectively (Fig. 5). Using these crustal ages, the μ and $^{232}Th/^{204}Pb$ required to evolve the SET and NWT crustal sources from the Pb evolution curve of Stacey and Kramers (1975) to the end-member composition of sources 1 and 2 were calculated. They are μ = 9.8 and $^{232}Th/^{204}Pb$ = 41 for the SET and μ = 8.4 and $^{232}Th/^{204}Pb$ = 35 for the NWT respectively. These values are in the range observed in subduction-related magmas (e.g. Kelemen et al., 2003) and they highlight the contrasting compositions of these two crustal sources.

In sections 5.3 to 5.6, samples associated with each of the principal source regions are discussed in more detail to evaluate further the processes behind the Pb isotope variation of Irish gold mineralisation (Fig. 6).

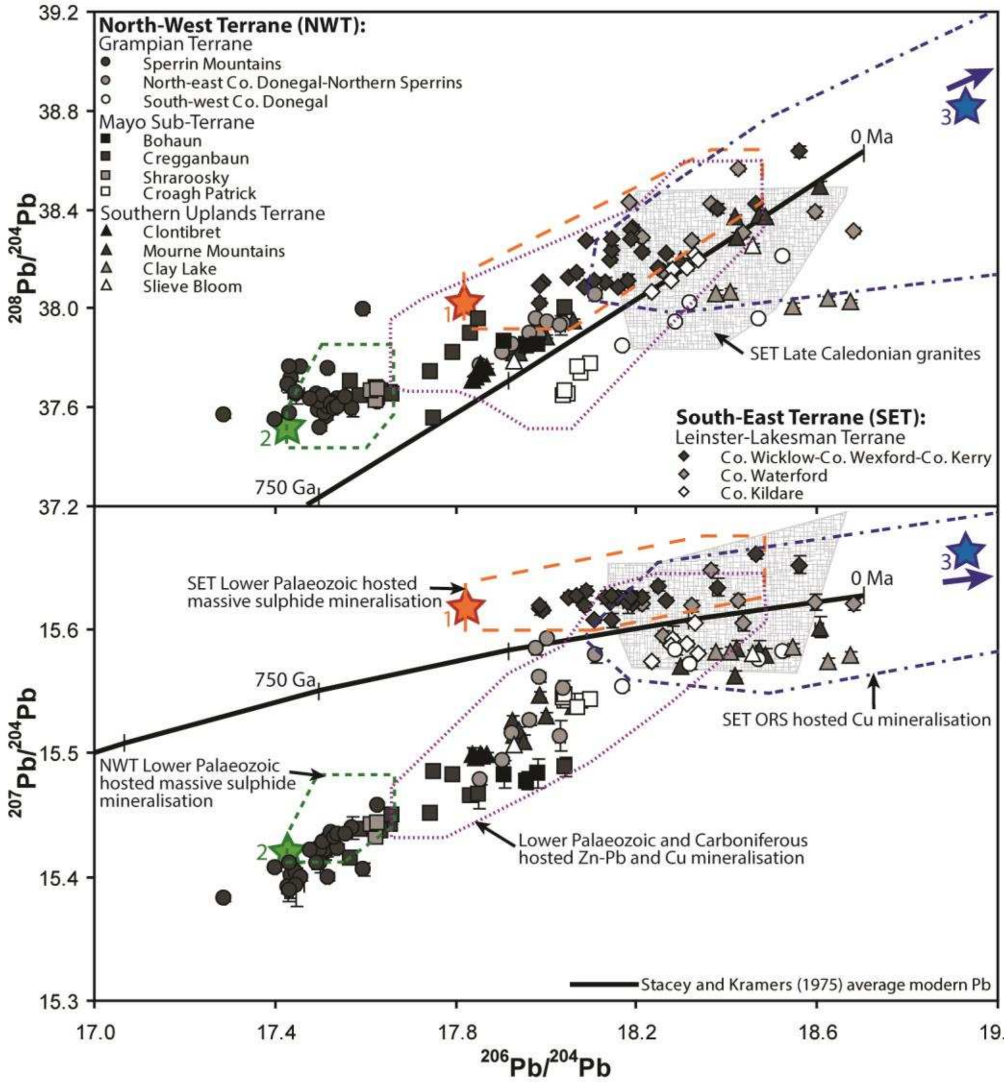

Fig. 6. Pb isotope composition of Irish gold occurrences relative to Stacey and Kramers (1975) Pb evolution curve (tick marks represent 250 Ma intervals), key Irish sulphide data fields presented in Fig. 2, and the isotopic signature of feldspars from SET Late Caledonian granites (data from Hampton and Taylor, 1983, and Everett et al., 2003 citing O'Keeffe, 1987).

5.3. Early and Late Caledonian NWT mineralisation and unradiogenic crustal Pb

The gold mineralisation of the Sperrin Mountains (dark grey circles, Fig. 6) of the Grampian terrane has the least radiogenic Pb isotope compositions of the Irish gold deposits studied, and therefore best defines the isotopic composition of source 2.

Evidence for a magmatic influence also exists, including sulphur isotope data from Curraghinalt (Earls et al., 1997; Parnell et al., 2000), and Bi telluride inclusions in the veins at Curraghinalt and Cavanacaw and as inclusions in placer gold collected locally at Curraghinalt (Chapman et al., 2000a, 2000b; Parnell et al., 2000). It can therefore be inferred that mineralisation inherited signatures from a range of local lithologies.

Parnell et al. (2000) proposed that the main phase of gold mineralisation at Curraghinalt occurred 470–400 Ma ago, and the consistency between the Sperrin Mountain data and the age of the Early Caledonian Charlestown massive sulphide deposit (Cummins, 1954; O'Connor and Poustie, 1986) supports the hypothesis of a Caledonian mineralsation age. This age has been further constrained to c.460–450 Ma using Re-Os and Ar-Ar (Rice et al., 2013) and as such it closely post-dates the main Caledonian metamorphic event. The median Pb-Pb model age for the Dalradian-hosted Sperrin Mountains mineralisation (487 Ma) indicates that some pre-Caledonian material was also involved in the mineralisation.

The slightly dissimilar Pb isotope ratios of samples from the Cregganbaun region of the Mayo sub-terrane (light and dark grey squares, Fig. 6) include some that are consistent with the Sperrin Mountains data. This suggests an association with a similar crustal Caledonian Pb source, again with a contribution from mantle derived sources based on the presence of pentlandite and millerite inclusions in placer gold from this region (dark grey squares, Fig. 6) which are taken to indicate associations with ultramafic source rocks (Chapman et al., 2000b). Mineralisation is associated with Ordovician volcano-sedimentary (turbiditic) formations that contain a significant component of ultramafic material (Thompson et al., 1992). Pb-Pb model ages for the Shraroosky deposit range from 446 to 417 Ma (n = 4), slightly older than the Late Caledonian mineralisation age preferred by Aherne et al. (1992).

5.4. Early and Late Caledonian SET mineralisation and radiogenic crustal Pb

Gold mineralisation sampled from the Leinster-Lakesman terrane/SET (diamonds, Fig. 6) is principally associated with Late Proterozoic basement or associated Lower Palaeozoic crustal Pb (source 1). SET placer gold records the sulphide-sulpharsenide inclusion suite and simple Au-Ag alloy typical of orogenic mineralisation, alongside copper contents up to 0.19 % (Chapman et al., 2006). Gold grains from this region can also include Ni-rich inclusions that suggest associations with ultramafics, consistent with contributions from Lower Palaeozoic sequences that contain arc-related and ultramafic formations (Max et al., 1990).

The SET mineralisation has variable $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ relative to $^{207}Pb/^{204}Pb$, indicating Pb isotope evolution from a source with variable μ and $^{232}Th/^{204}Pb$. Placer samples from Co. Wicklow-Co. Wexford-Co. Kerry (dark grey diamonds, Fig. 6) have variable model ages (Fig. 5, supplementary data) with the majority (70 %) ranging between 500 Ma and 360 Ma, and peaking at c.460 Ma contemporary with the Early Caledonian. This spread in ages may be the result of two mineralisation events that inherited Pb from similar source reservoirs over a period of c.140 My. Moreover, mineralisation in the Early Caledonian is supported by the age of the Avoca deposit dated to the Llandeilo-Ashgill divisions of the Ordovician by Williams et al. (1986).

Such a two-stage model is consistent with previous studies for vein gold mineralisation by the Goldmines Rivers (Ixer et al., 1990) and at Kilmacoo (Milner and McArdle, 1992). Ixer et al. (1990) linked the second (Late Caledonian) stage of mineralisation with magmatic processes, and this may have been responsible for the more radiogenic and isotopically variable Pb (source 3). Furthermore, gold alloys with appreciable copper, such as those under discussion here, could be associated with remobilisation linked to intrusive activity (Moles et al., 2013). Data fields for feldspars from SET Late Caledonian granites (from both Britain and Ireland, but including the Leinster granite itself) are plotted in Fig. 6. The signature of the granites is consistent with the more evolved Co. Wicklow-Co. Wexford-Co. Kerry gold samples (i.e. those with higher $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) along with the remaining Leinster-Lakesman terrane/SET mineralisation (light grey and white diamonds, Fig. 6). At the very least, it seems likely that both the SET gold mineralisation and the Leinster granite inherited Pb from similar crustal sources at approximately the same time, and as the Leinster granite crystallised at 404 ± 24 Ma (Rb/Sr; O'Connor and Brück, 1978), this adds further support for a Late Caledonian phase of mineralisation.

5.5. Late Caledonian NWT mineralisation and radiogenic crustal Pb

Irish mineral deposits of Late Caledonian or younger ages, such as Carboniferous/Lower Palaeozoic hosted Pb-Zn mineralisation (Fig. 2 & 4), and most of the remaining NWT gold occurrences, define a mixing trend between the more radiogenic crustal (source 1) and less radiogenic crustal (source 2) end members. In most cases this mixing can be explained if Pb was partially inherited from Silurian or later sources formed by sedimentation of eroded SET and NWT derived material (see Dixon et al., 1990; O'Keeffe, 1986).

Gold-bearing antimony-arsenic mineralisation at Clontibret has been linked to igneous processes based on the isotopic composition of oxygen, carbon and sulphur (Morris et al., 1986; Steed and Morris, 1997), whilst the presence of a Ni-rich inclusion in placer gold from the area favours an ultramafic association (Chapman et al., 2000a). The Pb isotope data for vein-hosted sulphides (black triangles, Fig. 6) are consistent with a source dominated by less radiogenic crustal Pb, yet with some input from a more radiogenic crustal source. With placer gold grains characterised by broadly orogenic signatures (Chapman et al., 2000a), the Pb isotope signature could be explained by contributions from local mafic rich greywackes or a concealed volcanic arc (see Steed and Morris, 1997) during the Late Caledonian following SET-NWT mixing. Gold-bearing mineralisation at Clontibret is considered to be Late Caledonian in age, and pre-dates stibnite mineralisation that is older than 360 ± 7 Ma based on K-Ar dating of associated clay minerals (Halliday and Mitchell, 1983). Pb-Pb model ages of 390 Ma to 363 Ma for the Clontibret sulphides support this Late Caledonian age.

Mineralisation at Croagh Patrick (Mayo sub-terrane) is hosted by greenschist facies Silurian metaquartzites that overlie slates and ultramafics, and it has been linked to the final (D_3) Caledonian deformation event (Aherne et al., 1992; Wilkinson and Johnston, 1996). The inclusion assemblage of both vein and placer gold grains consist of the typical orogenic sulphide-sulpharsenide suite, along with a number of Ni-rich species of ultramafic affinity (Chapman et al., 2000a). However it has higher $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ (white squares, Fig. 6) than Cregganbaun (dark and light grey squares, Fig. 6), suggesting a contribution of more radiogenic crustal Pb alongside the less radiogenic crust derived Pb that dominated the Shraroosky occurrence.

The high $^{206}Pb/^{204}Pb$ placer gold from Cregganbaun (dark grey squares, Fig. 6) indicates a second source of Pb, more radiogenic in nature, was involved in the mineralisation together with source 2. The radiogenic Cregganbaun end member has similar isotopic ratios to vein gold from Bahaun, Co. Galway (also the Mayo sub-terrane), and Lusty et al. (2011) proposed an association with post-Caledonian

(Carboniferous or later) Cl-rich basinal brine-type fluids, similar to those involved in red-bed Au-Pd mineralisation (see Chapman et al., 2009) and one of the four mineralisation phases at Curraghinalt (Parnell et al., 2000). However such gold typically contains very low Ag, has alloys in the Au-Pd-Hg system, and is characterised by an inclusion suite containing selenides and tellurides and absent of sulphides. In contrast, gold from Bohaun has none of these features, and it contains up to 40 mass % Ag (Lusty et al., 2011). The mineralisation instead appears similar to relatively shallow 'epizonal' orogenic gold from the Yukon, Canada (Allan et al., 2013), where mineralisation was ascribed to telescoping of an orogenic system during rapid uplift, one of the scenarios specified by Yardley and Cleverly (2013) as a potential setting for orogenic gold formation through metamorphic processes. An orogenic model would link the Bohaun deposit with other better known gold occurrences in the Mayo sub-terrane, such as Croagh Patrick and Cregganbaun, and the more radiogenic Pb input could be attributed to local Silurian sediments. In such a model the increasingly radiogenic Pb may have been sampled by the mineralising fluids at shallow depths above the level of the Shraroosky type Cregganbaun mineralisation, and the presence of similar signatures in some Cregganbaun placer gold could indicate shallow mineralisation is also present there.

5.6. NWT mineralisation and the potential role of intrusions

The alloy composition and mineral inclusion suite of placer gold from south-west Donegal (Grampian terrane) and the Mourne Mountains (Southern Uplands terrane) tend to be similar to those for orogenic mineralisation found elsewhere in Ireland (Chapman et al., 2000a, 2000b; Moles et al., 2013). However atypical compositions with high Cu contents and Cu-sulphide inclusions have been recorded at Balwoges in south-west Donegal and in the Mourne Mountains (Chapman et al., 2000a; Moles et al., 2013). Such copper bearing gold alloys are typically associated with non-orogenic styles of mineralisation and have been considered characteristic of magmatic associations (for example relating to porphyry and intrusion related gold; Chapman et al., 2011), but they can also be associated with zonation within an orogenic hydrothermal mineralising system or with remobilisation of orogenic mineralisation by later intrusive activity (Moles et al., 2013).

Localities with atypical, copper rich, alloy compositions have variable Pb isotope signatures that can not be explained by simple linear mixing between the principal NWT and SET Pb sources. They are characterised by the most radiogenic NWT Pb recorded (white circles and dark grey triangles, Fig. 6), and reflect mixing between a primary basement Pb source (similar to those orogenic gold occurrences discussed in section 5.5) and a secondary radiogenic crustal source characterised by high $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ (source 3). It is therefore inferred that the combination of high copper and radiogenic Pb both reflect an involvement from the same crustal source, and this source may be linked to intrusion related processes either directly (i.e. Balwoges), or indirectly (i.e. the Mournes Mountains) through remobilisation of pre-existing orogenic mineralisation (see Moles et al., 2013). In relation to the Mourne Mountains placer gold, the radiogenic Pb is likely to have been derived from the Lower Palaeozoic sediments of the Southern Uplands which were derived in part from the more radiogenic SET crust (Hutton and Murphy, 1987; Murphy, 1987).

6. GOLD MINERALISATION AND THE TECTONIC EVOLUTION OF IRELAND

The Pb isotope ratios in both lode and placer gold mineralisation are consistent with the broad story of Pb isotope evolution for Ireland proposed for Irish sulphide mineralisation (Dixon et al., 1990; Kinnaird et al., 2002; LeHuray et al., 1987; O'Keeffe, 1986;), and relate to the tectonic evolution of Ireland. Prior to the Caledonian Orogeny, Ireland was divided by the Iapetus Ocean (Fig. 7). The NWT (Laurentia) consisted of Palaeoproterozoic and younger crust relatively depleted in radiogenic Pb, whilst SET (Avalonian) crust was dominated by Late Proterozoic rocks (minimum age of 626 ± 6 Ma; Max and Roddick, 1989) relatively enriched in radiogenic Pb. The overlying volcanic arc and marine floor sequences up to Ordovician in age were partially derived from corresponding basement sources, and so the Laurentian and Avalonian plates constitute two key, discrete, Pb isotope reservoirs (see also Nd model ages, Fig. 5). Volcanic arc sequences and ophiolitic complexes, such as the Tyrone Igneous Complex, constitute an additional source of less radiogenic Pb (derived from the upper mantle), and play a more dominant role in the NWT.

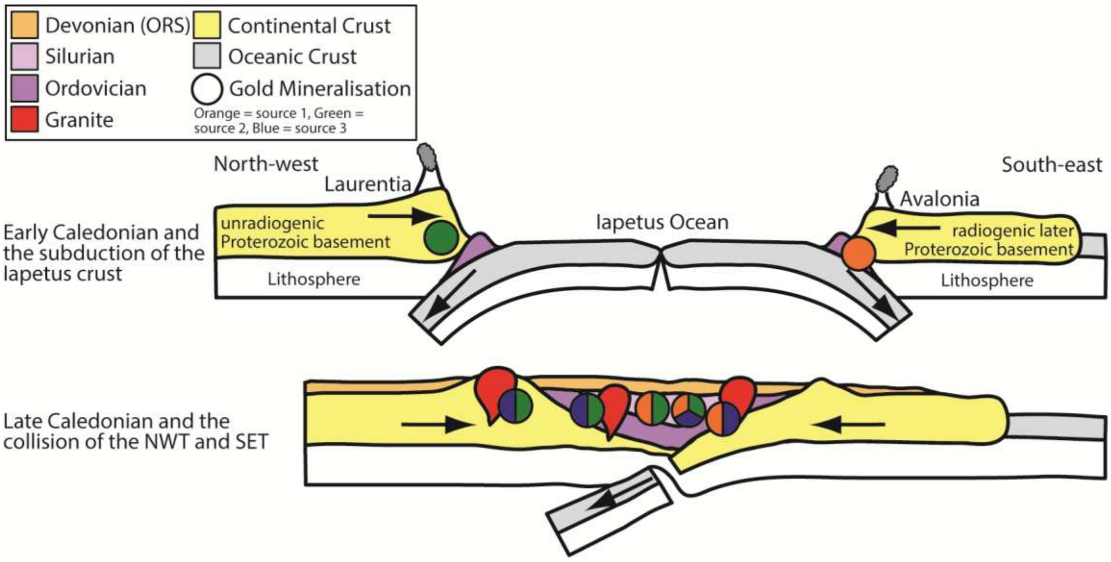

Fig. 7. Simplified schematic depicting key phases of Irish gold mineralisation. Pie charts represent the key Pb sources sampled by mineralisation in different geological settings, and correspond to those used in previous figures. Early Caledonian mineralisation sampled Pb from discrete SET and NWT sources depending on geographic location relative to the Iapetus Suture. Late Caledonian mineralisation could sample Pb from any combination of the three key Pb reservoirs.

During the Early Caledonian (Fig. 7) there was dual subduction of the Iapetus ocean crust beneath Laurentia to the north (immediately post-dating the Grampian Orogeny, see Cooper et al., 2011) and Avalonia to the south (Max et al., 1990). Associated gold mineralisation inherited Pb primarily from one of the two discrete, crustal, Pb sources depending on whether it was north or south of the Iapetus Suture. Such mineralisation in Co. Wicklow-Co. Wexford-(Co. Kerry) characterises the isotopic composition of the principal SET end member Pb reservoir that is dominated by more radiogenic crustal Pb (source 1). Microchemical signatures of these deposits are consistent with orogenic mineralisation, The Sperrin Mountains gold mineralisation (NWT) also formed at approximately the same time, and these deposits typify the less radiogenic NWT end member reservoir dominated by Pb derived from less radiogenic crust (source 2).

During the Late Caledonian, the continents of Laurentia and Avalonia collided following the closure of the Iapetus Ocean (Fig. 7). This collision led to a series of basins with Silurian sedimentary sequences (Hutton and Murphy, 1987) and henceforth sediments could be derived from both NWT and SET sources. As a result, the Pb isotope composition of Silurian or younger lithologies constitute mixtures, in varying proportions, between the radiogenic SET and less radiogenic NWT reservoirs. Microchemical characterisation favours an orogenic style for the vast majority of Irish gold deposits, and those that can be explained isotopically by simple linear mixing between the principal SET and NWT isotopic compositions are likely to be consistent with this model (such as the Croagh Patrick occurrence).

There is also evidence for the involvement of a third reservoir in certain mineralising episodes that is enriched in radiogenic Pb (source 3), often corresponding with gold occurrences favouring an intrusion related microchemical signature (for example the Balwoges placer occurrence). This third source is therefore thought to represent Pb with a magmatic origin, or at least distinctive Pb sampled through magmatic processes, and it could have been incorporated either during mineralisation associated with the intrusions or by intrusion-related remobilisation and mixing of pre-existing orogenic mineralisation.

Due to the complex mixing of multiple Pb sources, including one that is characterised by anomalous radiogenic Pb, Pb isotope ratios cannot be used to distinguish between Late Caledonian and younger mineralising episodes. Microchemical characterisation has demonstrated that most gold occurrences are consistent with an orogenic style of mineralisation associated with the Caledonian Orogeny, and Pb-Pb model ages of Irish gold mineralisation are consistent with Pb remobilised shortly before or during the Caledonian orogeny.

7. SUMMARY

A large-scale lead isotope study of Irish placer and lode gold grain populations has provided new perspectives on the sources of ore fluids and metals involved in gold mineralisation hosted by orogenic belts.

Placer gold inherited Pb from sources similar to those of both lode gold and sulphide mineralisation, and there is no evidence that Au mineralisation was associated with distinctive source regions. It is inferred that the principal controls on the Au mineralisation are most likely structural, and gold could be present anywhere in Ireland where lithologies affected by the Caledonian Orogeny are located. This is consistent with the geographical distribution of gold occurrences in Ireland.

The isotopic composition of most gold occurrences can be explained by Pb derived from two principal geochemical reservoirs during either the Early or Late Caledonian: 1) a more radiogenic crustal SET source, and/or 2) a less radiogenic crustal NWT source. The continental crust is therefore seen to play a key role in the genesis of Irish orogenic gold mineralisation, and in most cases mineralisation appears to have inherited signatures from a range of local lithologies. A third source is characterised by more radiogenic Pb isotope ratios and is a feature of some Late Caledonian gold occurrences. It is argued that this material is associated with magmatic processes, either as the source of the Pb, or as agent through which the Pb was remobilised. This highlights that intrusives were an important factor in the genesis of certain Irish gold occurrences and they may also have played a less direct role in other Late Caledonian deposits, for example in providing a heat source. In Ireland it appears that the gold occurrences considered to be of greatest economic importance are characterised by less radiogenic Pb.

The strategy of targeting placer deposits appears to have successfully sampled the key geochemical sources involved in Irish gold mineralisation, and future in-depth isotopic studies of placer gold are likely to provide a true reflection of lode mineralisation in a study region. Lead isotope analysis of gold has the potential to provide important new insights into the genesis of gold mineralisation worldwide.

ACKNOWLEDGEMENTS

R. Standish and G. Baddeley are thanked for fieldwork assistance, whilst N. Moles and R. Warner kindly donated additional placer gold samples for analysis. The authors would also like to thank the many landowners who granted access for fieldwork, and a number of mining and exploration companies who donated ore samples for study and provided useful discussions on their respective mineral deposits. Constructive comments of two referees and the editor helped to improve this paper. Funding was provided by the Natural Environment Research Council (NERC) in the form of a research studentship to CS.

REFERENCES

Allan M. M., Mortensen J. K., Hart C. J. R., Bailey L. A., Sánchez M. G., Ciolkiewicz W., McKenzie G. G. and Creaser R. A. (2013) Magmatic and metallogenic framework of west-central Yukon and eastern Alaska. In Tectonics, Terranes, Metallogeny and Discovery in the northern circum-Pacific region (eds. M. Colpron, T. Bissig, B. Rusk and J. Thompson). Society of Economic Geologists, Special Publication 17. pp. 111–168.

Aherne S., Reynolds N. A. and Burke D. J. (1992) Gold mineralization in the Silurian and Ordovician of south Mayo. In The Irish Minerals Industry 1980–1990 - A Review of the Decade (eds. A. A. Bowden, G. Earls, P. G. O'Connor and J. F. Pyne). Irish Association for Economic Geology, Dublin. pp. 39–49.

Arias D., Corretgé L., Suárez O., Villa L., Cuesta A. and Gallastegui G. (1996) Lead and sulfur isotope compositions of the ibias gold vein system (NW Spain): genetic implications. Econ. Geol. **91**, 1292–1297.

Baker J., Peate D., Waight T. and Meyzen C. (2004) Pb isotopic analysis of standards and samples using a ^{207}Pb-^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. Chem. Geol. **211**, 275–303.

Banks D. A., Boyce A. J. and Samson I. M. (2002) Constraints on the origins of fluids forming Irish Zn-Pb-Ba deposits: evidence from the composition of fluid inclusions. Econ. Geol. **97**, 471–480.

Blaxland A. B., Aftalion M. and Van Breemen O. (1979) Pb isotopic composition of feldspars from Scottish Caledonian Granites, and the nature of the underlying crust. Scot. J. Geol. **15**, 139–151.

Boast A. M. (1983) Discussions and contributions: T. I. Min. Metall. B **92**, 101.

Boast A. M., Swainbank I. G., Coleman M. L. and Halls C. (1981) Lead isotope variation in the Tynagh, Silvermines and Navan base-metal deposits, Ireland. T. I. Min. Metall. B **90**, 115–119.

Boyce A. J., Wilkinson J. J., Earls G., Boland M., Carey P. F., Fallick A. E., Hutton D. H. W., Johnston J. D., Legg I. C., Moles N. R. and Parnell J. (1997) Gold mineralization at Curraghinalt, Ireland: Multiple fluids in a mesozonal gold deposit (abstract). Geofluids II Conference, 10–14th March 1997, Queen's University of Belfast, Extended Abstracts, pp. 175–178.

Standish et al., 2014. Chemical Geology **378**–**379**, 40–51.

Calvert J. (1853) The Gold Rocks of Britain and Ireland. Chapman and Hall, London.

Caulfield J. B. D., LeHuray A. P. and Rye D. M. (1986) A review of lead and sulphur isotope investigations of Irish sediment-hosted base metal deposits with new data from the Keel, Ballinalack, Moyvoughly and Tatestown deposits. In Geology and genesis of mineral deposits in Ireland (eds. C. J. Andrew, R. W. A. Crowe, S. Finlay, W. M. Pennell and J. F. Pyne). Irish Association of Economic Geology, Dublin. pp. 591–615.

Chapman R. J., Leake R. C., Moles N. R., Earls G., Cooper C., Harrington K. and Berzins R. (2000a) The application of microchemical analysis of placer gold grains to the understanding of complex local and regional gold mineralization: A case study in the Irish and Scottish Caledonides. Econ. Geol. **95,** 1753–1773.

Chapman R. J., Leake R. C. and Moles N. R. (2000b) The use of microchemical analysis of placer gold grains in mineral exploration: experiences in Britain and Ireland. J. Geochem. Explor. **71**, 241–268.

Chapman R. J., Leake R. C., Warner R. A., Cahill M. C., Moles N. R., Shell C. A. and Taylor J. J. (2006) Microchemical characterisation of natural gold and artefact gold as a tool for provenancing prehistoric gold artefacts: A case study in Ireland. Appl. Geochem. **21**, 904–918.

Chapman R. J., Leake R. C., Bond D. P. G., Stedra V. and Fairgrieve B. (2009) Chemical and Mineralogical Signatures of Gold Formed in Oxidising Chloride Hydrothermal Systems and their Significance within Populations of Placer Gold Grains Collected during Reconnaissance. Econ. Geol. **104**, 563–585.

Chapman R. J., Mortensen J. K., Crawford E. C. and LeBarge W. (2010) Microchemical Studies of Placer and Lode Gold in the Klondike District, Yukon, Canada: 1. Evidence for a Small, Gold-Rich, Orogenic Hydrothermal System in the Bonanza and Eldorado Creek Area. Econ. Geol. **105**, 1369–1392.

Chapman R. J., Mortensen J. K. and Lebarge W. P. (2011) Styles of lode gold mineralization contributing to the placers of the Indian River and Black Hills Creek, Yukon Territory, Canada as deduced from microchemical characterisation of placer gold grains. Miner. Deposita **46**, 881–903.

Chew D. M. and Stillman C. J. (2009) Late Caledonian Orogeny and magmatism. In The Geology of Ireland, 2nd ed. (eds. C. H. Holland and I. S. Sanders). Dunedin Academic Press, Edinburgh. pp. 143–173.

Chew D. M., Daly J. S., Magna T., Page L. M., Kirkland C. L., Whitehouse M. J. and Lam R. (2010) Timing of ophiolite obduction in the Grampian orogen. Geol. Soc. Am. Bull. **122**, 1787–1799.

Clayton G., Graham J. R., Higgs K., Holland C. H. and Naylor D. (1980) Devonian rocks of Ireland: a review. J. Earth Sci. Dublin **2**, 161–183.

Cliff D. C. and Wolfenden M. (1992) The Lack gold deposit, Northern Ireland, In The Irish Minerals Industry 1980–1990 - A Review of the Decade (eds. A. A. Bowden, G. Earls, P. G. O'Connor and J. F. Pyne). Irish Association for Economic Geology, Dublin. pp. 65–75.

Clifford J. A., Earls G., Meldrum A. H. and Moore N. (1992) Gold in the Sperrin Mountains, Northern Ireland: An exploration case history, In The Irish Minerals Industry 1980–1990 - A Review of the Decade (eds. A. A. Bowden, G. Earls, P. G. O'Connor and J. F. Pyne). Irish Association for Economic Geology, Dublin. pp. 77–87.

Conroy Gold and Natural Resources Plc. (2012) Annual report and financial statements 2012. Dublin, Ireland.

Standish et al., 2014. Chemical Geology **378**–**379**, 40–51.

Cooper M. A., Collins D. A., Ford M., Murphy F. X., Trayner P. M. and O'Sullivan M. (1986) Structural evolution of the Irish Variscides. J. Geol. Soc. London **143**, 53–61.

Cooper M. R., Crowley Q. G., Hollis S. P., Noble S. R., Roberts S., Chew D., Earls G., Herrington R. and Merriman R. J. (2011) Age constraints and geochemistry of the Ordovician Tyrone Igneous Complex, Northern Ireland: implications for the Grampian Orogeny. J. Geol. Soc. London **168**, 837–850.

Cumming G. L. and Richards J. R. (1975) Ore lead isotope ratios in a continuously changing earth. Earth Planet. Sci. Lett. **28**, 155–171.

Cummins W. A. (1954) An Arenig volcanic series near Charlestown, Co. Mayo. Geol. Mag. **91**, 102–104.

Curti E. (1987) Lead and oxygen isotope evidence for the origin of the Monte Rosa gold lode deposits (Western Alps, Italy): a comparison with Archean lode deposits. Econ. Geol. **82**, 2115–2140.

Daly J. S. (2001) Precambrian. In The Geology of Ireland (ed. C. H. Holland). Dunedin Academic Press, Edinburgh. pp. 7–45.

Darling J. R., Hawkesworth C. J., Lightfoot P. C., Storey C. D. and Tremblay E. (2010) Isotopic heterogeneity in the Sudbury impact melt sheet. Earth Planet. Sci. Lett. **289**, 347–356.

Davies G., Gledhill A. and Hawkesworth C. (1985) Upper crustal recycling in souterhn Britain: evidence from Nd and Sr isotopes. Earth Planet. Sc. Lett. **75**, 1–12.

Dixon P. R., LeHuray A. P. and Rye D. M. (1990) Basement geology and tectonic evolution of Ireland as deduced from Pb isotopes. J. Geol. Soc. London **147**, 121–132.

Earls G., Hutton D. H. W., Wilkinson J. J., Moles N. R., Parnell J., Fallick A. E. and Boyce A. J. (1996) The gold metallogeny of northwest Northern Ireland. Geological Survey of Northern Ireland Technical Report GSNI/96/6.

Earls G., Hutton D., Wilkinson J., Johnston D., Parnell J., Moles N., Carey P., Boyce A., Fallick A., Boland M., Finlay S., Phelan G. and Legg I. (1997) The gold metallogeny of the Dalradian metasediments of the Sperrin Mountains, Northern Ireland. Irish Association for Economic Geology 1997 Annual Review. pp. 41–49.

Eugster O., Niedermann S., Thalmann C., Frei R., Kramers J., Krahenbuhl U., Liu Y. Z., Hofmann B., Boer R. H., Reimold W. U. and Bruno L. (1995) Noble gases, K, U, Th, and Pb in native gold. J. Geophys. Res. Sol. Ea. **100**, 24677–24689.

Everett C. E., Rye D. M. and Ellam R. M. (2003) Source or sink? An assessment of the role of the old red sandstone in the genesis of the Irish Zn-Pb deposits. Econ. Geol. **98**, 31–50.

Faure G. and Mensing T. M. (2005) Isotopes: Principles and Applications, 3rd ed. John Wiley and Sons, Hoboken NJ.

Fettes D. J., Long C. B., Bevins R. E., Max M. D., Oliver G. J. H., Primmer T. J., Thomas L. J. and Yardley B. W. D. (1985) Grade and time of metamorphism in the Caledonide Orogen of Britain and Ireland. Geol. Soc. London Mem. **9**, 41–53.

Gaboury D. (2013) Does gold in orogenic deposits come from pyrite in deeply buried carbon-rich sediments?: Insight from volatiles in fluid inclusions. Geology **41**, 1207–1210.

Geological Survey of Ireland (2007) 1:500,000 Bedrock Geology of Ireland Digital Map. Geological Survey of Ireland, Dublin.

Goldfarb R. J., Baker T., Dubé B., Groves D. I., Hart C. J. R. and Gosselin P. (2005) Distribution, Character, and Genesis of Gold Deposits in Metamorphic Terranes. Econ. Geol. 100th Anniversary Volume, 407–450.

Graham J. R. (2001) Variscan Structures. In The Geology of Ireland (ed. C. H. Holland) Dunedin Academic Press, Edinburgh. pp. 313–330.

Groves D. I., Goldfarb R. J., Robert F. and Hart C. J. R. (2003) Gold deposits in metamorphic belts: overview of current understanding, outstanding problems, future research, and exploration significance. Econ. Geol. **98**, 1–29.

Halliday A. N. and Mitchell J. G. (1983) K-Ar ages of clay concentrates from Irish orebodies and their bearing on the timing of mineralization. T. Roy. Soc. Edin. Earth **74**, 1–14.

Halliday A. N., Aftalion M. and Leake B. E. (1980) A revised age for the Donegal granites: Nature **284**, 542–543.

Hamilton P. J., Evensen N. M., O’Nions R. K. and Tarney J. (1979) Sm-Nd systematics of Lewisian gneisses: implications for the origin of granulites. Nature **277**, 25–28.

Hampton C. M. and Taylor P. N. (1983) The age and nature of the basement of southern Britain: evidence from Sr and Pb isotopes in granites. J. Geol. Soc. London **140**, 499–509.

Hennessey B. T., Foo B., Damjanović B., Villeneuve A. and Jacobs C. (2012) A Preliminary Economic Assessment of the Curraghinalt Gold Deposit, Tyrone Project, Northern Ireland. Micon International Ltd. Report NI 43–101.

Holdsworth R. E., Woodcock N. H. and Strachan R. A. (2000) Geological framework of Britain and Ireland. In Geological History of Briatain and Ireland (eds. N. H. Woodcock and R. A. Strachan). Blackwell Science Ltd, Oxford. pp. 19–37.

Hutton D. H. W. and Murphy F. C. (1987) The Silurian of the southern Uplands and Ireland as a successor basin to the end-Ordovician closure of the Iapetus. J. Geol. Soc. London **144**, 765–772.

Ixer R. A., McArdle P. and Stanley C. J. (1990) Primary gold mineralization within metamorphosed iron ores, Southeast Ireland. Geol. Sur. Ireland Bull. **4**, 221–226.

Jolley D. W. and Bell B. R. (2002) The evolution of the North Atlantic Igneous Province and the opening of the NE Atlantic rift. In The North Atlantic Igneous Province: Stratigraphy, Tectonic, Volcanic and Magmatic Processes (eds. D. W. Jolley and B. R. Bell). The Geological Society of London, London. pp. 1–13.

Kamenov G. D., Melchiorre E. B., Ricker F. N. and DeWitt E. (2013) Insights from Pb Isotopes for Native Gold Formation During Hypogene and Supergene Processes at Rich Hill, Arizona. Econ. Geol. **108**, 1577–1589.

Kelemen P. B., Hanghøj K. and Greene A. R. (2003) One view of the geochemistry of subduction-related magmatic arcs, with an emphasis on primitive andesite and lower crust. In Geochemistry of the Crust (ed. R. L. Rudnick). Elsevier. pp. 593–659.

Kinahan G. A. (1882) On the mode of occurrence and winning of gold in Ireland. Sci. Proc. Roy. Dublin Soc. **3**, 263–285.

Kinahan G. H. (1883) On the possibility of gold being found in quantity in the County Wicklow. Sci. Proc. Roy. Dublin Soc. **4**, 39–42.

Kinnaird J. A., Ixer R. A., Barreiro B. and Nex P. A. M. (2002) Contrasting sources for lead in Cu-polymetallic and Zn-Pb mineralization in Ireland: constraints from lead isotopes. Miner. Deposita **37**, 495–511.

Kramers J. D. and Tolstikhin I. N. (1997) Two terrestrial lead isotope paradoxes, forward transport modelling, core formation and the history of the continental crust. Chem. Geol. **139**, 75–110.

Leake R. C., Chapman R. J., Bland D. J., Condliffe E. and Styles M. T. (1997) Microchemical characterization of gold from Scotland. T. I. Min. Metall. B **106**, 85–98.

LeHuray A. P., Caulfield J. B. D., Rye D. M. and Dixon P. R. (1987) Basement Controls on Sediment-Hosted Zn-Pb Deposits: A Pb Isotope Study of Carboniferous Mineralization in Central Ireland. Econ. Geol. **82**, 1695–1709.

Lusty P. A., Naden J., Bouch J. J., McKervey J. A. and McFarlane J. A. (2011) Atypical Gold Mineralization in an Orogenic Setting - The Bohaun Deposit, Western Irish Caledonides. Econ. Geol. **106**, 359–380.

Lyle P. (1980) A Petrological and Geochemical Study of the Tertiary Basaltic Rocks of Northeast Ireland. J. Earth Sci. **2**, 137–152.

Lyle P. and Preston J. (1993) Geochemistry and volcanology of the Tertiary basalts of the Giants Causeway area, Northern Ireland. J. Geol. Soc. London **150**, 109–120.

MacCarthy I. A. J. (1990) Placer sedimentation patterns in the Munster Basin, Ireland. Sedimentology **37**, 685–712.

Maclaren M. J. (1903) The occurrence of gold in Great Britain and Ireland. Trans. Inst. Mining Eng. **25**, 435–508.

Marcantonio F., Dickin A. P., McNutt R. H. and Heaman L. M. (1988) A 1,800 million-year-old Proterozoic gneiss terrane in Islay with implications for the crustal structure and evolution of Britain. Nature **335**, 62–64.

Max M. D. and Long C. B. (1985) Pre-Caledonian basement in Ireland and its cover relationships. Geol. J. **20**, 341–366.

Max M. D. and Roddick J. C. (1989) Age of metamorphism in the Rosslare Complex, S.E. Ireland. P. Geologist. Assoc. **100**, 113–121.

Max M. D., Barber A. J. and Martinez J. (1990) Terrane assemblage of the Leinster Massif, SE Ireland, during the Lower Paleozoic. J. Geol. Soc. London **147**, 1035–1050.

McArdle P. and Warren W. P. (1987) The bedrock source and emplacement of placer gold at Goldmine River Valley, Co. Wicklow. Geol. Sur. Ireland Bull. **4**, 11–26.

McArdle P., Morris J. H. and Gardiner P. R. R. (1987) Gold in Ireland: the potential for mineralization. Geological Survey of Ireland, Report Series RS 87/1 (Mineral Resources).

McCann N. (1988) An assessment of the subsurface geology between Magilligan Point and Fair Head, Northern Ireland. Irish J. Earth Sci. **9**, 71–78.

McCann N. (1990) The subsurface geology between Belfast and Larne, Northern Ireland. Irish J. Earth Sci. **10**, 157–173.

McCormick A. G., Fallick A. E., Harmon R. S., Meighan I. G. and Gibson D. (1993) Oxygen and Hydrogen Isotope Geochemistry of the Mourne Mountains Tertiary Granites, Northern Ireland. J. Petrol. **34**, 1177–1202.

Meere P. A. (1995) Sub-greenschist facies metamorphism from the Variscides of SW Ireland: an early syn-extensional peak thermal event. J. Geol. Soc. London **152**, 511–521.

Milner A. I and McArdle P. (1992) Gold mineralization in Ordovician volcanic rocks at Kilmacoo, Co. Wicklow: its exploration and geological controls In The Irish Minerals Industry 1980–1990 - A Review of the Decade (eds. A. A. Bowden, G. Earls, P. G. O'Connor and J. F. Pyne). Irish Association for Economic Geology, Dublin. pp. 51–63.

Standish et al., 2014. Chemical Geology **378**–**379**, 40–51.

Moles N. R., Chapman R. J. and Warner R. B. (2013) The significance of copper concentrations in natural gold alloy for reconnaissance exploration and understanding gold-depositing hydrothermal systems. Geochem. Explor. Env. A. **13**, 115–130.
Morris J. H. (1987) The northern belt of the Longford Down Inlier, Ireland, and southern Uplands, Scotland - an Ordovician back-arc basin. J. Geol. Soc. London **144**, 773–786.
Morris J. H., Steed G. M. and Wilbur D. G. (1986) The Lisglassen-Tullybuck deposit, County Monaghan: Sb-As-Au vein mineralization in Lower Palaeozoic greywackes. In Geology and genesis of mineral deposits in Ireland (eds. C. J. Andrew, R. W. A. Crowe, S. Finlay, W. M. Pennell and J. F. Pyne). Irish Association of Economic Geology, Dublin. pp. 103–120.
Murphy F. C. (1987) Late Caledonian granitoids and timing of deformation in the Iapetus suture zone of eastern Ireland. Geol. Mag. **124**, 135–142.
Murphy J. B., Strachan R. A., Nance R. D., Parker K. D. and Fowler M. B. (2000) Proto-Avalonia: A 1.2–1.0 Ga tectonothermal event and constraints for the evolution of Rodinia. Geology **28**, 1071–1074.
Naylor D. (1992) The post-Variscan history of Ireland. In Basins on the North Atlantic Seaboard: petroleum geology, sedimentology, and basin evolution (ed. J. Parnell). The Gological Society, London. pp. 255–275.
O'Connor P. G. and Poustie A. (1986) Geological setting and alteration associated with the Charlestown mineral deposit. In Geology and genesis of mineral deposits in Ireland (eds. C. J. Andrew, R. W. A. Crowe, S. Finlay, W. M. Pennell and J. F. Pyne). Irish Association of Economic Geology, Dublin. pp. 89–102.
O'Connor P. J. (1975) Rb-Sr whole-rock isochron for the Newry granodiorite, NE Ireland. Proc. Royal Dublin Soc. A. **5**, 407–413.
O'Connor P. J. (1989) Chemistry and Rb-Sr age of the Corvock granite, western Ireland. Geol. Sur. Ireland Bull. **4**, 99–105.
O'Connor P. J. and Brück P. M. (1978) Age and origin of the Leinster Granite, J. Earth Sci. Dublin **1**, 105–113.
O'Connor P. J. & Gallagher V. (1994) Gold prospectivity in the Caledonides of southeast Ireland: application of the upper-crustal reservoir model. T. I. Min. Metall. B **103**, 175–187.
O'Keeffe W. (1986) Age and postulated source rocks for mineralization in Central Ireland, as indicated by lead isotopes. In Geology and genesis of mineral deposits in Ireland (eds. C. J. Andrew, R. W. A. Crowe, S. Finlay, W. M. Pennell and J. F. Pyne). Irish Association of Economic Geology, Dublin. pp. 617–624.
O'Keeffe W. (1987) A regional lead isotopic investigation of mineralization in Ireland. Ph. D. thesis, University College Dublin.
O’Nions R. K., Hamilton P. J. and Hooker P.J. (1983) A Nd isotope investigation of sediments related to crustal development in the British Isles. Earth Planet. Sc. Lett. **63**, 229–240.
Parnell J., Earls G., Wilkinson J. J., Hutton D. H. W., Boyce A. J., Fallick A. E., Ellam R. M., Gleeson S. A., Moles N. R., Carey P. F. and Legg I. (2000) Regional fluid flow and gold mineralization in the Dalradian of the Sperrin Mountains, northern Ireland. Econ. Geol. **95**, 1389–1416.
Pettke T. and Frei R. (1996) Isotope systematics in vein gold from Brusson, Val d’ Ayas (NW Italy), 1. Pb/Pb evidence for a Piemonte metaophiolite Au source. Chem. Geol. **127**, 111–124.

Standish et al., 2014. Chemical Geology **378**–**379**, 40–51.

Phelps R. and Mawson M. (2013) Technical report on the Omagh gold project County Tyrone, Northern Ireland. Galantas Gold Corporation. Report NI43-101, 2013 Revision.

Phillips G. N. and Powell R. (2010) Formation of gold deposits: A metamorphic devolatilization model. J. Metamorph. Geol. **28**, 689–718.

Powell D. and Phillips W. E. A. (1985) Time of deformation in the Caledonide Orogen of Britain and Ireland. Geol. Soc. London Mem. **9**, 17–39.

Rice C. M., Mark D. F., Selby D. and Hill N. J. (2013) Dating vein-hosted gold deposits in the Caledonides of N. Britain (abstract). Mineral Deposits Studies Group 36th Annual Winter Meeting, 3rd–4th January 2013, University of Leicester, UK.

Ridley J. R and Diamond L. W. (2000) Fluid Chemistry of Orogenic Lode Gold Deposits and Implicatoins for Genetic Models. In Gold in 2000 (eds. S. Hagemann and P. Brown). Society of Economic Geologists, Reviews in Economic Geology Volume 13. pp. 141–162.

Seedorf E., Dilles J. H., Proffett J. M., Einaudi M. T., Zurcher L., Stavast W. J. A., Johnson D. A and Barton M. D. (2005) Porphyry Characteristics and Origin of Hypogene Features. Econ. Geol. 100th Anniversary Volume, 251–298.

Simmonds S. F., White N. C. and John D. A. (2005) Geological Characteristics of Epithermal Base and Precious Metal Deposits. Econ. Geol. 100th Anniversary Volume, 485–522.

Smith C. G., Smith R. T., Leake R. C., Styles M. T. and Legg I. C. (1996) Mineral exploration in the Hilltown and Slieve Croob areas, County Down. Geological Survey of Northern Ireland, Technical Report GSNI/96/2, 18 p.

Smith M. H., Furlong D. and Sweeney J. (2003) The Longford-Down Massif: A new gold province in the Appalachian-Caledonian Orogeny (abstract). North Atlantic Minerals Symposium Abstracts Volume, September 2003, Dublin, Ireland, pp. 110–113.

Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet. Sci. Lett. **26**, 207–221.

Standish C., Dhuime B., Chapman R., Coath C., Hawkesworth C. and Pike A. (2013) Solution and laser ablation MC-ICP-MS lead isotope analysis of gold. J. Anal. Atom. Spectrom. **28**, 217–225.

Stanley G., Carroll B., Connolly J. and Doyle E. (2000) A review of Ireland's potential for bedrock gold mineralization. Geological Survey of Ireland.

Steed G. H. and Morris J. H. (1997) Isotopic evidence for the origins of a Caledonian gold-arsenopyrite-pyrite deposit at Clontibret, Ireland. T. I. Min. Metall. B **106**, 109–118.

Stevenson C. T. E. and Bennett N. (2011) The emplacement of the Palaeogene Mourne Granite Centres, Northern Ireland: new results from the Western Mourne Centre. J. Geol. Soc. London **168**, 831–836.

Stillman C. J. and Williams C. T. (1978) Geochemistry and tectonic setting of some upper Ordovician volcanic rocks in east and southeast Ireland. Earth Planet. Sc. Lett. **41**, 288–310.

Strelow F. W. E. (1978) Distribution coefficients and anion-exchange behavior of some elements in hydrobromic-nitric acid mixtures. Anal. Chem. **50**, 1359–1361.

Strelow F. W. E. and Toerien F. Von S. (1966) Separation of lead(2) from bismuth(3), thallium(3), cadmium(2), mercury(2), gold(3), platinum(4), palladium(2), and other elements by anion exchange chromatography. Anal. Chem. **38**, 545–548.

Thompson S. J., Shine C. H., Cooper C., Halls C. and Zhao R. (1992) Shear-hosted gold mineralization in Co. Mayo, Ireland. In The Irish Minerals Industry 1980–1990 - A Review of the Decade (eds. A. A. Bowden, G. Earls, P. G. O'Connor and J. F. Pyne). Irish Association for Economic Geology, Dublin. pp. 21–37.

Thorogood E. J. (1990) Provenance of the pre-Devonian sediments of England and Wales: Sm-Nd isotopic evidence. J. Geol. Soc. London **147**, 591–594.

Thorpe R. S., Beckinsale R. D., Patchett P. J., Piper J. D. A., Davies G. R. and Evans J. A. (1984) Crustal growth and late Precambrian-early Palaeozoic plate tectonic evolution of England and Wales. J. Geol. Soc. London **141**, 521–536.

Todd S. P., Murphy F. C. and Kennan P. S. (1991) On the trace of the Iapetus suture in Ireland and Britain. J. Geol. Soc. London **148**, 869–880.

Tomkins A. G. (2013) On the source of orogenic gold. Geology **41**, 1255–1256.

Whitehouse M. J. (1988) Granulite facies Nd-isotopic homogenization in the Lewisian complex of northwest Scotland. Nature **331**, 705–707.

Whitehouse M. J. (1993) Age of the Corodale Gneisses, South Uist. Scot. J. Geol. **29**, 1–7.

Whitehouse M. J. and Moorbath S. (1986) Pb-Pb systematics of Lewisian gneisses - implications for crustal differentiation. Nature **319**, 488–489.

Wilkinson J. J. (2003) On diagenesis, dolomitisation and mineralization in the Irish Zn-Pb orefield. Miner. Deposita **38**, 968–983.

Wilkinson J. J. and Johnston J. D. (1996) Pressure fluctuations, phase separation, and gold precipitation during seismic fracture propagation. Geology **24**, 395–398.

Williams F. M., Sheppard W. A. and McArdle P. (1986) Avoca mine, Co Wicklow: a review of geological and isotopic studies Avoca mine, Co Wicklow: a review of geological and isotopic studies. In Geology and genesis of mineral deposits in Ireland (eds. C. J. Andrew, R. W. A. Crowe, S. Finlay, W. M. Pennell and J. F. Pyne). Irish Association of Economic Geology, Dublin. pp. 71–82.

Yardley B. W. D. and Cleverley J. S. (2013) The role of metamorphic fluids in the formation of ore deposits. In Ore Deposits in an Evolving Earth (eds. G. R. T. Jenkin, P. A. J. Lusty, I. McDonald, M. P. Smith, A. J. Boyce and J. J. Wilkinson). Geological Society, London, Special Publications, Volume 393.

Zartman R. E. and Doe B. R. (1981) Plumbotectonics - the model. Tectonophysics **75**, 135–162.

APPENDIX: Pb isotope signature of Irish gold mineralisation discussed in the text

Geological Terrane	Location Name	Location Number[a]	Further Details	Placer/Lode	Easting[b]	Northing[b]	$^{206}Pb/^{204}Pb$	2 SE	$^{207}Pb/^{204}Pb$	2 SE	$^{208}Pb/^{204}Pb$	2 SE	Pb-Pb Age[c]
Grampian	Attagh Burn	1	Sperrin Mountains	Placer	2567	3865	17.437	0.003	15.401	0.003	37.718	0.008	500
							17.287	0.003	15.382	0.002	37.567	0.008	584
							17.447	0.004	15.403	0.004	37.653	0.011	496
	Balwoges	2	SW Co. Donegal	Placer	1764	3819	18.320	0.004	15.572	0.004	38.022	0.011	170
							18.525	0.005	15.582	0.004	38.208	0.012	33
	Berry Burn	3	Northern Sperrins	Placer	2473	4110	17.853	0.004	15.478	0.003	37.767	0.011	332
							17.985	0.005	15.561	0.003	37.886	0.009	405
							17.926	0.007	15.516	0.004	37.851	0.010	359
							18.040	0.008	15.552	0.007	37.938	0.019	342
							17.977	0.006	15.584	0.005	37.956	0.014	460
							18.109	0.006	15.579	0.006	38.056	0.017	331
							18.002	0.004	15.592	0.003	37.945	0.009	345
	Burntollet River	4	Sperrin Mountains	Placer	2502	4107	17.629	0.004	15.458	0.003	37.620	0.008	451
	Cabry River	5	NE Co. Donegal	Placer	2514	4314	18.031	0.010	15.514	0.012	37.932	0.040	268
							17.965	0.004	15.527	0.004	37.896	0.012	346
							17.906	0.004	15.494	0.002	37.825	0.008	331
	Cavanacaw	6	Sperrin Mountains	Lode	2404	3701	17.497	0.004	15.423	0.002	37.586	0.008	498
							17.513	0.004	15.420	0.004	37.563	0.011	479
							17.509	0.009	15.422	0.008	37.578	0.022	486
							17.519	0.004	15.430	0.003	37.604	0.008	495
	Cavanacaw (ga)	6	Sperrin Mountains	Lode	2404	3701	17.534	0.004	15.432	0.004	37.598	0.014	488
							17.538	0.003	15.435	0.002	37.601	0.008	490
							17.480	0.004	15.422	0.003	37.632	0.010	509
							17.572	0.008	15.440	0.009	37.594	0.031	474
	Cavanacaw (py)	6	Sperrin Mountains	Lode	2404	3701	17.525	0.004	15.434	0.003	37.619	0.009	498
							17.507	0.004	15.428	0.003	37.643	0.009	499
							17.526	0.004	15.436	0.003	37.616	0.008	501
	Curraghinalt (ars)	7	Sperrin Mountains	Lode	2623	3858	17.557	0.004	15.434	0.003	37.638	0.008	474
							17.399	0.003	15.407	0.002	37.552	0.008	543
	Curraghinalt (py)	7	Sperrin Mountains	Lode	2623	3858	17.431	0.008	15.389	0.007	37.762	0.017	479
							17.596	0.007	15.406	0.005	37.996	0.014	384
	Curraghinalt Burn	8	Sperrin Mountains	Placer	2571	3866	17.432	0.004	15.412	0.003	37.575	0.009	527
							17.458	0.004	15.400	0.003	37.763	0.008	480

							17.499	0.004	15.421	0.003	37.517	0.010	492
	Glencurry Burn[d]	9	Sperrin Mountains	Placer	2502	3767	17.499	0.007	15.411	0.007	37.620	0.017	470
							17.429	0.013	15.391	0.012	37.691	0.030	486
							17.446	0.019	15.393	0.017	37.657	0.045	476
							17.495	0.005	15.411	0.005	37.655	0.013	474
							17.517	0.004	15.400	0.003	37.754	0.010	435
							17.538	0.005	15.424	0.003	37.635	0.011	467
	Lougheraherk	10	SW Co. Donegal	Placer	1592	3882	18.171	0.003	15.553	0.002	37.847	0.007	243
							18.288	0.004	15.583	0.003	37.947	0.010	218
							18.473	0.004	15.576	0.003	37.958	0.009	59
Leinster-Lakesman	Ballybrack	11	Co. Waterford	Placer	2434	1079	18.184	0.004	15.628	0.004	38.427	0.012	388
							18.324	0.005	15.619	0.004	38.275	0.014	265
							18.595	0.006	15.623	0.006	38.390	0.020	68
							18.425	0.005	15.624	0.004	38.567	0.012	200
							18.211	0.005	15.621	0.004	38.285	0.010	352
							18.257	0.005	15.596	0.004	38.153	0.011	266
	Ballykale	12	Co. Wexford	Placer	3159	1565	17.994	0.004	15.616	0.003	38.104	0.009	502
	Boley	13	Co. Wexford	Placer	3069	1562	17.985	0.003	15.620	0.002	38.094	0.008	518
							18.105	0.003	15.608	0.002	38.112	0.007	407
	Gibbett Hill	14	Co. Wexford	Placer	2961	1575	18.189	0.005	15.627	0.005	38.280	0.014	381
							18.088	0.004	15.632	0.004	38.277	0.012	465
	Goldmines East River[d]	15	Co. Wicklow	Placer	3180	1745	17.985	0.005	15.617	0.005	38.025	0.016	513
							18.087	0.004	15.619	0.003	38.087	0.011	442
							18.212	0.005	15.626	0.004	38.229	0.013	362
							18.141	0.004	15.622	0.002	38.194	0.008	408
							18.147	0.005	15.608	0.006	38.234	0.018	423
							18.131	0.005	15.626	0.005	38.106	0.018	367
							18.192	0.004	15.621	0.003	38.326	0.011	384
							18.187	0.004	15.627	0.002	38.322	0.008	384
	Knockmore	16	Co. Kerry	Placer	666	1046	18.069	0.005	15.627	0.004	38.144	0.015	470
	Millshoge	17	Co. Wexford	Placer	3065	1520	18.378	0.008	15.634	0.007	38.402	0.018	255
							18.146	0.004	15.628	0.003	38.280	0.008	416
	Ow River	18	Co. Wicklow	Placer	3111	1800	18.560	0.006	15.653	0.007	38.635	0.023	157
							18.267	0.003	15.624	0.002	38.220	0.008	317
							18.050	0.004	15.626	0.003	38.128	0.010	482

							18.160	0.005	15.626	0.005	38.086	0.015	402
							18.181	0.010	15.623	0.009	38.115	0.024	379
							18.464	0.004	15.661	0.003	38.424	0.012	246
							18.246	0.005	15.635	0.004	38.163	0.012	356
	Walishtown	19	Co. Kildare	Placer	2940	2156	18.329	0.003	15.606	0.002	38.217	0.007	234
							18.233	0.004	15.574	0.003	38.070	0.009	240
							18.280	0.012	15.593	0.010	38.161	0.025	244
							18.314	0.003	15.588	0.002	38.162	0.007	210
							18.276	0.004	15.588	0.003	38.114	0.009	236
							18.337	0.004	15.582	0.003	38.197	0.008	177
	Whelanbridge	20	Co. Waterford	Placer	2513	1088	18.366	0.004	15.649	0.003	38.425	0.009	293
							18.679	0.004	15.621	0.004	38.312	0.013	0
							18.435	0.008	15.606	0.007	38.305	0.018	153
Mayo	Bohaun	21		Lode	1006	2557	17.909	0.012	15.483	0.011	37.866	0.029	298
							17.957	0.007	15.478	0.007	37.845	0.021	250
							17.981	0.012	15.484	0.011	37.855	0.029	243
	Bunowen River	22	Cregganbaun	Placer	8640	2743	17.589	0.004	15.438	0.004	37.646	0.013	456
							17.752	0.004	15.485	0.003	37.553	0.010	426
	Carrownisky River	23	Cregganbaun	Placer	0830	2725	17.625	0.004	15.432	0.003	37.681	0.008	416
							17.793	0.004	15.482	0.003	37.820	0.010	389
							17.743	0.005	15.452	0.005	37.741	0.017	363
							17.655	0.005	15.443	0.005	37.660	0.016	415
							17.634	0.004	15.437	0.003	37.668	0.008	420
							17.834	0.004	15.466	0.003	37.902	0.009	321
							17.851	0.012	15.467	0.011	37.959	0.028	308
							18.043	0.009	15.489	0.008	38.000	0.019	207
							17.659	0.004	15.450	0.003	37.651	0.008	427
							17.567	0.004	15.415	0.004	37.705	0.010	427
	Croagh Patrick	24		Placer	0896	2804	18.044	0.004	15.542	0.004	37.653	0.013	317
							18.076	0.004	15.542	0.003	37.736	0.010	291
							18.048	0.004	15.543	0.003	37.651	0.010	315
							18.040	0.004	15.545	0.004	37.649	0.012	327
							18.044	0.005	15.547	0.005	37.668	0.016	329
	Lecanvy Stream	25	Croagh Patrick	Placer	0890	2815	18.100	0.003	15.543	0.002	37.773	0.008	277
							18.069	0.004	15.537	0.003	37.763	0.009	287
	Shraroosky	26	Cregganbaun	Lode	0797	2715	17.623	0.004	15.432	0.003	37.632	0.008	417

							17.623	0.003	15.432	0.002	37.627	0.007	418
	Shraroosky (ga)	26	Cregganbaun	Lode	0797	2715	17.613	0.003	15.442	0.002	37.664	0.007	446
							17.628	0.004	15.444	0.003	37.672	0.008	438
Southern Uplands	Ballincurry	27	Mourne Mountains	Placer	3216	3157	18.605	0.009	15.602	0.009	38.492	0.025	15
	Camcor River	28	Slieve Bloom, Co. Offaly	Placer	2201	2062	17.928	0.005	15.507	0.006	37.791	0.018	334
							18.459	0.003	15.581	0.002	38.257	0.008	80
	Clay Lake (ars)	29		Lode	2817	3357	18.548	0.004	15.587	0.002	38.012	0.007	26
							18.624	0.004	15.575	0.003	38.040	0.009	n/a
							18.674	0.004	15.579	0.003	38.029	0.008	n/a
	Clay Lake (py)	29		Lode	2817	3357	18.409	0.004	15.582	0.003	38.069	0.009	122
							18.376	0.003	15.582	0.002	38.064	0.007	147
	Clontibret (ars)	30		Lode	2755	3301	17.837	0.005	15.499	0.005	37.712	0.015	390
							17.845	0.006	15.497	0.006	37.721	0.016	378
							17.856	0.003	15.499	0.002	37.776	0.007	375
							17.857	0.003	15.498	0.002	37.736	0.007	371
							17.870	0.003	15.499	0.002	37.765	0.008	363
	Leitrim River (Lower)	31	Mourne Mountains	Placer	3218	3285	17.999	0.004	15.531	0.003	37.887	0.009	329
							17.928	0.004	15.515	0.003	37.824	0.009	351
							17.987	0.004	15.548	0.003	37.944	0.009	374
							18.297	0.004	15.571	0.003	38.198	0.008	185
							17.926	0.005	15.526	0.004	37.845	0.012	377
	Leitrim River (Upper)	32	Mourne Mountains	Placer	3215	3259	18.420	0.004	15.563	0.003	38.370	0.009	72
							18.471	0.006	15.584	0.007	38.378	0.022	78
	River Bann	33	Mourne Mountains	Placer	3220	3290	18.424	0.006	15.585	0.006	38.287	0.021	116
							17.941	0.004	15.519	0.003	37.821	0.009	349
							18.061	0.003	15.538	0.002	37.949	0.008	297
	Rocky River	34	Mourne Mountains	Placer	3234	3277	18.486	0.005	15.580	0.004	38.372	0.013	58
							17.949	0.006	15.509	0.006	37.867	0.019	322

Notes: All analyses performed on gold unless otherwise stated: ars = arsenopyrite, ga = galena, py = pyrite. Errors ± 2 standard errors of the mean of 50 integration cycles. [a]Numbers refer to those on Figure 2, [b]Irish National Grid, [c]Pb-Pb model ages (Ma) based on Stacey and Kramers (1975), [d]Previously published: Standish et al. (2013).