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Economic Geology

Integration of detrital gold microchemistry, heavy mineral distribution and sediment geochemistry to clarify regional metallogeny in glaciated terrains: application in the Caledonides of southeast Ireland

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Abstract:	<p>Regional exploration for rare and precious metal enrichment traditionally uses multi-element geochemical analysis of the fines (<150 µm) fraction of stream sediments, however these data can be misleading in glaciated regions with complex geology. Here we compare the spatial distributions of data from sediment fines with distributions of heavy mineral concentrates including detrital gold in the same region. Gold grains are characterized according to abundance and morphology, plus a 'microchemical signature' from the combination of alloy analysis and systematic identification of mineral inclusions revealed in polished sections. These inclusions survive indefinitely and are indicative of hypogene mineralogy, whereas the metal loadings of fines may be affected by weathering or anthropogenic activity. All three approaches are mutually supportive: sediment fines analyses provide a basis for more labour-intensive targeted gold grain studies, which in turn highlight specific gold-element associations useful for interpretation of geochemical datasets. Spatial distributions of resistate heavy mineral suites constrain the directions and extents of glacial transport which facilitates more confident interpretations of placer-lode relationships from gold grain studies.</p> <p>Characterisation of 2160 gold grains from 40 localities in the auriferous region of southeast Ireland provided a clear indication of proximity of gold to source, and identified gold derived from different episodes of mineralization. A distinction is apparent between gold in the south of the region (Wexford), likely derived from widespread stratabound Au-As-Fe-S mineralization, and that in the north (Wicklow) where the historical placer mining district of the Goldmines River yielded gold with inclusions exhibiting a distinctive Pb-Bi-As association. The Goldmines River placers formed by the efficient accumulation and preservation of detrital gold derived from several discrete intra-valley sources. We recommend that a combination of classical stream sediment geochemistry, heavy mineral analysis, and gold grain studies is used more widely to provide additional insights on the location and nature of gold mineralization and regional metallogeny in regions of poor exposure and complex geology.</p>

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Integration of detrital gold microchemistry, heavy mineral distribution and sediment geochemistry to clarify regional metallogeny in glaciated terrains: application in the Caledonides of southeast Ireland

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Abstract

16 Regional exploration for rare and precious metal enrichment traditionally uses multi-element
17 geochemical analysis of the fines (<150 µm) fraction of stream sediments, however these data can be
18 misleading in glaciated regions with complex geology. Here we compare the spatial distributions of
19 data from sediment fines with distributions of heavy mineral concentrates including detrital gold in
20 the same region. Gold grains are characterized according to abundance and morphology, plus a
21 'microchemical signature' from the combination of alloy analysis and systematic identification of
22 mineral inclusions revealed in polished sections. These inclusions survive indefinitely and are
23 indicative of hypogene mineralogy, whereas the metal loadings of fines may be affected by
24 weathering or anthropogenic activity. All three approaches are mutually supportive: sediment fines
25 analyses provide a basis for more labour-intensive targeted gold grain studies, which in turn highlight
26 specific gold-element associations useful for interpretation of geochemical datasets. Spatial
27 distributions of resistate heavy mineral suites constrain the directions and extents of glacial transport
28 which facilitates more confident interpretations of placer-lode relationships from gold grain studies.

33 Characterisation of 2160 gold grains from 40 localities in the auriferous region of southeast Ireland
34 provided a clear indication of proximity of gold to source, and identified gold derived from different
35 episodes of mineralization. A distinction is apparent between gold in the south of the region
36 (Wexford), likely derived from widespread stratabound Au-As-Fe-S mineralization, and that in the
37 north (Wicklow) where the historical placer mining district of the Goldmines River yielded gold with
38 inclusions exhibiting a distinctive Pb-Bi-As association. The Goldmines River placers formed by the
39 efficient accumulation and preservation of detrital gold derived from several discrete intra-valley
40 sources. We recommend that a combination of classical stream sediment geochemistry, heavy mineral
41 analysis, and gold grain studies is used more widely to provide additional insights on the location and
42 nature of gold mineralization and regional metallogeny in regions of poor exposure and complex
43 geology.
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50 **Key words:** Placer gold, detrital gold, heavy minerals, stream sediment geochemistry, glaciated
51 terrain, metallogeny, orogenic gold, microchemical characterization, Caledonides
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Introduction

1 Stream sediment geochemical datasets are traditionally applied during mineral exploration to identify
2 vectors to mineralized areas (e.g. McLenaghan and Cabri, 2011). Two approaches are commonly
3 employed in tandem, one centering on the chemical composition of a fine fraction (typically <150
4 μm) and the other on the chemistry or mineralogy of a panned concentrate. The ‘fines’ fraction is
5 often preferred in regional studies as it can identify broad anomalies at spacing of one sample per a
6 few square kilometres. The panned concentrate (hereafter ‘heavy mineral concentrate’), may be useful
7 in directly identifying ore minerals whose longevity in the surface environment is limited, but which
8 may be present close to their bedrock source. Regional geochemical studies using these techniques
9 commonly contribute to initial evaluations of the prospectivity of an area of interest and may be
10 undertaken by Government agencies whose aim is to stimulate further, focussed exploration.
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15 Southeast Ireland has a maritime climate and a well-developed drainage network due to the hilly
16 topography. Mineral exploration in the region has benefitted from an extensive regional stream
17 sampling and geochemical analysis program (‘Tellus’) which has generated high resolution (1 per 4
18 km^2) data sets mostly in the counties of Wicklow and Wexford (Fig. 1) (Knights and Heath, 2016).
19 Regional lithologies comprise an assemblage of Palaeozoic metasedimentary, volcanic and igneous
20 intrusive rocks that were deformed in the Late Ordovician – Early Silurian during the Caledonian
21 orogeny. The region is of interest because of Kuroko-style volcanogenic massive sulphide
22 mineralization at Avoca in County Wicklow that has yielded around 100,000 tonnes of copper metal
23 (Tietzsch-Tyler et al., 1994) and because of historical placer gold extraction. In 1795, the Ballinvally
24 area ~7 km south of the Avoca mines was the scene of Ireland’s only historical ‘gold rush’ for placer
25 resources. It has been estimated (Reeves, 1971) that up to 300 kg of placer gold was recovered from
26 gravels in the Ballinvally and Monaglogh River valleys (Fig. 1) and surrounding area. Some of the
27 gold was very coarse-grained, the largest mass being the ‘Wicklow nugget’ weighing 22 ounces (682
28 g) which became the property of George III. A replica of this nugget is in the Natural History
29 Museum, London. However, despite intense exploration during the following century, the bedrock
30 source or sources were not identified. The Ballinvally and Monaglogh Rivers collectively became
31 known as ‘Goldmines River’. Modern exploration since the 1980s has extended the area of interest to
32 the south and southwest, and several areas prospective for gold mineralization have been identified by
33 mineral industry exploration using soil geochemistry, geophysical surveys, trenching and drilling
34 (Fig. 2). Current exploration company interest in the region is at least in part a consequence of the
35 Tellus data releases.
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43 Two major challenges face such exploration programmes; firstly the paucity of bedrock exposure
44 typical of areas subjected to Quaternary glaciation, and secondly the complex geology comprising
45 metasedimentary and metavolcanic rocks and igneous intrusions which provide the possibility of
46 different styles of gold mineralization. In common with many orogenic belts worldwide, the
47 abundance and distribution of placer gold in SE Ireland provides the most powerful indicator of local
48 mineralization, even though the location(s) of the source remain unclear. Analyses of gold grain alloy
49 chemistry, combined with the mineralogy of opaque mineral inclusions revealed in polished sections
50 through grains, generates a ‘microchemical signature’ which has been used to advantage in such
51 scenarios to distinguish different styles of mineralization from which the detrital gold is derived (e.g.
52 Chapman et al., 2017). This approach has been used to illuminate local variation in orogenic gold
53 signatures (Chapman et al., 2010a,b; Chapman and Mortensen, 2016) and to infer spatial variation in
54 mineralization within intensely glaciated areas of the British Caledonides where bedrock exposure is
55 scarce (Leake et al., 1998, Chapman et al. 2000a). This methodology appears ideally suited to
56 generating new insights into the metallogeny of the study area.
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1 This study considers data derived from three approaches to geochemical exploration which utilise
2 material collected from fluvial environments; the recently published Tellus data set, and two new
3 databases describing the mineralogy of heavy mineral concentrates and detrital gold.

4 **Geological background**

6 *Geology and tectonic setting*

8 Southeast Ireland comprises a NE-SW oriented belt of Cambrian and Ordovician sedimentary and
9 volcanic rocks (Fig. 1) that were tectonically deformed and metamorphosed during the Lower
10 Palaeozoic. Cambrian turbidites outcrop to the SE and NW with Ordovician basinal strata in a central
11 belt. In the lower Ordovician, thick laminated mudstones were deposited: the striped appearance of
12 these gave rise to the name 'Ribband Group'. The Cambrian and lower Ordovician strata were
13 deformed in mid-Ordovician time by an orogenic event, the Monian, which was localised to the
14 Leinster region and affected the southeast of the region more intensely than the northwest (Tietzsch-
15 Tyler et al., 1994; Gallagher et al., 1994). In the upper Ordovician, further sediments and volcanic
16 formations were deposited on the submerging Monian landmass, forming the Duncannon Group.
17 Outcrops occur in Wicklow in the Avoca district, and in Wexford as a 6-8 km wide belt sandwiched
18 to the north and south by Ribband Group metasediments (Figs. 1 and 2). In Wicklow the Duncannon
19 Group incorporates the Avoca Volcanic Group (AVG, formerly the Avoca Formation) which
20 comprises dominantly rhyolitic lavas, chloritic tuffs and slaty mudstones and hosts stratiform sulphide
21 mineralization, described below. In earlier interpretations (e.g. Brück et al., 1979) the Duncannon
22 Group was regarded as mainly volcanic, whereas Tietzsch-Tyler et al. (1994) include all post-Monian
23 sedimentary rocks in this Group.
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30 During the Late Silurian to Early Devonian Caledonian Orogeny, the previously deformed pre-
31 Monian rocks were further folded together with the younger Ordovician rocks. A major period of
32 shearing towards the end of the orogeny generated northeast-oriented deformation zones, one of
33 which occurs in the Avoca – Goldmines River area (Williams et al., 1986). The Leinster Granite
34 batholith and satellite granitic plutons (Fig. 1) were emplaced into these actively deforming shear
35 zones in the Early Devonian around 405 Ma (O'Connor and Brück, 1978; Gallagher et al., 1994).
36 Gold, tungsten, tin and lead-zinc mineralization is associated with thermal metamorphism and
37 hydrothermal fluid circulation accompanying batholith emplacement (McArdle et al., 1989).
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41 In the vicinity of the Goldmines River (Fig. 3), bedrock comprises low-grade metasedimentary rocks,
42 mainly dark grey phyllites and quartzites of the Kilmacrea Formation, with intrusive sheets of granite,
43 felsite and dolerite oriented parallel to the regional schistosity. Subordinate basic to intermediate lavas
44 and tuffs, metamorphosed to chloritic and sericitic schists, occur within the Ribband Group succession
45 which is stratigraphically overlain to the northwest by the AVG. The AVG outcrop width tapers
46 southeastwards and the tapered end abuts the sigmoidal-shaped Croghan Kinshelagh Granite (Fig. 3)
47 although some authors (e.g. Fritschle et al., 2018) consider the Duncannon Group to extend further
48 southwest enveloping the granite outcrop.
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52 The bedrock geology of North Wexford is similar to that of southern Wicklow, although the AVG is
53 not represented in Wexford. Duncannon Group metasediments and volcanic rocks, comprising the
54 Campile Formation, form a NE-SW belt which is demarcated on the south side by the Courtown-
55 Tramore Fault (Tietzsch-Tyler et al., 1994). This fault abuts the Campile Formation against Lower
56 Ordovician slates and siltstones (the Ballyhoge Formation). To the north of the Campile Formation
57 outcrop are stratigraphically older grey, green and purple slates of the Ribband Group (the Oaklands
58 and Ballylane Formations). In the Duncannon Group outcrop, volcanic rocks comprise around one
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1 quarter of the rock volume, and are mainly felsic with lesser intermediate and mafic volcanic rocks
2 and dolerite sills. The felsic rocks include rhyolitic lavas, tuffs and agglomerates within grey and
3 brown slaty mudstones. Sheet-like intrusive masses of granite occur in this belt to the southwest of
4 Enniscorthy, notably in the Adamstown area included in this study (Fig. 1). West of the study area,
5 the Leinster Granite outcrop forms upland moors. This granite is dominantly a two-mica granodiorite-
6 granite of S-type affinity which has higher concentrations of large-ion lithophile and light rare earth
7 elements than typical granite (Brück and O'Connor, 1977). Chemical characteristics of the granites
8 and volcanic rocks suggest that during their formation, the Leinster region was in a transitional
9 position between a volcanic island arc that extended from County Waterford to the English Lake
10 District and a back-arc basin in North Wexford – Wicklow.

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13 Gallagher et al. (1994) demonstrated that the Croghan Kinshelagh Granite (Figs. 2 and 3; Croghan
14 Complex of recent literature), cropping out west of the Goldmines River, is an older intrusion than the
15 Leinster Granite. Instead, this granite intrusion is contemporaneous with Upper Ordovician
16 (Llandeilo- Ashgill) volcanic rocks that outcrop around Avoca. Relatively high Th, Y, Nb and REE
17 concentrations contrast the Croghan Kinshelagh Granite to other granite types in SE Ireland.
18 However, recent geochronological and geochemical studies (Fritschle et al., 2016; Fritschle et al.,
19 2018) have established that the Croghan Complex comprises discrete older and younger units. The
20 older granite is correlative with AVG volcanism and has been deformed with a penetrative fracture
21 cleavage similar to the AVG rocks, as described by Gallagher et al. (1994). The younger granite
22 intrusion is undeformed and cuts across S1 deformation in the wallrock. Crystallization ages of 456.9
23 ± 2.4 Ma and 455.4 ± 2.8 Ma for the younger granite are c. 6 Ma younger than the AVG age of 462.6
24 ± 3.5 Ma (Fritschle et al., 2016). These dates and structural features constrain the date of deformation
25 representing a major arc accretion event at c. 460 Ma.

31 *Bedrock mineralization*

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33 Table 1 and Fig. 2 summarise occurrences of bedrock mineralization in the area under consideration.
34 Whilst the Avoca VMS deposit is clearly the most economically significant mineralization in the
35 region, it is unlikely to have contributed placer gold to the Goldmines River area to the southwest.
36 This is because of Avoca's peripheral geographical position, the very fine particle size of gold reported
37 from the VMS mineralization (Milner and McArdle, 1992), the size range of gold associated with
38 similar deposits elsewhere (Huston, 2000), and the prevailing glacial transport regimes discussed
39 below.
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43 Banded iron formation that crops out on the Moneyteige–Ballycoog Ridge adjacent to the Ballinvally
44 River (Figs. 2 and 3) hosts minor epigenetic Cu-Pb-Zn-Bi-Au mineralization described by McArdle
45 and Warren (1987 a,b), Ixer et al. (1990) and Milner and McArdle (1992). McArdle and Warren
46 (1987b) note that the major iron minerals are magnetite and siderite with sparsely disseminated pyrite
47 and chalcopyrite, and that the mineralization is richest where it has been remobilised along faults.
48 Chalcopyrite-rich samples assayed 0.2–0.5 ppm Au suggesting that gold is associated with
49 chalcopyrite, which at outcrop weathers to hematite and limonite thereby liberating the gold.
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53 Elsewhere in the Goldmines River area, stratabound Au-As-Fe-S mineralization has been identified
54 by company exploration at the Mary Ellen and Maclaren zones (Figs. 2 and 3). These stratabound
55 zones occur in the top-most interval of the Ribband Group marking the transition from sedimentary
56 facies to volcano-sedimentary facies of the Duncannon Group (McKillen, Tyler and Associates,
57 2009). Similar associations have been reported from various localities throughout the study area in
58 County Wexford. For example, exploration results reported by IMC (2013) in the Knockbrandon,
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1 Kilmichael-Ballyowen-Ballygarrett and Boley prospects in County Wexford (Fig. 2) indicate that,
2 although broadly stratabound, the mineralization occupies ENE trending shear zones that are slightly
3 oblique to lithological strike. Visible gold occurs in quartz veins within the shear zones. No detailed
4 mineralogical information is available concerning this form of mineralization. However, it appears to
5 be structurally controlled, often occurring at lithological contacts, and may be comparable in origin to
6 the sulfide-hosted gold mineralization in the Kilmacoo deposit (Table 1).
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8 *Quaternary geology*

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10 Geochemical and mineralogical studies of sediments need to take into account the mobilization of
11 material by various surface processes. Ireland was repeatedly glaciated during the Pleistocene, and at
12 various times ice sheets covered most if not all of the area shown in Fig. 1, and certainly all of the
13 area shown in Fig. 2 (Knight et al., 2004). In Ireland the most recent glacial epoch is referred to as the
14 Midlandian. Consequently a wide variety of glacial and fluvio-glacial erosional landforms and deposits
15 occur in the study area. Located west of the area, the Wicklow Mountains supported an ice dome from
16 which ice flowed radially (Warren, 1993). In the Avoca – Goldmines River area, SE- to ESE-oriented
17 glacial striae mapped by McArdle and Warren (1987a,b) indicate that this radial ice flow would have
18 dispersed detritus southeastwards across the study area (Fig. 2). Avoca and Goldmines River lie
19 several kilometres beyond the western limit of shell-bearing glacial sediments deposited by
20 southward- and south-westward-flowing ice streams in the Irish Sea basin (Fig. 2). Consequently, we
21 assert that glacial processes could not have transported detritus from the Avoca VMS deposit or
22 Kilmacoo Au deposit south-westwards to the Goldmines River area during the Midlandian glaciation.
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28 In Wicklow, the effects of glacial processes are dependent upon valley orientation. East of Aughrim,
29 the Aughrim River valley follows a ESE-trending course cutting through the prevalent structural grain
30 (Figs. 2 and 3) and during glaciations is likely to have experienced a large ice flux (ice streaming)
31 with associated transport of detritus. Perpendicular to this ice flow direction is the Goldmines River
32 valley in which valley-side deposits are more prominent on east-facing slopes in the lee of the ice
33 flow. McArdle and Warren (1987b) noted that sections through valley-side deposits show a
34 stratigraphy of two distinct Quaternary deposits: a compact till unit up to 6 m thick overlies a clast-
35 supported deposit of angular, locally-derived bedrock fragmented by gelifluxion. Underlying the till
36 unit in the valley bottom, the geliflucted debris interdigitates with stream-washed debris. This
37 suggests that the Ballinvally placer deposit was contained in sediments which pre-dated the
38 Midlandian glaciation. McArdle and Warren (1987b) conclude that preservation of these pre-glacial
39 sediments was facilitated by the transverse direction of the ice flow across the deeply incised valleys
40 now occupied by the Ballinvally and Monaglogh Rivers (Fig. 3).
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46 In Wexford south of the Croghan Kinshelagh upland area (Fig. 2), the outcrop extent of the Ribband
47 Group is characterised by relatively low, subdued topography extensively covered by glacial deposits.
48 Igneous rocks in the Duncannon Group form ENE-WSW oriented bedrock ridges. Gaps in these
49 ridges, where the present day rivers flow across the structural grain, may have resulted from erosion
50 along N-S oriented faults that segment the Duncannon Group outcrop (Fig. 2).
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53 **Methodology**

54 *Collection of placer gold and other heavy minerals*

55 Gold grains were collected using the specialist field techniques described by Leake et al. (1997)
56 which permits co-collection of heavy mineral concentrates (HMC). Material was collected from 30
57 sites in the study area selected for their potential to host elevated concentrations of gold particles, such
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1 as bedrock traps and point bars. All samples were collected from active, modern fluvial systems.
2 Samples from 'first order' streams were favoured because these yield more valuable information on
3 the provenance of placer gold than samples from trunk drainages which may contain gold grains from
4 disparate sources (e.g. Chapman et al., 2010a).

5
6 Leake et al. (1997) suggested that a sample population of 30 particles would provide a satisfactory
7 inclusion signature, based on their experience of observing inclusions in around 20% of the gold
8 grains. This study has adopted a methodology in which far more gold grains have been collected,
9 firstly, because the inclusion abundance in some samples was far lower, which necessitated
10 resampling, and secondly because studies such as Moles and Chapman (2013) and Chapman et al.
11 (2016) illustrate the benefit of larger data sets when characterizing populations of placer gold grains
12 derived from multiple sources. Even so, in some cases only small numbers of inclusions were
13 observed (e.g. Askamore: Table 2). Resampling over a period of several years also permitted
14 evaluation of the reproducibility of alloy data for specific stream locations. Figure 4 A shows that
15 very similar cumulative percentile Ag plots were obtained when resampling the same locality. This
16 increases confidence that differences in the shape of the curves between sites are geologically
17 significant and are not a consequence of sampling variations.

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19 A total of 2160 detrital gold particles were used in this study, the data for 619 of which were
20 previously reported by Chapman et al. (2006). Although detrital gold was recovered at every locality,
21 the abundance varied enormously (Table 2). Collection of HMC samples was undertaken in order to
22 provide semi-quantitative data on the abundance of heavy minerals other than gold, with a view to
23 illuminating particle mobility in the surficial environment and potentially identifying mineral species
24 genetically linked to gold mineralization (McClenaghan, 2011).

30 *Analysis*

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32 Field-panned HMC were refined at the University of Brighton using heavy liquid separation (di-
33 idiomethane) to remove mineral particles with a specific gravity of less than 3.3. Estimates of the
34 modal mineralogy of HMC were obtained using X-ray diffraction (XRD) of powdered sub-samples,
35 followed by mineral matching and semi-quantitative processing of the spectra. It is emphasized that
36 the study aimed to compare the bulk mineralogy of the samples: the techniques employed do not
37 reveal minerals in the HMC that are present in trace amounts (<1-2%). Portable XRF measurements
38 of compressed powdered samples were used to qualitatively confirm the identity of minerals which
39 have similar XRD spectra but contrasting geochemistry, such as cassiterite and magnetite. Due to
40 spectral similarities, staurolite is difficult to distinguish from garnet in samples with large proportions
41 of garnet and lesser staurolite.

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43 The gold grains were mounted in resin blocks which were ground and polished to expose cross-
44 sections through grain cores for microchemical analysis at the University of Leeds according to the
45 methods of Chapman et al. (2000b). Quantitative analysis of gold and alloying elements was carried
46 out using a Cameca SX50 automated electron microprobe (EMPA), fitted with three wavelength
47 spectrometers and an Oxford Analytical 10/55s Energy Dispersive System (EDS). The EMPA was
48 operated at 20kV and 50 nA, with a 30 second counting time for each element. Background counts
49 were determined by a 30 s count off-peak. The standards employed were pure Au, Ag, Cu, and HgS.
50 An internal standard of 81.5 % Au and 18.5 % Ag was employed in each batch of analyses. Detection
51 limits were Ag: 350 ppm, Hg: 2,800 ppm, and Cu: 200 ppm. All analyses are reported in terms of
52 mass % unless otherwise stated. Identification of specific mineral inclusion species was carried out
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1 using a Camscan Series 4 scanning electron microscope (SEM) operated at 25 kV fitted with an
2 Oxford Analytical 10/25s EDS system, also at the University of Leeds.

3 *Data presentation*

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5 Heavy mineral assemblages and Tellus geochemical data have been depicted as pie charts and
6 proportional symbols respectively on maps of the study area (Figs. 5 and 11). It is emphasized that
7 heavy minerals are expressed as proportions of the HMC sample which constitutes a variable fraction
8 of the bulk sediment. Consequently no direct relationship is expected between these mineral
9 proportions and the Tellus data for geochemical compositions of sieved stream sediment samples.
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13 The abundance of detrital gold is typically highly variable in auriferous regions, but local high
14 abundances may provide useful information on the distribution of bedrock source(s) particularly in
15 first order drainage. Meaningful quantification of detrital gold grain abundance is challenging because
16 of the extreme variation in concentrations at specific sampling sites due to hydrodynamic processes
17 and operator skill, as discussed later. The locations of old placer workings provide a clear indication
18 of local high concentrations, although abundances of detrital gold may now be low due to historical
19 extraction. Elsewhere, detrital gold abundance at sample localities has been defined as very low, low,
20 medium or high (Table 2, Fig. 6 A) where ‘high’ corresponds to recovery rates of dozens to hundreds
21 of grains per hour of sluicing and panning activity, whereas ‘very low’ corresponds to a recovery rate
22 of one or two grains per hour.
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27 Representation of information generated by microchemical characterization is less straightforward to
28 present spatially. Silver compositions of individual sample populations reflect either the
29 compositional variation of a single source or the compositional ranges of multiple sources. In the
30 second case, the presentation of a single statistical measure such as a median is usually inappropriate,
31 and representation by use of cumulative percentile plots for each population is preferred (e.g. Fig. 4).
32 Using this form of presentation, the Ag range and relative proportion of grains of similar Ag contents
33 may be easily seen, and comparisons between samples quickly established. In Wexford, the majority
34 of sample populations yielded sub-parallel shallow-gradient cumulative frequency trends with 5–20%
35 of particles forming a steeper ‘tail’ of Ag-rich compositions (Fig. 4 B). In such cases the populations
36 may be adequately represented by a median value (i.e. %Ag content at the 50% percentile), and this
37 measure has been depicted on maps for comparison with other data sets. Class intervals have been
38 defined on the basis of breaks in the slope of the cumulative Ag curve (Fig. 4 C) depicting the median
39 values for all localities at which 4 or more gold grains were obtained (Table 2).
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45 In contrast, sample populations from the environs of Croghan Kinshelagh in Wicklow generally
46 exhibit a wide variation both in Ag content, and in profiles on a cumulative frequency plot (Fig. 4 D).
47 Considerations of specific inclusion assemblages in conjunction with limited ranges of alloy
48 composition have identified specific gold ‘types’ defined by their microchemical signatures. These
49 types are present to different extents at each locality, explained below. In this particular area the
50 distribution of these gold types is informative, whereas information is lost through the adoption of a
51 single statistical measure such as the median %Ag value.
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55 In this study, 20 opaque mineral species have been recorded as inclusions within gold grains (Table
56 2). Spider diagrams (Chapman et al., 2017b) permit quick comparison of the importance of major
57 inclusion species whilst also recording the presence of small numbers of unusual minerals, such as
58 native bismuth, whose presence may be informative.
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1 While we focus on the microchemical signature of gold grains from sample localities, in some cases it
2 has been helpful to consider the size and morphology of gold grains within a population to provide an
3 additional context for the interpretation of compositional data.

4 **Results**

5 *Mineralogy of heavy mineral concentrates*

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7 Proportions of heavy minerals in the concentrates are given in Table 3 and displayed as pie charts in
8 Fig. 5. Garnet is ubiquitous throughout the region and staurolite is commonly associated with garnet
9 in the north and south of the study area, consistent with previous HMC analyses by Malone (2007).
10 These minerals are constituents of Ribband Group metasediments within the aureole of the Leinster
11 granite and we ascribe their eastwardly dispersion to glacial transport during the Midlandian and
12 perhaps also earlier glaciations. Locally, the dominance of garnet is reduced because of
13 geographically focussed inputs of other heavy minerals derived from local lithologies. Ilmenite is an
14 important component of the HMC at localities in the environs of mafic lithologies within the
15 Duncannon Group in Wexford and the Ribband group in Wicklow (Fig. 2). Other minerals are
16 recorded in elevated concentrations in spatially coherent clusters, for instance monazite in central
17 Wexford, cassiterite at Askamore, Boley Lower and Milshoge in Wexford and some localities in
18 Wicklow, ferberite at Askamore and Boley Lower, and chrome spinel at Ballygarrett and nearby sites.
19 In the Goldmines River area, locally abundant hematite is most likely derived from the BIF outcrop
20 on the Ballycoog-Moneyteige Ridge, as discussed later. Magnetite is abundant only in samples from
21 Coolbawn River and from the Ballinvally River sampled at the main historical extraction site, the
22 'Red Hole'. The concentrates at these two sites have a striking similarity in heavy mineral proportions
23 which contrast with surrounding sites (Fig. 5).
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31 *Detrital gold characteristics*

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33 As shown in Fig. 6 A, the abundance of detrital gold in stream sediment varies widely across the
34 study area. The historical gold workings in Wicklow likely exploited concentrations of placer gold far
35 in excess of those present at sample localities in Wexford where there is no history of artisanal
36 mining. In north Wexford, scattered sites returned relatively high abundance against a background of
37 average to low abundance. Relatively high abundances were recorded at four localities: Boley Lower,
38 Milshoge, Ballykale and Ballygarrett (Fig. 6 A).
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42 High abundance of detrital gold may be ascribed to either autochthonous or allochthonous processes
43 and it is clearly advantageous to know which is prevalent in areas that are the focus of exploration
44 campaigns. In this regard, information on gold particle size and morphology may be usefully applied.
45 The coarse particle size of rough gold near the Red Hole in the Ballinvally River strongly suggests
46 very local derivation (Maclaren, 1903), as does the apparent influx of gold particles to around 1g in
47 the middle reaches of the Monaglogh River recorded during the present study (Fig. 7 A, B). Flaky
48 gold from Milshoge (Fig. 7 C) is typical of gold particles recovered in Wexford, although rough gold
49 characteristic of proximal derivation is dominant at Ballygarrett and Boley Lower.
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53 Polished sections through gold grains embedded in resin exhibit various microtextural features when
54 viewed with a scanning electron microscope in back-scattered electron mode. Small inclusions of
55 sulfides and other metallic minerals represent the associated hypogene mineralogy (Fig. 8 A, B).
56 Commonly observed gold-rich rims are attributed to silver depletion in the modern surficial
57 environment (Groen et al., 1990), and are not considered further. Internally, gold grains from the
58 Goldmines River area are mostly homogeneous in alloy composition (e.g. Fig. 8 C), but in contrast,
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1 many gold grains from the Wexford localities show internal heterogeneity (Figs. 8 D, E). These grains
2 commonly have complex textures in which Ag-rich alloys appear to have overprinted a pre-existing
3 alloy and a third phase of nearly pure gold forms rims and/or tracks. Processes that contributed to this
4 heterogeneity, and the significance of the contrasting appearance of Wicklow and Wexford gold
5 alloys, are discussed later.
6

7 Evaluations of the microchemical information exhibited by regional sample sets normally start with
8 consideration of the alloy content of the various sample populations (e.g. Moles and Chapman, 2013;
9 Chapman and Mortensen, 2016). While silver is ubiquitous as an alloy component, Cu and Hg were
10 recorded only sporadically in grains from the region. The highest Cu values of 4.6% and 4.3%,
11 recorded in gold grains from Ballyshannon and Ballykale respectively, are anomalous whereas the
12 majority of grains have values close to or below the instrumental detection limit of 0.02% Cu.
13 Therefore Cu values do not constitute a robust data set for quantitative treatment. Similarly, detectable
14 Hg values were largely absent. Consequently neither Cu nor Hg are considered further as
15 discriminants.
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19 Sample suites from Wicklow and Wexford differ fundamentally in the nature of the ranges of silver
20 present within individual sample populations. As discussed above, the generic form of the cumulative
21 frequency curves of %Ag in all Wexford sites has allowed their characterization using a single median
22 value, presented in Table 2, ranging from 3.2% Ag at Coolnacon Bridge to 8.3% Ag at Huntingtown.
23 Three class intervals of median %Ag (low <5.5, medium 5.5-7.5, high >7.5) were chosen on the basis
24 of the form of a cumulative percentile plot of median % Ag values (Fig. 4 C) and these categories
25 have been indicated on Fig. 6 B. There appears to be little or systematic variation in Ag content of the
26 Wexford sample suites with location, except that those around Adamstown in the south appear to
27 contain slightly less Ag. Neither is there an overall correlation between Ag content and underlying
28 lithology or heavy mineral association (Fig. 5), or spatial relationships correlating with ice flow
29 direction (Fig. 2).
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34 Contrasting characteristics are exhibited by detrital gold from each of the most important historical
35 placer mining localities around Croghan Kinshelagh namely Ballinvally, Coolbawn and Monaglogh
36 Rivers (Figs. 3 and 6 B). Gold from the Monaglogh River exhibits a high Ag sub-population that
37 comprises around 40% of the grains (Fig. 9 A). This high-Ag alloy is largely absent at the other two
38 localities. The relatively wide range of Ag contents observed within these populations, which
39 invalidates the use of median %Ag values for classification, has directed our attention to the use of
40 inclusion assemblages as the primary discriminants. At all three locations, the majority of arsenopyrite
41 inclusions are hosted by gold grains with a narrow range of c. 9-14% Ag as shown in Fig. 9 A. Galena
42 and native bismuth inclusions have been grouped because of their intimate association (e.g. Fig. 8 C)
43 and these inclusions were observed within gold alloy of a lower Ag range (indicated by a horizontal
44 line in Fig. 9 A). These tend to be mutually exclusive with the alloy range of gold grains that host
45 arsenopyrite inclusions.
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50 The Ag ranges of detrital gold samples collected to the north and northwest of Croghan Kinshelagh
51 are depicted in Fig. 9 B. In these samples are dominated by low Ag gold alloys (type 1) that account
52 for 50% to 90% of the total inventory (cumulative percentile), with very few grains containing $\geq 15\%$
53 Ag. The plots for samples from the Clone and Ballintemple streams are strikingly similar. The low
54 Ag, galena-bearing gold type identified in Fig. 9 A is also displayed in Fig. 9 B, where it corresponds
55 to the low Ag portion of all other curves. Gold alloy in the range 9-14% Ag containing arsenopyrite
56 inclusions is an important component of the overall population in the Goldmines River samples, but is
57 absent in gold from the Ow and Clone localities.
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1 Apart from galena and arsenopyrite, other mineral species occur in these samples, but their low
2 overall abundance (Table 2) precludes a similar analytical approach. Gold ‘types’ identified by
3 inclusion suites and range in Ag content of the host alloy have been defined broadly in Table 4. These
4 types are interpreted to represent gold sourced from different mineralizing events, but there is no
5 necessity for each type to exhibit mutually exclusive Ag contents, and no reason why a ‘diagnostic’
6 inclusion in one type should not be present, although rare, in another type.
7

8 The spatial variation in microchemical signature of detrital gold in the Ballinvally and Monaglogh
9 River valleys was investigated by sampling upstream of the main placer areas and in tributary
10 streams. Gold from upstream of the old workings yielded very similar Ag profiles to the richer areas
11 downstream, whereas samples from tributaries showed a narrower compositional range (Fig. 9 C, D).
12 Galena and arsenopyrite are the most common inclusion species although their proportions vary
13 between gold types, as shown in Table 4. Type 1 gold exhibits the highest ratio of galena to
14 arsenopyrite. Inclusions of native bismuth are extremely rare in general in gold grains, but the three
15 observed here all conform to the type 1 alloy signature. In type 2 gold, the proportions of galena and
16 arsenopyrite are approximately equal. In type 3 gold, arsenopyrite is far more common than galena
17 and there is a higher abundance of pyrite with occasional pyrrhotite. Chalcopyrite is present in gold
18 types 1 and 2 but is absent in type 3.
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23 The above discussion has focussed on arsenopyrite and galena because these are the most abundant
24 inclusion species. Using the full inclusion suite (Table 2), ‘spider plots’ have been generated (Fig. 10)
25 by which the entire suite of inclusion minerals may be compared. Fig. 10 A shows the contrasting
26 assemblages within the three gold types identified in the Croghan Kinshelagh area of County
27 Wicklow as described above. For this geographically broader comparison, the plots incorporate
28 inclusions recorded within all sample populations from each main valley, i.e. they also include
29 inclusion data for gold obtained from tributaries and headwaters.
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33 Presentation of the inclusion data for the Wexford sample suite is more challenging. The small
34 number of inclusions recorded at each locality precludes meaningful comparison of individual
35 assemblages such that some form of grouping into data sets is required, but this approach could mask
36 locally dominant signatures. Two rationales for data grouping have been explored. Figure 10 B
37 compares the inclusion signatures of gold from sample localities in the central Wexford area grouped
38 according to bedrock stratigraphy at sample sites. In this approach each group shows broad
39 mineralogical similarities, although Sb-bearing inclusions are present only at Boley Lower within the
40 Ribband Group, and at Hyde Park near the Ribband/Duncannon Group contact.
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44 A second approach is to use the heavy mineral concentrate data as a guide to forming the data sets. As
45 noted earlier, heavy mineral assemblages at Boley and Askamore are atypical as they are dominated
46 by cassiterite, ferberite and monazite. This suggests the presence of local felsic igneous bedrock,
47 which in turn raises the possibility of different styles of local gold mineralization. Figure 10 C
48 compares the inclusion signatures of gold from Askamore and Boley Lower with others from
49 localities within the Ribband Group outcrop. The gold from Boley generally conforms to the regional
50 signature, except the proportion of Sb-bearing inclusions is notably higher. In contrast, gold from
51 Askamore differs from the regional norm through the absence of galena and the relatively strong Te
52 and Se signature of the inclusion suite.
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57 *Results of the regional stream sediment geochemistry program*
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1 O'Connor and Reimann (1993) reported the first comprehensive regional geochemical study of SE
2 Ireland. This was based on analyses of nearly 2000 sieved (fine fraction) stream sediment samples
3 that were collected in the period 1986-1990 from 1st and 2nd order streams at an average spacing of 1
4 per 4 km². In this dataset, they identified three significant geochemical associations: (i) a close spatial
5 correlation of Li, Ta, U and W with granitic lithologies, (ii) a Cu, Sb and Au signature interpreted as
6 indicative of a volcanic association, and (iii) a Cr-Ni association which they ascribed to small local
7 occurrences of ultramafic lithologies. Relative to regional values, elevated Au concentrations were
8 found throughout the Ribband and Duncannon Group outcrop on the SE side of the Leinster Granite,
9 with anomalous Au values in samples in the Tinahely-Shillelagh zone of tourmaline-bearing Ribband
10 Group metasediments (Fig. 2). Samples from the Avoca – Goldmines River area did not show Au
11 enrichment relative to the regional levels although a single high value (discussed later) was found in
12 the Coolbawn River.
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16 The current, Ireland-wide, Tellus regional geological surveying program included re-analysis by XRF
17 of the original sieved sediment samples obtained for the study reported by O'Connor and Reimann
18 (1993). The re-analyses, using methods reported by Smyth (2007), were undertaken by the Geological
19 Survey of Ireland and funded by the Department of Communications, Energy and Natural Resources.
20 The new data set was made publically available in 2016 (Knights and Heath, 2016). Several examples
21 of the data sets are presented in Figure 11. The concentrations and distribution of various elements
22 reported in the Tellus database can be interpreted in the light of their probable significance for gold
23 mineralization. Elements such as Cu, Sb, As, Pb and Bi could be associated with specific gold
24 sources, whereas Sn, W, Cr and Ni are more likely to be derived from other styles of mineralization
25 but their distribution may provide evidence for glacial dispersion (McClenaghan and Paulen, 2018)
26 which may have also influenced detrital gold distribution (discussed later).
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31 Less than 5% of the stream sediment samples collected within the study area returned elevated
32 concentrations of gold in the range 0.1 to 1.5 ppm (Fig. 11 A). Fine fraction sediment samples with
33 >0.5 ppm Au are mostly located in a southeast-northwest trending belt between Camolin and Carnew.
34 There appears to be no spatial association between bedrock geology and Au enrichment in sediments,
35 indeed the SE-NW trending belt is perpendicular to the 'Caledonian' trend of the bedrock and crosses
36 outcrops of both Ribband and Duncannon Group rocks. This belt encompasses the Tombreen,
37 Askamore, Boley, Kilcloran, Milshoge and Ballyeden detrital gold sites of the present study (Fig. 2).
38 In addition, to the east of this belt, an isolated auriferous stream sediment sample is located close to
39 the Ballygarrett auriferous float occurrence documented by Chapman et al. (2006). Further stream
40 sediment Au anomalies occur west and southwest of Arklow and southwest of Camolin although
41 these areas were not sampled during the gold grain study reported here.
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46 Detrital gold was recovered during the current study from several areas where the Tellus data
47 indicates that fine-fraction sediment is not auriferous. Examples are south of Camolin (South
48 Corbetstown), south of Gorey (Coolnaveagh and Ballykale), west of Ballycanew (Ballyduff) and east
49 of Inch (Hyde Park and Cullenoge) (Table 2, Figs. 2 and 11 A). In the Avoca – Goldmines River area,
50 concentrations of Au >0.1 ppm occur in only one Tellus sample (Fig. 11 A) which is located
51 downstream of the Coolbawn River detrital gold sample site of the present study. Interestingly,
52 sediment samples from the Monaglogh and Ballinvally River catchments, re-analysed in the Tellus
53 programme, do not contain detectable levels of Au. Possible explanations for this are discussed later
54 but it is noteworthy that studies of other glaciated terranes show little correlation between gold in
55 sieved sediment and in heavy mineral fractions (McClenaghan and Paulen, 2018).
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1 Neither Cu or As show close associations with Au values in the Tellus dataset (Fig. 11 D, E) which is
2 perhaps surprising given the regional descriptions of Au-As-Fe-S bedrock mineralization. Higher Cu
3 and As values were recorded around Avoca and there are clusters of As values in known auriferous
4 areas such as the Goldmines River and in the west of the study area (4 km north and 5 km east of
5 Carnew). Antimony concentrations in fine fraction sediments range up to 12 ppm and display a strong
6 spatial trend (Fig. 11 F) with values >3 ppm Sb largely confined to Kilmacrea Formation (Duncannon
7 Group) metasediments on the southeast side of the Avoca – Ballycoog-Moneyteige zone, i.e. in the
8 stratigraphic footwall to the stratabound Cu-Fe mineralization. Additionally, high Sb values are
9 recorded in the central sections of the Ballinvally and Monaglogh Rivers. Moderate Sb concentrations
10 occur east of this and in the southern part of the study area in Wexford. Lead (Fig. 11 C) shows
11 anomalous concentrations at Avoca in the same sediments that are enriched in Sb, and in one sample
12 from the west of Croghan Kinshelagh. Similarly, Bi is enriched in the fine fraction stream sediment in
13 the environs of the Croghan Kinshelagh granite, the BIF on the Moneyteige ridge, and the AVG
14 outcrop (Fig. 11 B). There is also an isolated high Bi anomaly 2-3 km ESE of Camolin.

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19 The distribution of Cr, Ni, W and Sn correlates to specific lithologies and in some cases provides an
20 indication of general glacial dispersion. Chromium concentrations are generally <200 ppm except for
21 a prominent linear belt extending 6-8 km NNW from Ballygarrett to Cummer (Fig. 11 G) where
22 values up to 1000 ppm are recorded. The linear anomaly lies within Ribband Group metasediments
23 but is discordant to the country rock strike, and can be ascribed to glacial and fluvial dispersion
24 southeastwards from the chromite-bearing serpentinite outcrop near Cummer in north Wexford
25 (Gallagher, 1989). Moderate Ni enrichment (Fig. 11 H) is associated with the Cummer serpentinite
26 and with Duncannon Group outcrop between Avoca and Arklow. Tin concentrations are highest at the
27 margins of the Leinster and Croghan Kinshelagh granites (Fig. 11 I). The distribution of Sn and of W
28 (Fig. 11 J) indicates mineralization at these granite margins, notably the Ballinglen-Tinahely zone of
29 W-Sn-Au mineralization described by Steiger and Bowden (1982) and Kennan et al. (1986) (Table 1),
30 showing a broad dispersion consistent with the prevailing ice flow direction towards the southeast, as
31 described above.
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36 Discussion

37 *Implications of the stream sediment geochemistry dataset for regional gold mineralization*

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39 There are two ways in which the stream sediment geochemistry data set can inform exploration for
40 gold mineralization within the study area.
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44 Firstly, the data set permits evaluation of the dispersion of chemically distinctive mineral particles
45 within a surficial environment which has been subject to multiple episodes of glaciation. Tungsten, tin
46 and chromium exhibit well defined dispersion trains from source lithologies as described above. As
47 discussed in a later section, these elements are likely contained within the resistate oxide minerals
48 ferberite, cassiterite and chrome spinel. The linear pattern of down-ice dispersion of chromium from a
49 point source serpentine outcrop (Fig. 11 G) indicates the potential distance and direction of dispersion
50 of other resistate minerals such as gold.
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54 Secondly, the abundance of gold and its correlation with other elements commonly regarded as
55 ‘pathfinders’ may generate a multi element anomaly suggestive of a particular style of mineralization,
56 which may then be correlated with our understanding of bedrock geology. Elevated gold
57 concentrations in stream sediment, indicated by the Tellus analyses, are widespread in the study area
58 but there is little correlation between Au values and other potential gold indicators such as As and Sb
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1 which occur sporadically (Fig. 11 E and F). Bismuth enrichment in fine fraction stream sediments
2 (Fig. 10 B) appears to be a generic marker for mineralization associated with the Croghan Kinshelagh
3 granite and with the contemporaneous volcanic-hydrothermal expressions at Moneyteige Ridge and
4 Avoca. The Tellus results for the Avoca area broadly correspond with till geochemistry reported by
5 Moon and Hale (1983) who found that As, Sb and Bi enrichment in near-surface glacial sediments
6 reveal the concealed Avoca mineralization which otherwise has a weak geochemical expression at
7 surface.
8

9 Other element signatures may be related to known mineral occurrences, or specific lithologies.
10 Anomalously high Pb and Cu occur in stream sediments in the vicinity of the disused mines at Avoca
11 and at one site southwest of Croghan Kinshelagh (Fig. 11 C, D). Clusters of sites with relatively high
12 Pb values occur southwest of Tinahely and of Camolin (Fig. 11 C) suggesting that Pb-bearing
13 mineralization is also present in these areas. Moderately elevated Pb is spatially associated with the
14 Duncannon Group outcrop in southern Wicklow, but not in Wexford where there is no difference
15 between the Duncannon and Ribband Groups in terms of Pb concentrations in fine fraction sediments.
16 Nickel is relatively enriched in sediments in the Duncannon Group outcrop in County Wicklow with
17 anomalous levels south of Avoca (Fig. 11 H). Although a cluster of Ni enrichment is evident
18 associated with the Cummer serpentinite outcrop east of Carnew, Ni does not show the extensive
19 eastwards dispersion shown by Cr (Fig. 11 G), probably as a consequence of the relative instability of
20 Ni-bearing minerals such as pentlandite in the weathering environment.
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25 *Interpretation of the HMC data set*

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28 Garnet and staurolite are volumetrically abundant constituents of Ribband Group metasediments
29 within the aureole of the Leinster granite and we ascribe their eastwardly dispersion to glacial
30 transport and post-glacial fluvial reworking into modern stream sediments.
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32
33 The major gold-bearing catchments of Coolbawn, Ballinvally and Monaglogh all exhibit a strong
34 magnetite signature, usually with haematite, although hematite has a low abundance in the Monaglogh
35 River (Table 3, Fig. 5). Magnetite could be derived either from the oxidised granites of the Croghan
36 Complex which outcrops at the Coolbawn site and in the headwater of the Ballinvally River, or from
37 BIF formations (McArdle and Warren, 1987b; Ixer et al., 1990; Wheatley, 1971). Wheatley (1971)
38 records the supergene alteration of magnetite to hematite (martitization) which would account for the
39 spatial overlap of these iron oxides and variations in their relative proportions between sample sites.
40 This precludes using magnetite as a diagnostic marker for erosional products of the BIF. Gallagher et
41 al. (1994) mentions 'accessory Fe ore' in the Croghan Kinshelagh granite and mapped 'magnetite-rich
42 tuffs' in that area. Localities of high ilmenite concentrations are focussed around the Croghan
43 Kinshelagh granite and associated dolerite intrusions in Wicklow, but are more consistent throughout
44 Wexford suggesting that minor intrusions of dolerite are widespread in the Ribband Group.
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49 Barite was recorded in the HMC from Ballygarrett (Table 3, Fig. 5) which is suggestive of local
50 mineralization since barite is mechanically unstable during transport in the surficial environment.
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53 The local concentrations of cassiterite, ferberite and tantalite at Askamore (Fig. 5) and to a lesser
54 extent at localities eastwards along the general glacial dispersion direction, suggest derivation from a
55 currently unrecorded granitic intrusion.
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57 Overall the HMC samples owe their diversity to a variety of local overprints of the ubiquitous garnet
58 + staurolite signature. Minerals associated with 'point sources', notably monazite, cassiterite,
59 ferberite, magnetite and chrome spinel, appear to have been dispersed in the region of a few
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1 kilometres eastwards of bedrock sources. This transport distance and direction accords with the
2 dispersion of W and Cr from parent lithologies, as shown by the Tellus sediment geochemistry data
3 set.

4 *Interpretation of detrital gold characteristics in southeast Ireland*

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6 Internal alloy heterogeneity, ranges of alloy compositions, and mineral inclusion suites may all be
7 used to compare gold from different sampling localities and in some cases to infer the nature of the
8 source mineralization.
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11 The contrasting internal textures of gold grains from Wicklow and Wexford (Fig. 8 D-F) indicate
12 different conditions of mineralization. In Wicklow, alloy homogeneity suggests a stable precipitation
13 environment and a single episode of deposition, although the exact conditions may vary spatially or
14 temporarily, yielding gold grains of different compositions. In contrast, the texturally complex gold
15 particles from Wexford may indicate episodic fluid influx and spatial dispersion of the mineralizing
16 fluids, as discussed by Chapman et al. (2010a). Within the cores of heterogeneous grains, Ag-rich
17 gold always postdates Au-rich alloy (e.g. (Fig. 8 E, F). Veinlets of nearly pure gold may cross cut
18 these features but these have been ascribed to surficial alteration penetrating along crystal boundaries
19 (Hough et al., 2009). Thus only the progression to Ag-rich alloy reflects evolution within the
20 hypogene environment, a trend that is consistent with both falling temperature and decreasing
21 availability of gold in the later stages of the hydrothermal regime (Gammons and Williams-Jones,
22 1995).
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28 Our relatively high sampling density in the Goldmines River area, together with specific gold alloy
29 inclusion associations replicated at different localities in this area, has enabled the definition of three
30 gold types as summarised in Table 4, and illustrated spatially in Fig. 12 using pie charts. In the
31 historic placer mining area, type 1 gold was identified in the Monaglogh and Ballinvally Rivers, but
32 only as a minor component in the Coolbawn River (as evident in Fig. 9 A). The abundance of type 2
33 gold varies between the three main auriferous drainages but forms the majority of the population in
34 the Coolbawn site. Type 3 gold is abundant only in the Monaglogh River.
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38 Linking placer gold analyses to statistics describing production data to establish the signature of the
39 most promising exploration target was advocated by Chapman and Mortensen (2016) and has proved
40 useful again here. We can compare our results for the median Ag values of gold from the Goldmines
41 River (Ballinvally and Monaglogh Rivers samples combined: 8.5%) and from the Coolbawn River
42 (11.2%) against the bulk assay of historically recovered gold (7.82% Ag) recorded in returns to the
43 Irish Mint (Kinahan, 1882). Given that type 1 gold has the least Ag, this suggests that type 1 gold
44 contributed a disproportionately large mass with respect to the overall inventory of recovered placer
45 gold, and hence probably represents the most attractive target for future exploration projects.
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50 Figure 12 shows that the Ballinvally and Monaglogh River placer occurrences are adjacent to zones of
51 Au-As-Fe-S mineralization. However, Fig. 9 B shows that arsenopyrite-bearing gold is typically
52 associated with an Ag range of 9-14%. Thus in these catchments the known in situ localities appear
53 not to match the most important placer signature, either in terms of alloy composition or mineralogy.
54 The inclusion mineralogy of type 1 gold appears similar to the mineralogy of sulfide-sulfosalt
55 mineralization (chalcopyrite, galena, sphalerite Cu-Pb-Bi sulfosalts) hosted by the BIF on Moneyteige
56 Ridge (Fig. 12) reported by Ixer et al. (1990). These authors suggested that hydrothermal systems
57 associated with local basic intrusions introduced the metals into the vein systems. McArdle and
58 Warren (1987a,b) suggested that regional structural development may have formed conduits for fluids
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1 associated with the cooling of the Leinster Granite. Such a wider scale event better explains the
2 distribution of type 1 gold (Fig. 12).

3 Ixer et al. (1990) comment on the close association of galena and native bismuth within samples of
4 mineralized BIF. They ascribe this association to exsolution of previously existing more complex
5 minerals. Figure 8 C shows a galena–native Bi inclusion in a gold grain from the Monaglogh River.
6 Native Bi is the dominant mineral and it may be that the other native Bi inclusions observed in this
7 study are also associated with minor amounts of other minerals which have not been revealed in
8 section. The similarity between inclusion suites in type 1 gold and the mineralization at Moneyteige
9 Ridge is consistent with the scenario of multiple occurrences of this gold type within the Wicklow
10 study area. The Ag plots presented in Figures 9 C and D show variation between samples from within
11 the catchments of the Ballinvally and Monaglogh rivers respectively. The most plausible explanation
12 for the variation in signatures of sample populations from trunk drainage and tributaries is that
13 different sources account for each.
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18 Arsenopyrite was not recorded in either type 1 gold or in the hypogene mineralogy at Moneyteige
19 Ridge reported by Ixer et al. (1990). Therefore type 2 gold may correspond to the Au-As-Fe-S type
20 mineralization reported at such localities as the Mary Ellen Zone and the Maclaren zone (Table 1, Fig.
21 12). However arsenopyrite inclusions were not observed in gold from the Coolbawn River and the
22 source association for this placer gold remains unclear. Type 3 gold may represent a compositional
23 end member of type 2 gold.
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27 The mineral inclusion assemblage of Wexford gold also shows a galena-arsenopyrite signature (Fig.
28 10 B). Bismuth minerals are absent whereas chalcopyrite, sphalerite and pyrite are more common
29 than in the Wicklow samples. This inclusion mineralogy is compatible with the compositional range
30 of Phanerozoic orogenic gold recorded throughout the British and Irish Caledonides as summarized
31 by Chapman et al. (2000b).
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34 The inclusion signature of the gold from Askamore appears different from the regional signature (Fig.
35 10 C), although the alloy composition is otherwise typical of gold in the region. The inclusion
36 signature is based on a small sample set, but appears to indicate very low fS_2 , owing to the presence of
37 altaite (PbTe) and clausthalite (PbSe) but not galena. A distinctive heavy mineral suite dominated by
38 cassiterite and ferberite with minor tantalite strongly suggests a previously unrecognised concealed
39 granitic body, and this atypical local lithology may provide an underlying reason for the unusual
40 inclusion mineralogy.
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44 The diverse mineral inclusion assemblage in gold from Boley Lower contains a distinct antimony
45 signature which distinguishes it from other samples in the region (Table 2, Fig. 10 C). The discovery
46 of nearby in situ mineralization provides a plausible local source, but neither descriptions of the
47 borehole lithologies nor the inclusion suite suggest a magmatic influence on the gold mineralization.
48 In this case, the origin and significance of the ferberite and cassiterite components of the heavy
49 mineral concentrate are uncertain but they likely represent glacial dispersion from the postulated
50 granitic outcrop at Askamore and are probably unrelated to the gold mineralization. It seems more
51 likely that the gold at Boley Lower is derived from a proximal source as suggested by the local
52 abundance, gold morphology and distinctive microchemical signature.
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57 *Re-evaluation of previous models accounting for the Wicklow placer resource*

58 Correlation of gold microchemical signature with the current limited understanding of in situ
59 mineralization allows a re-evaluation of previous hypotheses which proposed various models for the
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1 source of gold in the Wicklow placers. These have ranged from local intra-valley sources (Weaver,
2 1835; Maclaren, 1903), sulfide mineralization at Moneyteige Ridge (Smyth, 1853; Kinahan, 1883;
3 McArdle and Warren, 1987a and 1987b; Ixer et al., 1990), and auriferous gossans at Avoca (O'Brien,
4 1959). The potential of Avoca as a source may be discounted on the basis of ice flow directions
5 (McArdle and Warren, 1987b), patterns of heavy mineral distribution (Fig. 5) and gold signature (Fig.
6 9 D). The potential for the BIF-hosted mineralization on the Moneyteige Ridge to represent an
7 example of type 1 gold has been discussed above, as is the likelihood that such mineralization is more
8 widespread in the region and not confined just to BIF host rocks.
9

10 The differences in signatures of sample populations of detrital gold from within individual drainages
11 (Figs. 9 C, D and 12) leads us to favour a model in which intra-valley type 1 mineralization
12 supplemented gold from the local Au-As-Fe-S style (gold types 2 and 3) to form rich gutter placers in
13 a ravine-like setting at the Red Hole. In Fig. 12, pie charts representing the proportions of gold types
14 are superimposed colour-coded catchment areas representing heavy mineral proportions, from which
15 it is apparent that these show no consistent relationship. The decoupling of gold types from HMC
16 mineralogy suggests that in the Goldmines River area, bedrock gold mineralization is not
17 lithologically controlled, and is instead probably structurally controlled. This concurs with Standish et
18 al. (2014) who, in interpreting lead isotope ratios in placer gold from southeast Ireland, favour two
19 mineralization events that peaked at c.460 Ma contemporary with the Early Caledonian orogenesis
20 and at c.400 Ma coincident with Late Caledonian granite emplacement.
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26 *Evaluation of glacial impact*

27 The general lack of information describing in situ mineralization throughout the study area clearly
28 inhibits proposing specific placer-lode relationships. In addition, speculation of these relationships
29 based on microchemical characterization of detrital gold grains must take into account potential
30 transport by glacial processes. In Wicklow, it is possible to infer limited transport of gold in the areas
31 of historical gold working on the basis of the local large particle size of gold, detrital gold abundance
32 and the distinctive and geographically constrained associated HMC signatures (Fig. 12). Elsewhere in
33 Wicklow the overall similarity between HMC signatures irrespective of bedrock lithology (Fig. 5) is
34 suggestive of a strong glacial influence. At many localities the low abundance of detrital gold is
35 compatible with reworking from regionally-derived till. There are notable exceptions: both the
36 Ballintemple and the Clone streams were minor targets during the gold rush, and gold from these
37 localities produces a very similar Au alloy signature (Figs. 9 B and 12). Lyburn (1901) reported placer
38 gold workings in the upper reaches of the Ow River, in the aureole of the Leinster Granite. It seems
39 most likely that local occurrences of bedrock mineralization have generated these modest placers, but
40 that some gold has been glacially transported and ultimately manifests as low concentrations in
41 drainages elsewhere (e.g. Knockanode and Castlemacadam: Table 2, Figs. 3 and 12).
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48 The degree to which glaciation has influenced the distribution of gold in the Wexford localities is less
49 clear. Evidence from the dispersion of heavy mineral indicators has provided a guide to the direction
50 and extent of glacial transport which, coupled with multiple occurrences of auriferous bedrock, would
51 generate the Au distribution observed in both the Tellus dataset and the gold-grain study. At
52 Ballygarrett, derivation of the placer gold from proximal bedrock is considered as likely based on (i)
53 the discovery of nearby in situ mineralization (Table 1), (ii) relatively high abundance of detrital gold,
54 and (iii) the abundant barite which is not observed in HMCs elsewhere (Fig. 5). Further evidence for
55 specific local sources is provided by the abundance and pristine nature of gold grains at Boley Lower.
56 At other localities, low abundances of gold are compatible with glacial-fluvial transport away from
57 localised Fe-As-S mineralization, most of which probably remains undiscovered. We propose that
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1 multiple occurrences of a broadly similar of style of mineralization, coupled with small scale
2 dispersion, account for the general similarity in compositional signatures of gold in the Wexford study
3 area.

4 *Evaluation of the strengths and weaknesses of each method and the advantages of a combined*
5 *approach*
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8 The widespread Au enrichment in fine fraction sediment revealed in the Tellus dataset highlights
9 southeast Ireland as a prospective region for gold mineralization. The sampling and analytical
10 protocols ensure comparability across the region, and the geochemical data provide an efficient means
11 of identifying broad areas of interest for multiple elements simultaneously. Conversely the
12 methodology may be hampered by the ephemeral nature of non-resistate mineral species in the
13 surficial environment, such as sulfides and sulfarsenides. This might explain why sediment
14 geochemistry data for Au and As in Wexford does not show a spatial correlation.
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18 The presence of Au within fine fraction sediments may be a consequence of ‘invisible’ gold within
19 sulfides or attributable to small particles of native gold. In Wexford, where derivation from Au-As-
20 Fe-S mineralization is proposed, the lack of correlation between Au and As suggests that any original
21 mineralogical association between arsenopyrite and gold has been eradicated by chemical
22 degradation. The same reasoning may be applied to any invisible gold once hosted by pyrite.
23 Therefore, the gold values recorded in the Tellus data set almost certainly indicate small particles of
24 free gold. The recovery of gold grains less than 150 µm in diameter ensures comparability between
25 samples and is independent of the skill of field operatives. In some areas, detrital gold is almost all
26 below this size threshold, for example in the present study, the Tellus data reports anomalous Au in
27 tributaries of the Avoca River where coarser gold is extremely scarce (Table 2). This disparity may be
28 a consequence of the predominantly fine size of gold grains present in the nearby Avoca VMS and
29 Kilmacoo Au deposits.
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34 The very high density of native gold enhances local segregation in a fluvial environment. The sample
35 collection methodology used in O’Connor and Reimann’s (1993) survey and in the more recent Tellus
36 programmes involve sampling the centre of the active channel, as this sedimentary environment is
37 reproducible between sites. However, such high energy zones are unfavourable environments for the
38 accumulation of particles of very high density. Additionally, gold grains are normally relatively scarce
39 in sediment, and so a sampling protocol which involves collection of a fixed volume of sieved
40 sediment does not offer the best methodology to establish the presence of detrital gold. In the present
41 study, gold grains were recorded in moderate abundance at some Wexford localities (e.g. Camolin,
42 Hyde Park and Ballykale) but this result is not reflected in the Tellus geochemical data set. In the
43 Goldmines River area of Wicklow, the relatively coarse particle size range of gold may have
44 influenced the collection of gold grains during O’Connor and Reimann’s (1993) survey, although
45 other factors most likely influenced the generally low regional values. These factors include QA/QC
46 issues in sample collection of the stream sediments in this area (K. Knights, pers. commun., 2018),
47 and gold depletion owing to historical mining which frequently involved re-routing of the watercourse
48 to yield a relatively impoverished channel.
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54 Exploration programmes which involve the collection specifically of detrital gold grains adopt a
55 completely different approach in which atypical sedimentary environments that preferentially
56 concentrate gold are targeted (e.g. Leake et al., 1997). The success of sampling may be contingent
57 upon the ability of the field operative to identify such areas, particularly if gold particles are scarce.
58 This methodology involves spending sufficient time at one location to collect a sample, and
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1 consequently the period required to complete a survey may be difficult to predict. Sample collection
2 by panning does not necessitate a pre-screening other than to remove >1 cm clasts. While offering the
3 advantage of collection of gold particles with diameters >150 µm, retention of smaller gold grains
4 during sluicing and panning is most certainly a function of the skill of the field operative.
5

6 In the present study, consideration of HMC mineralogy has helped to constrain the degree of glacial
7 dispersion of minerals released from a point source, and this appears to broadly accord with similar
8 conclusions drawn from the fine fraction sediment geochemistry. This information has been used to
9 explore possible relationships between the microchemical signatures of gold from localities that could
10 feasibly be within a dispersion train. For example, Avoca is an inadmissible source for gold in the
11 Goldmines River area when HMC signatures are inspected (Fig. 5). Analysis of HMC samples
12 provides an additional advantage in that this may reveal minerals which can only be ascribed to
13 specific lithologies, which may not appear on existing geological maps due to poor exposure. At
14 Askamore, this approach has permitted a robust interpretation of the mineralization which would not
15 otherwise have been possible. In some cases, the same mineral may be derived from two or more local
16 lithologies which can complicate interpretation of the mobility of the mineral in the surficial
17 environment. For example, magnetite may be derived from granite and from BIF, as discussed above.
18 In these cases it may be possible to establish the host lithology source of mineral grains through trace
19 element analysis (e.g. Canil et al., 2016; Nakashole et al., 2018). HMC data sets rarely provide direct
20 information on the nature of source Au mineralization because sulfides and other ore minerals do not
21 survive in oxidising surficial environments. This observation is consistent with the decoupling of As
22 and Au recorded in the Tellus stream sediment geochemistry dataset.
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28 Distinctive gold particle size and/or morphology may help to infer the presence of local bedrock
29 sources, particularly when used in tandem with compositional studies of the same sample population.
30 Alloy heterogeneity may indicate whether the parameters controlling alloy composition were stable,
31 suggestive of a regime which is sufficiently robust to buffer against chemical or physical change, or
32 whether gold mineralization is a consequence of episodic, smaller volume fluid influx. Inclusions
33 preserve the mineralogy of the hypogene source even when other components (sulfides etc.) are no
34 longer represented in surface sediments, or potentially where the original Au-metal relationships have
35 been obscured by anthropogenic contamination. Establishing the inclusion assemblage may also
36 confirm the validity of a potential local hypogene source, or indeed categorically exclude it. Clear
37 indications of specific possibilities of sources in areas of complex geology and geomorphology can
38 indicate whether gold is likely derived from a single point source or multiple bedrock occurrences,
39 and whether all in situ mineralization is genetically related. Such insights can greatly inform deposit
40 models with the associated benefits for exploration targeting. In academic studies of gold
41 metallogenesis, a further refinement is the use of lead isotope analysis of gold grains (Standish et al.,
42 2014).
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48 However, there are limitations to the adoption of gold grain studies. Firstly the technique is specific to
49 gold, although Chapman et al. (2017, 2018) have advocated the use of detrital gold as a pathfinder for
50 copper porphyry mineralization. Secondly, substantial field time may be required to collect sufficient
51 detrital particles for study, particularly in areas where overall abundance is low. Selection of sample
52 sites is of paramount importance, and the use of experienced field personnel is particularly
53 advantageous in this regard, whereas the field skills required for collection of fines and HMC are
54 relatively easily learned. Time spent searching for gold grains when they are in fact absent, is clearly
55 inefficient and consequently gold grain studies may benefit from the results of previous standard
56 stream sediment geochemistry to delineate areas for focussed study – although this was not the case in
57 Wicklow. Thirdly, preparation and analysis, whilst not particularly difficult, are currently the preserve
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1 of a small number of facilities, and are time consuming and expensive in comparison to the
2 established automated analytical procedures applied to sediment samples.

3 Whilst reconnaissance geochemical studies can provide a geographical focus for gold grain studies,
4 the specific gold–element association revealed by analysis of inclusion suites may also inform
5 interpretation of geochemical data bases. For example, the presence of arsenopyrite inclusions may
6 underline the importance of As values in stream sediments. A spatial coincidence of Au and Pb
7 sediment anomalies in urban areas could be ascribed to anthropogenic contamination, but knowledge
8 of the gold grain inclusion suite may confirm whether such associations are genetic.
9

10 11 **Conclusions**

12 Each of the techniques employed here has contributed to an improved understanding of the gold
13 metallogeny of SE Ireland and we propose that such an approach could be used to advantage in other
14 regions of complex geology and poor exposure. The information provided by regional programs of
15 fine sediment analysis is widely appreciated, and this study underlined the value of this standard
16 approach, in that the geochemical dataset confirmed the widespread distribution of detrital gold in the
17 study area. Nevertheless, on the basis of stream sediment geochemistry alone it would be reasonable
18 to conclude that gold mineralization in Wexford represents the most attractive target, whereas
19 interpretation of gold grain studies, together with consideration of historical accounts of mining,
20 would strongly favour a larger gold endowment in Wicklow.
21

22 Co-collection of gold and heavy mineral suites provides two independent measures of heavy mineral
23 dispersion, i.e. through mineralogical studies and consideration of gold particle size, morphology and
24 composition. Studies of heavy mineral concentrates provide a context to interpret results of gold grain
25 studies through evaluation of the mobility of resistate minerals in the surficial environment. However,
26 unless source-specific indicator minerals are recovered in the HMC samples, they provide only
27 indirect evidence for the nature and location of gold sources.
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29 Gold grain collection programs are comparatively time-consuming and their success may be
30 dependent on the skill of field operatives. However, compositional characterization of gold provides
31 an effective way to establish whether sets of detrital grains from different localities share a common
32 origin. This information may be applied in specific areas to prove or disprove genetic links between
33 target in situ mineralization and local accumulations of placer gold. Assumptions of a genetic link
34 between placer and lode gold may provide rationales for exploration projects but the hypotheses are
35 rarely tested. In addition, the mineral inclusion suites permit direct correlation with global templates
36 that link inclusion mineral species or assemblages to specific styles of hypogene mineralization. In
37 this way, gold characterization studies provide more compelling evidence to interpret regional
38 metallogeny than may be inferred by considering only the co-variance of elements in stream sediment
39 geochemical datasets.
40

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Figures (placed in Publisher / PDF file)

1
2 FIG. 1. SE Ireland map with outlines of the Ribband and Duncannon Groups and the Leinster
3 Granite, locating the main towns and study area map shown in Fig. 2 (red dashed boxes indicate
4 the main map area and the Enniscorthy inset map). Inset reproduced with permission from the
5 Geological Survey of Ireland: map of interpolated Au in Tellus sediments in SE Ireland showing
6 an area of relatively high values in north-central Wexford and scattered high values in Wicklow
7 and Carlow; small map shows map location within Ireland.
8
9

10 FIG. 2. Geologic map of the North Wexford – South Wicklow study area (after Tietzsch-Tyler et
11 al., 1994) with occurrences of detrital gold and various styles of bedrock mineralization based on
12 O'Connor and Gallagher (1994) and exploration company reports (see Table 1 for sources). Blue
13 arrows indicate ice flow directions during previous glaciations (Warren, 1993). Star symbols are
14 sample locations in this study, letters designate Wicklow sites and numbers designate Wexford
15 sites: refer to Table 2 for locality names. Dotted black line is the N11/M11 highway. Green box is
16 the area of Fig. 3.
17
18

19 FIG. 3. Topographic and geologic map of the Goldmines River area with sample locations and
20 features referred to in the text. Weaver's trenches are excavations through overburden to bedrock
21 instigated by Thomas Weaver (1835). Red stippling indicates river sections that were worked
22 historically for placer gold (after Reeves 1971) implying relatively high abundances. Star symbols
23 are sample locations in this study (Table 2).
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26 FIG. 4. Ag distributions in detrital gold samples underpinning approaches to data interpretation
27 used in this study. A: reproducibility of Ag contents of samples obtained from two locations
28 sampled on different occasions. B: all Wexford samples, showing a common plot form and
29 providing justification for locality definition using a single statistical measure (median %Ag). C:
30 cumulative plot of median %Ag values for the 46 samples from the study area in which 4 or more
31 gold grains were obtained, with 'low' to 'high' categories defined (data in Table 2). D: selected
32 Wicklow samples showing wide variation in plot form (details in Fig. 9).
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35

36 FIG. 5. Pie charts of heavy mineral proportions in panned concentrates from sample sites on an
37 outline geology map of the study area. Inset map at the same scale shows the Adamstown area;
38 for location refer to Fig. 1. Locality names and data in Table 3.
39

40 FIG. 6. Outline geology of the study area (refer to key in Fig. 2) with symbols at sample sites
41 indicating (A) detrital gold abundance, with 'high*' indicating concentration of detrital gold
42 previously sufficiently high to support historical exploitation, and (B) median %Ag categories at
43 sites from which 4 or more gold grains were obtained (Table 2 and Fig. 4 C).
44
45

46 FIG. 7. Morphology and size of gold grains from selected sites in Wexford and Wicklow. Scale
47 bars 1mm. A: Nuggets to 1g from Monaglogh River. B: Rough gold to 0.5g showing morphology
48 consistent with limited transport, from Ballinvally River sampled near the Red Hole. C:
49 Relatively waterworn gold from Milshoge, Wexford.
50

51 FIG. 8. Examples of microtextures revealed in polished sections of detrital gold grains. A, B:
52 typical examples of arsenopyrite and galena inclusions observed in gold from throughout the
53 study area. C: native bismuth and galena inclusions in gold from Monaglogh River. D: typical
54 homogenous Au alloy of gold grains from the Monaglogh and Ballinvally Rivers. E, F: examples
55 of alloy heterogeneity frequently observed in gold grains from Wexford.
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58 FIG. 9. Characteristics of gold populations in Wicklow indicated by variation in Ag signatures in
59 the Wicklow sample sites. A: Definition of gold types 1 and 2 according to Ag range of Pb-Bi
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association and As-Pb association (horizontal line). B: Sample localities north of Croghan Kinshelagh. C and D: Comparison of samples from within the catchments of the Ballinvalley and Monaglogh Rivers respectively.

FIG. 10. Depiction of inclusion assemblages. Mineral abbreviations as in Table 2. Additional abbreviations: Hs = hessite, Cl = clausthalite. A: Comparison of gold types 1–3, Wicklow region. B: Comparison of inclusion signatures of gold hosted in the Duncannon and Ribband Groups, Wexford. C: Inclusion assemblages of Wexford sites that have atypical heavy mineral concentrates (Askamore, Boley) compared with other Ribband Group localities.

FIG. 11 A-J. Study area outline geology (refer to key in Fig. 2) with Tellus fine fraction stream sediment sample geochemical data for Au, Bi, Pb, Cu, As, Sb, Cr, Ni, Sn, and W. Inset map at the same scale shows the Adamstown area (for location refer to Fig. 1).

FIG. 12. Outline map of south Wicklow showing historical placer workings, zones of stratabound Au-As-Fe-S mineralization, and proposed bedrock sources and transport processes affecting placer gold accumulations. Catchment areas are colour-coded according to the proportions of hematite, magnetite and ilmenite in HMC samples with opacity in proportion to abundance of these components (data in Table 3). Pie charts show the proportions of gold types 1-3 in each main area (data in Table 4).

Tables (placed at end of this manuscript and also available as individual Word and Excel files)

TABLE 1. Summary of auriferous bedrock mineralization reported in the southeast Ireland study area, excluding the Avoca and Kilmacoo ore deposits. Localities are shown in Fig. 2. Sources: 1: Milner and McArdle (1992). 2: Shepherd (1980) and Williams et al. (1986). 3: McArdle (1993). 4: Ixer et al. (1990). 5: Downes and Platt 1978. 6: McArdle and Warren (1987a, b). 7: McKillen, Tyler and Associates (2009). 8: Dana Exploration PLC (1992). 9: Riofinex North Limited (1993 and 1994). 10: McKillen, Tyler and Associates (2009). 11: Kennan et al. (1986) and Steiger and Bowden (1982). 12: Geological Survey of Ireland (2000). 13: IMC Exploration PLC (2013).

TABLE 2. Sample locality names and codes (numbers indicate Wicklow, letters indicate Wexford), detrital gold abundance, median % Ag in gold alloy, and inclusion assemblages. Mineral abbreviations: Py = pyrite, Po = pyrrhotite, Gn = galena, Cpy = chalcopyrite, Sph = sphalerite, CuSbS = chalcostibite, Ars = arsenopyrite, Grs = gersdorffite and similar FeNi(Co)AsS minerals, Alt = altaite, Bi = native bismuth. Duplicate samples indicated by boxed rows, with inclusion species tallied in the two samples. ^ indicates sites sampled in 2013 by Christopher Reynolds and Christopher Smith. High* indicates concentration of detrital gold previously sufficiently high to support historical exploitation.

TABLE 3. Percentages (volume %) of minerals in heavy mineral concentrates from sample sites in the study area.

TABLE 4. Characteristics of detrital gold types 1–3 in the Goldmines River area (Wicklow) and the proportions of each type at sites where a sufficient number of grains was recovered to permit microchemical characterization.

TABLE 1 (Word file)

County	Locality	Setting/description/mineralogy	Gold grade/concentration / composition	Comments
Wicklow	Kilmacoo	Orogenic remobilisation of gold precipitated in sulfide-rich, silicified chloritic tuffs ¹	Riofinex best intersection 30 m at 4.4 g/T. Gold within sulfides typically <10 micron, gold within quartz veins typically ~20 micron ¹	Tabular zone 30 m thick by >150 m along strike. Considered to have formed by preferential deposition of Au in veined/sheared rock ¹
	Avoca	Kuroko style Volcanogenic Massive Sulfide deposit ^{2,3}	Typically <10 micron grains, 12-15% Ag ²	Historically mined, sub-economic resource remains ³
	Ballycoog–Moneyteige Ridge	Banded Iron Formation containing siderite and magnetite with minor (<1%) sulphides ^{4,6}	Native Au hosted in sulfides contains 17% Ag (2 analyses) ⁴	Considered to be a exhalative equivalent of the Avoca volcanogenic sulphide deposits ^{5,6}
	Maclaren Zone, Monaglogh River	Stratabound Au-As-Fe-S comprising veins and disseminations of pyrite and arsenopyrite hosted in chloritic, sericitic and felsic tuffs ^{7,8,9}	Road cut exposes 1.3 m with 3 g/T Au. Up to 12.55 g/T Au in rock chip samples ¹⁰	
	Mary Ellen Zone, Ballinvally River		GSI borehole 94/2 included 2.2 m at 1 g/t Au ⁶ . Trenching included 3 m at 1.28 g/T with grab samples containing 3.45 to 42.5 g/T Au ^{7,8,9,10}	20 m thick Au-enriched stratabound zone extending >400 m along strike at contact between Ribband and Duncannon Groups ^{7,8,9}
	West Slievefoore Zone			60 m thick Au-enriched stratabound zone extending along strike for >3 km ⁸
	Kingston and Killshelagh	Chalcopyrite-bearing quartz veins enriched in As, Au and Ag	Up to 0.45 g/T Au in pyritic breccia ⁸	Outcropping mineralization considered to be part of a swarm of Au-As-Fe-S veins ⁸
	Croghan Complex	Granite-hosted Sn-W-Au greisen	‘Low grade’ ⁸	
	Ballinglen	W-Sn mineralization in greisenized albitic microtonalite sheets. Stage 1: scheelite, arsenopyrite, pyrrhotite. Stage 2: sphalerite, galena, chalcopyrite, pyrite, stannite, cassiterite. ¹¹	Bi-Mo-Au enrichment noted	Main locality near Ballinglen is part of an extensive weakly mineralized zone (Fig. 2)
Wexford	Kilmichael-Ballyowen-Ballygarrett	Au-As-Fe-S mineralization in tuffs	Borehole 13.5 m intercept at 3.5 g/T Au, including 0.7m at 10 g/T Au. Trench sample 30 m at 0.38 g/T plus 3 m at 3.6 g/T ⁷ . Float to 980 g/T ^{12,13}	Potential mineralized zone of 6.5 km in strike length reported by IMC in 2013 ¹¹
	Boley	Oakland Formation phyllites with auriferous quartz veins	1.5 m intercept at 354 g/T Au within 13.5 m averaging 3.5 g/T ¹³	Proposed structural control at intersection of ENE trending fractures and regional strike ¹³
	Craan Hill - Knockbrandon	Auriferous quartz veins and sulfide mineralization	0.25 m intercept at 9.6 g/T Au. Quartz float to 18 g/T, ‘mineralized boulders’ to 32 g/T ^{12,13}	
	Tombreen	Stratabound Au-As-Fe-S mineralization in sheared felsic tuffs and phyllites	Intercepts of 0.38 m at 11.65 g/T, 0.5m at 18.4 g/T. Float to 286 g/T ^{12,13}	Close to mapped contact of the Maulin and Ballylane formations
	Knocknalour	Stratabound Au-As-S mineralization in sheared felsic tuffs and phyllites	Borehole intercepts 0.4 m at 19.9 g/T Au, 0.3 m at 10.45 g/T Au ^{12,13}	
	Churchtown	Au-As-Fe-S mineralization hosted by rhyolite in a shear zone	Borehole intercept 8m at 0.2 g/T Au ¹²	

TABLE 3 (Excel file)

Site code	Site / river name	Barite	Hematite	Magnetite	Ilmenite	Rutile	Chrome spinel	Cassiterite	Ferberite	Tantalite	Monazite	Zircon	Garnet	Staurolite
1	Kilmacoo north	-	13	-	-	-	-	-	-	-	-	-	75	12
2	Knockanode	-	8	-	-	-	-	-	-	-	-	-	80	12
3	Avoca tributary	-	-	-	-	-	-	-	-	-	-	-	86	14
4	Ow River	-	-	-	-	-	-	-	-	-	-	-	85	15
5	Castlemacadam	-	27	-	10	-	-	-	-	-	-	-	42	21
6	Clone stream	-	-	-	5	-	2	5	2	-	-	-	68	18
7	Ballintemple stream	-	11	2	5	-	2	9	-	-	-	-	56	15
8	Tomnaskela River	-	-	-	75	-	3	6	2	-	-	2	12	-
9	Coolbawn River	-	20	37	30	-	-	-	5	-	-	-	8	-
9n	Moneyteige North	-	18	11	25	-	3	9	3	-	2	-	22	7
11	Ballinvally River, Red Hole	-	16	32	42	-	-	-	-	-	-	-	10	-
13	Monaglogh R trib., Rostygah	-	40	4	2	-	-	4	2	-	-	-	33	15
14	Monaglogh River	-	4	19	40	10	-	3	-	-	-	-	19	5
A	Kilcloran	-	11	-	50	-	-	2	2	-	16	3	16	-
B	Hyde Park	-	12	-	38	-	-	4	2	-	3	-	41	-
C	Cullenoge	-	15	-	55	-	-	-	-	-	-	8	22	-
D	Coolnacon Bridge	-	-	5	60	4	-	5	-	-	-	-	17	9
E	Misterin	-	-	5	68	6	-	2	-	-	-	-	13	6
F	BallyShannon	-	-	-	57	4	-	7	-	1	2	-	17	12
G	Boley Lower	-	9	-	7	-	3	17	19	2	29	-	14	-
H	Rossminogue south	-	-	-	39	-	10	5	-	-	20	2	24	-
I	Ballykale	-	8	-	39	-	12	4	2	1	-	2	32	-
J	Newbridge Wood	-	-	-	66	-	-	4	-	-	16	-	14	-
K	Askamore	-	-	-	5	-	-	54	10	4	3	-	24	-
L	Milshoge	-	9	-	54	9	-	12	-	-	10	-	6	-
M	Knockrobin Lower	-	7	-	60	6	-	-	-	-	-	-	27	-
N	Ballyeden	-	11	-	45	3	-	3	-	-	-	4	34	-
P	Bolinready	-	9	-	39	-	-	-	-	-	-	-	52	-
Q	Huntingstown	-	3	-	67	-	6	3	-	-	-	3	18	-
R	Ballygarrett / Ballyowen	13	6	-	21	-	21	9	3	-	18	-	9	-

TABLE 4 (Word file)

Type	1	2	3
%Ag range in alloy	0 – 9	9 – 15	>15
Defining inclusion mineralogy	Galena ± native bismuth	galena, arsenopyrite	arsenopyrite
Locality	% type 1	% type 2	% type 3
Ballinvally River	43	51	6
Monaglogh River	47	20	33
Coolbawn River	20	65	15
Clone stream	73	24	3
Ballintemple stream	73	24	3
Ow River	90	9	1

Fig. 1

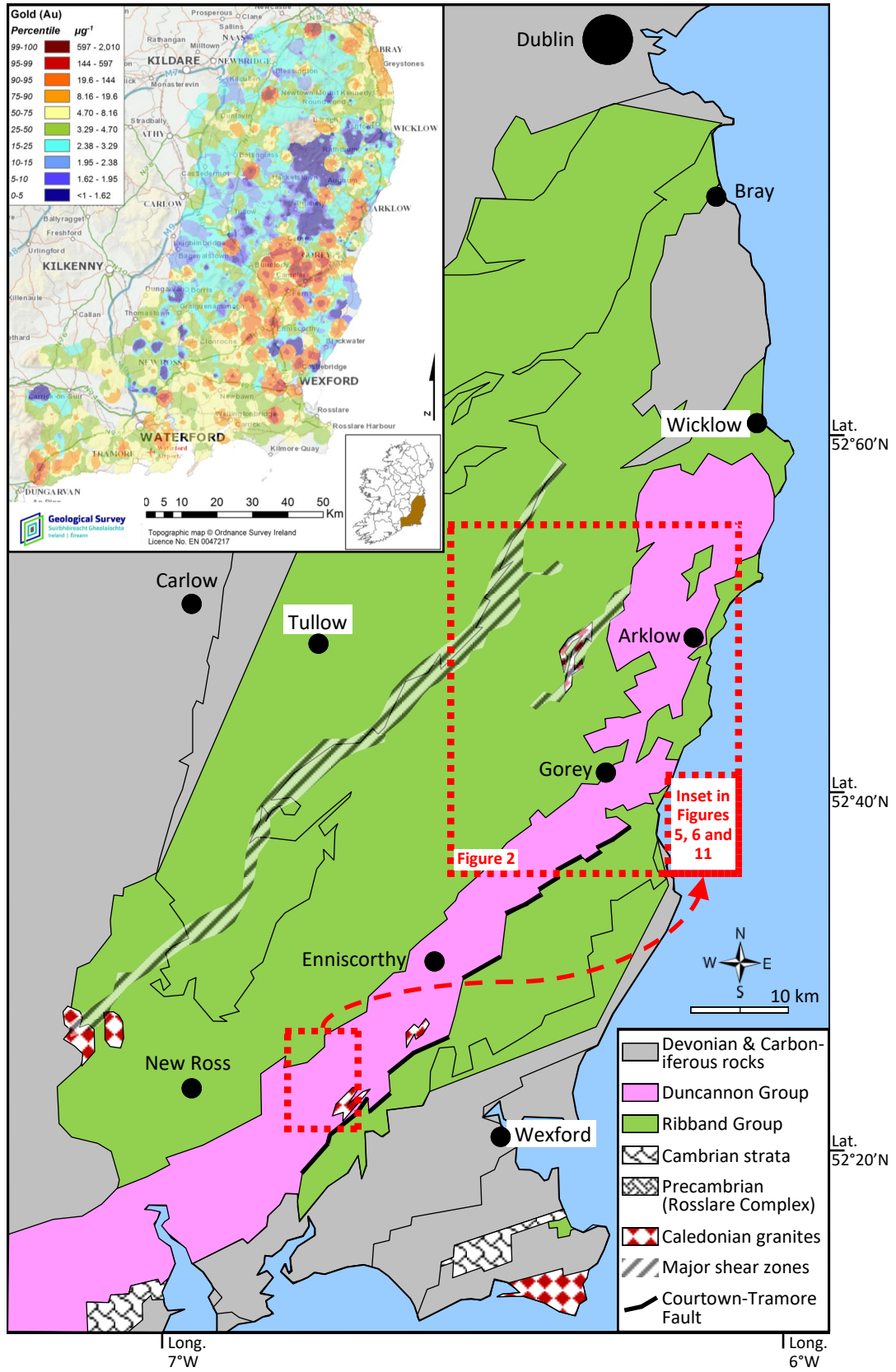


Fig. 2

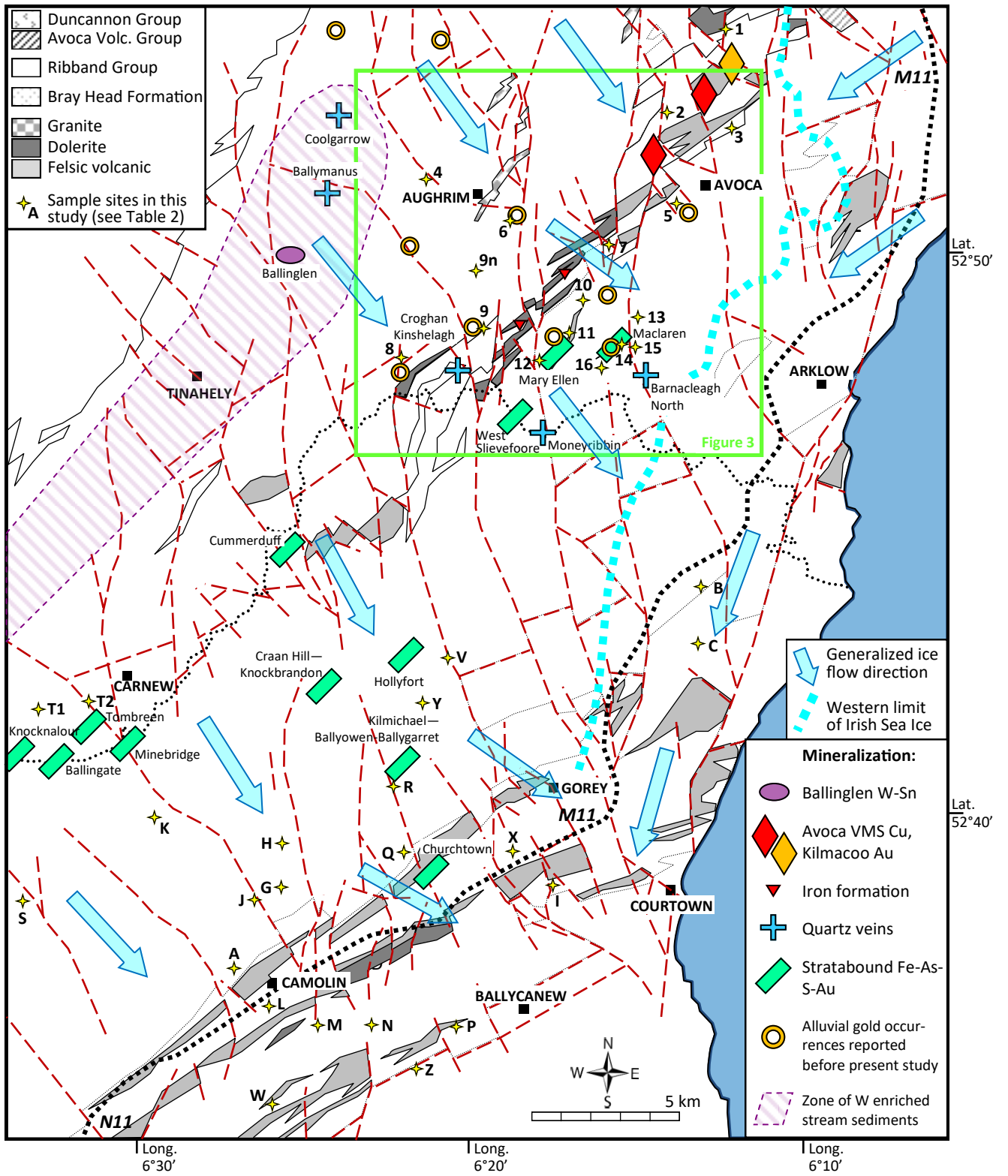


Fig. 3

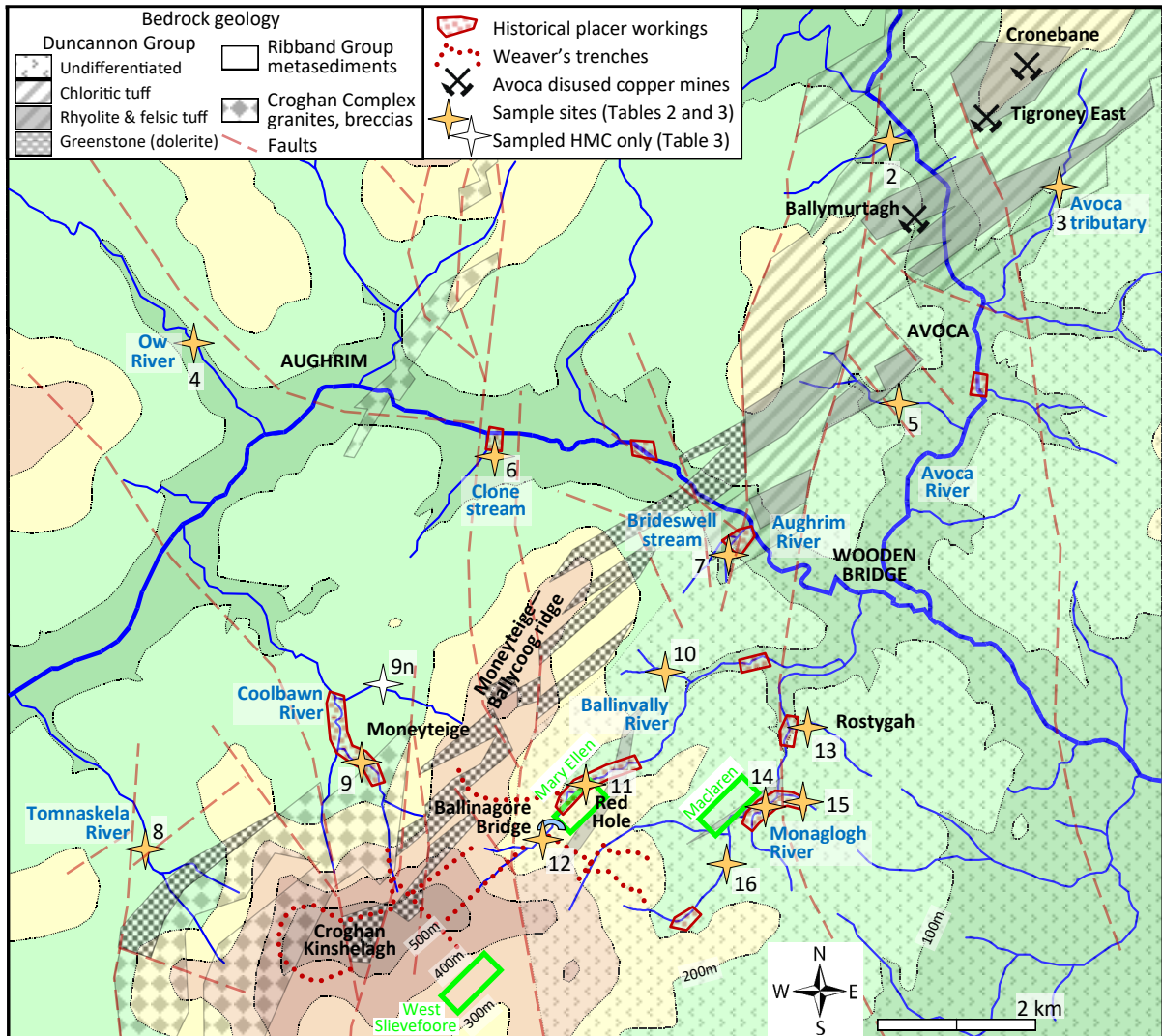


Fig. 4 A—D

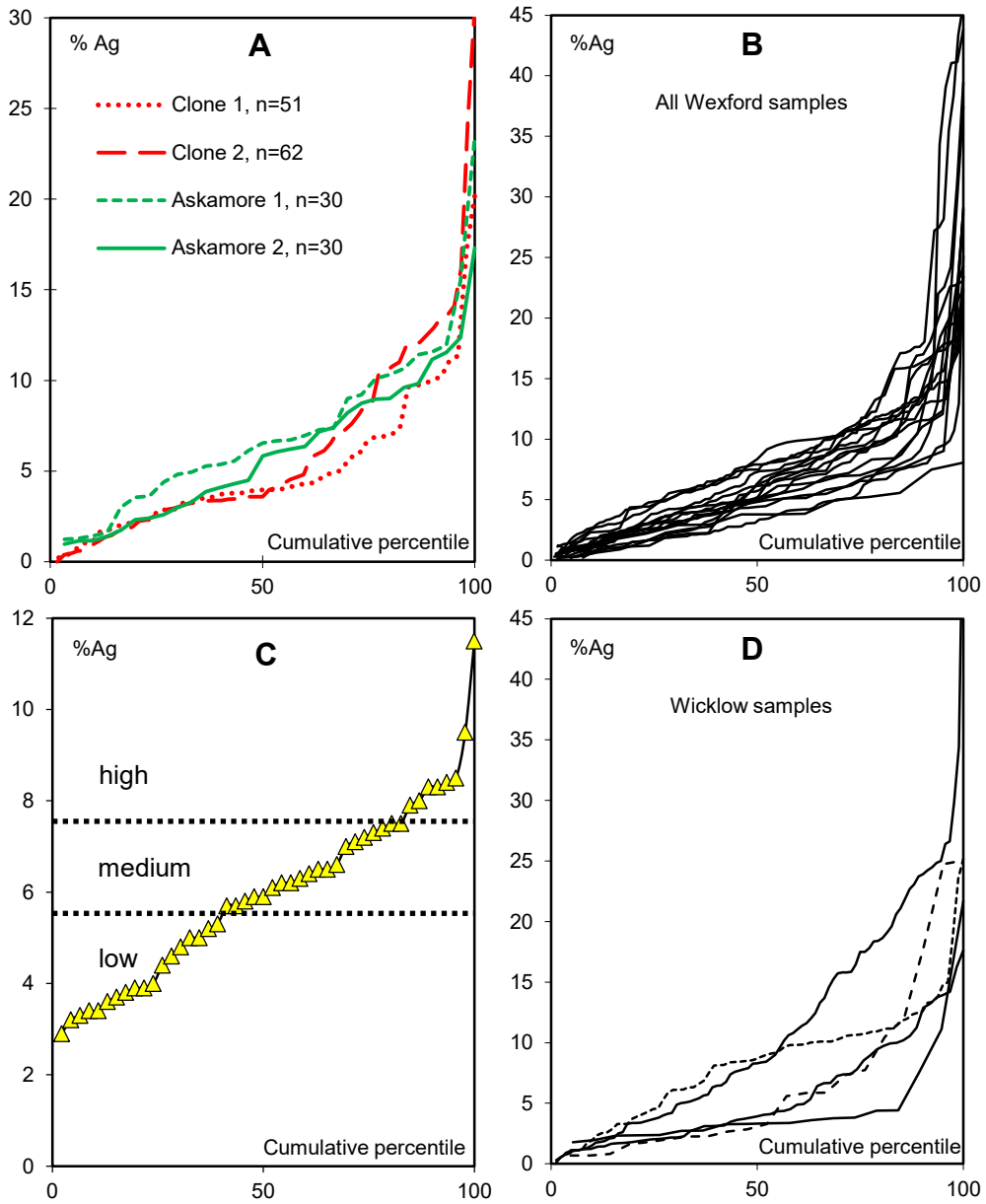


Fig. 5

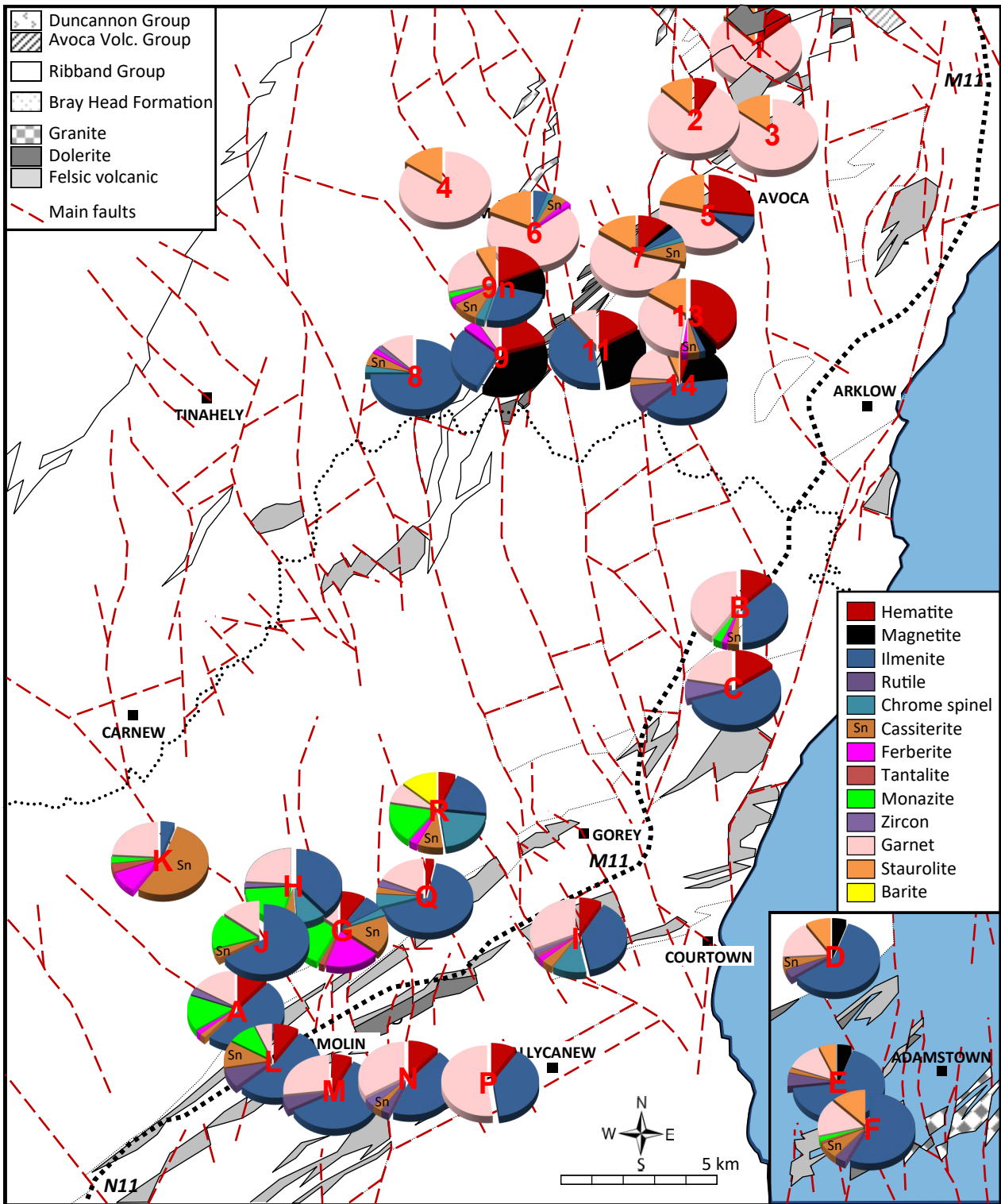


Fig. 6 A and B

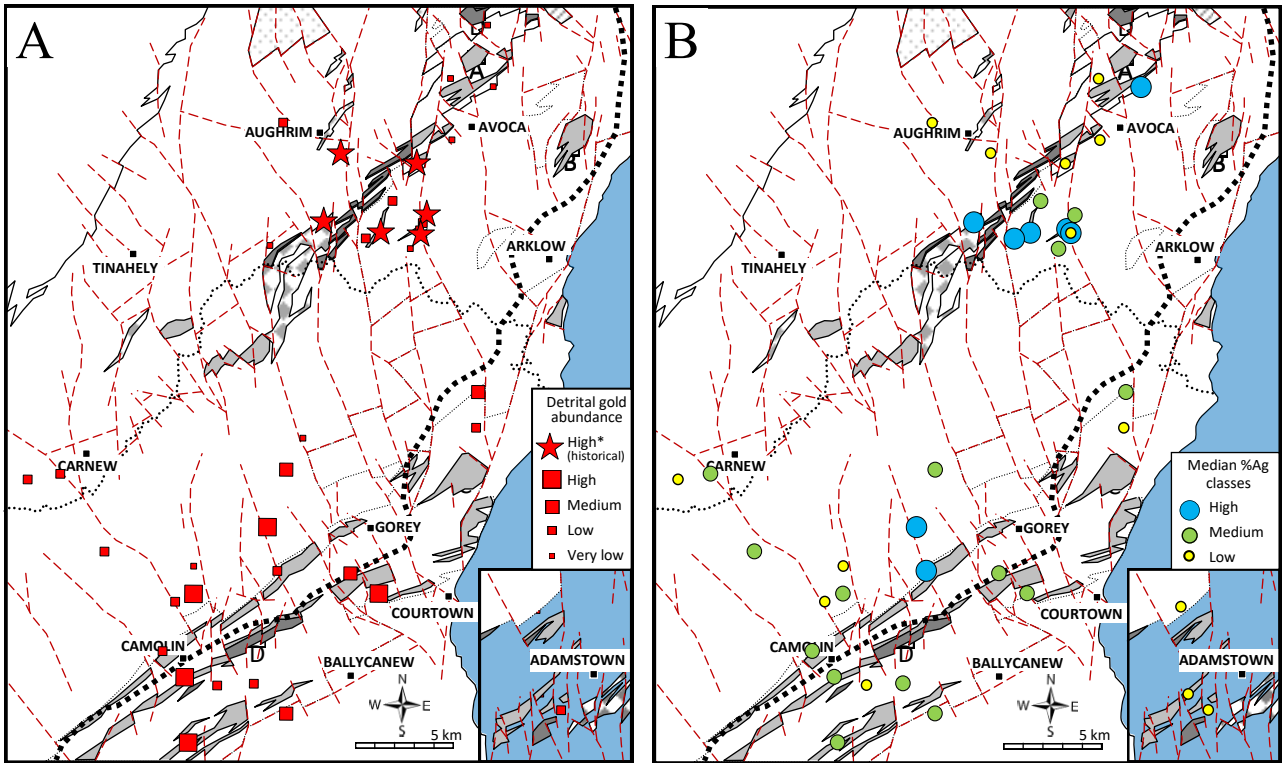


Fig. 7 A—C

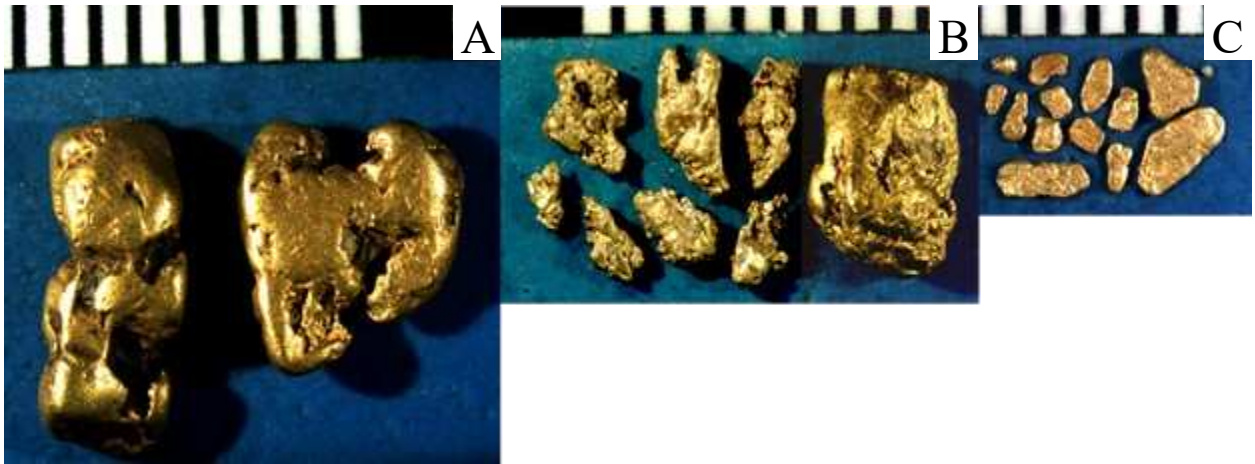


Fig. 8 A—F

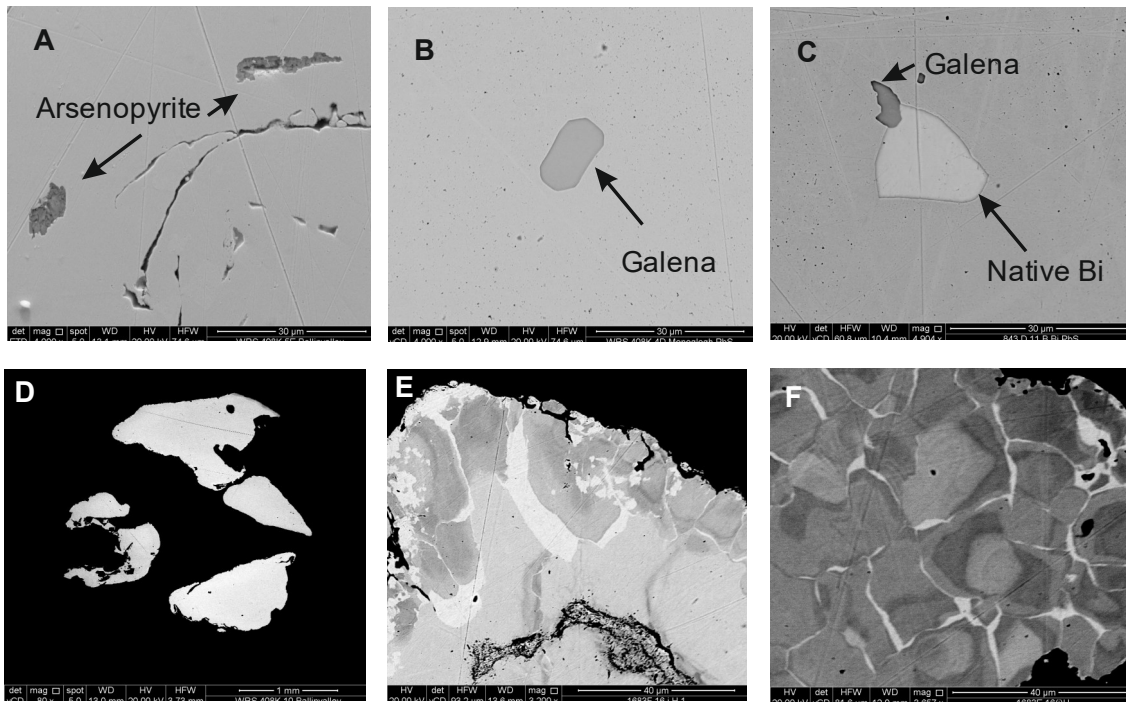


Fig. 9 A–D

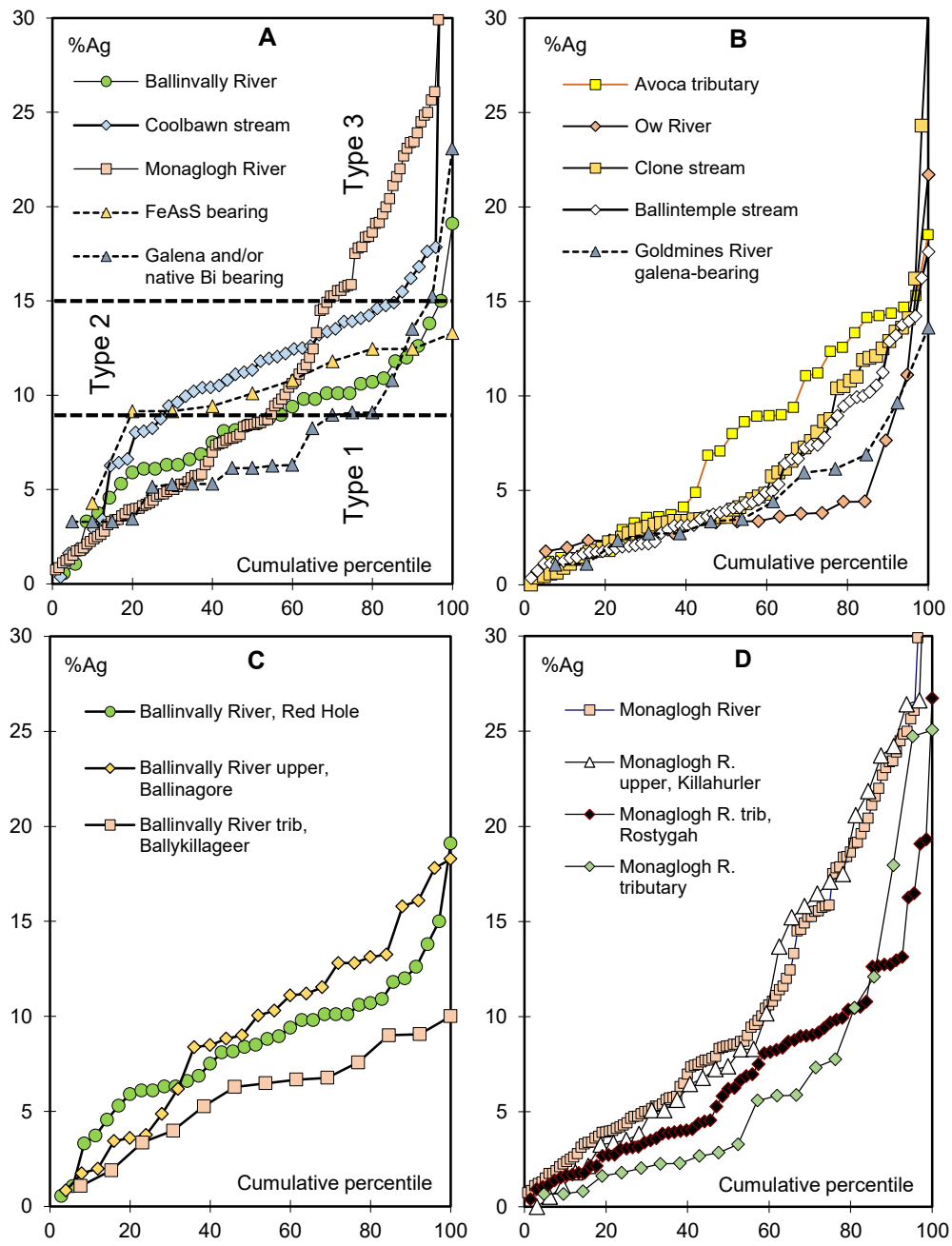


Fig. 10 A—C

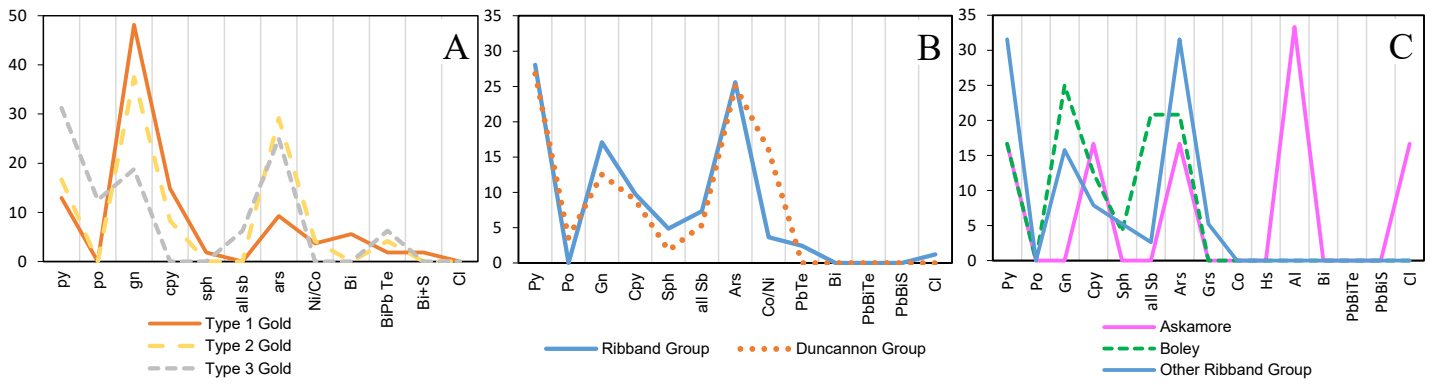


Fig. 11 A–F

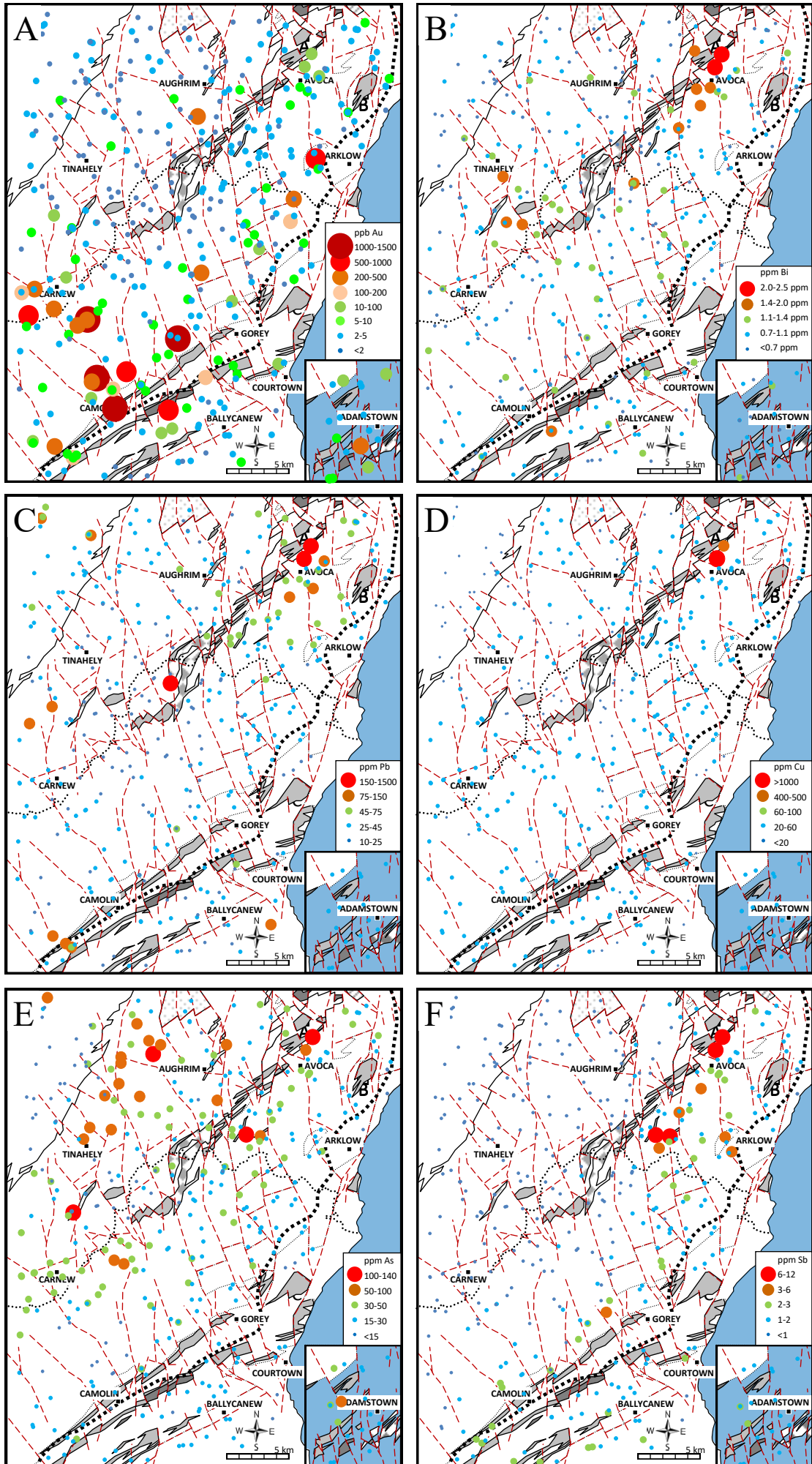


Fig. 11 G—J

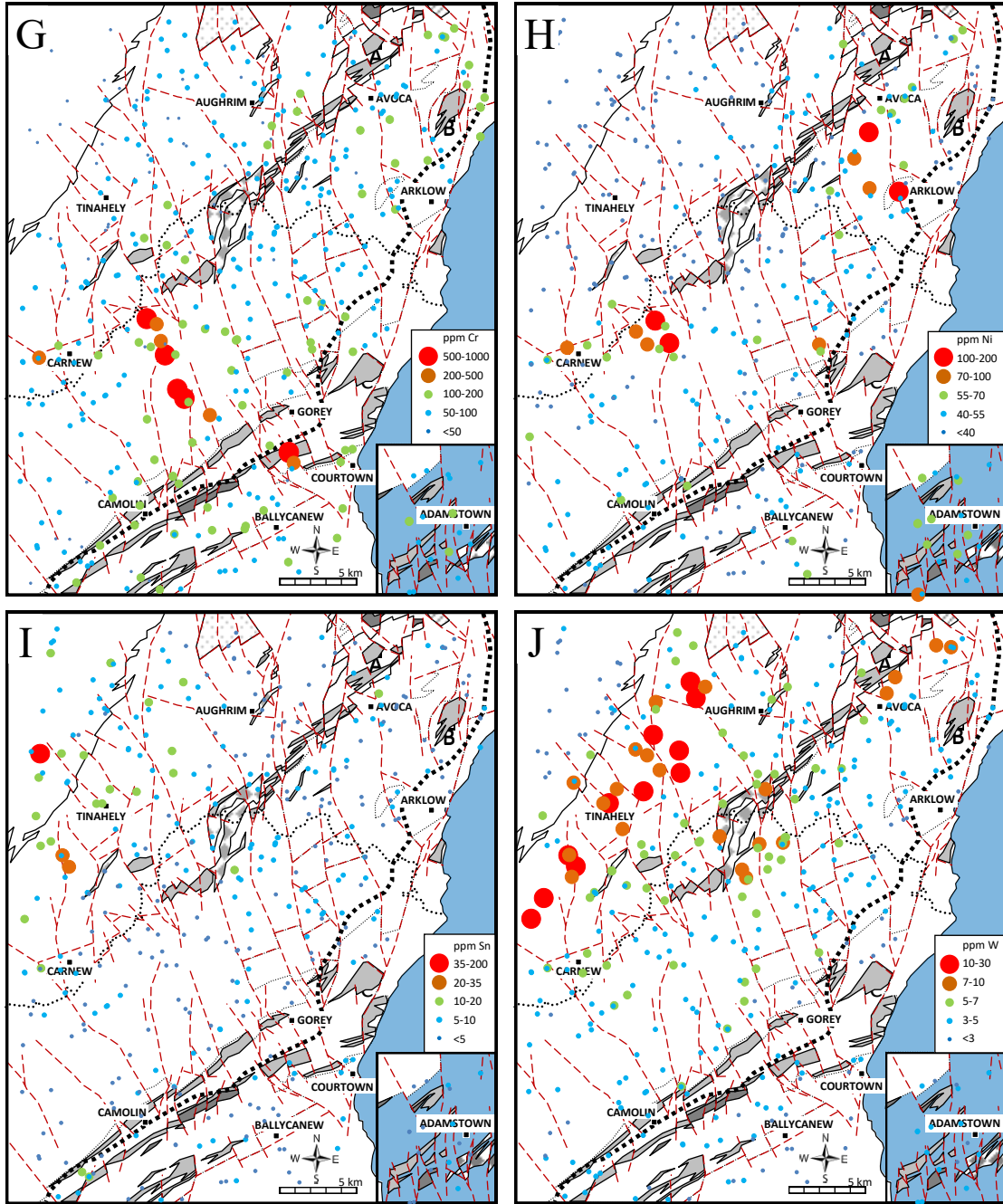
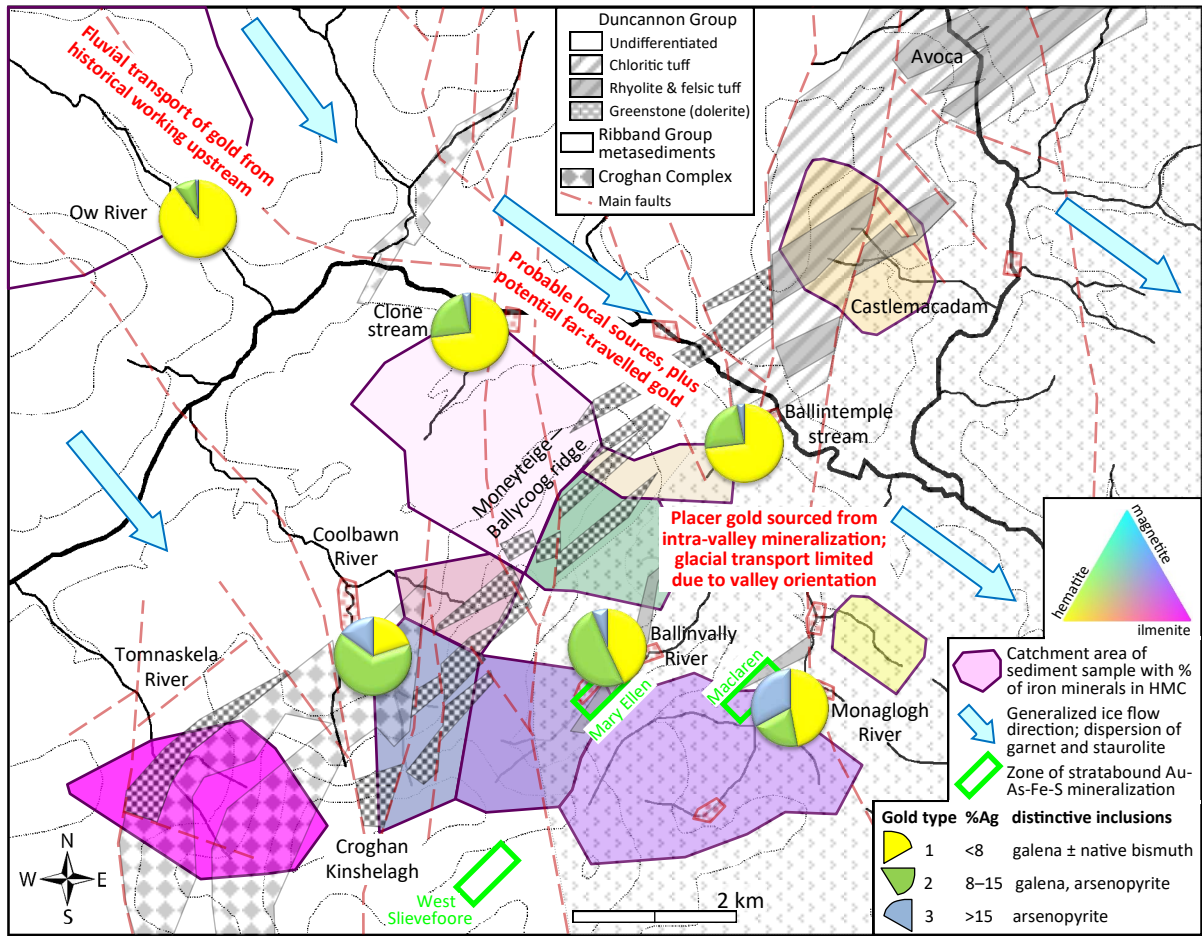


Fig. 12



Moles & Chapman - SE Ireland placer gold - Table 2

Map code	Site / river name	County	Irish Grid ref.	Abundance	Number of grains	Median %Ag	Median %Ag category	No. grains with inc.	% with inc.	Total no. inclusions	Metalliferous inclusion species											
											Py	Po	Gn	Cpy	Sph	CuSbS	Ars	GrS	Alt	Bi	Others	
1	Kilmacoo north	Wicklow	T 211 850	very low	2	-	-	0	0	0												
2	Knockanode	Wicklow	T 193 823	very low	4	3.7	low	1	25	2			1									Native As
3	Avoca tributary	Wicklow	T 214 819	low	33	8.0	high	6	18	7	1		1	1		1	3					
4	Ow River	Wicklow	T 111 800	low	19	3.4	low	6	32	8	1	1	4	2								
5	Castlemacadam	Wicklow	T 194 792	very low	4	3.4	low	0	0	0												
6	Clone stream	Wicklow	T 140 785	high*	62	3.6	low	5	8	6												
6	Clone stream	Wicklow	T 140 785	high*	51	4.0	low	5	10	6			9	2	1							
7	Ballintemple stream	Wicklow	T 177 780	high*	62	3.9	low	9	15	11	3		1	1			3		2			Wittichenite
8	Tomnaskela River	Wicklow	T 105 738	very low	2	-	-	0	0	0												
9	Coolbawn River	Wicklow	T 132 750	high*	46	11.5	high	3	7	3			3									
10	Ballinvally River trib., Ballykillageer	Wicklow	T 165 761	low	13	6.5	medium	1	8	1			1									
11	Ballinvally River, Red Hole	Wicklow	T 160 745	high*	81	8.5	high	16	19	22	5		5	1			5	1			2	Plumbogummite x3
12	Ballinvally River upper, Ballinagore	Wicklow	T 152 742	low	25	9.5	high	3	8	3	1			1								Tsumoite
13	Monaglogh R trib., Rostygah	Wicklow	T 182 754	high*	68	6.2	medium	15	22	17	3		9	1			2	1				Unidentified CuAsS
14	Monaglogh River	Wicklow	T 180 745	high*	60	8.4	high	6	10	8												
14	Monaglogh R duplicates 2 & 3	Wicklow	T 178 747	high*	73	8.3	high	9	12	12	4	1	7	1		1	4	1		1		
15	Monaglogh tributary	Wicklow	T 180 750	low	21	3.3	low	3	14	3							2	1				
16	Monaglogh R upper, Killahurler	Wicklow	T 174 737	very low	5	7.2	medium	0	0	0												
A	Kilcloran	Wexford	T 054 533	low	46	6.2	medium	3	7	3	2		1									
B	Hyde Park	Wexford	T 208 665	medium	81	5.7	medium	9	11	11	2		4				4	1				
C	Cullenoge	Wexford	T 207 647	low	50	5.0	low	5	10	12	4		2	3				2	1			
D	Coolnacon Bridge	Wexford	S 839 307	medium	91	3.2	low	8	9	8	2		1	3	1			1				
E	Misterin	Wexford	S 842 264	very low	13	3.8	low	1	8	1											1	
F	Ballyshannon	Wexford	S 850 255	low	48	4.4	low	2	4	3	1										2	
G	Boley Lower	Wexford	T 069 562	high	192	5.9	medium	17	9	24	4		6	3	1	5	5					
H	Rosminoge South	Wexford	T 069 576	very low	20	5.0	low	0	0	0												
I	Ballykale	Wexford	T 160 563	high	167	7.5	medium	13	8	19	4	1	3	3				7	1			
J	Newbridge Wood	Wexford	T 060 558	low	21	4.8	low	1	5	1												
K	Askamore Burn	Wexford	T 025 585	low	30	6.5	medium	4	13	4												
K	Askamore duplicate	Wexford	T 024 583	low	30	5.8	medium	2	7	2	1			1				1		2		Clausthalite
L	Milshoge	Wexford	T 065 520	high	96	7.3	medium	3	3	4	1			1								
M	Knockrobin Lower	Wexford	T 082 516	low	18	5.2	low	1	6	1												
N	Ballyeden	Wexford	T 099 517	low	68	6.3	medium	6	9	5	2	1										
Q	Huntingtown	Wexford	T 110 574	low	41	8.3	high	5	8	5	3						1	1				
R	Ballygarrett (Ballyowen)	Wexford	T 105 596	high	64	7.9	high	2	3	2												
R	Ballygarrett duplicate^	Wexford	T 115 607	high	114	7.5	medium	6	5	6	3		1		1	1	2					
S	Gibbett Hill	Wexford	S 961 576	medium	55	5.9	medium	3	5	3	1		1					1				
T1	Tombreen 1	straddle	T 003 622	low	30	7.4	medium	2	7	2												
T2	Tombreen 2	straddle	S 987 619	low	28	5.3	low	3	11	4			2	1				2	1			
V	River Bann, Holyfort	Wexford	T 122 641	very low	3	3.9	-	0	0	0												
W	S. Corbetstown^	Wexford	T 067 487	high	93	6.6	medium	3	3	3	3											
X	Coolnaveagh^	Wexford	T 146 573	medium	57	6.4	medium	4	7	5	1						1	1	1			Cobaltite
Y	Kilmichael^	Wexford	T 114 625	medium	30	7.0	medium	2	7	2	1			1								
Z	Ballyduff^	Wexford	T 115 502	medium	43	7.1	medium	5	12	8	1				1	1	3	1				Boulangerite
Total:					2160			198		247	54	4	62	26	5	15	52	12	4	3		10

Site code	Site / river name	Barite	Hematite	Magnetite	Ilmenite	Rutile	Chrome spinel	Cassiterite	Ferberite	Tantalite	Monazite	Zircon	Garnet	Staurolite
1	Kilmacoo north	-	13	-	-	-	-	-	-	-	-	-	75	12
2	Knockanode	-	8	-	-	-	-	-	-	-	-	-	80	12
3	Avoca tributary	-	-	-	-	-	-	-	-	-	-	-	86	14
4	Ow River	-	-	-	-	-	-	-	-	-	-	-	85	15
5	Castlemacadam	-	27	-	10	-	-	-	-	-	-	-	42	21
6	Clone stream	-	-	-	5	-	2	5	2	-	-	-	68	18
7	Ballintemple stream	-	11	2	5	-	2	9	-	-	-	-	56	15
8	Tomnaskela River	-	-	-	75	-	3	6	2	-	-	2	12	-
9	Coolbawn River	-	20	37	30	-	-	-	5	-	-	-	8	-
9n	Moneyteige North	-	18	11	25	-	3	9	3	-	2	-	22	7
11	Ballinvalley River, Red Hole	-	16	32	42	-	-	-	-	-	-	-	10	-
13	Monaglogh R trib., Rostygah	-	40	4	2	-	-	4	2	-	-	-	33	15
14	Monaglogh River	-	4	19	40	10	-	3	-	-	-	-	19	5
A	Kilcloran	-	11	-	50	-	-	2	2	-	16	3	16	-
B	Hyde Park	-	12	-	38	-	-	4	2	-	3	-	41	-
C	Cullenoge	-	15	-	55	-	-	-	-	-	-	8	22	-
D	Coolnacon Bridge	-	-	5	60	4	-	5	-	-	-	-	17	9
E	Misterin	-	-	5	68	6	-	2	-	-	-	-	13	6
F	BallyShannon	-	-	-	57	4	-	7	-	1	2	-	17	12
G	Boley Lower	-	9	-	7	-	3	17	19	2	29	-	14	-
H	Rosminogue south	-	-	-	39	-	10	5	-	-	20	2	24	-
I	Ballykale	-	8	-	39	-	12	4	2	1	-	2	32	-
J	Newbridge Wood	-	-	-	66	-	-	4	-	-	16	-	14	-
K	Askamore	-	-	-	5	-	-	54	10	4	3	-	24	-
L	Milshoge	-	9	-	54	9	-	12	-	-	10	-	6	-
M	Knockrobin Lower	-	7	-	60	6	-	-	-	-	-	-	27	-
N	Ballyeden	-	11	-	45	3	-	3	-	-	-	4	34	-
P	Bolinready	-	9	-	39	-	-	-	-	-	-	-	52	-
Q	Huntingstown	-	3	-	67	-	6	3	-	-	-	3	18	-
R	Ballygarrett / Ballyowen	13	6	-	21	-	21	9	3	-	18	-	9	-