

Detrital gold, heavy minerals and sediment geochemistry elucidate auriferous mineralization in southeast Ireland

Moles, Norman R.

School of Environment and Technology, University of Brighton, UK

Chapman, Robert J.

Ores and Mineralization Group, School of Earth and Environment, University of Leeds, UK

Abstract. Recently published Tellus geochemical data for sediment fines in SE Ireland show extensive Au anomalies in north Wexford, but few anomalies in Wicklow despite historical extraction from the Goldmines River. Discovery of bedrock sources is hampered by glacial dispersion and scarce bedrock exposure. Here we describe a novel approach to characterizing regional gold metallogeny which involves the synthesis of data sets from stream sediment surveys, analysis of heavy mineral concentrates (HMCs) and detrital gold. Mineralogical characterization of HMCs and 2160 gold grains from 40 localities in the auriferous region provides a clear indication of proximity of gold to source and genetic origins. Detrital gold in the south of the region (Wexford) is most likely derived from the widespread stratabound Au-As-Fe-S reported by exploration companies, whereas the distinctive Pb-Bi-As mineral inclusion signature in detrital gold from the Goldmines River area is suggestive of a magmatic influence. Combining data sets from the different techniques yields superior information than is possible using each approach in isolation.

1 Introduction

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 or due to anthropogenic influences. In particular, the extreme density of gold results in highly localized concentrations within fluvial sediments, an effect exacerbated as gold particle size increases. Thus classical stream sediment sampling may under-represent gold. Conversely, establishing placer-lode relationships for gold can be challenging if only gold particles are collected because the particles may be recycled into successive surficial environments. Heavy mineral concentrates co-collected with gold particles may be used to investigate spatial relationships between sediments and local lithologies. Here we compare the spatial distributions of data from sediment fines with distributions of heavy mineral concentrates (HMCs) including detrital gold in southeast Ireland, where the relationships are poorly understood between historically exploited Cu-Au volcanogenic massive sulphide (VMS) mineralization, placer gold, and widespread Au anomalies in stream sediment fines.

2 Geology and mineralization

Southeast Ireland comprises a NE-SW oriented belt of Cambrian – Ordovician sedimentary and volcanic rocks that were deformed and metamorphosed during later Palaeozoic orogenic events (Gallagher et al. 1994). Lower Ordovician thick laminated mudstones of the ‘Ribband Group’ were followed by clastic sediments and volcanic rocks of the Duncannon Group (Brück et al. 1979). In Wicklow the latter incorporates the Avoca Volcanic Group (AVG) which comprises dominantly rhyolitic lavas, chloritic tuffs and slaty mudstones.

A major period of shearing towards the end of the Caledonian orogeny generated NE-oriented deformation zones, one of which occurs in the Avoca – Goldmines River area. The Leinster Granite batholith and satellite granitic plutons, including the Croghan Kinshelagh complex south of the Goldmines River, were emplaced into these actively deforming shear zones (Gallagher et al., 1994). Recent geochronological and geochemical studies (Fritschle et al. 2018) have established that the Croghan Kinshelagh complex comprises discrete older and younger units. The older granite is correlative with AVG volcanism and has been deformed with a penetrative fracture cleavage similar to the AVG rocks, whereas the younger granite intrusion is undeformed.

Metalliferous mineralization is widespread in SE Ireland. The AVG hosts VMS ore that was previously mined at Avoca yielding around 100,000 tonnes of copper metal (Tietzsch-Tyler et al. 1994; Williams et al. 1986). Banded iron formation crops out on the Moneyteige–Ballycoog Ridge adjacent to the Ballinvally River (Fig. 4) and hosts epigenetic Cu-Pb-Zn-Bi-Au mineralization (McArdle & Warren 1987; Ixer et al. 1990; Milner & McArdle 1992). In the Goldmines River area (Ballinvally, Monaglogh and Coolbawn catchments) and extending southwest into Wexford, company exploration has identified Au-As-Fe-S mineralization which is in part stratabound and in part associated with shear zones that are slightly oblique to lithological strike (IMC 2013). Visible gold occurs in quartz veins within the shear zones. Adjoining the Leinster Granite, Au, W, Sn and Pb-Zn mineralization is associated with hydrothermal fluid circulation accompanying late Caledonian shearing and granite intrusions (McArdle et al. 1989).

In 1795, the Goldmines River area was the scene of Ireland’s only historical gold rush (Maclaren 1903). It has been estimated (Reeves 1971) that up to 300 kg of placer gold was recovered from gravels in the Ballinvally and

Monaglogh Rivers (Figs. 2 and 4) and surrounding area. Some of the gold was very coarse-grained, the largest mass being the 'Wicklow nugget' weighing 22 ounces (682 g). However, despite intense exploration, bedrock sources have not been identified.

Various exploration campaigns since the 1980s identified several gold prospects using soil geochemistry, geophysical surveys, trenching and drilling. Exploration in the region has recently benefitted from a release (Knights & Heath 2016) of high precision re-analyses of fine fraction sieved stream sediments originally collected in the 1980s (O'Connor & Reimann 1993). Over 2000 samples had been obtained at a density averaging 1 per 4 km². About 5% returned elevated concentrations of gold in the range 0.1 to 1.5 ppm (Fig. 1). Samples with >0.5 ppm Au are mostly located in a NW-SE trending belt between Camolin and Carnew in north Wexford. There appears to be no spatial association between bedrock geology and Au enrichment in sediments, indeed the belt is perpendicular to the 'Caledonian' trend and crosses outcrops of both Ribband and Duncannon Group rocks. In the Avoca – Goldmines River area, values of Au >0.1 ppm occur in only one Tellus sample, from the Coolbawn River, but not at other localities of historical gold winning.

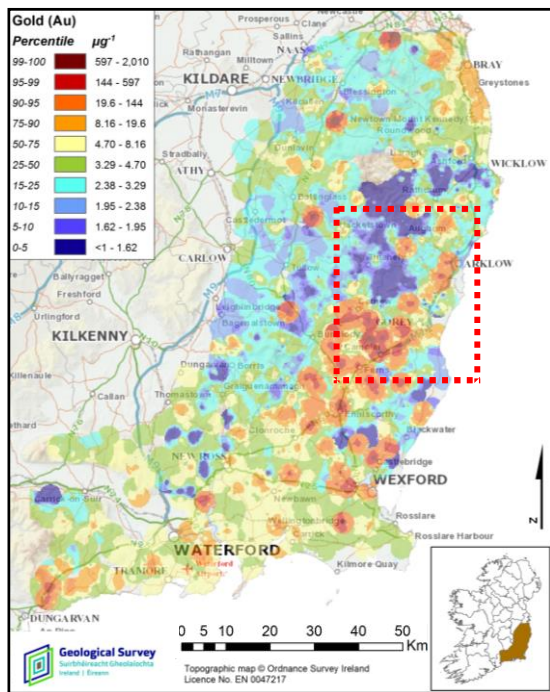


Figure 1. Au concentrations in fine fraction sediments in SE Ireland, showing an area of relatively high values in north-central Wexford and mostly low values in Wicklow and Carlow. Tellus map reproduced with permission from the Geological Survey of Ireland. Red box indicates the study area shown in Figure 2.

3 Methods and results

3.1 Detrital gold characterization

New data describing the alloy compositions and mineral inclusions within 1541 detrital gold particles was augmented by a similar data set for 619 grains reported

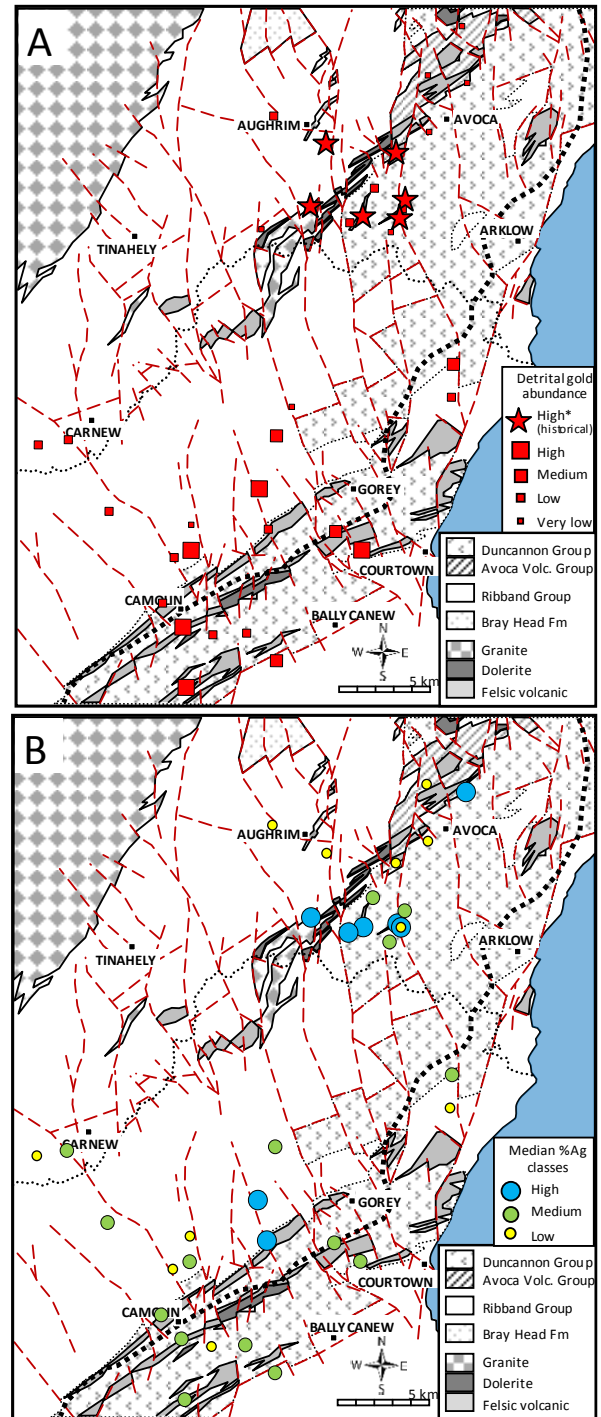


Figure 2. Outline geology of the study area with symbols at sample sites indicating (A) detrital gold abundance, with 'high*' indicating concentration previously sufficiently high to support historical exploitation in the Goldmines River area, and (B) median %Ag classes at sites from which 4 or more gold grains were obtained.

by Chapman et al. (2006). A total of 40 localities in south Wicklow and Wexford are represented. Although gold was recovered at every locality, abundances varied enormously (Fig. 2A). In north Wexford, scattered sites returned relatively high abundance against a background of average to low abundance. The coarse particle size and rough morphology of gold grains from near the

former placer working ('Red Hole') in the Ballinvally River strongly suggests very local derivation, as suggested by Maclaren (1903). Rough gold characteristic of proximal derivation was found at Ballygarrett and Boley Lower in Wexford, while elsewhere much of the gold is flaky indicating transport and less proximal derivation.

Electron microprobe analyses of gold alloy in grain cores revealed that Ag is ubiquitous, whereas Cu and Hg are detected only sporadically. A generic form of the cumulative frequency curves of wt% Ag in Wexford samples allowed their characterization using a single median value. Three class intervals of median wt% Ag (low <5.5, medium 5.5-7.5, high >7.5) were selected and the spatial distribution of these categories is presented in Fig. 2B. No spatial association is apparent between Ag content and underlying lithology, HMC mineralogy, or ice flow direction in Wexford. In the Goldmines River area correlation of Ag range with inclusion type has yielded three generic gold types (Fig 3). Most arsenopyrite inclusions are hosted by gold grains of c. 9-14 wt% Ag, (Type 2). The majority of galena and native bismuth inclusions, grouped because of their intimate association, occur within gold containing <9 wt % Ag (Type 1: Fig. 3).

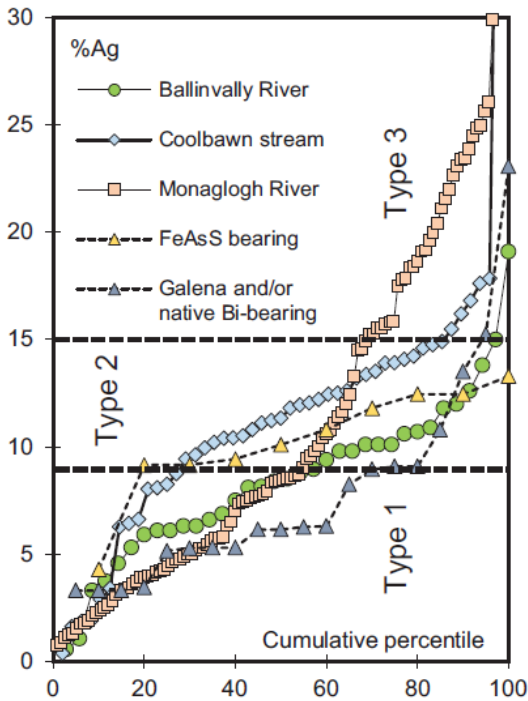


Figure 3. Silver content of gold populations from three catchments in Wicklow showing definition of gold types 1 to 3 according to the Ag ranges grains with arsenopyrite and galena-bismuth inclusions.

Chalcopyrite associates mostly with Types 1 and 2 and is absent from Type 3 gold. Individual catchments show different gold signatures according to these gold types (Fig. 3) which suggests local sources in each case. Ixer et al. (1990) comment on the close association of galena and native bismuth in samples of mineralized BIF from the Ballycoog–Moneyteige Ridge (Fig. 4). The similarity between inclusion suites in Type 1 gold and this mineralization is consistent with a scenario of multiple occurrences of this gold type in Wicklow.

Comparison of wt% Ag ranges of gold types 1-3 against the bulk assay of historically recovered gold (7.82% Ag) recorded in returns to the Irish Mint (Kinahan 1882) shows Type 1 gold to be the most important overall signature. Consequently Type 1 gold probably represents the most attractive target for future exploration projects.

The mineral inclusion assemblage of Wexford gold also shows a galena-arsenopyrite signature. Bismuth minerals are absent whereas chalcopyrite, sphalerite and pyrite are more common than in the Wicklow samples. This inclusion mineralogy is compatible with the compositional range of Phanerozoic orogenic gold recorded throughout the British and Irish Caledonides as summarized by Chapman et al. (2000).

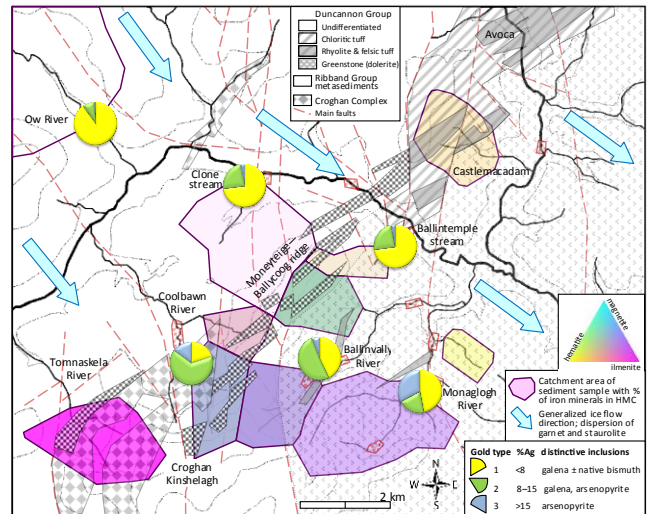


Figure 4. Outline geology of south Wicklow showing historical placer workings (red stippled boxes along rivers), sampled catchment areas colour-coded according to the proportions of hematite, magnetite and ilmenite in HMC samples with opacity in proportion to abundance of these components, and pie charts indicating the proportions of gold types 1–3 in each area.

3.2 Heavy mineral characterization

Semi-quantitative analysis of mineral abundances in HMCs was undertaken to investigate resistate particle mobility in the surficial environment and potentially identify mineral species genetically linked to gold mineralization. As shown in Fig. 4, HMC mineralogy is diverse in the Goldmines River area with differing proportions of hematite, magnetite and ilmenite in adjacent tributaries. There are no clear associations between HMC mineralogy, gold abundance and the proportions of the gold types. However in Wexford, atypical HMC mineralogy at Askamore, which included abundant cassiterite and ferberite, correlates with a distinctive gold signature which, in combination, indicate a local source of granite-associated Au mineralization.

4 Implications for bedrock mineralization

Given the current limited understanding of in situ Au-bearing mineralization in SE Ireland, we can apply the spatial associations between detrital gold abundance,

microchemical signatures, and bedrock geology to re-evaluate previous hypotheses for the source of gold in the Wicklow placers. The potential of Avoca as a source may be discounted on the basis of ice flow directions (McArdle & Warren 1987), patterns of heavy mineral distribution (Fig. 4), and gold abundance and Ag contents (Fig. 2). The potential for the BIF-hosted mineralization on the Moneyteige Ridge to represent an example of Type 1 gold has been discussed above, although elsewhere Type 1 gold is hosted by other lithologies.

The differences in signatures of sample populations of detrital gold from within individual drainages (Figs. 3 and 4) leads us to favour a model in which intra-valley mineralization with magmatic-hydrothermal characteristics (gold type 1 with bismuth inclusions) supplemented gold from the local stratabound Au-As-Fe-S style (gold types 2 and 3) to form rich gutter placers in ravine-like settings in the Goldmines River particularly the Red Hole.

The decoupling of gold types from HMC mineralogy suggests that in the Goldmines River area, bedrock gold mineralization is not lithologically controlled. Instead, mineralization is likely to be controlled by tectonic structures and proximity to the Croghan Kinshelagh granites. This concurs with Standish et al. (2014) who, in interpreting lead isotope ratios in placer gold from southeast Ireland, favour two separate mineralization events associated with the Early Caledonian orogenesis and with Late Caledonian granite emplacement.

5 Evaluation of exploration methods

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 (Moles & Chapman 2019). Spatial distributions of heavy mineral suites constrain the directions and extents of glacial transport, which facilitates more confident interpretations of placer-lode relationships from gold grain studies. Microchemical characterization of gold establishes genetic relationships and clear links with known types of hypogene mineralization.

Acknowledgements

We thank John Ashton of New Boliden Tara Mines Limited for supporting the sampling program in Wexford, and IMC Exploration Group plc for their support of follow-up fieldwork in Wicklow. The University of Brighton provided facilities for XRD, SEM and XRF analyses of heavy mineral concentrates. The University of Leeds provided EMPA and SEM facilities for analysis of the gold grains. We are indebted to Colin Kimberley and John Krenc, Christopher Reynolds, Christopher Smith and Hamidullah Waizy for their assistance with sampling and analysis.

References

Brück PM, Colthurs, JRJ, Feely M, Gardiner PRR, Penney SR, Reeves TJ, Shannon PM, Smith DG, Vanguetaine M (1979) Southeast Ireland: Lower Palaeozoic stratigraphy and depositional history. In: Harris AL, Holland CH, Leake BE (editors) *The Caledonides of the British Isles – Reviewed*. Geol Soc London Special Publication 8: 533-544.

Chapman RJ, Leake RC, Moles NR, Earls G, Cooper C, Harrington K, Berzins R (2000) The application of microchemical analysis of gold grains to the understanding of complex local and regional gold mineralization: a case study in Ireland and Scotland. *Econ Geol* 95: 1753-1773.

Chapman RJ, Leake RC, Warner RA, Moles NR, Cahill MC, Shell, CA, Taylor JJ (2006) Microchemical characterization of natural gold and artefact gold as a tool for provenancing prehistoric gold artefacts: A case study in Ireland. *J Applied Geochem* 21: 904-918.

Fritschle T, Daly JS, McConnell B, Whitehouse MJ, Menuge JF, Buhre S, Mertz-Kraus R, Döpke D (2018) Peri-Gondwanan Ordovician arc magmatism in southeastern Ireland and the Isle of Man: Constraints on the timing of Caledonian deformation in Ganderia. *GSA Bulletin* 130 (11-12): 1918-1939.

Gallagher V, O'Connor P, Aftalion M (1994) Intra-Ordovician deformation in southeast Ireland: evidence from the geological setting, geochemical affinities and U-Pb zircon age of the Croghan Kinshelagh granite. *Geol Mag* 131: 669-684.

IMC Exploration PLC (2013) Boley-Kilmichael Gold Project, County Wexford, Ireland. Presentation available from company website <http://imcexploration.com/images/Wexford-Project.pdf>.

Ixer RA, McArdle P, Stanley CJ (1990) Primary gold mineralization within metamorphosed iron ores, Southeast Ireland. *Geological Survey of Ireland Bulletin* 4: 221-226.

Kinahan GA (1882) On the mode of occurrence and winning of gold in Ireland. *Scientific Proceedings of the Royal Dublin Society* 3: 263-285.

Knights KV, Heath PJ (2016) Quality control and statistical summaries of Tellus stream sediment regional geochemical data: analytical data 2016. *Geological Survey of Ireland*, 252 p.

Maclaren MJ (1903) The occurrence of gold in Great Britain and Ireland. *Trans Inst Mining Engineers* 25: 435-508.

McArdle P, Warren WP (1987) Iron formation as a bedrock source of gold in southeast Ireland and its implications for exploration: *Trans Inst Mining Metallurgy (Section B Applied Earth Sciences)* 96: 195-200.

McArdle P, Fitzell M, Oosterom MG, O'Connor PJ, Kennan PS (1989) Tourmalinite as a potential host rock for gold in the Caledonides of Southeast Ireland. *Mineralium Deposita* 24: 154-159.

Milner AL, McArdle P (1992) Gold mineralization in Ordovician volcanic rocks at Kilmacoo, County Wicklow: its exploration and geological controls. In: Bowden AA, Earls G, O'Connor PG, Pyne JF (editors). *The Irish Minerals Industry 1980–1990*. Irish Association for Economic Geology. 51-63.

Moles NR, Chapman RJ (2019) 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. *Econ Geol* 114: xx-xx.

O'Connor PJ, Reimann C (1993) Multi-element regional geochemical reconnaissance as an aid to target selection in Irish Caledonian terrains. *J Geochem Exploration* 47: 63-89.

Reeves TJ (1971) Gold in Ireland. *Geological Survey of Ireland Bulletin* 1: 73-85.

Standish CD, Dhuime B, Chapman RJ, Hawkesworth CJ, Pike AWG (2014) The genesis of gold mineralisation hosted by orogenic belts: a lead isotope investigation of Irish gold deposits. *Chemical Geology* 378-379: 40-51.

Tietzsch-Tyler D, Sleeman AG, McConnell BJ, Daly EP, Flegg AM, O'Connor PJ, Warren WP (1994) *Geology of Carlow – Wexford: A geological description to accompany the bedrock geology 1:100,000 map series, sheet 19, Carlow–Wexford*. Geological Survey of Ireland.

Williams FM, Sheppard WA, McArdle P (1986) Avoca Mine, County Wicklow: A review of geological and isotopic studies. In: Bowden AA, Earls G, O'Connor PG, Pyne JF (editors). *The Irish Minerals Industry 1980–1990*. Irish Association for Economic Geology. 71-82.