Title: Tin sources for prehistoric bronze production in Ireland.

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The importance of Ireland in the early metallurgy of northwestern Europe and the huge number of Early Bronze Age metal artefacts found there must not be downgraded by the absence of tin sources in the country. Despite having the distinctive Irish impurity pattern, the earliest tin-bronzes found in Ireland may not have been made there as this pattern may have resulted from a particular smelting technology applied to ores from a number of geographical sources.

Ireland is important in the early metallurgy of northwest Europe, for it has given us a large majority of the Early Bronze Age artefacts from the whole British Isles. Is there tin-ore to have been mined in early Ireland to produce this bronze or must it have come from elsewhere?

Ireland and early metallurgy

For many years Ireland has been central to interpretations of the earliest metallurgy in the British Isles, and ongoing excavations at Ross Island in Killarney look set to confirm an early origin for extractive copper metallurgy in the country (O'Brien pers. comm.). Well over 2000 Early Bronze Age copper-based artefacts have been attributed to Ireland (Harbison 1969a; 1969b) compared with a few hundred from England, Scotland and Wales (Burgess 1974; Coles 1968-9; Savory 1980). Proposals that this distribution indicated an Irish origin of British metallurgy received considerable support from compositional analysis of British and Irish metalwork (Case 1954; 1966; Coghlan & Case 1957) and hand specimens of Irish copper ores (Coghlan 1963; Butler 1963). Case (1966) concluded that the earliest metal artefacts in circulation in the British Isles were predominantly produced in Ireland by an 'industry' based in that country. These artefacts, characterized by a high arsenic, antimony and silver impurity pattern, were, it was suggested, made from sulfide ores of the fahlerz type (Coghlan 1963). At the time it was proposed that such ores were being mined in antiquity from Mount Gabriel in southwestern Ireland (Jackson 1968; 1979). Detailed re-examination of the ores, however, has shown that arsenic- and antimony-bearing minerals are totally absent from Mount Gabriel (Ixer 1990; O'Brien 1990; O'Brien et al. 1990), although they have been found elsewhere in southwestern Ireland (Ni 1991). Recent schemes have divided the Early Bronze Age of the British Isles into numerous technological stages (Burgess 1974; 1979) which have been associated with characteristic impurity patterns (Northover 1980a; 1980b; 1982), but Case's (1966) thesis, that all of the earliest material was produced in Ireland, has remained unchallenged.

Much of the Early Bronze Age metalwork from the British Isles, in common with that from elsewhere in Europe, has a high arsenic content. The supposed advantages of arsenical copper and the possibility of its deliberate production in the European Chalcolithic have been discussed by Wertime (1964), Charles (1967; 1979; 1980; 1982), Eaton & McKerrell (1976), Rapp (1988), Northover (1989) and Budd (1991). Some researchers saw early British arsenical coppers as intentional products from the smelting of arsenic-bearing sulfide (McKerrell & Tylecote 1972; Craddock 1979), or oxide (Tylecote 1976; Charles 1985), zone minerals. More recent work has shown that British and Irish 'arsenical copper' is unlikely to have been deliberately produced; it may have resulted from the primitive smelting of arsenic-bearing cupriferous ores (Thomas 1990; Pollard et al. 1990; 1991; Budd et al. 1992).

If arsenical coppers were not deliberately produced, it is the earliest tin-bronzes which must be considered as the first true alloys with specific physical or mechanical properties achieved by mixing different metals or their ores. Until now, it has been proposed that the practice of alloying copper and tin to produce bronze, like metallurgy itself, developed first in Ireland and later spread to mainland Britain. Ireland is still held to be the sole source of copper for the earliest tin-bronzes both in Ireland and mainland Britain (Northover 1980b). If, as Northover (1982) proposes, alloying with tin was carried out near the copper production centres, it follows that local tin resources must have been available in Ireland in the earliest part of the Bronze Age.

Both Jackson (1979; 1991) and Northover (1988) have concluded that accessible tin resources may have occurred in the Gold Mines River of Co. Wicklow. As its name suggests, the river is known to have contained exploitable concentrations of gold; Jackson (1979) argued that abraded crystals of cassiterite (Sn[O.sub.2]) were volumetrically as abundant as gold in the placer -- a secondary ore deposit formed by the erosion and sorting of minerals from a primary ore deposit by river action. Jackson (1991) proposed that tin ore occurred in 'quite substantial quantities' and that cassiterite was probably present in the oxidized secondary enrichment zones at Avoca, 7 km northeast of the Gold Mines River (Jackson 1991). Neither of the last two assertions can be substantiated and one, perhaps both, can be shown to be incorrect. The errors may have been based on the mistaken belief that the sources of tin and gold in the Gold Mines River placer, and hence their relative abundances, were the same. This is not so.

Primary and secondary tin and gold ores

The primary tin minerals are cassiterite and complex copper-iron-tin- and, possibly, zinc-sulfides, collectively known as 'stannite'. These, together with tungsten, arsenic and bismuth minerals, form part of a characteristic high-temperature hydrothermal mineralization associated with some 'fertile' granites. Copper ores associated with acid volcanic rocks have slightly enhanced tin values, but the tin is not carried as cassiterite; rather it is present as very fine-grained stannite or, more often, is locked into the iron-copper sulfides. In both cases it is invisible to the naked eye and cannot have been exploited in antiquity.

Cassiterite is the only tin-bearing mineral found in placer deposits. On oxidation stannites alter to very fine-grained, often colloidal, mixtures of iron and copper sulfides and poorly hydrated tin oxides (Russel & Vincent 1952; Alderton 1993) which are lost during weathering and erosion. As a consequence, secondary (placer) tin deposits formed from stannite-rich ores are extremely rare and require the primary ore to be exceptionally rich (Ramdohr 1969); this is one reason why the potential tin grade of placer deposits cannot be determined from the grade of the source rocks. If the primary tin mineral is stannite, there may be no secondary deposit. If the tin minerals are a mixture of stannite and cassiterite, or are just cassiterite, the resulting placer is poorer, the same, or, more commonly, richer than the primary ore.

Gold is a surprisingly widespread element. Although a large number of primary gold-bearing minerals are known, secondary gold is found almost exclusively as native gold or gold-silver-copper alloys with or without palladium. As for tin deposits, the grade of primary gold ores is not reflected in their secondary deposits, especially as some gold in placer deposits has precipitated from surface waters to form gold-rich rims and nuggets (Ixer 1990). Many placer gold deposits are therefore richer than their source rocks.

Although some volcanogenic copper ores carry trace amounts of tin and gold, primary gold-tin ores are not known; hence the sources of the two metals in a gold- and tin-bearing placer will be separate. The volcanogenic copper ores at Avoca, gold-bearing and with enhanced background tin values, are close to the Gold Mines River; their role as a possible source for the Gold Mines River placer is discussed below.

Sources of tin in Ireland

Many Irish gold localities have been, are being, or have the potential to be, exploited (McArdle 1989). Their number and history of exploitation contrasts sharply with the paucity of tin in Ireland. Macalister said (1949: 15), 'Ireland's resources of tin are insignificant'. This is still true, for despite 40 more years of intense and successful metal exploration, no economic nor sub-economic tin deposits are known; even recorded tin localities are rare (Jackson 1979; Penhallurick 1986). Jackson's list of eight localities includes three unconfirmed historical citations, three of cassiterite associated with granites (including two associated with the Leinster Granite), one of waterworn cassiterite from the Gold Mines River placer and one of stannite from the Avoca ores. Anomalous tin values (17 ppm), but no tin minerals, have since been recorded from Pre-Cambrian granite--gneiss bodies in Co. Mayo (Winchester & Max 1983) and minor amounts of stannite, together with even less cassiterite in acid intrusive rocks, from the Aughrim-Tinahely area close to the eastern edge of the Leinster Granite (Steiger & Bowden 1986).

Other reports of enhanced tin values in copper ores include 0.05 wt. % Sn for Ross Island (Co. Kerry), 0-035 wt. % Sn for Avoca, and up to 0.015 wt. % Sn for mines in counties Cork and Kerry. Three points must be made. The tin values relate to single hand specimens (Butler 1963); they cannot represent the tenor of the copper ores. Both the method of analysis and its results must be treated with scepticism. Recent detailed and comprehensive mineralogical investigation of all the named ore deposits has recognized no tin minerals larger than 2[[micro]meter] in diameter (Ni 1991; Ixer 1992).

This lack of tin in Ireland must be contrasted with the abundance of primary and secondary tin deposits in southwest England (which were of world class importance) and themselves associated with Variscan 'fertile' granites (Alderton 1993). Although Ireland has granite bodies of different ages, notably Caledonian and Tertiary, there are no Variscan granites. Only the Aughrim--Tinahely tungsten mineralization and the gold-bearing river placers of the Gold Mines River area appear to have tin in other than trivial amounts.

The Gold Mines River as a source of tin

The mineralogy of the Gold Mines River placer is recorded as magnetite ([Fe.sub.3][O.sub.4]), quartz, chlorite, iron ochre (limonite, FeO(OH)), haematite ([Fe.sub.2][O.sub.3]), pyrite (Fe[S.sub.2]), gold plus wolframite ((Fe,Mn)W[O.sub.4]), molybdenite (Mo[S.sub.2]) and abraded crystals of cassiterite (Sn[O.sub.2]) (Mills et al. 1801; Mallet 1851). As sulfides oxidize very quickly and so are rarely found in modern placers (except for proximal ones), the unusual presence of pyrite suggests that some of the source rocks providing the heavy minerals were close by. However, the abraded nature of the cassiterite, a very hard mineral, is more consistent with a distal source.

McArdle & Warren (1987a) and Ixer et al. (1990) have suggested that outcrops of auriferous banded iron formations close to the Gold Mines River were the primary source of the gold. These iron formations comprise quartz-chlorite with siderite (FeC[O.sub.3]), magnetite plus lesser amounts of pyrite and chalcopyrite (CuFe[S.sub.2]). Native gold, present in trace amounts, is associated with chalcopyrite, galena (PbS), sphalerite (ZnS) and copper-lead-bismuth sulfosalts (Ixer et al. 1990). Gold values for the iron formations run at 0.2 to 0.5 ppm gold, but chalcopyrite concentrates have 3-18 ppm gold (McArdle & Warren 1987a). Despite a complex mineralogy, no tin or tin-bearing minerals, nor any tungsten and molybdenum ones, were found. If the mineralogy of the gold-bearing iron formations is subtracted from that of the river placer (primary siderite forms secondary iron ochre) then cassiterite, wolframite and molybdenite remain: an assemblage characteristic of high temperature 'granitic' mineralization. The nearest granite is the Leinster Granite, the main body of which is approximately 12 km northwest of the Gold Mines River.

There are three possible source rocks for the tin-tungsten-molybdenum minerals. From the least likely to most likely they are; gossans from the Aveca copper ores (Jackson 1979; 1991); erosion of the tungsten-tin deposits at Aughrim-Tinahely; erosion and concentration of the background tin mineralization within the main Leinster Granite. Jackson (1979) cites an unconfirmed mid-19th centuryreference to stammine [stannine/stannite] being present at Cronbane, part of the volcanogenic massive copper sulfide mineralization at Avoca, northeast of the Gold Mines River. He infers it would alter to cassiterite in the overlying gossan and then be transported southwestwards by glacial action into the placer deposits. None of the modern detailed geological and mineralogical descriptions of the Avoca ores (Wheatley 1971; Platt 1977; Pointon 1979; Willlams et al. 1986; Ixer 1992), have confirmed the presence of any tin minerals. Had stannite been present, it would have been exceptional for it to produce significant amounts of cassiterite on weathering. Finally, the evidence is against any glacial movement from Avoca towards the Gold Mines River (McArdle & Warren 1987b). There can, therefore, be very little support for a genetic relationship between the primary mineralization at Avoca and tin minerals in the river placer.

Tin is a minor constituent of the underground sub-economic tungsten mineralization that belongs to a zone of microgranite sheets lying between Aughrim and Tinahely on the eastern flank of the Caledonian Leinster Granite batholith (Kennan et al. 1986; Steiger & Bowden 1986). Here, scheelite (CaW[O.sub.4]), the only tungsten mineral, is accompanied by arsenopyrite (FeAsS) and minor amounts of base metal sulfides and -- very locally -- by stannite and traces of cassiterite and molybdenite. The mineralization, approximately 8 km to the northwest of the Gold Mines River, lies in direct line and 'upstream' of glacial movements in the Pleistocene (McArdle & Warren 1987b). Although this mineralization potentially could provide cassiterite and molybdenite to the placer, it is problematic as a source. Both wolframite and molybdenite are only found in proximal placers requiring a near-by source rock, whereas the cassiterite is abraded. Wolframite, recorded from the placer, is absent from the mineralization at Aughrim--Tinahely, where the only tungsten mineral is scheelite. Although scheelite can be replaced by wolframite and vice versa, the panned river sediments overlying the buried tungsten--tin mineralization only contain scheelite; replacement of scheelite by wolframite during weathering and erosion of the primary mineralization is not indicated. The Aughrim--Tinahely mineralization is an unlikely source of the cassiterite.

All that remains is the Leinster Granite. The cassiterite, wolframite and molybdenite may come from the widespread weathering and erosion of this granite, the main body of which lies 12 km to the northeast of the placer deposits. Although the Leinster Granite cannot be compared to the tin-rich Variscan Cornish granites, it has intruded into metasediments that have geochemically enhanced tin values, which in turn have caused the granite to be stanniferous at very low concentrations. Crystals of cassiterite have been recorded from the south of the batholith as a minor constituent of lithium-bearing pegmatites (Kennan et al. 1986) as well as to the north from Dalkey, near Dun Laoghaise, and from a weathered glacial erratic in the boulder clay at Greystones, near Bray (Jackson 1979). This last report is of interest as McArdle & Warren (1987a) record that between 1 and 3% of the material from the Gold Mines River placer is Leinster Granite. If a few per cent of the granite has survived weathering, erosion and glacial transport, then the more stable components of the granite (oxides and silicates of the heavy mineral suite) must also be present. Although their concentrations will be higher than in the granite source rock (a source rock with 10-20 ppm tin), even if all of the tin is cassiterite, it cannot lead to the formation of a rich placer.

Therefore, although cassiterite is present in the Cold Mines River placers, reports of its richness are, at best, over-enthusiastic; like many other reports of Irish mineralization in the 19th century, they may have had a speculative purpose. Whilst trace amounts of cassiterite in the placers are consistent with the geology of the area, cassiterite in 'quite substantial quantities' (Jackson 1991) is not.

Conclusions

Because tin in the Gold Mines River placer was said to be as abundant as gold, Jackson assumed that this was the case in prehistory; since gold had been extracted from the placer in the historic period, the tin must have been exploitable in the past. This assumption was unfounded, and Jackson's conclusion must now be regarded as erroneous. The tin mineralization of the area is not derived from the same source as the gold, and the concentration of the two metals in the Gold Mines River is in no way mutually dependent. Whereas it is possible that gold was collected from the river in the Early Bronze Age, it is inconceivable, contrary to Jackson (1979; 1991), that the tiny traces of cassiterite that may have been present were noticed and exploited.

The absence of tin sources in Ireland which could have been exploited to produce the earliest tin bronzes does not diminish the significance of early metallurgy in the country nor of the large number of Early Bronze Age metal artefacts that have been recovered there. Indeed, it seems highly likely that Ireland was an important source of copper and arsenical copper in this period. There are, however, objections to the idea that Ireland was the only source of copper at this time and supplied the whole of the British Isles even after the introduction of tin-bronze. If this were so, where did the tin in early Irish bronzes come from? Was tin imported to Ireland to make bronze in the Early Bronze Age and the alloying carried out at a remote distance from the tin source? Or were the first tin-bronzes produced in tin-bearing regions like Cornwall or Brittany? If the earliest tin-bronzes found in Ireland were not made there then why do they have the distinctive 'Irish' impurity pattern? The answers to these questions may lie in the interpretation of the analytical data. Recent work has proposed that the reduction of ore to metal during the Early Bronze Age may have involved temperatures lower than were used in later periods (Craddock & Meeks 1987; Pollard et al. 1991; Budd et al. 1992). Under these circumstances it has been shown that specific smelting temperature and ore benefication regimes are as important in determining the trace and minor element pattern of the smelted metal as the provenance of the ore (Pollard et al. 1991; Budd et al. 1992). This work calls into question the validity of linking groups of compositionally similar artefacts with particular ore sources without a detailed understanding of production processes. It may not be possible to define an 'Irish' copper type on compositional grounds; the characteristic impurity pattern may be a product of a particular smelting technology which may have been applied to ores from any one of a number of geographical sources. If metal with an arsenic-antimony-silver impurity pattern was not regarded as exclusively Irish then it would not be necessary to promote the idea of tin-bronze metallurgy developing in a region with no tin.

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