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Where is the tin?

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In spite of the great quantities of bronze from prehistoric times recovered during excavations, relatively few finds of the main alloying element, tin, which would be required for addition to the copper base, have occurred. This phenomenon is examined in some detail, with the conclusion that trade, and addition to copper, could have been as cassiterite or other tin-bearing minerals which may not have been recognized and recorded by excavators in the past.

Various forms of cassiterite and other possible tin-bearing additions are described and illustrated and methods of identification outlined in order that excavators dealing with hoards or smelting sites may be aware of significant material. Dr Charles, Fellow of St John's College, Cambridge, and Lecturer in the Department of Metallurgy and Materials Science of the University of Cambridge, has written for us before (1968, 278; 1970, 207; 1972, 134).

It is not the object of this article to advance opinions as to the various possible origins of bronze metallurgy and its dispersion by trade and migration, nor to assess in detail the likely sources of the raw materials that were employed, although in the case of the tin addition this is proving a fascinating study. The purpose is to discuss why it is considered that direct mineral addition may have been the route to bronze, and to draw attention to the types of mineral that may have been used, and how they can be recognized. It is thus hoped that hard evidence may be forthcoming from future excavations where there is an awareness of specific materials to be recognized.

It is unfortunate that there are no smiths' graves from the Bronze Age in which assembled tools or raw materials gathered in one place could give a clearer picture of the technology practised. It has been considered that probably the early smiths were not a socially significant class, as is the case in some primitive tribes today. Thus, if not perhaps highly regarded, or if they were even detribalized as Tylecote (1962, 16) suggests, they were to a degree liberated from the bonds of local custom and had greater freedom to travel, and perhaps settle elsewhere where they could find markets for their products—possibly even abroad.

Since copper and, more particularly, tin ores are restricted to certain well-defined areas, the smith had to have trade contacts. He may have mined his own material in specific areas, smelted it, and then carried his finished product around a 'territory' in the early stages, but in the case of bronze, only rarely do copper and tin ores occur in reasonable juxtaposition and a more likely development would be an itinerant caster with moulds travelling an area, collecting scrap from customers and calling at intervals on the smelters or miners to replenish his primary supplies. With further development and increasing status, as his products became inseparable from tribal dominance, he would either become more settled with supplies traded to him or move with other smiths as a separate community. The large hoards of bronze objects from the Late Bronze Age show clearly that the industry had expanded greatly in terms of scale, organization and technology and would have involved organized trade in raw materials and products.

THE NATURE OF TIN SOURCES

To produce the bronze, ores of copper and of tin were required and strategically this hinges on the less plentiful sources of tin, which are almost all now in the form of cassiterite, tin

ANTIQUITY

oxide. In only rare instances do copper and tin ores occur in association, such that the fortuitous production of bronze would result, although this is not to say that the origins of bronze may not be associated with such mixed ores. This could have happened, for example, with material from one area in Cornwall. Some of the older Cornish mines like Dolcoath were first worked as copper mines. As the ore was followed in depth it changed more or less gradually from copper to copper-tin, tin-copper and then eventually to tin, although the copper-tin zone is usually not rich in the minerals of either copper or tin. Furthermore, where ingot metal forms are found they are almost always of pure copper, with only relatively few instances of copper/tin alloy, and then only at low tin contents of the order of 2 per cent. Such could, indeed, have been a smelting product from the use of a mixed ore, since ingot forms would be most likely to arise from primary extraction, but alternatively it might have come from the remelting of scrap. In any event, the tin content in these cases is lower than that employed most usefully for bronze artifacts. The use of mixed ores in other than the early development stages is thus considered unlikely.

Tin, unlike copper, does not occur in metallic form in nature, and nowhere in the world have tin minerals been formed *in situ* except where the mineralization is genetically related to granite, or to the granite family rocks—magmatic quartz veins, aplites, pegmatites, rhyolites and quartz porphyries or 'elvans' as they are known in Cornwall. Tin lodes may be mined some distance from the granite origin, as in the Cornish 'killas' and in metamorphosed sedimentary rocks elsewhere, but always in these cases the cassiterite is in veins or lodes consisting of material originally derived from the granitic magma—the molten mass from which the granite rocks were formed on solidification. The cassiterite in alluvial stanniferous deposits is derived from mineralized areas also intimately associated with these types of igneous rocks. Thus the occurrence of tin minerals can be related to types of rock.

There is strong evidence that most tin was

carried from acid igneous magma in the formation of granite, mainly in combination with fluorine and boron. By interaction with water vapour the metal was deposited as tin oxide, $\text{SnF}_4 + 2\text{H}_2\text{O} = \text{SnO}_2 + 4\text{HF}$. The hydrogen fluoride thus released attacked some of the existing minerals: e.g. feldspar to form topaz $(\text{AlF})_2\text{SiO}_4$, and tin oxide is usually found in association with fluorides such as topaz, tourmaline, fluorspar. The absence of tin in basic rocks may well be connected with the immobilization of the fluorine by its strong combination with alkalis.

Copper ores are widely found in igneous, sedimentary and metamorphic rocks in a great variety of forms. There is strong evidence, however, that in most cases the copper minerals were originally deposited by hot ascending solutions emanating from an igneous source.

The main difference between the occurrence of copper and tin is, of course, concerned with the high stability of cassiterite which has a negligible solubility in water, as compared to the solubility of copper minerals, particularly the sulphides (of which chalcopyrite, CuFeS_2 , is the most common), under natural weathering processes. Thus, in copper deposits, the surface zone is leached to low copper content and enriched in iron as limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) to form a reddish-brown 'gossan' or capping, referred to by miners as the 'iron hat', but still sometimes containing blue and green zones of the copper carbonates and silicates. The copper initially carried downwards in solution as soluble sulphate may be redeposited some distance below the surface in zones of 'secondary sulphide enrichment' to give chalcocite (Cu_2S) and bornite (Cu_5FeS_4), enargite (Cu_3AsS_4) and 'fahlerz'—tetrahedrite (Cu_3SbS_3 with replacement of some Sb by As). The upper zones may subsequently be oxidized to the carbonates, malachite and azurite, the oxide, cuprite, and the silicate, chrysocolla. Arsenic contents will be reflected in arsenates.

With tin, the richest sources have always been from detrital alluvial or eluvial deposits, i.e. stream tin, where weathering processes have destroyed the host rock and have deposited the chemically and physically stable, dense (SG

WHERE IS THE TIN?

6.5–7) and hard (Moh's hardness 6–7) cassiterite mineral in a natural physical concentrating process. In such detrital deposits, although they are often quite dilute, the cassiterite is present as grains or pebbles in a range of sizes up to ~30 mm., although larger pieces are not unknown. The particles are normally clean and not attached to any gangue (other unwanted rock or earthy substance).

Tin also occurs to a lesser extent as the sulphide stannite ($\text{Cu}_2\text{SFeS.SnS}_2$), which occurs with chalcopyrite and pyrite (FeS_2) and which resembles arsenopyrite (FeAsS) and enargite in its silvery semi-metallic appearance. The only clue to the presence of tin in the mineral is the increased weight. Stannite occurs in copper deposits (e.g. in Cornwall) and may thus have been the first source of tin to be alloyed with copper through the smelting of mixed sulphidic material, or of mixed oxidized material from such a deposit—where the cassiterite produced as finely divided 'needle-tin' or as more massive 'wood-tin' would be mixed with the oxidized copper ores such as malachite. In this category would come the use of stanniferous gossan from the oxidized cap of the deposit where the insoluble cassiterite remains concentrated in the iron oxide-rich material, which may have been used initially as a flux for smelting the main copper ore. Such upper zones in a mixed deposit could, in some cases, still be selectable as copper-bearing in that they would exhibit the colours associated with the basic copper carbonates.

The occurrence of these mixed deposits is, however, relatively rare, and whatever significance they may have had in the origins of bronze, the production of tin almost certainly became established quite early on the basis of separate cassiterite raw material.

TIN FROM PREHISTORY

In spite of the large amount of bronze of usefully high tin content which has been discovered from the Bronze Age, frequently associated with finds of pure copper, where we can be confident that in the main it was obtained by the purposeful addition of tin by some means to copper, finds of tin metal itself are strikingly rare. It is

strange that a metal which constitutes a major technological change in society and which presents no problems in extraction to those who are able to reduce copper ores, should be scarcely evident in its own right. This, of course, adds some weight to the arguments of those who maintain that bronze as an 'improved copper' was obtained by using particular ores or fluxes in the manufacture of the material without the recognition of tin as a separate metal. But some tin does exist. Dated earlier than 2000 BC the only finds known to the author have been a bangle made of two twisted strands of tin wire, found by Dr Lamb at Thermi in Lesbos and identified by Dr Desch (1936, 215). There is also a cast tin bottle and a tin ring from Egypt, probably of the later years of the eighteenth dynasty, but except for these four objects no articles made of pure tin or tin ingots have been recovered until after a date origin of 1500 BC, and even then the evidence is fairly scanty. Beads of tin occurred at Sutton Veney in Wiltshire, and were included with amber and faience in the famous Odoorn necklace from Drenthe in Holland. Coghlan and Case (1957) list items of personal adornment, armlets and a torc from the Irish Late Bronze Age which were made of tin.

In the context of the scarcity of tin finds it is necessary to consider the stability of the metal. The chemistry of the metal itself and the fact that objects do survive in good condition indicates that it is not particularly prone to complete corrosion and disintegration in deposits. A consideration which always has to be borne in mind, however, is that the allotropic modification to the grey tin ('tin pest') powder could occur in high purity material if it were subjected to low temperature for substantial periods. Although the allotropic transformation occurs at 13.20°C , much lower temperatures are necessary to induce the change in practice and even then, prior mechanical deformation may be required. The grey tin appears as isolated dark spots which spread over the surface of the metal. Since grey tin is less dense than normal β white tin, these spots of grey tin swell and break down to a powder. Most impurities, however, inhibit the

ANTIQUITY

transformation and it is this aspect which gives confidence that the relative scarcity of tin finds is unlikely to be primarily due to disintegration by the pest. From the chemical stability point of view, massive tin is only slightly attacked by any cold reagents, and with the survival of copper and bronze objects there can be no reasonable doubt that white tin would have survived also.

BRONZE AGE HOARDS

In founders' hoards it is common to discover 'bun' or 'plano-convex lump' ingots of copper, together with bronze artifacts and bronze scrap from previously used failed artifacts or failed scrap castings. The ingots represent the raw material which the itinerant founder received from the copper smelter, and with rare exceptions are always of almost pure copper without significant contents of tin, above that which might be expected as a normal impurity. As a typical example, the hoard from Stuntney Fen, near Ely, Cambs., which has been examined recently in great detail by Dr E. A. Slater and the author, contained 42 pieces of copper bun ingots. The original weight of these pieces is recorded by Clark at 43 lb. 2 oz. (1940, 58). The analysis of these by Dr Slater revealed only three with significant tin content (0.88, 1.13 and 2.08 per cent) and this in the context of a bronze hoard, where the majority of the artifacts contained 6-10 per cent tin.

The strange thing about this material, and the numerous other founders' hoards so far recorded, is the apparent absence of any raw material for the tin addition to make bronze, whether this was in the form of tin metal, a very high tin copper/tin alloy, cassiterite or a special flux derived from sulphidic deposits. If trade were in the form of already alloyed bronze from central smelting sites, then the unformed crude ingots of bronze would appear in hoards together with already used bronze scrap, but, in fact, the ingot material is almost always pure copper. The presence together of crude forms of copper and scrap or finished bronze implies that the founder also possessed a form of tin addition used to bring the melt up to the desired composition.

THE PROBLEM

Given the observations that there are very few tin objects from the Bronze Age, and that no tin ingot forms are found to match the raw copper so commonly associated with founders' hoards, what has happened to the tin-rich material that the smith must have had available to add to the copper he possessed to make bronze, and what form might it have taken?

As regards the use of metallic tin, the high chemical stability of tin and its oxide have been described and, although a possibility, the formation of grey tin powder from original white tin by allotropic modification is unlikely, in that some white tin has persisted from prehistory at quite high purities, and that we know that relatively small amounts of impurity are sufficient to prevent the change occurring. Tin is difficult to refine and the purity of smelted tin will depend directly on the purity of the cassiterite, and is not likely to have reached the levels where such allotropic change would occur. In any case, the presence of grey tin powder agglomerate in association with bronze hoards should have been noticeable. The remaining possibility is that the tin was added to the copper from a mineral form, without prior reduction to tin, even in conditions of itinerant founding. It is an interesting idea that because of the fact that stannite may contain substantial arsenic and because of its similarity of appearance with the arsenic-bearing arsenopyrite and enargite, experimentation by early smiths with stannite deposits, eventually leading to the use of oxidic tin material, marked the transition from arsenical copper to tin bronze. Even where no arsenical copper technology seems to have existed before, the initial use in this case of a material similar in appearance to that used to harden copper elsewhere could still point to stannite and thus to tin bronze.

The addition of tin to copper by a cementation process in which tin is reduced directly into molten copper from a surface covering of oxide tin materials and charcoal is practicable and has been demonstrated by the author. It is also evident from other recent practical work by Eaton (Eaton and McKerrell, pers. comm.) that arsenic and tin may be similarly added by

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WHERE IS THE TIN?

the use of sulphide minerals, to include stannite. Assuming a move from stannite to oxide materials in due course, the trade in tin to the founder could well have been in these mineral forms, to be used as such directly in the production of bronze. Perhaps initial trade in stannite, or in tin-rich limonite flux (gossan)—the earthy and predominantly dark brown material with occasional blue/green copper-rich areas, was replaced by cassiterite once the connexion of materials in terms of origin had been noticed and related to the intensity of effect on the copper to which they were added. The critical addition would have been identified, and purer, more concentrated, sources sought. These would take the form of placer deposits of cassiterite pebbles. There is little doubt that they were already aware of the relationship of waterborne, concentrated, placer deposits in relation to the occurrence of dispersed gold in its original host rock, and similar deduction could be applied to the occurrence of cassiterite, which in some cases could easily occur with such gold deposits, as has been noted.

That cassiterite became the main raw material in its own right must be assured in relation to the relative scarcity of mixed deposits, stannite or tin-rich gossans, and to the need for high tin sources to give ease of addition and a consistently high tin content in the bronze. The discovery of such concentrated sources would not have presented the same difficulties as today. The occurrence of near-surface waterborne oxidized deposits from weathering at large lump size, and other rich surface mineral concentrations, obviously would have been much more widespread than today. In the early days of mineral exploration in N America in the nineteenth century, where relatively little mineral exploration by man had previously occurred, surface gold and native copper were found at large size and locally high concentrations. Early man scavenged the surface of useful material built up over previous millennia, and the condition cannot be repeated and is scarcely represented today. It is not at all unlikely that coarse, readily recognizable surface placer deposits of cassiterite would have been available.

It is the aim of this article to suggest the possibility for the trade and use of tin as cassiterite, limonitic material bearing cassiterite, or stannite and secondly, to provide information as to the appearance of the relevant minerals in the field and tests which may be applied for the recognition of cassiterite. It is hoped that, armed with this knowledge, excavators may be alert to their possible existence, both in the context of association with hoards or smelting sites, and, possibly, in hitherto unknown small-scale ore deposits.

THE APPEARANCE OF TIN MINERALS

So far as occurrence in Europe and the Near East is concerned, the only minerals, and by far the most common, are cassiterite, SnO_2 , known as tinstone, and stannite, $\text{SnS}_2 \cdot \text{Cu}_2\text{SFeS}$. SnO_2 also occurs as souxite ($\text{SnO}_2 \cdot x\text{H}_2\text{O}$, i.e. agglomerated colloidal SnO_2), also known as wood tin because of its concentric 'tree ring' appearance. Whilst crystalline cassiterite may be found in lodes exhibiting the tetragonal form, where twinning is very common, the alluvial deposits are usually of more or less rounded pebble or stone form. While the mineral cassiterite is usually shades of brown to black from iron contamination, it may be almost any colour and be thus confused with others.

Stannite may be steel-grey, greenish-grey or bronze-coloured; in all cases there is more or less metallic lustre. While it may be confused with pyrite, chalcopyrite, tetrahedrite or arsenopyrite, in certain cases, the more striking and metallic appearance of all of these is hardly likely to have escaped notice in excavations.

Gossans will be similar in appearance to limonitic iron ore—earthy in texture and shades of brown in colour, but sometimes with streaks or zones of coloured copper minerals. Samples of Cornish gossan from the Woodwardian Collection in the Geology Department at Cambridge are illustrated (FRONTISPICE *a*). This collection was made in the late seventeenth century and illustrates material that would be difficult to find today. Three of the specimens exhibit copper coloration of the limonite, whilst the other contains a substantial amount

ANTIQUITY

of sulphidic remnant as chalcopyrite. FRONTIS-PIECE *b* illustrates the main forms of high concentration tin mineral and it is hoped that this will be of assistance to archaeologists in recognition, both in terms of the possible presence of the mineral in a smelting hearth or hoard context, or in recognition of an ore source associated with metallurgical activity.

IDENTIFICATION OF CASSITERITE IN THE FIELD

In addition to the appearance there are several simple tests that can be applied in the field to distinguish cassiterite.

The density (6.5-7) is the most obvious clue to its identity. Other brown to black minerals which might be confused with it in terms of appearance are of generally much lower density (e.g. Zircon 4.7). Brown to black oxide minerals of iron have densities in the range 4-5. Stannite also has a lower density of approximately 4.5.

The density (gm/cc) can be rapidly assessed by weight and volume derived from the displacement of water in a measuring cylinder.

A special reaction frequently employed to distinguish cassiterite is by cathodic reduction to tin metal using metallic zinc. The material is placed in a zinc metal cup or dish made from zinc sheet and dilute hydrochloric acid (equal parts concentrated acid and water) is added. After a few minutes the acid is poured off and replaced by clean water to wash. Where

the mineral has been in contact with the zinc it is reduced to a dull grey coating of metallic tin. Where the pieces of mineral are large enough, this may be polished on the palm of the hand or on cloth to give a bright silver-white coating. Alternatively, pieces of zinc or zinc dust may be used mixed with the mineral in a non-reactive container, but care must then be taken in not mistaking aggregated zinc for coated tin oxide material.

Whilst these tests would enable the identification of cassiterite itself fairly readily, and sulphide would be obvious from its appearance, the recognition of tin-bearing gossan would be less readily obtained. For this reason any dark brown earthy material which does not clearly belong to the natural strata should be recorded and set aside for laboratory examination.

CONCLUSION

The identification of tin sources in prehistory and the extent of trade from these sources is a fascinating study. The discovery of the tin raw material associated with this trade would not only largely identify the technology involved, but could also give clues to the ancient tin sources. It is hoped that with the information given in this article, archaeologists may be aware of the significance of what might otherwise appear to be uninteresting material in an excavation, and be able to recognize it.

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