

A RE-EXAMINATION OF AN ALLEGED STANNIFEROUS DEER'S-HORN FROM THE CORNISH TIN-BEARING ALLUVIALS

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Abstract

A portion of an antler, which was found in the tin-bearing alluvials of Pentewan, Cornwall, and which was reported by Collins (1881) to contain 2.60 per cent of syngenetic stannic oxide, has been shown, on re-examination, to be almost devoid of tin. (Of the 19 samples analyzed, 18 contained less than 10 p.p.m. Sn, whilst the remaining one, a surface sample, contained c. 296.)

Examination of thin and polished sections failed to reveal any cassiterite, but established that syngenetic pyrite lines some of the Haversian spaces and fills many of the smaller canals and the adjacent lacunae and canaliculi. The genesis of the pyrite is discussed.

It is concluded that either the original investigator examined a part of the specimen which was quite unrepresentative of the whole or his analysis and microscopy were in error. No evidence has been found in support of his contention that syngenetic cassiterite was deposited in the fossil.

INTRODUCTION

Because Edwards and Baker (1954) established that supergene cassiterite had developed from stannite in the zone of secondary sulphide enrichment at the Sardine Tin Mine, Queensland, the writer decided to re-examine a portion of a deer's antler (the property of the Royal Cornwall Geological Society) which had been found in the Pentewan alluvial-tin deposits of Cornwall (Fig. 1), and which was reported by Collins (1881) to contain 2.6 per cent of stannic oxide which he believed was deposited from cold surface water. It was also considered that the study might enable further details to be added to the still incomplete picture of the liberation of tin from the parent ore-body and the subsequent migration and deposition of this element in the adjacent soil and drainage system.

COLLINS' RESULTS AND OBSERVATIONS

Collins (op. cit.) makes the following points regarding the deer's horn in question :—

- i. It is probably a part of the antler of the red deer (*Cervus elephas*) and has a specific gravity of 2.7 : that of the unaltered recent horn of the fallow deer is only 1.26.

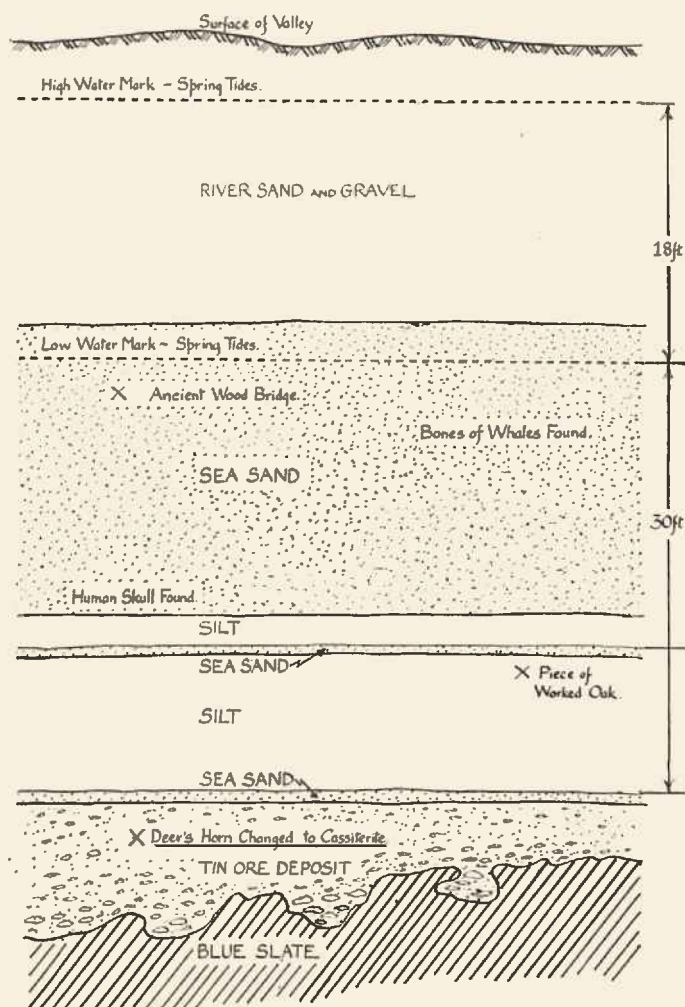


FIG. 1. Section of Pentewan alluvial deposit.

ii. It contains only 12 per cent of organic matter, whereas recent horn contains 62 per cent.

iii. The analysis of the fossil horn is :—

Calcium phosphate	...	...	80.04
„ carbonate	...	...	2.24
„ fluoride	...	...	0.50
Ferrous sulphide	...	...	1.66
Ferric oxide	...	...	0.62
Stannic oxide	...	...	2.62
Silica	...	...	0.22
Organic matter and loss	...		12.12
			100.00

iv. “The microscopic appearance of the horn, as seen in thin sections, shows that the oxides of tin and iron, and the iron pyrites, have found their way to the interior of each cell and are visible throughout the structure, although somewhat more abundant near the periphery than in the interior. The mode of occurrence shows that these substances reached the cells in a state of solution, and percolated through the walls. . . . we can only suppose that the tin was brought to the horn in the state of soluble salt, such as the fluoride or the chloride.”

In the same paper Collins claims that in the British Museum there are several fragments of deer-horn from Cornwall containing “a large proportion” of oxide of tin and that “in some parts the original horn structure seems to be almost entirely preserved or reproduced in oxide of tin, and there are even minute crystals of this substance visible in places”.

RESULTS OF THE RE-EXAMINATION

No cassiterite was recognised during the examination of several transverse and longitudinal thin-sections of the fossil horn, but pyrite occurs abundantly in the Haversian canals, lacunae and canaliculi, and locally the ground substance—particularly the outermost 2 mm.—is stained, and probably replaced, by brown ferric oxide.

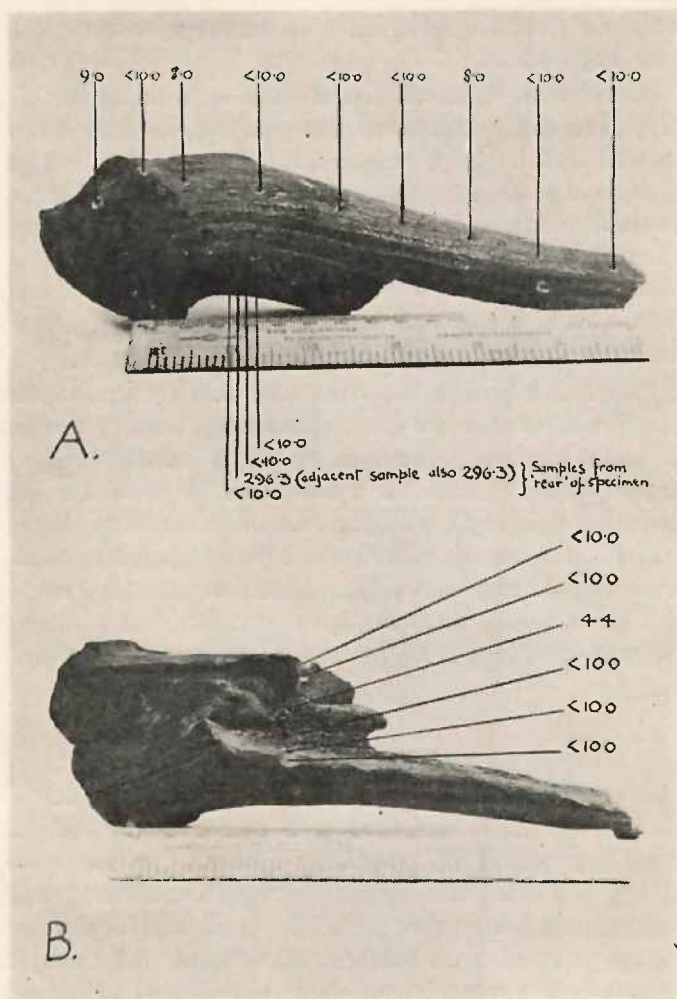


PLATE I.

- A. Photograph of the exterior of the fossil horn, showing sampling points and tin-content (parts per million).
- B. The interior of the horn showing sampling points and tin-content (parts per million).

That tin is virtually absent from that portion of the horn from which the sections were cut (and from where Collins obtained the material he examined) was confirmed by carrying out several tin determinations on c. 6g. — samples by the Beringer method. In no case was any tin found.

Because it was realised that if there were tin in the horn it might be irregularly distributed, nineteen samples were taken (by means of a small tungsten carbide drill) along the axis, around the periphery and across the diameter, and the tin in each of these was determined colorimetrically by the gallein method. In eighteen of the samples the tin-content did not exceed 10 p.p.m., but in the remaining one it reached 296. (Plate I.) A further sample taken from near the anomalous one confirmed the presence of a peripheral zone in which the tin content is comparatively high (216 p.p.m.)

Finally, as it seemed likely that fine sand (quartz, cassiterite, etc.) could become attached to the exterior of a horn by a veneer of ferric oxide, and might occur in the larger canals, having been washed in via the broken end, a portion of the specimen was decomposed by warming it with nitric acid and the insoluble residue was examined under the microscope. This was found to consist of small sub-angular fragments of quartz admixed with a few fragments of horn which would, doubtless, have been dissolved had the acid attack been somewhat more prolonged: cassiterite, however, was absent.

CONCLUSIONS

The present investigation has been disappointing in that it has failed to demonstrate whether cassiterite can or cannot be deposited by syngenetic means in tin-bearing alluvials. It has, however, established that either Collins examined a portion of the horn which was quite unrepresentative of the whole, or his analytical work and microscopy were in error. Furthermore, it seems abundantly clear that a deer-horn could become highly stanniferous as a result of "normal" fine-grained cassiterite being entrapped in the Haversian spaces, etc., and being cemented to the surface by limonite.

In view of the fact that some doubt must now be cast on the validity of Collins' work and conclusions, and because the question of the development of syngenetic cassiterite in alluvials is of considerable geochemical importance, it is hoped that this paper will

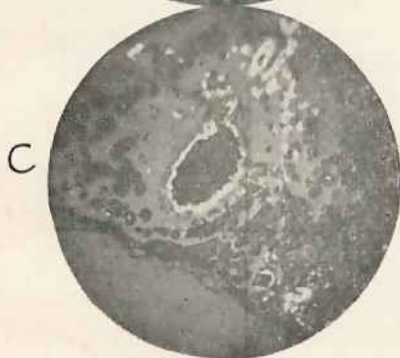
PLATE 2.



- A. Photomicrograph in ordinary light of a thin transverse section of the compact part of the horn, showing Haversian canals, lacunae, and canaliculi infilled with pyrite (black). (X370).



- B. Photomicrograph of a polished transverse section of the horn showing pyrite (white) lining fissures which intersect the surface. (X185).



- C. Photomicrograph of a polished transverse section of the horn showing pyrite (white) lining one of the Haversian spaces. (X185).

persuade the mineralogists of the British Museum to examine those specimens of Cornish stanniferous deer-horn which Collins believed to be in their collection: if this happens this communication will have been worthwhile.

A NOTE ON THE SYNGENTIC PYRITE OF THE HORN

The syngenetic pyrite in the horn is worthy of further comment. It occurs most profusely in the ochre-yellow compact intermediate part, and there it completely fills many of the Haversian canals and associated lacunae and canaliculi (plate 2, A). In transverse section some of the larger of these pyrite masses are cracked in such a way which suggests that they have been derived from gels. In longitudinal section crudely parallel pyritised zones are separated by zones which are essentially free from pyrite. Possibly this pattern reflects the paths along which iron-bearing solutions migrated. It seems likely that at least some of the sulphide sulphur used in the development of this pyrite was derived from the decomposition of the proteins of the horn by biological agents. It is also possible that protein-derived sulphide ions would diffuse from iron-free areas into the zones where pyrite deposition was taking place.

In the peripheral, 2 mm.-thick layer — which is dark-brown because of a considerable accumulation of limonite there — pyrite is only sparsely distributed, but it does tend to line the radial fissures which intersect the surface (plate 2, B), a fact which suggests that this pyrite may have developed from components which migrated into the horn: it also indicates that the limonite in the peripheral layer was probably deposited directly as such and is not a product of oxidation of originally deposited pyrite.

In the central spongy part of the horn most of the large Haversian spaces are lined with pyrite (plate 2, C). These linings — whose "free" surfaces are irregularly undulating — are of variable thickness and composed of loosely packed pyrite masses. Some of the components are crudely spherical and on occasion, at least, some of the spheres are hollow and possibly developed around spherical micro-organisms (though this has not been demonstrated). However, small pyrite cubes do occur and in one polished section several small octahedra were also noticed, so that a portion of the pyrite, at least, was probably deposited by "normal" inorganic means. Locally, associated with the pyrite masses, are aggregates of

distorted thin-walled cellular material which may be remnants of tissue originally occupying the Haversian spaces. Whatever their true nature, they are of interest in that some of them contain solitary small pyrite spheres of pyrite which may owe their origin to the work of micro-organisms. (See footnote.)

To summarise, there are indications that, in part, the syngenetic pyrite of the horn was deposited by inorganic means and in part by biological agents. Whilst the iron of the pyrite doubtless migrated into the horn, there is reason to believe that at least some of the sulphide sulphur used in the synthesis was obtained by decomposition of the proteins of the horn (probably by micro-organisms).

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Footnote. The writer has recently demonstrated the occurrence of framboidal pyrite (i.e., spheres of pyrite whose texture is reminiscent of that of a strawberry) in several Cornish lowland-peat deposits. Each of these bodies consists of a spherical micro-organism coated with pyrite. Further details will be reported subsequently.