

III. *Observations on the changes which have taken place in some antient alloys of copper.* By JOHN DAVY, M. D. F. R. S. In a Letter to Sir HUMPHRY DAVY, Bart. Pres. R. S.

Read November 17, 1825.

PERMIT me through you to lay before the Royal Society, the results of some experiments and observations on the incrustations of certain antient alloys of copper, which I trust may not be undeserving of notice, whether considered in connexion with the arts of Antient Greece, or in relation to the slow play of chemical affinities acting during a long period of time.

I shall commence with the most interesting object that I have examined since I have been in the Mediterranean, for which I am indebted to His Excellency Sir FREDERICK ADAM, His Majesty's Lord High Commissioner in the Ionian islands. This is a bronze helmet of the antique Grecian form, recently found in a shallow part of the sea, between the citadel of Corfu, and the village of Castrades. Both internally and externally it is partially encrusted with shells, and a deposit of carbonate of lime. The surface of the helmet generally, both under the incrustation, and where freed from it, is of a variegated colour, mottled with spots of green, dirty white, and red. On minute inspection, the green and red patches exhibit a crystalline structure, and the red very distinctly; and on examining them with a lens, they were found to be

formed of octohedrons of the red oxide of copper, intermixed with crystals of the same form of metallic copper. These crystals are most distinct at the surface; they even adhere to the calcareous crust, and may be detached with it, presenting well-formed facets towards the part from which they have been separated. Chemical examination shows that they are actually composed of metallic copper, without the least tarnish, and of the pure ruby protoxide of copper; and that the green rust consists principally of carbonate and submuriate of copper, and the dirty white chiefly of oxide of tin. The mineralizing process (if I may be allowed the expression) which has produced these new combinations, in general has penetrated very little into the substance of the helmet. The incrustation and rust removed, the metal is found bright beneath; in some places considerably corroded, in others very slightly. It proves on analysis to be copper alloyed with 18.5 per cent. of tin. Its colour is that of our common brass, and it possesses a considerable degree of flexibility.

An antient nail from a tomb in Ithaca, and an antient mirror from a tomb at Samos, in Cephalonia, have afforded me results very similar to the preceding, excepting that the mineralized part, consisting of oxide of tin, submuriate, carbonate, and protoxide of copper, each more or less collected apart from the others into little masses, has exhibited rather a crystalline structure than distinct well-formed crystals, and has been without any appearance of crystals of metallic copper. The copper in the mirror I have found alloyed with about 6 per cent. of tin, and a very minute quantity of arsenic and zinc.

I have examined a select number of antient coins, purposely chosen from the fine collection of Dr. DEMETRIO PETRIZZOPULO, of Santa Maura, to whose kindness I am indebted for them. The results too which they have afforded are in conformity with the preceding. As this part of my subject may be interesting to the antiquarian, as well as to the chemical enquirer, I shall treat it a little in detail. The very pale incrustations, consisting of a mixture of green and white particles, contain a large proportion of oxide of tin, and a little carbonate of copper, or submuriate of copper, or both. They appear to owe their light hue to the accumulation of the oxide of tin at the surface. The black incrustations owe their colour to the predominance of the black oxide of copper, which is commonly mixed with a little protoxide of the same metal, and a minute quantity of oxide of tin, and of the carbonate and submuriate of copper. The coins that I have examined with this crust have contained very little tin. The bluish-green incrustations consist chiefly of carbonate of copper, either without oxide of tin, or mixed with a small proportion of this metal. The emerald-green incrustations abound in the submuriate of copper, and the red consist almost entirely of the protoxide of copper. These two compounds I have never witnessed spread over the whole of a coin, but more or less mixed with rusts of a different kind, studding the surface in the form of little crystalline elevations.

It is natural to enquire—is there any connexion between the chemical composition of the incrustations of antient coins, and their texture; some being remarkably smooth, and as

it were polished, preserving admirably the original impression of the die ; whilst others are rough and deformed ? I am disposed to reply in the negative, not having yet discovered such a connexion ; excepting thus far, that the protoxide of copper, and its submuriate, frequently appear in minute crystalline elevations rising above the surface of the coin. Generally, I suspect the difference of texture in question depends on other circumstances, and very likely in different degrees of rapidity of operation of the mineralizing cause.

It is a curious question for consideration, the manner in which the crystalline structure is acquired exhibited by these incrustations ; and still more so, how crystals are formed, especially such as were discovered on the helmet, and on the adhering calcareous deposit. There being no reason to suppose deposition from solution, are we not under the necessity of inferring, that the mineralizing process witnessed in its effects, depends on a slow motion and separation of the particles of the original compound ? and, must we not conclude, that this motion is connected with the operation of electrochemical powers ?* Supposing the oxides first formed upon the bronze in a state of negative electricity, with respect to the metal, their agency, in a long course of ages would be to separate the least oxidable metal, the copper, in its pure form ; and all the changes are such as may be accounted for from agencies of the same kind, but of different intensity. And may not similar explanations be given of other like

* The separation of the copper from the tin in the bronzes found in the ancient cities destroyed by volcanic eruptions, must be referred to another source ; namely, the crystallizations dependent upon degrees of heat a little below the point of fusion of the alloy.

phænomena, which often seem to occur in the mineral kingdom? These facts offer an obvious practical application, both in determining the antiquity and genuineness of ancient works of art; for ærugo of the kind which I have described could not be successfully imitated by any artificial processes; and a very slight chemical examination, or even one by the lens, would be sufficient to expose any fraud attempted to be practised by substituting modern imitations for ancient works.

I am, most truly yours,

J. DAVY.

To Sir H. Davy, Bart.

Pres. R. S.