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NOTES ON DIFFUSION IN ANCIENT ALLOYS

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INTRODUCTION

Ancient alloys offer a number of physico-chemical features that are connected with the fact that they are ancient. The diffusion of impurities in the course of time is one of the phenomena that contribute to give these alloys such specific characteristics which, if known, can be used to interpret some of the results yielded by the analysis of archaeological objects.

In the particular case of ancient copper-silver coins, we shall study the influence of diffusion in the course of time on the distribution of some of the impurities that are most common with such monetary alloys.

METHODS OF APPROACH

Analyses were made at the surface of the coins at four different points of the field, generally in the reverse field which is wider than the obverse field. The coins were then worn in a parallel direction to the surface of the field. Analyses were carried out at various levels, on the perpendiculars to the field that pass through the surface points analysed.

Analyses were performed by emission spectrometry (condensed spark). As the lines of impurities are often not very apparent, the background was corrected on the graphic recording of the spectra. For each spectrum, the ratio of the intensity between the lines of impurities and the same silver line was measured. The results for each impurity were plotted onto a graph, with the ratio between the concentration of the impurity (relative to silver) at a given level to the concentration of the same impurity measured at the surface plotted as the ordinate, and the depth of each level plotted as the abscissa (Appendix II).

MATERIAL STUDIED

Analyses were first carried out on various specimens belonging to the 177-211 B.C. series of Roman denarii, which had previously been studied from another angle and reported in this bulletin (Condamin and Picon 1964a). We should like to recall that, with these coins, silver percentages vary from 40 to 50%. A few older denarii, dating back to the Republic and the beginning of the Empire, were added to the first ones because of the high silver content. Lastly, a few antoniniani of Caracalla were also studied with them.

EXPERIMENTAL RESULTS

The two diagrams (figures 1 and 2) are a fairly accurate summary of the whole of the phenomena that were observed. Figure 1 was obtained from a denarius of Augustus (RIC p. 90, n° 351 - 95% Ag) and figure 2 was from an antoninianus of Caracalla (RIC p. 249, n° 258 - 45% Ag).

INTERPRETATION OF CURVES

(i) Curves in figure 1 are for elements that are more oxidisable than silver: Cu, Pb, Sn, and are easily explained by the standard theories on oxidation (Bénard 1962, 1964). Diffusion may result from mere capture, near the surface, of the

elements that have most affinity for oxygen. Let us note that the formation of corrosion substances such as carbonates and hydrocarbonates above the metal surface does not modify at all the fundamental mechanism of diffusion. The latter always occurs through capture of the oxidisable elements near the surface. Such capture explains both the superficial enrichment in impurities and the impoverishment of areas situated right under the surface, as well as the bell profile of concentrations inside the coins. These features are shown in figure 1.

An important remark follows, concerning the localisation of impurities that are more oxidisable than silver. Such impurities seem to be concentrated under the form of oxides or of carbonates *above* the metal surface (Appendix II). Even if the alloy is rich in copper and internal oxidation of this element results in the formation of an important layer of corrosion substances above the metal surface, it looks as if there was a definite concentration of impurities that are more oxidisable than copper at the base of this layer, near the primitive surface of the alloy (Appendix II). This, as a matter of fact, agrees with the fundamental laws of oxidation in alloys (Bénard 1962, 1964), in the hypothesis of extremely slow phenomena. The part which might be played by the solubility of impurities at ordinary temperatures in the basic metal has not been very apparent till now.

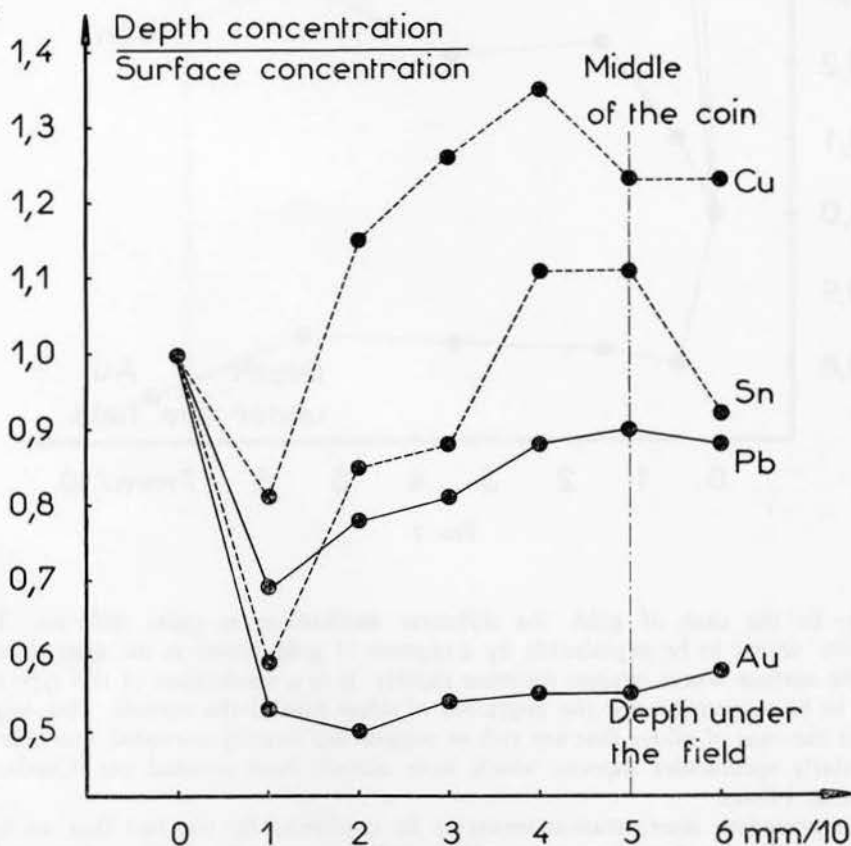


FIG. 1.

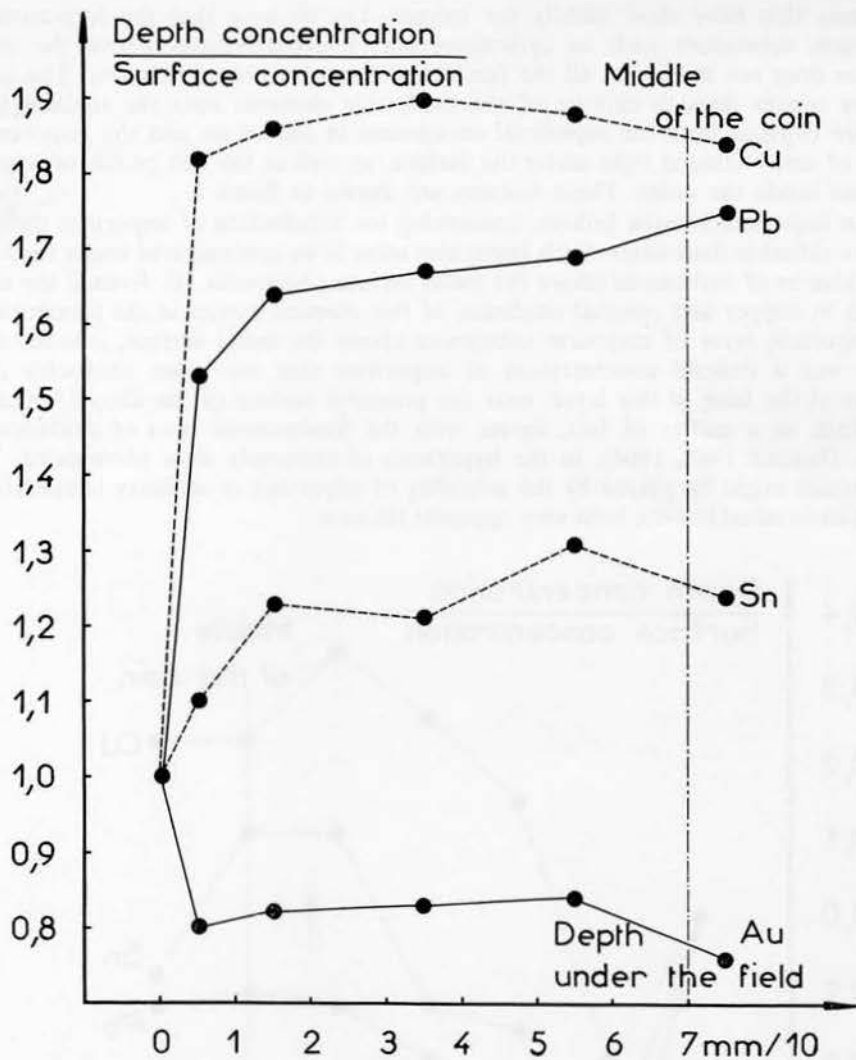


FIG. 2.

(ii) In the case of gold, the diffusion mechanism is quite different. This diffusion seems to be explainable by a capture of gold atoms in the area situated near the surface where stresses decrease rapidly. It is a mechanism of this type that seems to be responsible for the migration of silver toward the outside. This migration, in the case of alloys that are rich in copper and heavily corroded, can take on particularly spectacular aspects, which have already been pointed out (Condamin and Picon 1964a).

The preceding interpretation seems to be confirmed by the fact that we have noted no diffusion of gold atoms in alloys rich in copper (Cu 20% to 60%) when the oxidation of this element is responsible for important stress in the area situated

near the surface. This interpretation is also indirectly confirmed by the *very frequent* disappearance of the superficial enrichment in oxidisable elements when coins are being cleaned. The curve of gold, on the contrary, does not appear to be very much affected by this operation, which could be easily explained if the gold enrichment was situated under the surface of the coin and not above.

It therefore looks as if it were possible to pass from a diagram of the figure 1 type to a diagram of the figure 2 type, merely through a cleaning operation of the coins. This explains both the fact that the second type of diagram is more frequent than the first, and the almost constant presence of superficial gold enrichment in all ancient coins.

APPLICATION TO PROBLEMS IN ARCHAEOLOGICAL ANALYSIS

It is obvious that phenomena connected with diffusion play a prominent part in the study of ancient techniques in metal coating: gold-plating, silver-plating, etc. In particular, when an ancient object in a perfect state of preservation has appeared, not requiring energetical scraping of the surface, superficial concentrations which are extremely high and due to mere diffusion can sometimes be found. For example, the surface of some copper-silver coins with X-ray fluorescence gave a lead rate of about 20% while the total concentration of this element was inferior to 1%. Now, in this case, metallographic and X-ray study allowed the definite conclusion of diffusion. It looks as if it was such phenomena that have sometimes been interpreted wrongly as intentional plating (Weill 1964). In many other cases, much greater prudence should also have been used in the interpretation of results yielded by analysis (Salin and France-Lanord 1946, Banderet and Bastien 1961).

The cases just mentioned however remain fairly exceptional. The usual scraping of the surface of almost every ancient object, more or less corroded, decreases the risks due to superficial enrichment in impurities. Excellent results deduced from the statistical interpretation of semi-quantitative analyses of impurities at the surface of coins are sufficient to prove the point.

Let us lastly add that if ancient coins could be had that had never been cleaned, it would be very useful to know, for each one of the impurities, what fraction of it has passed to the outside in the course of time.

APPENDIX I

With the condensed spark technique, the intensity of spectra taken from the surface of ancient coins is always much superior to that of spectra from the internal areas. A number of analyses performed through arc spectrography and X-ray fluorescence have allowed the preceding results to be checked, on the hypothesis of important perturbations in the emission of the superficial layer. It does not appear that these perturbations can alter the general results given here.

APPENDIX II

The X-ray diffraction diagrams ($\text{MoK}\alpha$) which are taken with an incident beam making a small angle, inferior to 10° , with the field of ancient copper-silver coins, allow the following remarks to be made: in the case of denarii whose percentage of silver ranges between 40 and 50%, the diagrams of most specimens show the bright lines of oxide Cu_2O and the very much dulled lines of copper. It is

easy to understand that if X-ray fluorescence analysis is carried out under similar geometrical conditions, the copper emission will be greatly reduced owing to the transformation of a part of this metal into less compact oxide. For higher silver-contents, it becomes more difficult to show the superficial oxidation film, but we think that this superficial oxidation, in the condensed spark technique and in X-ray fluorescence, always constitutes the main factor of the superficial enrichment (Condamin and Picon 1964b).

It seems useful to point out here that if care is taken to choose coins that were strongly drawn in the course of minting, the X-ray diagrams which have been already mentioned, show the orientation of the crystals in the drawn areas of the field. Now, in such cases, the oxide Cu_2O which has replaced the copper grains of the alloy near the surface has kept the same crystallographic orientation of these grains. On the other hand, the Cu_2O formed above the surface has lost its orientation. In the same way, the lead and the tin oxides that frequently appear in such diagrams also lose their orientation. All these oxides which appear above the surface are formed through diffusion, without any epitaxy. It is quite certain that lead always appears without any orientation in coins in which this element is plentiful, but what should be stressed here is the superficial concentration of elements whose rate remains very much inferior to 1% in the other parts of the coins, and the opposition between the two kinds of Cu_2O which is formed either on the spot or after diffusion.

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