THE INFLUENCE OF CORROSION AND DIFFUSION ON THE PERCENTAGE OF SILVER IN ROMAN DENARII

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INTRODUCTION

The exact chemical composition of an ancient coin in its present state can be determined at present by means of non-destructive methods; in particular the method of activation analysis seems to be becoming more widely used in the study of ancient coins. Yet, in numismatics, an important problem has to be dealt with: to what extent is the chemical composition of a coin, in its present state, representative of the chemical composition of this coin at the time of its minting?

We shall concern ourselves with this problem in the case when the coins are copper-silver alloys. After having pointed out the causes which may produce a difference between the original and the present compositions, we shall discuss quantitatively the variations of the percentage of silver and the average frequency of these variations.

MATERIALS USED

The following observations and measurements have been carried out on a series of 90 Roman denarii, from the period 177-211 A.D. We were able to use half of each coin, the other half having been used a few years ago, for a chemical analysis.[1] The coins which have been studied were divided into two sets of approximately equivalent numbers. The average silver-content of the first set was about 72%; that of the other one about 47%. The division of the denarii into two sets, one with high silver-content and the other with low silver-content, results from historical considerations (devaluation of Septimius Severus 194 A.D., see legend fig. 4). Some exceptional specimens deviate considerably from the relevant average value quoted above (corrosion, bad manufacture, intermediate coinage, etc.). This purely historical classification is only used in fig. 4 and its legend. In the remaining part of the text, the expression "denarii with low silver-content" means *all* denarii whose original percentage of silver was below 55%, and likewise "denarii with high silver-content" means *all* denarii whose original percentage of silver was above 55%.

The denarii studied come from different sources; so we may assume that the frequency of the phenomena observed represents the probability of finding such phenomena in ancient denarii in general.

CAUSES OF THE VARIATIONS IN THE RELATIVE SILVER-CONTENT WITH TIME

The only change that may occur, in the course of time, to a coin of copper-silver alloy is a variable loss of the most oxidizable element: copper. There is thus an increase of the average percentage of silver. This does not eliminate the possibility of a decrease in the relative silver-content at some particular points within the coin. The phenomenon of diffusion, which will be dealt with later, in particular may produce such a result. However, regarding the whole coin, the only decrease of concentration which will be seen is that of the copper. The principle phenomena

FIG. 1. Magnification × 50. No metallographical attack. Cross-section of a partly oxidized denarius. Average percentage of silver at present: 64%. Percentage of silver in the central part: 48%. The copper grains transformed into Cu_2O appear in grey. Note the distinctness of the separation between the two regions (consequence of diffusion).

responsible for variations of chemical composition are corrosion and diffusion. In the observation of these changes we shall limit ourselves to those having immediate archaeological consequences.

Corrosion The phenomenon of surface corrosion is deliberately ignored here. It plays a prominent part in surface enrichment but this enrichment has only a negligible effect on the average composition of the blank. On the other hand, internal corrosion entails an important increase of the percentage of silver. It may appear in two different forms often simultaneously in the same coin. (Appendix I)

(a) There may be within the coin a conversion of the copper grains of the alloy into the oxide Cu_2O. On the whole, the texture of the alloy does not change; the particles of oxide fill the place of the original copper particles. This transformation results in a volume increase. The volume of Cu_2O is about 1.7 times as large as the volume of the corresponding copper. Thus, as the oxidation proceeds, it is necessary for the copper to diffuse toward the surface, where it will be either eliminated or involved in the formation of various corrosion products. The analyses made by emission spectrometry (condensed spark) and measured at different depths in the partly oxidized coins (fig. 1) confirm this view.

If we take into account the possible diffusions—which will be dealt with later—we may assume that the original composition of the coin is generally little different from that of the inner portion not reached by the oxidation. This is so, for example, for the following cases, the second of which is illustrated in figure 1 and the third in figure 2.

Present total silver-content	*Silver-content of the non-oxidized interior portion*
81%	71%
64%	48%
59%	49%
58%	45%

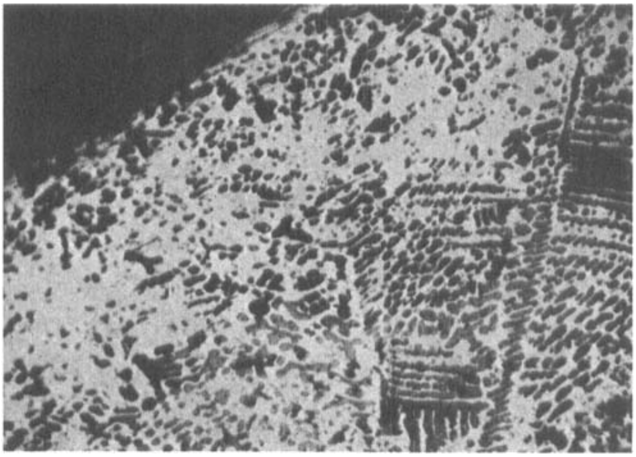


FIG. 2. Magnification × 100. No metallographical attack. External part of an equatorial section of a partly oxidized denarius. Average percentage of silver at present: 59%. Percentage of silver in the central part (not visible on the negative): 49%. The pits appear in black, the copper grains appear in grey.

The enrichment is often greater than that which would result from simply replacing the copper by Cu_2O. This is because numerous corrosion pits frequently appear at the surface, at the expense of the particles of oxide. (fig. 2)

Almost complete oxidation of the alloy (volume oxidized greater than 80% of the total volume) was found in more than 10% of the 90 coins which were examined. The denarii affected by such an oxidation can be divided as follows: 5 of a high silver-content, 4 of a low silver-content. The others show only a weak internal oxidation. It should be noted that denarii of a high silver-content are a little less numerous than those of a low silver-content among the 90 coins dealt with (36 to 54).

Among the nine heavily oxidized coins indicated above, the fraction of the copper which has been lost compared with the amount existing originally in the whole coin varies from $\frac{1}{3}$ to $\frac{1}{2}$.

(b) The phenomenon of corrosion may take a second form, characterized by the predominance of pits. However, the latter are always accompanied by a more or less extensive oxidation.[2] In most cases the pits are limited to the volume of the grains. Larger pits are very rare. They are not, of course, pits or fissures initially present and more or less increased by corrosion; they always remain very localized accidents and are involved but little in the variation of the composition.

As a rule, the corrosion with formation of pits at the expense of the copper is a phenomenon more confined to the surface than the oxidation previously discussed, but its influence on the variations of the percentage of silver is important because of the almost complete disappearance of the copper particles affected by this corrosion. The very nature of this corrosion accounts for an extremely variable decrease of the proportion of copper in the corroded part. When the part is extensive enough to be easily studied, it is found that the quantity of copper that has disappeared is generally greater than two-thirds of the copper originally present in the corroded layer.[3]

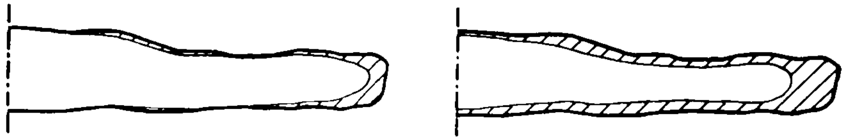


FIG. 3.

The frequent importance of this kind of corrosion all around the circumference of the coin accounts for the large volume of the corroded part, although this corrosion is generally superficial. For instance, the volumes hatched in fig. 3 form one sixth and one half, respectively, of the total volume. The disappearance of two-thirds of the copper in these parts causes the relative silver-content to change from 47% to 50% and 57% respectively (fig. 3). The coins that have lost at least one-fifth of the copper initially present are 5 in number (out of 90). They belong to the set of the low-silver content coins. The upper limit of the fraction of copper lost is one-third. This loss of copper is thus less important than in a simple oxidation; but we must not forget that we have arbitrarily distinguished between two phenomena which, in fact, are connected.

Diffusion Interpretation of the diffusion phenomena is very complicated. We must separate effects arising from segregation and diffusion occurring during minting from those resulting from slow diffusion in the course of time. Only the latter is of interest to us. Though the problems to be solved are still numerous, some points are sufficiently well established to enable us to determine the role of diffusion in the variation of the relative silver-content with time. Here we shall deal only with the diffusion of the major constituents: copper and silver. This diffusion arises essentially from the existence of a concentration gradient or internal-stress gradient. The general principles were already given in this journal.[4]

(a) The diffusion of the copper may result from the existence of a concentration gradient created by the elimination at the surface of this element by corrosion. The atoms of copper carried away by diffusion toward the surface of the coin may, in turn, be eliminated; hence a progressive enrichment in silver of the coin will occur. The role of diffusion is obvious in the mechanism of corrosion in which oxidation predominates but it also plays a part in the formation of pits at the expense of copper grains. On the other hand, the action of this diffusion becomes quickly negligible in the interior of the coin as one moves away from the corroded layer. Concerning the coins studied, it does not seem that we could ascribe to this phenomenon a loss of copper in the non-corroded portion greater than one-twentieth of the amount originally present in this part. Actually, only diffusion in the inner part of the corroded layer may have an effect upon the over-all percentage of silver. Note that a similar mechanism cannot be invoked for silver, a metal nobler than copper, except in the case of original segregation. Besides, in that exceptional case, the diffusion occurs without any component being eliminated.

(b) The second mechanism of diffusion, the effects of which are observed in ancient coins, arises from the existence of internal stresses created at the time of the minting. The internal-stress gradient controls the relative displacements of the atoms of copper and silver. These are inclined to migrate toward regions of low stress, especially toward the surface of the coin. This diffusion causes local rearrangements without any loss of the constituents. It has thus no influence on the over-all composition. Yet, its importance is very great in other respects (Appendix II) and we must take it into account in the estimation of the original composition of the coin starting from the composition of the inner portion which is not corroded.

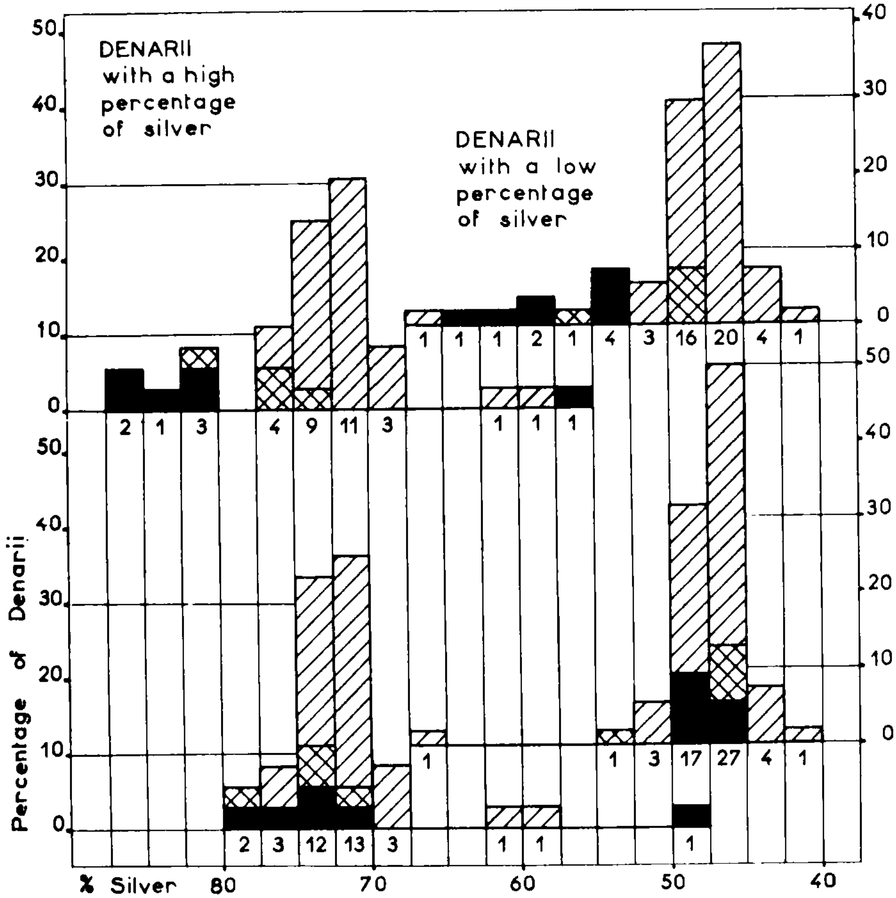


FIG. 4. The series of denarii of a high silver-content includes:

a) 33 coins from the period 177 up to and including 193 A.D., previous to the devaluation of Septimius Severus (194 A.D.). (The 3 coins with a percentage of silver less than 65% date from the year 192.)

b) The 3 coins of the year 196 represent a very particular coinage (Albinus at LYONS) apparently maintained in the old percentage of silver by this rival of Septimius Severus.

The series of denarii of a low silver-content includes 54 denarii from the years 194-211 A.D. Most of them come from Rome.[6] The two upper diagrams represent, for each of the preceding series, the present dividing up of the coins in terms of the percentage of silver known thanks to chemical analysis. The number of the coins in each interval of percentage is indicated below the corresponding column. The two lower diagrams show how the coins were probably divided originally. The black parts correspond to denarii which have lost more than one-fifth of the copper originally present. The cross-hatched parts represent denarii having lost from one-fifth to one-tenth of copper.[7]

GENERAL CONSEQUENCES

To sum up the consequences of the preceding phenomena it is sufficient to mention that about 15% of the coins have lost more than one fifth of all the copper originally present and that this loss does not exceed one half in any case. To this may be added a few intermediate cases, in which the loss of copper, less than in the preceding case, is yet greater than one tenth (this value being regarded as the limit prescribed by the precision of the measurements). The number of the intermediate cases seems to range from 5 to 10% approximately.

As the origins of the coins studied are varied, these values are not likely to be very different from the average values that would be observed in all Roman denarii.

The influence of the loss of a fraction of the copper on the over-all composition is, of course, much more important for the low-silver content coins than for those of a high silver-content. For instance the initial values of 47% and 72% would become 53% and 76% respectively after the loss of one fifth of the copper; they would become 64% and 84% after the loss of one half of the copper.[5]

The importance of the differences due to the preceding phenomena is illustrated in the diagrams of fig. 4. These diagrams clearly show that the percentage of the large differences is too small to have an influence on the characteristic median of each of the sets. It will always be so for the series where the relative silver-content of the coins varies little.

It is advisable to be cautious when the composition of certain coins belonging to a large group shows, compared to the median of this group, an over-all enrichment in the range of those which we have discussed. On the other hand, particular attention must be paid to the case of monetary treasures. If the conditions of burial were the same for the various coins found and if these conditions were favourable for an increase in the percentage of silver it may be assumed that this increase is general for the treasure considered.

A FEW REMAINING PROBLEMS

As a rule, it is of interest to compare the theoretical conclusions drawn from the observations with the results of additional measurements and observations. Besides verifying the general character of the preceding phenomena, it would be particularly interesting to determine the influence of factors such as the thickness of the coin and the manufacturing process, etc. on these phenomena.

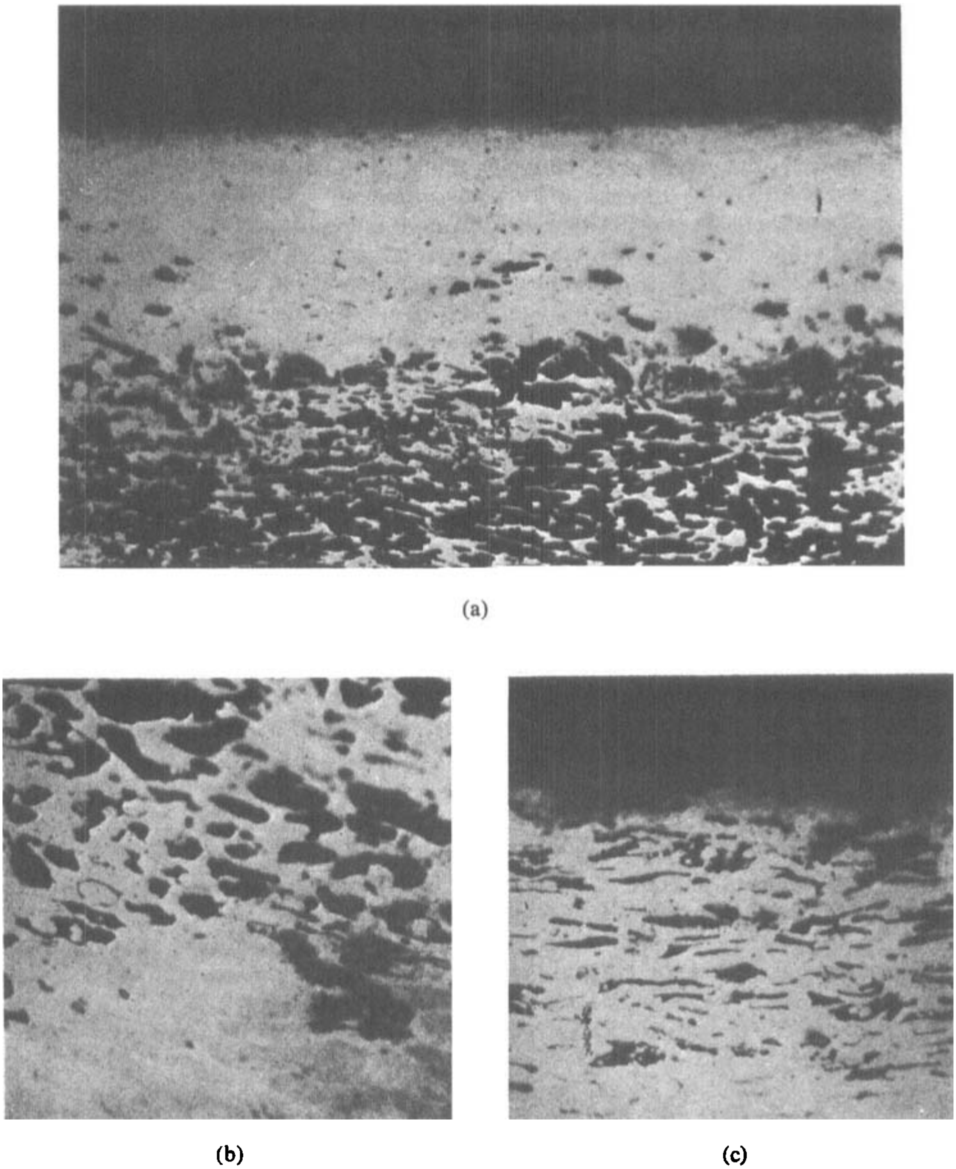
Moreover the conditions under which the coins were preserved would require a special study.

Research on diffusion should be carried out. Especially for the high percentages of silver it is necessary to determine the effects of the concentration gradient. For these percentages it would seem that this gradient might play a part not to be neglected even outside the corroded layer.

Furthermore, it seems possible, thanks to non-destructive testing processes, to detect the states of corrosion responsible for the differences between the original and the present compositions. This problem is being studied.

APPENDIX I

It is very important to stress that the state of corrosion visible on the surface is nearly always unrelated to the existence of internal corrosion. On the contrary, the outward aspect of the coins, the present composition of which is considerably



(a)

(b) (c)

FIG. 5. Cross-section of a partly corroded denarius. Average percentage of silver at present: 53%. Percentage of silver in the central part: near 45%.

a) Magnification × 200. The silver layer appears above the initial alloy the copper grains of which were dyed in black. A thin corroded layer separates the two regions.

b) Magnification × 600. No metallographical attack. Detail of the corroded layer which shows the progressive replacing of the copper grains by silver.

c) Magnification × 600. No metallographical attack. Detail of a part of the silver layer near that represented in a) and which shows numerous traces of the initial copper grains.

different from the original is, on the whole, much better than that of the coins unattacked by internal corrosion. We are concerned here with a secondary effect due to the diffusions involved in the very act of this internal corrosion. (cf. Appendix II)

APPENDIX II

Diffusion due to the existence of an internal-stress gradient seems to play a prominent role in the present heterogeneity of the ancient monetary alloys[7] and in the concentration of the impurities at the surface. The addition of effects due to both types of diffusion in the regions near the surface is responsible for a spectacular transformation of the alloy. We can notice (fig. 5) the progressive replacing by silver, which has diffused under stress, of the copper grains of the alloy gradually eliminated by diffusion due to the concentration gradient. There results from this, in the vicinity of the surface, formation of a compact layer of silver the thickness of which may attain 0.2 mm locally. It is a mechanism of this type which is responsible for the very beautiful aspect of numerous ancient coins and especially of those for which internal corrosion is extensive.

REFERENCES

1 J. Guey, Rev. Num. 1962, 73-128.
2 The corroded part presents the aspect of the more external region visible on fig. 2, but it reaches a more important part and the region of pure oxidation disappears almost completely.
3 The remarks previously made concerning the identity of the internal composition in the unattacked part and the original composition are also valid here.
4 A. P. Hornblower, *Archaeometry* 5, 1962, 108-112.
5 The loss of 1/10 of the copper would result in a percentage of silver of 50% and 74%.
6 J. Guey, *Rev. Num.* 1962, 73-128.
7 For further details (from the historical point of view) see J. Guey, *Rev. Num.* 1965 (in the press).
8 J. Guey and J. Condamin, *Rev. Num.* 1961, 51-73.