

**Antique AE Coins Depatination Experiment**  
**Composition Comparison Patina/Core Material - XRF Measurements**

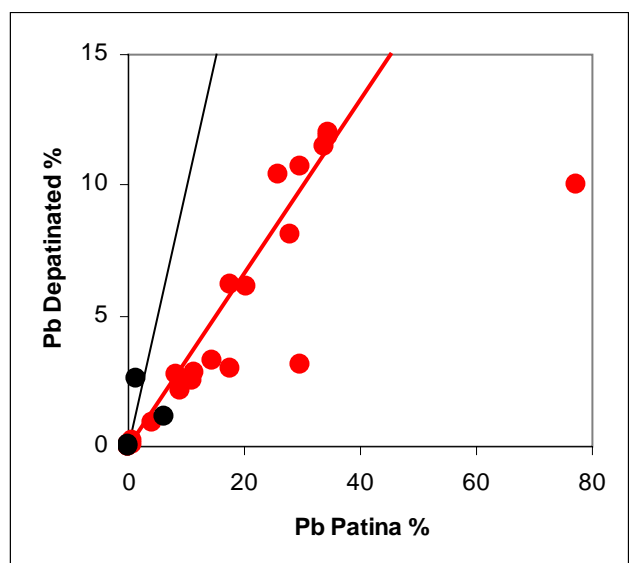
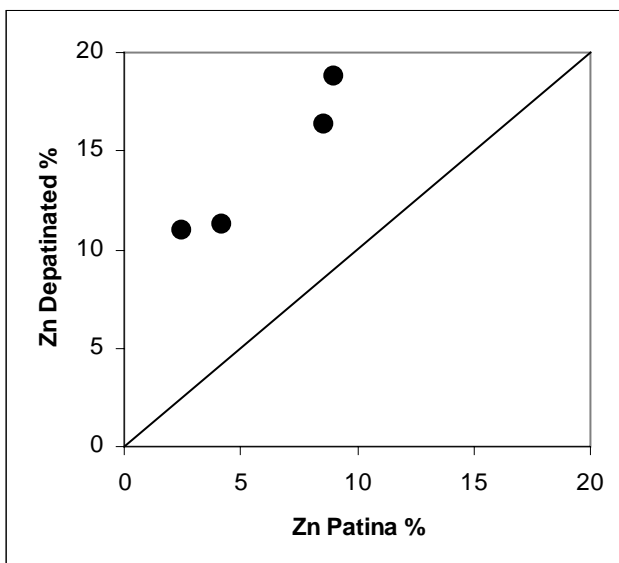
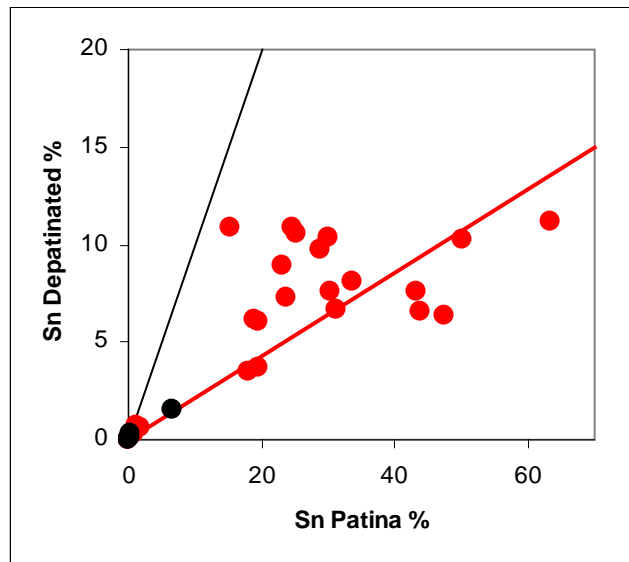
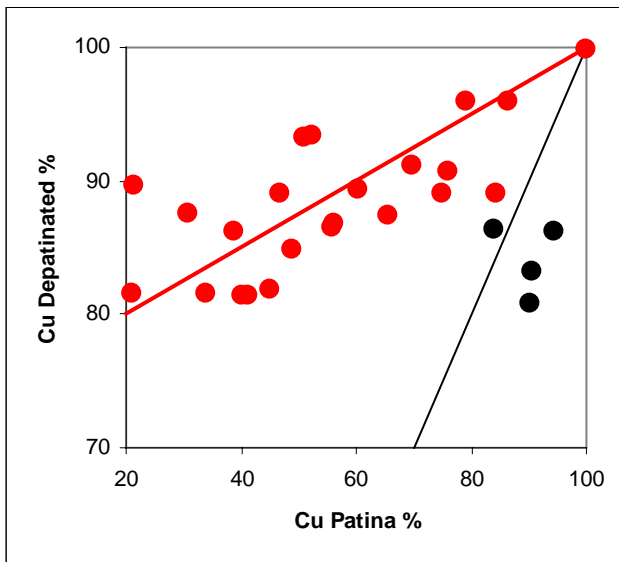
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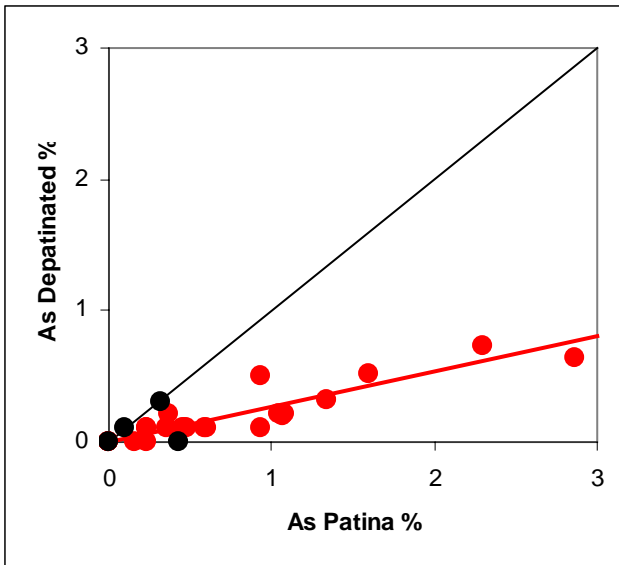
Preliminary evaluation of presently available data.

Material composition in the patina layer was measured on the original coin over the whole surface on an X-Ray Fluorescence facility. The patina was then removed by rigorous grinding and the measurement repeated. The experiments are still in progress and will last several more months.

Specimens for the investigation were provided by the members of the "Arbeitskreis Experimentelle Numismatik": Walter Neussel, Wittlich; Dietrich Klose, Staatliche Münzsammlung München; Florian Haymann, University of Freiburg; and Yannis Hourmouziadis, Falkensee.

Assuming that the core material consists primarily of Cu, Sn, Zn, Pb, and As, measured data was corrected to give 100 % for the sum of these elements. The results are shown in the following diagrams where concentrations after removal of the patina (core) are plotted against the patina value. Coins containing zinc (brass) behave somewhat differently and are distinguished with solid black symbols. The black straight lines indicate equal concentrations in the patina and the core material. The red straight lines indicate a very rough linear correlation (phenomenology) between the patina and core concentrations.

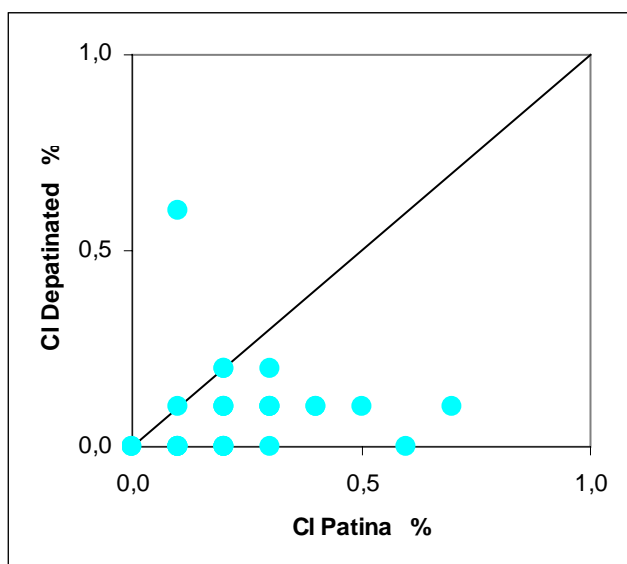
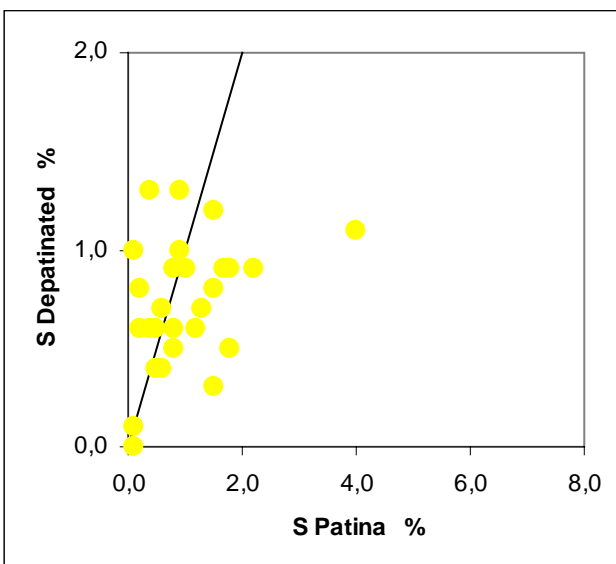


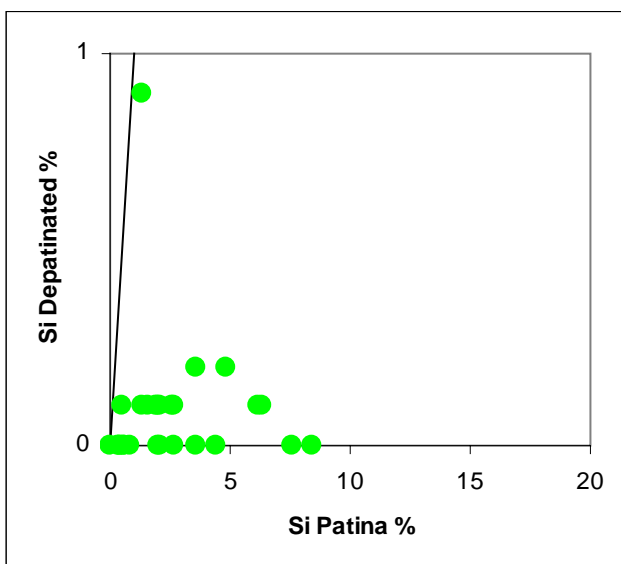
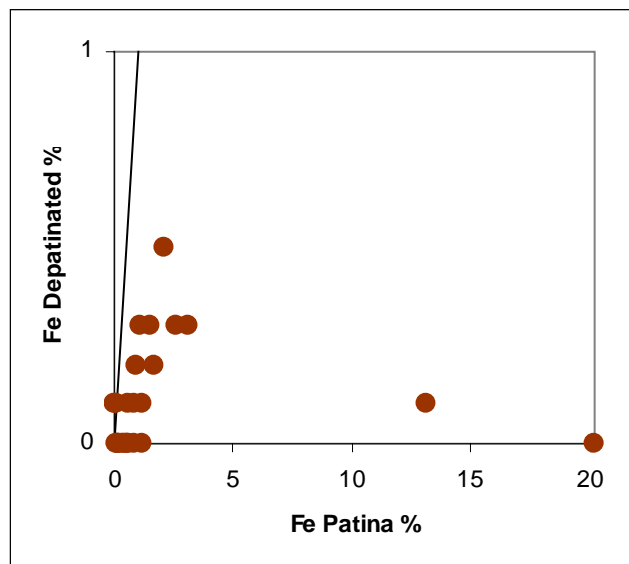
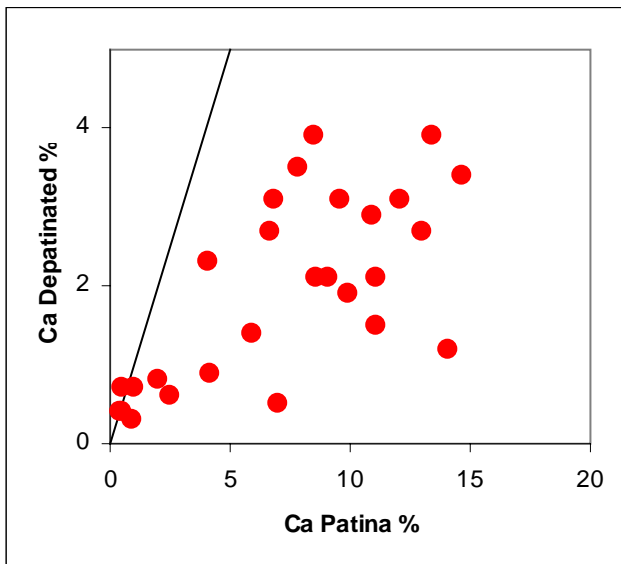
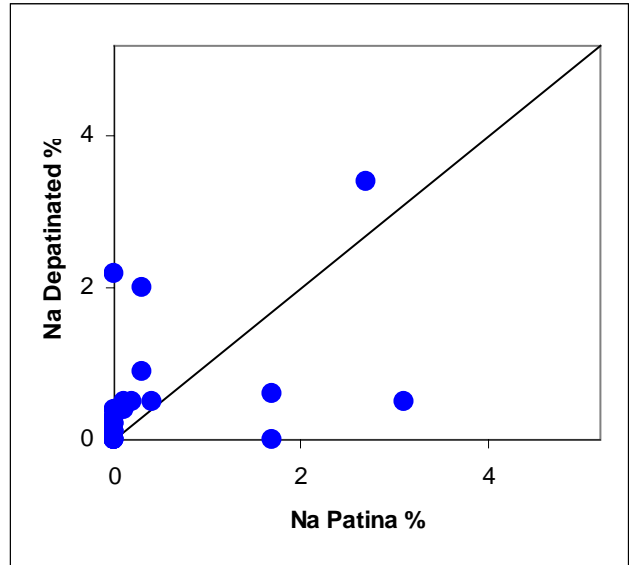
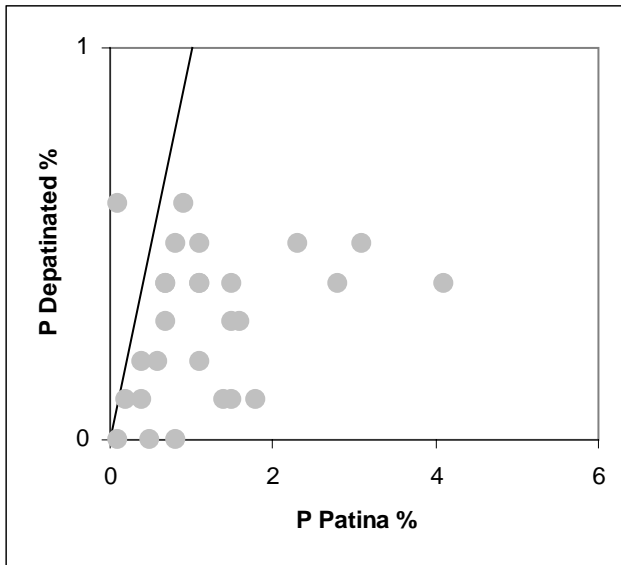


The results illustrate the known processes in the patina layer and will only be discussed shortly here.

- Cu is a rather volatile element. The chemical reactions during the patination process release a large portion into the ambient environment. Concentration in the patina can be less than half the value in the core material.
- Zn is even much more volatile. A major portion in the patina is diffused chemically into the surrounding material. Cu concentration in the patina can be higher than in the core, if the loss of Zn is stronger than that of Cu. It could also be possible that the chemical reactions of Zn during patination inhibit the release of Cu, however, this would require a chemical investigation.
- Sn appears merely to be enriched in the patina. Concentration there can be four times that of the core material.
- Pb behaves similarly, the enrichment being about three times that in the core. It should be noted that lead does not go into solution in the alloy, but exists in local pure Pb islands.
- As was added to copper in early antiquity in small quantities to improve castability and hardness. It is also a volatile element. Concentration in the patina layer drops to about one fourth of that in the core.

Elements that have been introduced from the environment into the patina are S, Cl, P, Na, Ca, Fe, and Si. They are present in more or less molecular combinations with C, O, H, and most of the basic elements of the core material. Concentrations for these elements are referred to the overall composition of patina, which does not include the contribution of C, O, and H.





Preliminary conclusions concerning the "intruders" from the environment are the following.

- S is present in the patina and the core material in about the same quantities. It is known from the chemical reactions involved that S contributes to the patination process. Obviously, in the course of these processes no enrichment occurs. However, it appears that S is present in the core in quantities of < 1 % and may have been introduced with the melted material for the blank, if S goes in such quantities in solution in an Cu/Sn/Pb-alloy.
- Cl is present in very small quantities in the patina and has been largely removed by the grinding. It should be noted that the measured concentrations are extremely low.
- P is also present in small quantities only (< 3 %) and has been essentially removed with the patina layer.
- Na was measured in quantities of < 3 %. The available data does not indicate obvious trends.
- Ca was found in larger quantities in the patina which were practically removed by grinding. The core material still exhibits a Ca content of up to 4 %. This could have been unwillingly introduced with the manufacturing of the blank, however, it is not known to what extent Ca will go into solution in an Cu/Sn/Pb-alloy.
- Up to 20 % Fe was measured in the patina. It was practically removed completely with the depatination.
- The same behaviour is observed for Si. Probably this is only sand that has been adsorbed onto the surface of the coin and consequently was removed by the grinding.

S, P, und Ca appear to be present in traces or small quantities in the core material. Cl, Fe, and Si were found in the patina layer only.