

THE ETRUSCAN-TO-MIDDLE AGE COPPER-SILVER-LEAD SLAGS FROM CAMPIGLIA MARITTIMA

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The Campiglia Marittima area (Southern Tuscany) has been long exploited for Cu-Pb-Ag mineralizations (skarn deposits formed mostly by hedenbergite, johannsenite and ilvaite with Cu, Pb, Zn and Fe sulphides).

An important mining activity started there in Etruscan time (8th–3rd c. BC). The mining activity was mostly addressed to the extraction of Cu (from chalcopyrite), Pb and Ag (from silver-rich galena). The centre of metal processing was the Capattoli Valley, where abundant slag heaps occur. The segregation of metals was obtained by smelting in appropriate ovens and subsequent gravimetric separation of metals (at the bottom of the oven) and silicate melts (at the top of the oven).

Slags are mainly formed by SiO₂ (mean value 27.7 wt%), FeO (47.5 wt%) and CaO (9.1 wt%), with minor Al₂O₃, MgO and MnO contents: major element contents reflect the original composition of the raw material used in the process. The Cu, Pb and Zn contents give information about the effectiveness in metal segregation. The Cu content is always low (mean value 2700 ppm), whereas Zn is systematically higher (mean value 36700 ppm), as this element was neglected in the smelting process. Pb occurs in variable amounts, ranging from 5300 to 33900 ppm. In particular, we identified two different compositional groups, high Pb in CaO-poor slags and low Pb in CaO-rich slags, the latter corresponding to higher segregation effectiveness.

The slags are mostly formed of olivine, with variable Fe/Ca ratio: in particular, CaO-poor slags consist of fayalite whereas CaO-rich slags contain two different olivines, a Ca-rich fayalite and a Fe-rich kirschsteinite. Pb and Zn occur as sulphides (galena and sphalerite, respectively), whereas no evidence for chalcopyrite has been found, possibly due to the low Cu content. Slags also contain an amorphous silicate glass, formed by Si, Ca, Fe and Al, with minor Na and K. Na and K could be derived from the charcoal and/or firewood as well as from the oven walls, which were built of porphyry and clays.

The mineralogical characterization of slags from Capattoli has been useful to understand the ancient metallurgic technique used in this area and the effectiveness of the metal segregation process. Cu segregation was attained in all the slag heaps. In contrast, the segregation of Pb was successfully attained only in the ovens working with CaO-rich charges: this could reflect different ore compositions as well as different processes (for instance, addition of limestone fluxes).