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Multidisciplinary investigation of seabed sediments in revealing the exploitation history and ore-types exploited, Lavrion, Greece

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Introduction – geology

Lavreotiki Peninsula is known for its mining activities from ancient times until late 20th century. First traces of exploitation go back to 3.000 B.C., whereas the first mines operated during the Classical period (6th to 4th century B.C.) for exploitation of Ag-bearing galena for the production of Ag, which contributed to the power of ancient Athens (Conophagos, 1980). During that period, the metallurgical process of "cupellation" was first established. The Lavrion mines re-opened during the mid-19th century and exploitation continued until the 1980s. The distinctive geotectonic evolution and hydrothermal activity in the Lavrion area resulted in the formation of several major and minor hydrothermal type sulfide ores including carbonate-replacement Pb-Zn-Ag, Skarn type, porphyry-style and vein-type mineralizations (Bonsall et al., 2011).

The aim of the present study is to correlate the radionuclide and geochemical data with the mineralogical investigation of core sediments in an attempt to provide new insights on the history of exploitation as well as the ore type exploited.

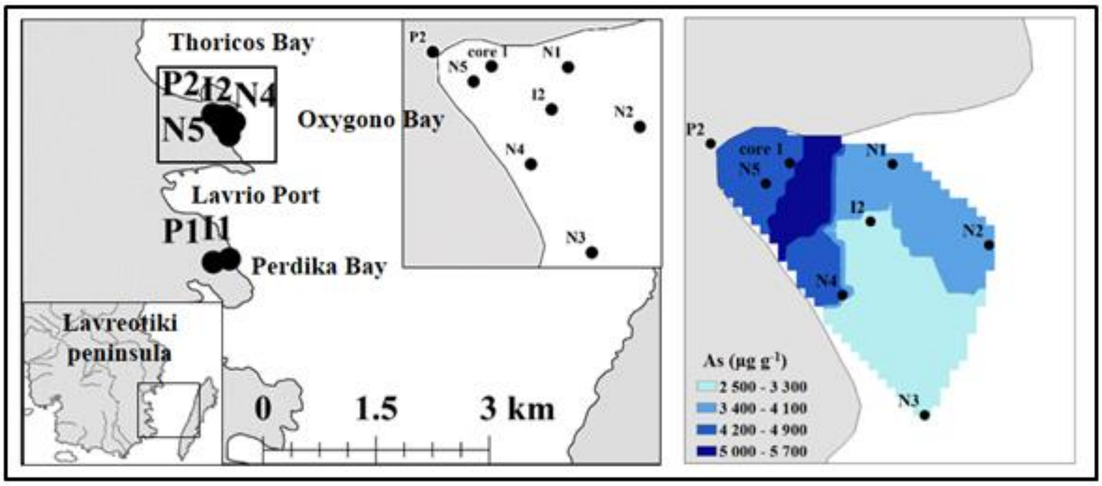

Figure 1. Sampling map of surface beach sands and seabed sediments (left), and spatial distribution of As (right) at Oxygono Bay, Lavrion (Pappa et al., 2018).

Sampling-Analytical methods

One seabed sediment core (core 1) of approximately 50 cm length was collected in 2014 at 50 m distance from the shore of Oxygono Bay. Sampling also included surficial beach sands and marine sediments (Fig. 1). The samples were primarily cleaned, sieved, and the fraction below 2mm was pulverized for radionuclide, geochemical and mineralogical analyses. The fine-grained fraction was selected for the mineralogical analysis in order to better correlate the geochemistry with the mineralogical assemblage of the samples. The radionuclide concentrations were determined via gamma ray spectroscopy at the Nuclear Laboratory of Physics, National Technical University of Athens utilizing a High-Purity Ge Detector (HPGe). The major elements and trace metals concentrations were calculated by means of X-ray Fluorescence at the Geochemistry Laboratory of the Hellenic Centre for Marine Research, whereas optical and Scanning Electron Microscopy was employed for the mineralogical investigation, and was carried out at the Laboratory of Mineralogy, Petrology and Economic Geology, Section of Geological Sciences, School of Mining and Metallurgical Engineering, National Technical University of Athens.

Results – Discussion

The spatial distribution of metals indicated a more contaminated area near the coast, as it is evident by the indicative spatial distribution map of As (Figure 1). Therefore a temporal study was performed in the coastal core (core 1) utilizing the metal profiles in combination with radio-chronological models. These models and in particular the sedimentation rate (SR) estimation based on natural radionuclides were employed for dating analysis (details in Pappa et al., 2018) resulting in the identification of three periods of mining activities in the Lavrion area (1860-1900, 1900-1930, 1930-1980), as well as a post-mining period (1980-2014). The corresponding depths for each period are 38-52 cm, 28-38 cm, 12-28 cm and 0-12 cm respectively (Fig. 2).

During the first period (1860-1900) the ancient slags were primarily utilized for the production of Ag and Pb, as evident by the very low Pb, As, Zn, Cu and Mn content of the sediments (Figure 2). Mineralogical investigation revealed that the sediments are dominated by silicate clasts, carbonates and biofragments, whereas only traces of authigenic framboidal pyrite are identified. In later years (1875-1900) exploitation was expanded to the primary sulfide ores also for the production of Ag and Pb, resulting in a slight increase in the sediment metal load. During the second and third period (1900-1930 and 1930-1980), a new flotation method was adopted mainly for the exploitation of Ag-bearing galena, whereas the other ore phases and metals (e.g. As, Zn, Mn) were not retrieved and were disposed. This observation is directly related to the geochemistry and mineralogy of the sediment core between 35 and 10 cm depth. In particular, the As, Zn and Mn content increases rapidly and remains constant until the surface (Figure 2). The mineralogy identified includes in ranging content primary ore phases (mainly pyrite and arsenopyrite with minor galena and sphalerite), waste rock clasts, slag fragments, gangue phases (quartz, micas, chlorite, ankerite-siderite, dolomite, barite), secondary phases [smithsonite, mimetite - $Pb_5(AsO_4)_3Cl$], and W-bearing phases (scheelite - $CaWO_4$, ferberite - $FeWO_4$, and hubnerite - $MnWO_4$). At the same time, the concentration of natural radionuclide (^{226}Ra) shows similar trend to As, Zn and Mn, indicating possible correlation. The presence of ^{226}Ra in the sediment may be related to the granitoids surrounding the primary ores, and in particular the Skarn-type mineralization (Leleu et al., 1973; Economou et al., 1981; Voudouris et al., 2008). The granitoids were extracted during exploitation along with the ore and were disposed as wastes.

Based on the mineralogy and geochemistry of the sediment core, as well as its radionuclide content, it is reasonable to assume that at some points during the second (1900-1930) and the third period (1930-1980), exploitation of the Plaka intrusion related system, and in particular the skarn type mineralization took place. The primary sulfide ore was mainly exploited by floatation for the extraction of Ag-bearing galena whereas the rest of the material including primary ore phases (arsenopyrite, sphalerite and pyrite), gangue (including carbonates and W-bearing phases), and waste granodiorite (as evident by the presence of natural radionuclide ^{226}Ra) were disposed and are now enriched in the sediment core at depths between 10 and 35 cm.

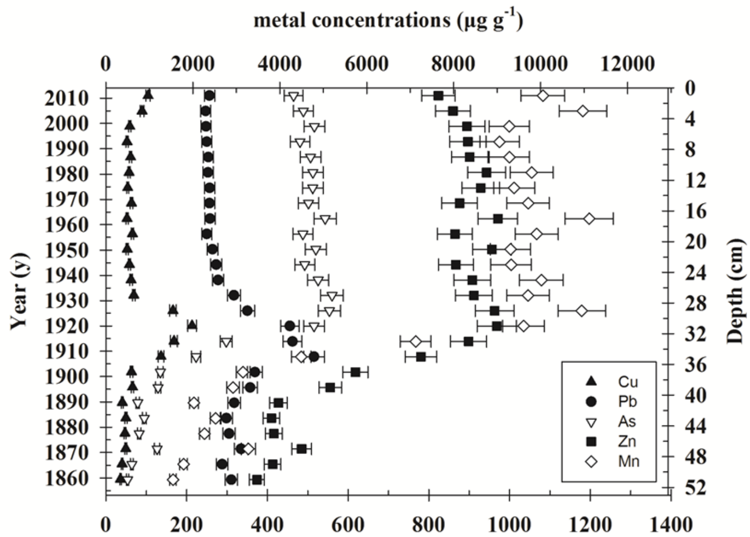

Figure 2. Vertical distribution of As, Pb, Cu, Zn and Mn in the sediment core from Oxygono Bay, Lavrio.

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