Environmental assessment using Zn-Cd-Pb isotopes at an abandoned old mining area

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São Domingos Mine (SDM), a copper-pyrite mine associated with a refining complex, located in the Iberian Pyrite Belt, Alentejo, southern Portugal, is abandoned since 1966. About 5Mt of waste deposits form large slag heaps that transfer large quantities of metals and metalloids (Pb, Zn, Cd, Cu, Fe, Al, Mn, Cr, As, Sn) to soils and waters presenting a high potential of negative impact on environment and public health. An acid mine drainage (AMD) system (pH=0.5-3) intensively affects the area.

We applied a multi-isotope study (Zn, Cd and Pb) to assess environmental impacts. As recently demonstrated, pyrometallurgical processes can fractionate Zn and Cd isotopes through evaporation-condensation processes involved in the sintering or smelting stages. Light isotopes are favoured in the exhaust emissions, while heavy isotopes are retained in the slag residues. We were then able to discriminate the relative contribution of different origins of dust pollution rich in trace metals which may represent important sources of exposure for inhabitants: 1) historical atmospheric deposition from the smelting-refining complex recorded on contaminated topsoils; 2) resuspension of slag residues; 3) resuspension of fine unprocessed ore from stockpiles.

Epiphytic lichens have been used to monitor atmospheric metal pollution and made possible to identify remote sources, long-range atmospheric transport in industrial and mining areas (Carignan et al., 1995; Cloquet et al., 2006b; Dolgopolova et al., 2006).

Samples of unprocessed ores, tailings, AMD salts, cultivated and village soils and lichens were analyzed for Zn, Cd and Pb isotopic compositions on a Nu-Plasma MC-ICP-MS (ULB, Brussels). Lead isotope ratios are homogeneous and confirm the primary pyrite ore body ($^{208}Pb/^{204}Pb$=38.253; $^{207}Pb/^{204}Pb$=15.636; $^{206}Pb/^{204}Pb$=18.173) as the main Pb source. Unprocessed pyrites show uniform $\delta^{66}Zn$ values (+0.07 to +0.1‰). In contrast, tailings and soils show strong Zn isotopic fractionation, with the highest $\delta^{66}Zn$ values (+0.53 to +0.61‰) in tailings close an abandoned sulphur refining factory and the lowest values (-0.69 to -0.18‰) in village soils, located 1.5 km North from the sulphur factory. Those soils may have recorded

deposition of particles emitted by the factory chimney. The $\delta^{66}Zn$ of the lichens define the same isotopic trend previously shown by the topsoils. Their Pb and Zn isotopic compositions reflect the strongest impact of the historical atmospheric emissions related to the factory chimney, and do not reflect traffic influence.

Comparisons between metal contents of soils and lichens show that Cd and Mn concentrations are correlated. Preliminary d114 Cd data clear reflect adsorption of Cd on Fe oxides and Mn-bearing hydroxides, which could probably explain the significant enrichment of soils in light Cd isotopes. $\delta^{66}Zn$ and d114 Cd data on AMD minerals jarosite ($KFe^{3+}_3(SO_4)_2(OH)_6$) and melanterite ($FeSO_4.7H_2O$) suggest fractionation related to Fe oxidation.

The use of Zn-Cd-Pb isotopic multitracer and lichens as bio-monitor revealed to be a sensitive tool to discriminate processes that might occur simultaneously in metal polluted environments.

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