



## **Isotopic study of two biolimiting metals (Zn and Cu) in industrial aerosols**

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The goal of the present isotopic study is to characterize atmospheric Zn and Cu flux from industrial activities. Zn and Cu belong to traditional biolimiting elements. The geochemical cycle of these elements in the Earth superficial envelopes influences the biological productivity in oceans or in soils and, in turn, the global environment (Maréchal et al., 2000; Pichat et al., 2003). Other than Zn and Cu arising from minor geogenic processes, all other sources of Zn and Cu are anthropogenic. Among world-wide anthropogenic sources of Cu and Zn aerosols, metallurgical processing for Cu and steel production, as well as coal production are among the major sources (Pacyna, 1998).

Samples from two metallurgical plants, a Pb-Zn refinery and an integrated steel mill located in Northern France not far away from the southern bight of the North Sea, are investigated in the present study. Samples are ores and dusts directly collected on filtration devices mounted on the main exhaust systems of the plants. Dry deposition plates were positioned near working units previously recognized as major aerosol emission sources (cf. Franssens et al., 2004): sintering plant and steel shop unit, and the main chimneystack.

Samples were taken into solution using standard  $\text{HF-HNO}_3(\pm\text{HClO}_4)$  wet acid digestion techniques. Cu and Zn fractions were then isolated from the sample matrix on a Biorad AG-MP1 resin by one step ion-exchange chromatography (slightly different relative to the Maréchal et al. (1999) and Zhu et al. (2002) methods). Full recover-

ies of Cu and Zn were quantitatively monitored to circumvent problems associated with isotopic fractionation on columns. Cu and Zn isotopic ratios were measured on a “Nu-Plasma” MC-ICP-MS (ULB-Brussels). Instrumental mass fractionation was controlled by using simultaneous external normalization (Cu-doping method for Zn, and Zn-doping method for Cu) and standard-sample bracketing with the Zn JMC and Cu NIST SRM 976 reference materials. A Ni correction was systematically applied. Every sample was analyzed at least in duplicate. Reference materials were repeatedly measured, giving a long-term reproducibility of  $\pm 0.07$  per mil for  $\delta^{65}\text{Cu}$  and  $\delta^{66}\text{Zn}$  ( $2\sigma$ ,  $n=158$ ). Total beam intensities averaged 6 V/ppm.

As a whole, ores and dust collected on filters from the two industries show  $\delta^{66}\text{Zn}$  and  $\delta^{65}\text{Cu}$  varying from -0.63 to 0.58 per mil and -0.62 to 0.21 per mil, respectively.

In the Pb-Zn refinery, Pb isotopic ratios were measured on the same samples and showed no significant variations with similar isotopic signatures for the Pb and Zn working unit emissions (Franssens et al., 2004). In contrast,  $\delta^{66}\text{Zn}$  and  $\delta^{65}\text{Cu}$  values are systematically lower for the Pb working unit emissions. This observation is especially obvious for Cu isotopic compositions, with negative  $\delta^{65}\text{Cu}$  (-0.22 to -0.62) for the Pb working unit emissions, while positive (0.04 to 0.21) for the Zn working unit emissions.

When both metallurgical plants are compared, data sets overlap with the lowest  $\delta^{66}\text{Zn}$  value for the Pb-Zn refinery and the highest  $\delta^{66}\text{Zn}$  for the steel mill plant. With that exception, no major difference is observed. Both data sets provide an interesting trend: throughout the process, continuous enrichment in light Zn isotopes is observed, with the lowest  $\delta^{66}\text{Zn}$  (-0.63) for the end-of-process sample (the Pb-Zn refinery main chimneystack sample). This isotopic fractionation may reflect an oxidation process occurring in the sintering plant and a high temperature liquid to gas phase transfer process in the steel shop unit.

Further investigation will be focused on the evolution of Cu and Zn isotopes fractionation during transport processes in the troposphere.

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