

Stable Cu and Zn isotope ratios as tracers of sources and transport of Cu and Zn in contaminated soil

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During the production of Cu metal, large amounts of Cu and Zn are released to the environment. We determined Cu and Zn concentrations and $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ values in three soils under forest at distances of 1.1, 3.8, and 5.3 km from a Slovak Cu smelter. Soils were sampled at different depths together with bedrock and smelter wastes to trace sources and transport of Cu and Zn in soils.

Soils were heavily contaminated with concentrations up to 8087 $\mu\text{g g}^{-1}$ Cu and 2084 $\mu\text{g g}^{-1}$ Zn in the organic layers. The $\delta^{65}\text{Cu}$ values varied little (-0.12 to 0.36‰) and overlapped in soils, bedrock, and most wastes. Therefore, no source identification was possible. In soils, Cu became isotopically lighter with increasing depth down to 0.4 m, likely because of equilibrium reactions between dissolved and adsorbed Cu species during transport of smelter-derived Cu. This suggests that Cu was leached at a mean rate of ca. 0.0067 m yr⁻¹ in the last 60 yr.

The $\delta^{66}\text{Zn}_{\text{IRMM3702}}$ values were isotopically lighter in ash (-0.41‰) and organic horizons (-0.85 to -0.32‰) than in bedrock (-0.28‰) and slag (0.18‰) likely because of fractionation during evaporation and thus allowed for separation of smelter-derived Zn from native Zn. In the organic horizons, Zn isotopes shifted to heavier $\delta^{66}\text{Zn}$ values with depth probably because of the mixing of smelter-derived Zn and native Zn in the soils and biogeochemical fractionation.

We conclude that Cu and Zn stable isotope ratios may serve as tracer of sources, vertical dislocation, and biogeochemical behavior of these metals in contaminated soils.

Parallel trends in Middle Eocene temperatures and atmospheric carbon dioxide concentration?

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The warmth of the Eocene 'greenhouse world' (56-35 Ma) is generally considered to be related to generally elevated atmospheric carbon dioxide concentrations ($p\text{CO}_2$). Evaluation of this relationship is however hampered by the absence of high-resolution $p\text{CO}_2$ -records. Here we present a reconstruction of $p\text{CO}_2$ and sea surface temperature (SST) over an episode of global warming, the Middle Eocene Climatic Optimum (MECO, ~40 Ma). Molecular paleothermometry (TEX_{86} , U^k_{37}) reveals an increase in Southwest Pacific Ocean SST by 5-6°C. Warming is furthermore manifested by the incursion of low-latitude dinoflagellate cysts at the expense of high-latitude taxa. These results confirm a major SST perturbation associated with the MECO.

We augmented the alkenone $p\text{CO}_2$ proxy with biotic information derived from microfossil assemblages in order to constrain soluble phosphate concentrations, a critical parameter for application of this proxy. The marked consistency between SST and $p\text{CO}_2$ during the MECO leads us to suggest that $p\text{CO}_2$ is not only a driver for long-term Paleogene climate trends, but also for transient anomalies like the MECO. The combined SST and $p\text{CO}_2$ -data contribute towards constraining high latitude climate sensitivity in the Paleogene 'greenhouse world'.