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Method development for Ultra-trace-level Cu isotope analysis and application to atmospheric particulate matter

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Copper (Cu) isotope composition in aerosols is commonly used as an effective tracer for distinguishing natural geochemical signals from anthropogenic pollution. However, recent literature suggests a strong correlation between water-soluble transition metals (particularly Cu) in particulate matter (PM) and its oxidative potential (OP, the overall production capacity of reactive oxygen species) [1]. Consequently, Cu isotope fractionation may offer deeper insights into the chemical evolution of PM.

This study analysed Cu isotope of aerosol with MC-ICP-MS under dry plasma since the sample amount is very limited. We developed a high-sensitivity method for Cu isotope measurement at trace levels (5 ng/mL) using Ni isotopes for mass-bias fractionation. An external reproducibility of delta $^{65/63}$Cu of ±0.06 ‰ (2 SD, n = 56) was achieved, marking a slightly improvement compare to previously reported result [2]. We also evaluated various Ni isotope pairs for mass bias correction. Results indicate that the ^{62}Ni/^{58}Ni ratio yields slightly better external precision compared to the ^{62}Ni/^{60}Ni ratio for Cu isotope measurement, likely due to the higher signal intensity of of ^{58}Ni relative to ^{60}Ni. The methods were applied to analyse water-soluble Cu in PM samples collected from Puli, central Taiwan. We observed a significant delta $^{65/63}$Cu variation (up to ~0.3‰) within a week, occurring simultaneously with substantial fluctuations in OP. Given that Cu isotope is redox-sensitive, these findings suggest that short-term Cu isotope variations are useful for studying the physical and chemical processes during atmospheric transport.

[1] Wu et al. (2025) Environ. Res. 278, 121661.
[2] Lauwens et al. (2018) Analytica Chimica Acta 1025, 69-79