Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.24503

Speciation and isotopic analysis of zinc and iron in size-fractionated aerosol samples related to its source and chemical processes

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Zinc (Zn) in aerosols plays important roles for biological activity and attracts public attention from the perspective of environmental measures. Because of its high volatility and water solubility, Zn is readily released into the atmosphere by human activities and supplied to natural water. To explore the origin and formation process of Zn in atmospheric aerosols, it is important to investigate isotopic (= δ^{66}Zn) and speciation information of Zn in size-fractioned aerosols. We measured light δ^{66}Zn (e.g., $\delta^{66}Zn_{IRMM\text{-}3702}$ = -1.32‰ as the lowest value) mainly for the particles ranging from 0.65 to 4.7 μm [1]. Zn species in aerosols were also estimated based on XANES and EXAFS spectroscopy [2], suggesting that (i) Zn oxalate and sulfate and (ii) Zn oxide, sulfide, and carbonate are main Zn species in fine and coarse particles, respectively. In particular, Zn chloride was found mainly in the middle particle size range, which corresponds to the range with light δ^{66}Zn, suggesting that the light δ^{66}Zn was caused by emission of Zn chloride during artificial combustion processes. The origins of Zn in aerosols are assumed to have three endmembers; (A) tire and brake wears and road dust, (B) industrial emissions, and (C) vehicular exhaust. Their formation mechanisms are related to vaporization and mixing processes based on the results of combined analysis of atmospheric concentration, speciation, and isotopic composition of Zn with different particle sizes. These trends could be successfully interpreted by species-specific δ^{66}Zn values: component (A) consisting mainly of Zn oxide and sulfide with relatively heavier δ^{66}Zn, component (B) Zn chloride and sulfate secondarily formed in the droplet mode having lightest δ^{66}Zn among all the species, and (C) Zn oxalate with δ^{66}Zn closer to 0‰ due to its emission by the complete combustion in vehicle engines. Species-specific Zn isotope data obtained for size-fractionated aerosols complementary provide novel information on the initial generation and secondary processes for the formation of Zn species in the aerosols. In addition, isotope fractionation during combustions processes will be also compared between Zn and iron in the presentation.

[1] S. Natori et al., Atmospheric Environment, 294, 119504.