Elucidating the sulfate formation during haze episodes in wintertime Beijing: insights from sulfur and triple oxygen isotope

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Frequently occurred severe haze events in heavily populated China in recent years have been attributed to extensive industrial and residential emissions, together with enhanced secondary aerosol formation under stagnant meteorological condition, especially in winter. Sulfate, as the major inorganic component of fine particles ($PM_{2.5}$), has been found to form rapidly under high relative humidity conditions. Currently, a large gap exists in model-estimated sulfate concentration and field observation, with the latter often being magnitudes higher. While model simulation is improving, multiple oxygen and sulfur isotopic compositions of atmospheric sulfate offer an independent, often specific constraint on atmospheric secondary sulfate formation pathways.

Here we report inorganic components, together with sulfur ($\delta^{34}S$) and triple-oxygen isotopes ($\delta^{18}O$, $\Delta^{17}O$) of sulfate in $PM_{2.5}$ samples collected every 12 hours in the city of Beijing, northern China in winter 2015. During the sampling period, $PM_{2.5}$ concentration went up to as high as 178.9 $\pm$ 154.9 $\mu g\ m^{-3}$. Sulfate had an average concentration of 20.9 $\pm$ 20.9 $\mu g\ m^{-3}$, with a mean $\delta^{34}S$ values of 5.5$\pm$2.4‰ ranging from 1.3‰ to 9.4‰ The $\delta^{34}S$ is higher during heavily polluted days (average at 6.8‰) than that during relatively clean days (average at 2.0‰). Meanwhile, the average sulfate $\Delta^{17}O$ ($\Delta^{17}O = \delta^{18}O - 0.5305 \times \delta^{17}O$) during heavy haze episodes was 0.62 $\pm$ 0.33‰ suggesting that aqueous oxidation pathway of S(IV)–H_2O_2 played a significant role on the enhanced sulfate formation during the evolution of haze episodes associated with fog processing.