

Multiple sulfur and oxygen isotope measurements on sulfates from high to low-temperature formation within volcanic and anthropogenic plumes.

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Variability in volcanic and anthropogenic emissions of sulfur dioxide is the main source of sulfate aerosols burden in our past and present atmosphere. Most of SO₂ is thought to be oxidized into sulfate within aqueous phase oxidation. Despite a good understanding of the sulfate aerosols formation according to the common oxidation pathways (i.e. O₃, H₂O₂, O₂-TMI) some observations remain mysterious.

S-MIF (sulfur anomaly, $\Delta^{33}\text{S}\neq 0\text{‰}$) in Archean rocks or in ice core data is thought to result from sulfur photochemistry in low pO₂ atmosphere and so under high levels of solar UV radiation which never occurs at tropospheric level in today's atmosphere. So far, it is the only known S-MIF mechanism. However, this mechanism cannot explain the small but very significant S-MIF ($\Delta^{33}\text{S}\approx 0.3\text{‰}$) measured on sulfate aerosols worldwide urban areas.

Here, we present a new data set of oxygen and sulfur isotope composition of sulfate aerosols monitored over the past 25 years in Mexico City and also sulfate extracted from fresh ash from Popocatepetl volcano tropospheric emissions. Multiple S- and O- isotope composition were analysed using SF₆ fluorination line and Ag₂SO₄ pyrolysis method.

Sulfate aerosols collected on urban area (low-temperature formation) and sulfate collected on volcanic ash (high and/or low temperature formation) present distinct $\Delta^{33}\text{S}$ and $\Delta^{17}\text{O}$ values meaning different origins, intermediates and chemical transformations. Concentrations of chemical compounds, isotopic fractionation values and Rayleigh distillation processes allow us to propose, in each case, different hypothesis on the formation pathways.