

S(IV) is oxidized by O₂, not NO₂, in microdroplets: Triple oxygen isotope evidence

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The oxidation of sulfur(IV) (S(IV)) by nitrogen dioxide (NO₂) or molecular oxygen (O₂) in atmospheric microdroplets remains a contentious issue, impeding our understanding of sulfur oxidation processes in the atmosphere. O₂, characterized by a small but resolvable negative $\Delta^{17}\text{O}_{0.5305}$ value of -0.50‰ , can be incorporated one oxygen atom into sulfate oxygen if indeed O₂ is the oxidant that turns S(IV) into sulfate in microdroplets. We anticipate that the $\Delta^{17}\text{O}$ value of the resulting sulfate would be more negative than -0.125‰ . However, if NO₂ is the oxidant, all sulfate oxygen should come from ambient water, thus bearing a $\Delta^{17}\text{O}$ value more positive than approximately -0.12‰ (changing with the corresponding $\delta^{18}\text{O}$ value). To test the hypothesis, we conducted chamber experiments by introducing sulfur dioxide (SO₂) into a set of controlled environments containing microdroplets, under conditions of O₂ and/or NO₂, to facilitate the formation of sulfate. The triple oxygen isotope composition of the produced sulfate has the $\delta^{18}\text{O}$ (sd = 0.2‰) and $\Delta^{17}\text{O}$ (sd = 0.02‰) values of 9.4‰ and -0.11‰ , respectively, when NO₂ was present. In contrast, when O₂ was present, these values were 9.1‰ and -0.16‰ , respectively. Notably, when both NO₂ and O₂ were present, the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of sulfate were 11.6‰ and -0.19‰ , respectively. These findings demonstrate unmistakably that O₂ oxidizes S(IV) to sulfate in microdroplets.