

降水中の過酸化水素 $\Delta^{17}\text{O}$ 値の変動要因の解明

Factors controlling the variability in $\Delta^{17}\text{O}$ values of hydrogen peroxide in precipitation

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Tropospheric ozone (O_3) is not only a major component of photochemical smog, causing respiratory diseases and damaging plants and crops, but also the third most important greenhouse gas after CO_2 and methane. Consequently, it is a key target for mitigation in air quality management. However, our understanding of the increase in tropospheric O_3 since the pre-industrial time (1850) to the present and the factors driving its variability remain limited. Direct observational data for tropospheric O_3 are available only since 1956 (Cooper et al., 2014). Moreover, because O_3 rapidly decomposes after deposition to the surface, it is not preserved in paleoclimate archives such as ice cores. Research has therefore focused on exploring alternative proxies, such as isotope ratios of impurities in ice cores, that might retain information on past O_3 levels (Alexander and Mickley, 2015).

To address this challenge, we focus on a novel proxy: the triple oxygen isotope composition ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of hydrogen peroxide (H_2O_2). Specifically high $\Delta^{17}\text{O}$ value in O_3 ($\approx 39\text{‰}$), in contrast to other oxygen species in the atmosphere (e.g., OH and O_2 , $\Delta^{17}\text{O} \approx 0\text{‰}$), is partially inherited to H_2O_2 through its formation processes. Consequently, $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ is expected to vary depending on the relative contributions of O_3 -involved reactions and other pathways. The existing measurements of $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ in precipitation samples collected in La Jolla, California, reported values ranging from 1.3 to 2.4 ‰ (Savarino and Thiemens, 1999); however, its relationship with ambient O_3 concentrations has not been examined. Moreover, the requirement of large sample volume (4 L) for analysis posed a major limitation, having hampered the $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ measurements of natural precipitation samples ever since.

In this study, we have developed a new analytical method for $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ using a continuous flow GC-IRMS system, successfully reducing the required sample volume to 200 mL. With this new method, we conducted an extended measurements of $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ in precipitation collected at Kanazawa (36.5°N, 136.7°E), from March through November 2025, to examine the relationship with O_3 concentration. $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ values varied between 1.1 and 2.5 ‰ ($n = 30$), which was broadly consistent with that reported in previous study at California. Importantly, the observed $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$ values were not correlated with O_3 concentrations in Kanazawa ($p = 0.40$). However, during the chemical conversion process of H_2O_2 in the samples to O_2 gas within the measurement, we observed an excessive amount ($>120\%$) of O_2 was produced for most cases ($n = 20$). This phenomena suggest a significant interference of the analysis by H_2O_2 or O_2 generated from sources other than the original H_2O_2 in precipitation. In this presentation, we discuss the sources of this interference and the potential approaches to avoid them.

キーワード：三酸素同位体組成、オゾン、過酸化水素、降水

Keywords: Triple Oxygen Isotopic Composition, Ozone, Hydrogen Peroxide, Precipitaion