Variations $\Delta^{17}O$ of H_2O_2 formed in electrical discharge with water vapor and oxygen

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Hydrogen peroxide (H_2O_2), being an important *oxidant* in the Earth's *atmosphere,* plays a crucial role in many atmospheric chemical cycles. The isotope anomaly ($\Delta^{17}O$) of H_2O_2 has been detected in rainwater [1] and laboratory experiments [2]. The $\Delta^{17}O$ anomalous of H_2O_2 derived from the photochemical produced ozone that possess excess ^{17}O [3]. Here we report results of laboratory experiments to measure the effect of $\Delta^{17}O$ in H_2O_2 formed from water vapor using a spark discharge in a helium continues flow system. The reaction was run into a glass reactor where water vapor was passed by bubbling helium flow (30 mL/min) through a water sample (1mL) at 100°C. The outflow from the reactor passed through a trap at liquid nitrogen temperature to collect the product of reaction. To investigate the variations of $\Delta^{17}O$ in H_2O_2, molecular oxygen O_2 was added to helium flow before it entered the reactor and was present at various concentrations at the reaction point. The oxygen isotopic composition of H_2O_2 was analyzed using $KMnO_4$ and MnO_2 and was measured with a MAT-253 mass spectrometer running in continuous flow mode. Precision of analyses was tested using solutions of commercial H_2O_2 (standard deviation of 0.6 ‰ for $\delta^{18}O$, 0.3‰ for $\delta^{17}O$, and 0.05‰ for $\Delta^{17}O$). Laboratory experiments demonstrated that isotopic variations in produced H_2O_2 depended on the concentrations of O_2 and were found to be: (a) $\Delta^{17}O$= 1.3-1.5‰ with the $\delta^{18}O$ value insignificantly different from the initial $\delta^{18}O$ value of water if the concentration of O_2 was very low (in the range of $\sim 10^{-6}$ % of the present atmospheric level (PAL)); (b) $\Delta^{17}O$= 2.5-3.0‰ with enriched in both ^{18}O and ^{17}O by 20-30‰ compared to the initial water as the concentration of O_2 increased to ~0.001, 0.01, and 1% of PAL. Note that the content of H_2O_2 produced in the spark discharge was in range of $(5\text{-}9)\cdot 10^{-5}$ mol/L and weakly correlated with the O_2 concentrations at the reaction point. This study was supported by the Russian Foundation for Basic Research, grant # 15-05-00794

[1] Savarino & Thiemens (1999) *Atmos. Environ.* **33**, 3683-3690. [2] Shaheen *et al.* (2010) *PNAS* **107**, 20213–20218. [3] Thiemens & Heidenreich (1983) *Science* **219**, 1073-1075.