

Clumped isotopes in firn air O₂ to study tropospheric O₃ variations in recent past

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The isotopic composition of O₂ in the atmosphere holds a unique record of biological, hydrological, and photochemical processes. With advanced analytical techniques such as the MAT 253 ULTRA stable isotope ratio mass spectrometer, it is now possible to carry out high precision measurements of multiply substituted isotopologues, called clumped isotopes. Clumped isotopes in O₂ are ¹⁸O¹⁸O, ¹⁸O¹⁷O and ¹⁷O¹⁷O, and their excess abundance over that expected from a stochastic (random) distribution, denoted by Δ_{36} , Δ_{35} and Δ_{34} , depend on their formation temperatures and other kinetic and statistical effects. The main challenge of ¹⁸O¹⁸O measurement is the separation from ³⁶Ar, which is easily achieved with the MAT 253 ULTRA. Δ_{36} and Δ_{35} in tropospheric O₂ have been found to be sensitive to O₃ concentration and troposphere-stratosphere transport [1]. We report high precision measurements of Δ_{36} and Δ_{35} along with the conventional stable isotopic compositions in O₂ extracted from firn air collected at several stations in Greenland and Antarctica, which have the potential to trace atmospheric oxidation chemistry. The sensitivity of Δ_{36} and Δ_{35} to O₃ and NO_x concentrations in the atmosphere, their preservation in firn and ice samples and the variation in oxidation chemistry in the earth's atmosphere in the recent past will be discussed.

[1] Yeung et al. (2016) *J. Geophys. Res.* 121, 12541-12559