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Measurements of $^{17}O^{18}O$ and $^{18}O^{18}O$ in atmospheric air O_2 and comparison with model simulations

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The conventional isotopic composition of atmospheric oxygen in governed by photosynthesis and hydrological process in the troposphere. However photochemical reactions also affect the isotopic compositions in the tropopause (TP) and stratospheric regions. In this study, we present measurements of doubly substituted $^{17}O^{18}O$ and $^{18}O^{18}O$ (known as clumped isotopes), denoted as Δ_{35} and Δ_{36}respectively, in atmospheric air samples collected from the surface to the lowermost stratospheric regions (LMS) of up to 20km. Isotope exchange between O_2 and $O(^3P)$, a product of photolytic dissociation of O_3, resets the isotopic signatures of oxygen. The clumped isotope signatures depend on the resetting ambient temperature as well as on the $O(^3P)$ concentrations. The Δ_{36} and Δ_{35} values are higher for air sampled at colder temperatures in the TP and LMS regions (2.9‰ to 3.1‰ for Δ_{36} ; 1.4‰ to 1.6‰ for Δ_{35}), whereas lower values (2.2‰ to 2.9 ‰ for Δ_{36} ;1.1‰ to 1.9‰ for Δ_{35}) are observed in the tropospheric regions. As a result of the high abundance of O_3 in the TP and LMS, the clumped isotope values are close to the isotopic equilibrium values there. In contrast, O_2 in the troposphere is a mixture of that has been isotopically exchanged at relatively warmer temperature in the troposphere, and the O_2 that has retained higher clumped isotopes values from the time that it was isotopically equilibrated in the cold stratosphere. Full isotopic equilibration in the troposphere does not occur due to the low O(3P) concentrations there. Thus, Δ_{36} values are influenced by atmospheric transport and circulation. To investigate this in more detail, the clumped isotopic composition of O_2 was modeled with the European Centre for Medium-Range Weather Forecasts – Hamburg (ECHAM)/Modular Earth Submodel System (MESSy) Atmospheric Chemistry (EMAC) model. The model resets the clumped isotopic composition of O_2 to the thermodynamically expected values depending on temperature during isotope exchange reactions, and it explicitly takes into account the transport. The model reproduces the mean measured tropospheric clumped isotope within the analytical uncertainty. The results obtained from the measurements and model will be discussed.