Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 6, 2073-2090, 2006
www.atmos-chem-phys.net/6/2073/2006/

Modelling the budget of middle atmospheric water vapour isotopes

A. Zahn[1], P. Franz[2,3], C. Bechtel[4], J.-U. Grooß[6], and T. Röckmann[2,5]
[1]Institute of Meteorology and Climate Research, Forschungszentrum Karlsruhe, Germany
[2]Max-Planck-Institute for Nuclear Physics, Heidelberg, Germany
[3]National Institute for Water and Atmospheric Research (NIWA), Wellington, New Zealand
[4]Robert Bosch GmbH, Bühl, Germany
[5]Institute for Marine and Atmospheric Research Utrecht, Utrecht University, The Netherlands
[6]Institute of Chemistry and Dynamics of the Geosphere, Forschungszentrum Jülich, Germany

Abstract. A one-dimensional chemistry model is applied to study the stable hydrogen (D) and stable oxygen isotope (^{17}O, ^{18}O) composition of water vapour in stratosphere and mesosphere. In the troposphere, this isotope composition is determined by "physical'' fractionation effects, that are phase changes (e.g. during cloud formation), diffusion processes (e.g. during evaporation from the ocean), and mixing of air masses. Due to these processes water vapour entering the stratosphere first shows isotope depletions in D/H relative to ocean water, which are ~5 times of those in $^{18}O/^{16}O$, and secondly is mass-dependently fractionated (MDF), i.e. changes in the isotope ratio $^{17}O/^{16}O$ are ~0.52 times of those of $^{18}O/^{16}O$. In contrast, in the stratosphere and mesosphere "chemical'' fractionation mechanisms, that are the production of H_O due to the oxidation of methane, re-cycling of H_2O via the HO_x family, and isotope exchange reactions considerably enhance the isotope ratios in the water vapour imported from the troposphere. The model reasonably predicts overall enhancements of the stable isotope ratios in H_2O by up to ~25% for D/H, ~8.5% for $^{17}O/^{16}O$, and ~14% for $^{18}O/^{16}O$ in the mesosphere relative to the tropopause values. The $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios in H_2O are shown to be a measure of the relative fractions of HO_x that receive the O atom either from the reservoirs O_2 or O_3. Throughout the middle atmosphere, MDF O_2 is the major donator of oxygen atoms incorporated in OH and HO_2 and thus in H_2O. In the stratosphere the known mass-independent fractionation (MIF) signal in O_3 is in a first step transferred to the NO_x family and only in a second step to HO_x and H_2O. In contrast to CO_2, $O(^1D)$ only plays a minor role in this MIF transfer. The major uncertainty in our calculation arises from poorly quantified isotope exchange reaction rate coefficients and kinetic isotope fractionation factors.

Final Revised Paper (PDF, 357 KB) Discussion Paper (ACPD)

Citation: Zahn, A., Franz, P., Bechtel, C., Grooß, J.-U., and Röckmann, T.: Modelling the budget of middle atmospheric water vapour isotopes, Atmos.

Chem. Phys., 6, 2073-2090, 2006. Bibtex EndNote Reference Manager