

STABLE ISOTOPE COMPOSITION OF H₂ IN THE TROPOSPHERE, STRATOSPHERE, AND MESOSPHERE

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Recent developments in continuous flow isotope ratio mass spectrometry allow us to obtain sufficiently precise data even using small volumes of air (0.4 L). Here we present hydrogen isotopic ratios (D/H) observed in the troposphere, the stratosphere, and the mesosphere. Tropospheric air has been collected with the CARIBIC (**C**ivil **A**ircraft for the **R**egular **I**nvestigation of the atmosphere **B**ased on an **I**nstrument **C**ontainer) Boeing 767 over Europe and Africa during 3 flights in May, July, and December. The D/H ratio as well as the H₂ concentration shows a clear seasonality in both hemispheres. The seasonal variation of H₂ is similar to that observed in the remote marine boundary layer. However, the D/H ratio varies out of phase with the H₂ concentration in the northern hemisphere, while varying in phase in the southern hemisphere. This suggests that the source or sink processes regulating the H₂ concentrations are different in each hemisphere. In addition, the H₂ in the southern hemisphere was on average 7 ‰ more enriched in deuterium than that in the northern hemisphere. Stratospheric air was collected by balloon flights in Aire sur l'Adour (France) in 2002 and in Kiruna (Sweden) in 2003. The D/H ratio increases with altitude, but the H₂ concentration shows no vertical gradient in the lower stratosphere due to the balance in the photochemical oxidation of CH₄ and H₂ by OH, Cl, and O(¹D) radicals. In a winter flight, we observed a breakdown of this steady state at high altitude, whilst the isotopic ratios kept increasing. By chance, mesospheric air, which had intruded into the stratosphere, was collected in the same flight. The H₂ concentrations rose up to 840 ppb and the D/H ratio decrease down to ~130 ‰ (vs. SMOW) simultaneously.