Geophysical Research Abstracts, Vol. 9, 03934, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-03934

0.1 Measuring the 17O excess of water with the equilibration method

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It is generally assumed that the variations of ^{17}O and ^{18}O contents of water samples are closely related for mass dependent fractionation processes. But it was shown, that the relation can differ between equilibrium and kinetic processes. Moreover there are mass independent fractionation processes that occur for example in the formation of ozone which leads to heavily ^{17}O enriched stratospheric water vapour and carbon dioxide. Therefore the ^{17}O excess defined here as (δ^{17}O+1-(δ^{18}O+1)$^{\lambda}$) can change in water and ice samples. This ^{17}O excess could give information on the past hydrological cycle and would have a significant effect on the ^{17}O correction for isotopic CO_2 analysis by mass spectrometry and therefore on the δ^{13}C measurements.

^{17}O of water can be determined from the measured δ^{45} values after equilibration with an isotopically known CO_2 gas. The reproducibility of this method for ^{17}O is, however, rather moderate with about 0.4 ‰ if one uses the same procedure as for the δ^{18}O measurements. Interference originates from small ^{13}C changes during equilibration. Minor changes in the carbonate chemistry for example during equilibration or between samples can lead to a 14-fold amplified impact on the measured δ^{17}O and therefore on the Δ^{17}O. The largest impact is due to fractionations of the carbon isotopes of the equilibration gas which is dependent on the distribution of the carbon species, that in turn depends on the pH-value of the equilibrated water. The pH-value after the equilibration is determined by the buffer capacity of the water sample. Therefore, when controlling the pH-value with a chemical puffer, it is expected that the reproducibility for Δ^{17}O can be improved to better than 0.1‰.