



Limitations in the determination of the ^{17}O excess of water and ice samples 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. CO_2 would transfer its enriched isotope signal to the water on the earth's surface via photosynthesis/respiration cycle and CO_2 hydration within sea and lake waters. Therefore the ^{17}O excess defined here as $(\delta^{17}\text{O}+1-(\delta^{18}\text{O}+1)^\lambda)$ 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 $\delta^{13}\text{C}$ 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 permil. The precision of δ^{45} measurement is in the order of 0.05 permil for water samples. Additional 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 14fold amplification impact on the measured ^{17}O . We discuss the influence of temperature, water amount, CO_2 pressure and its isotopic composition as well as the equilibration time on the measured ^{17}O . We reevaluated former $\delta^{18}\text{O}$ measurements from ice samples of the

two EPICA ice cores DomeC and EDML to determine ^{17}O excess. $\delta^{18}\text{O}$ values and rare data were made available to us from the Department of Earth Science, University of Parma and from the Isotope Laboratory of the Alfred Wegener Institute for Polar and Marine Research Potsdam. We found rather large variations in the ^{17}O excess up to 1 permil. We discuss whether these results represent real ^{17}O signals or are pseudo signals generated by the influenced parameters mentioned above. Based on those measurements we assess the limitations of the equilibration method for paleoclimatic use.