



Determination of $\Delta^{17}\text{O}$ in stratospheric CO_2 using oxygen isotope exchange with CeO_2

Dorota Mrozek and Thomas Röckmann
Poland (dorota.mrozek@gmail.com)

The characterization of the ^{13}C and ^{18}O content of carbon dioxide has played a significant role in the understanding of the global carbon cycle. Most isotope fractionations are mass dependent (MDF) because they arise from differences in chemical and physical properties that are dependent on mass. These processes obey the mass dependent fractionation equation $\Delta^{17}\text{O} = 17\text{O} - 0.52 \text{ }^{18}\text{O} = 0$. In the atmosphere, almost all atmospheric components show an oxygen isotope anomaly, i.e. $\Delta^{17}\text{O} > 0$. Such deviations in ^{17}O from a purely mass-dependent pattern are named mass-independent fractionation (MIF). Also stratospheric CO_2 shows mass independent fractionation.

Measurement of both oxygen isotopes in CO_2 is not easy because ^{17}O - and ^{13}C - substituted CO_2 cannot be distinguished by isotope ratio mass spectrometry. Therefore, CO_2 has to be either converted to O_2 or the oxygen it contains must be exchanged with oxygen of known isotopic composition. Most of these methods were initially developed as offline analytical techniques. We have established an online measurement system for $\delta^{17}\text{O}$ in CO_2 , based on complete oxygen isotope exchange with CeO_2 at 650°C (Assonov et al. 2001). Similar to the system by Kawagucci et al (2005), using CuO for exchange, the system allows analysis of ^{17}O on nanomolar quantities of CO_2 .

The approach involves measurement of CO_2 directly, and after isotope exchange. First, CO_2 is separated from the main air constituents by gas chromatography. One aliquot is then directly injected into the mass spectrometer, another aliquot is directed through a CeO_2 where it is isotopically equilibrated with the O_2 excess of CeO_2 at 650°C . The equilibrated CO_2 without anomaly is analyzed on the IRMS.

As a first application, we have determined the isotopic composition of stratospheric CO_2 on air samples obtained during the EU project RECONCILE in the Arctic winter/spring season with the high-altitude aircraft Geophysica.