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Online, high precision analytical method for determination of $\triangle$17O in stratospheric CO_2 with the use of CeO_2 isotopic exchange

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Isotope studies of carbon dioxide (CO_2) play an important role in understanding of the global carbon cycle. In the atmosphere CO_2 is an important greenhouse gas. Stratospheric CO_2 is known to undergo an isotopic exchange reaction with ozone (Yang et all 1991). Therefore, stratosphere CO_2 shows a mass independent fractionation (MIF) which is a deviation in the 17O content from a purely mass-dependent pattern (MDF): for MDF phenomena Δ17O = δ17O - 0.52 δ18O=0, for MIF phenomena Δ17O $\neq$ 0. The detail mechanism that controls the 17O anomalies in stratospheric CO_2 is not fully understood.

Interest in this field has caused innovations in analytical techniques based on Isotope Rato Mass Spectrometry (IRMS). Our approach was to design an analytical system that allows analysis of 17O on nanomolar quantities of CO_2 suitable for measuring oxygen isotope anomalies in the stratospheric air samples.

The standard continuous flow-IRMS techniques permit measuring small quantities of CO_2 but it is impossible to measure the 17O isotope at mass 45 due to the interference from the much more abundant 13C. 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. Based on complete oxygen isotope exchange with CeO_2 at 650°C (Assonov et al. 2001) we have established an online measurement system for δ17O in CO_2. The system allows analysis of 17O on nanomolar quantities of CO_2 with a good reproducibility of 0.08‰ for δ45CO_2.

The new technique is a valuable tool to study isotopic exchange mechanism between O_3 and CO_2 in the stratosphere. 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.