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Supplement of

A new set-up for simultaneous high-precision measurements of CO₂, δ¹³C-CO₂ and δ¹⁸O-CO₂ on small ice core samples

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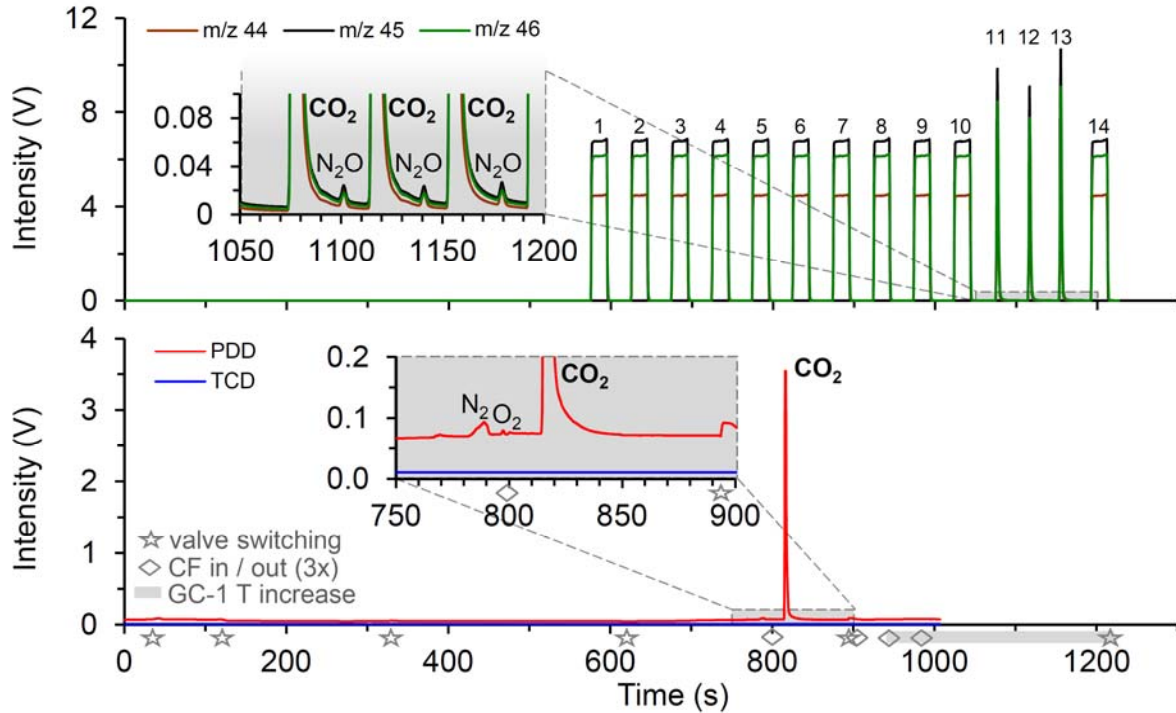


Figure S1: Chromatograms for the measurement of pure CO₂-WS injected into section B of the setup (Fig. 2 in the main manuscript) and subsequently passing the PreCon-GC system. Upper panel: IRMS signal intensity for mass 44, 45, and 46. Injections of the WS via the open split are identifiable by the flat-topped peaks. Peaks 1-9 are used to reach stable source conditions while peaks 10 and 14 before and after the samples (i.e. the WS passing the PreCon-GC system) are used for referencing. The inset shows baseline details and N₂O separation in detail. Lower panel: PDD and TCD intensity signal for CO₂ and air (not detected for the pure CO₂ sample injected here), respectively. Stars indicate valve switching, resulting in small variations in the PDD signal due to changes in pressure and flow (see inset, not detected by the less sensitive TCD). Diamonds indicate immersion of the three capillary traps into liquid nitrogen for CO₂ cryofocusing and their subsequent one by one release resulting in the three peaks of the split sample shown in the upper panel (peaks 11–13). Over the time period indicated by the grey bar the GC-1 temperature is increased to 150 °C in order to precondition the column for the next sample. The enlargement shows baseline details and the N₂ and O₂ signal of the system blank contribution.

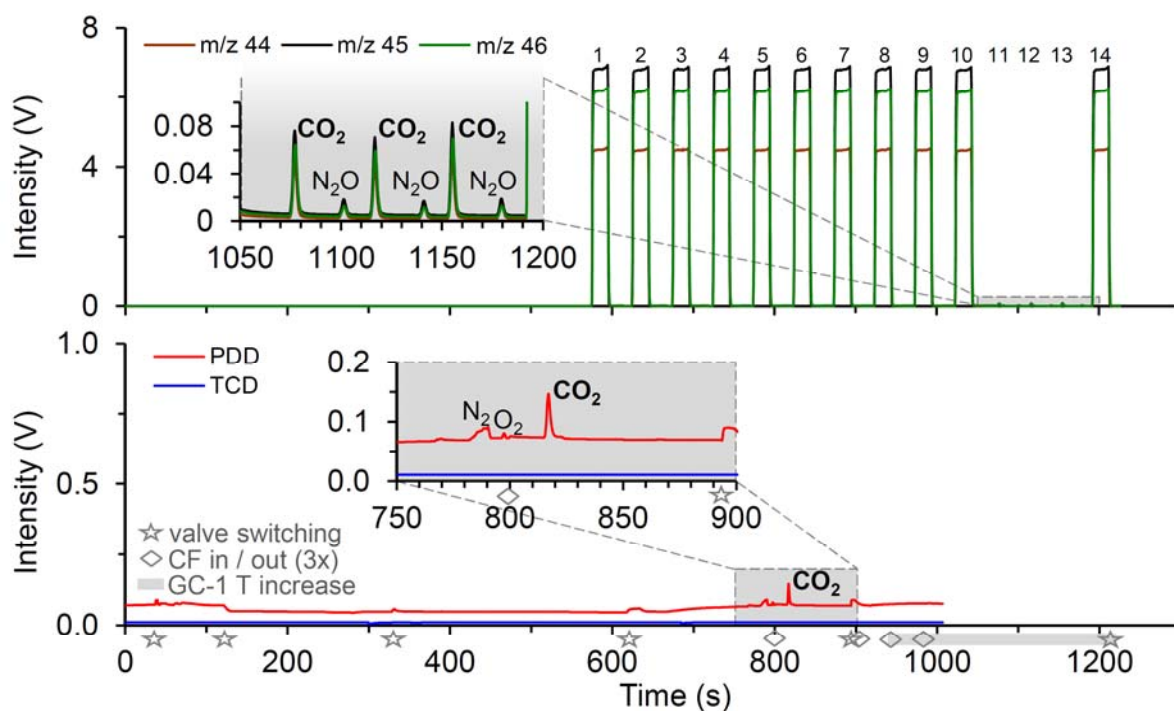


Figure S2: Chromatograms for the measurement of a system blank including both sections A and B (Fig. 2) and bellow compression (i.e. needle movement without ice). Upper panel: IRMS signal intensity for mass 44, 45, and 46. Injections of the WS via the open split are identifiable by the flat-topped peaks. Peaks 1–9 are used to reach stable source conditions while peaks 10 and 14 before and after the samples (i.e. the system blank) are used for referencing. The inset shows baseline details and the system blank signal of CO₂ and N₂O in detail. Lower panel: PDD and TCD intensity signal for CO₂ and air (not detected), respectively. Stars indicate valve switching, resulting in small variations in the PDD signal due to changes in pressure and flow (see inset, not detected by the less sensitive TCD). Diamonds indicate immersion of the three capillary traps into liquid nitrogen for CO₂ cryofocusing and their subsequent one by one release resulting in the three peaks of the split sample shown in the upper panel (peaks 11–13). Over the time period indicated by the grey bar the GC–1 temperature is increased to 150 °C in order to precondition the column for the next sample. The enlargement shows baseline details and the system blank contribution of N₂, O₂ and CO₂.

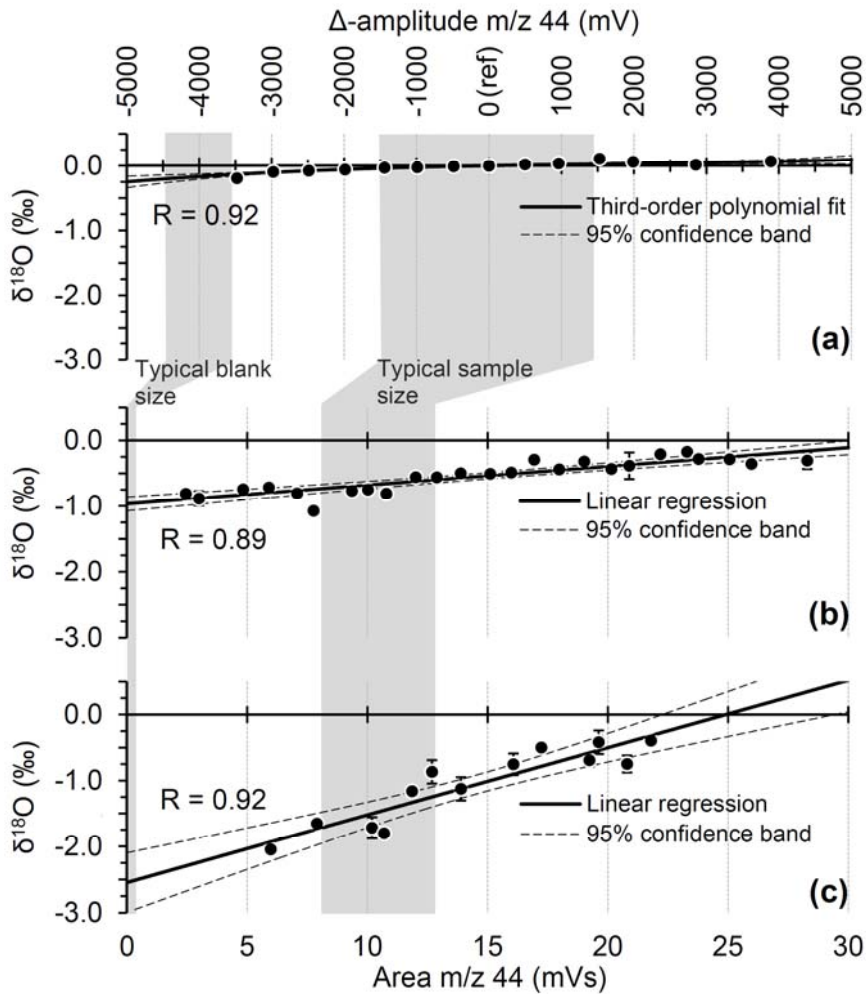


Figure S3: Fractionation effects for $\delta^{18}\text{O}$: (a) IRMS nonlinearity effect; $\delta^{18}\text{O}$ dependence on peak amplitude (top x axis), Δ -amplitude is the deviation in intensity (m/z 44) from the reference peak (ref, $\delta^{18}\text{O}$ and Δ -amplitude = 0). The data are obtained from a total of 177 measurements and mean values with the 1σ standard deviation are shown. (b) PreCon-GC linearity (bottom x axis); CO_2 sample size dependence for pure CO_2 working standard directly injected to section B. The data are obtained from a total of 318 measurements corrected for IRMS nonlinearity and blank; mean values with the 1σ standard deviation are shown. (c) Air amount dependence (bottom x axis); air sample size dependence for air standards/samples injected to section A. The data are obtained from a total of 46 measurements corrected for IRMS nonlinearity, PreCon-GC linearity and system blank. Mean values with the 1σ standard deviation are shown. The grey bars indicate the typical procedural blank and sample size range of air extracted from ice samples, respectively.

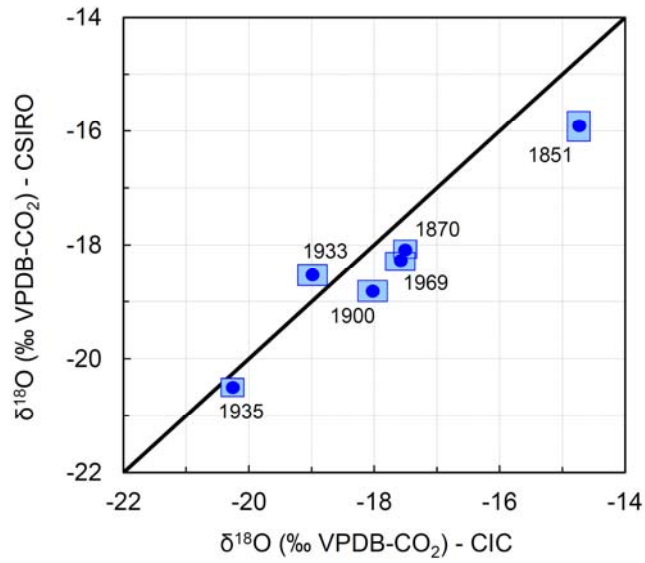


Figure S4: Laboratory comparison measurements of Law Dome ice samples covering the recent past (1851–1969 AD). $\delta^{18}\text{O}$ - CO_2 values measured at CIC (x axis) and CSIRO (y axis; M. Rubino, pers. comm.) are shown. Blue boxes indicate 1σ uncertainties defined for each laboratory by the respective side length.

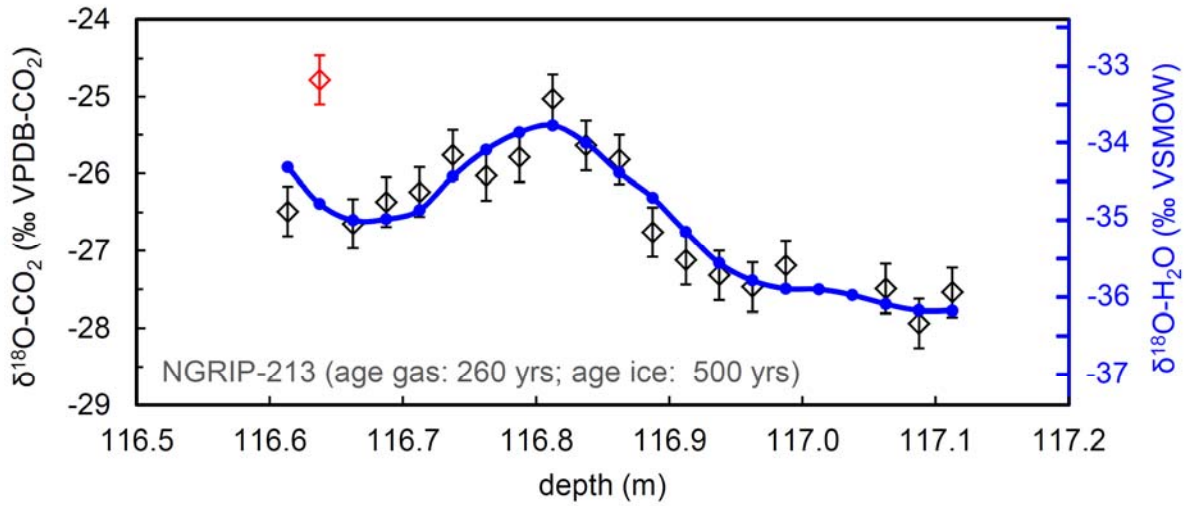


Figure S5: High resolution records of $\delta^{18}\text{O}-\text{CO}_2$ with error bars (1σ , left axis) and $\delta^{18}\text{O}-\text{H}_2\text{O}$ (right axis) for an ice section from NGRIP. The sample in red has been defined as an outlier (for details see Sect. 4.3 in the main manuscript).