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

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1 Supplement



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Figure S1: Chromatograms for the measurement of pure CO₂-WS injected into section B of 3 4 the setup (Fig. 2) and subsequently passing the PreCon-GC system. Upper panel: IRMS signal intensity for mass 44, 45, and 46. The flat-topped peaks are on/off peaks of the WS 5 injected via the open split. Peaks 1-9 are used to reach stable source conditions while peaks 6 7 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: 8 PDD and TCD intensity signal for CO₂ and air (not detected for the pure CO₂ sample injected 9 here), respectively. Stars indicate valve switching, resulting in small variations in the PDD 10 11 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 12 cryofocusing and their subsequent one by one release resulting in the three peaks of the split 13 sample shown in the upper panel (peaks 11–13). Over the time period indicated by the grey 14 bar the GC-1 temperature is increased to 150 °C in order to pre-condition the column for the 15 next sample. The enlargement shows baseline details and the N2 and O2 signal of the system 16 17 blank contribution.



2 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 but no ice). Upper panel: 3 4 IRMS signal intensity for mass 44, 45, and 46. The flat-topped peaks are on/off peaks of the CO₂-WS injected via the open split. Peaks 1–9 are used to reach stable source conditions 5 6 while peaks 10 and 14 before and after the samples (i.e. the system blank) are used for 7 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), 8 9 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). 10 Diamonds indicate immersion of the three capillary traps into liquid nitrogen for CO₂ 11 cryofocusing and their subsequent one by one release resulting in the three peaks of the split 12 sample shown in the upper panel (peaks 11–13). Over the time period indicated by the grey 13 bar the GC-1 temperature is increased to 150 °C in order to pre-condition the column for the 14 next sample. The enlargement shows baseline details and the system blank contribution of 15 N_2 , O_2 and CO_2 . 16

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Figure S3: Fractionation effects for δ^{18} O: A) IRMS nonlinearity effect; δ^{18} O dependence on 2 peak amplitude (top x-axis), Δ -amplitude is the deviation in intensity (mass 44) from the 3 reference peak (ref. δ^{18} O and Δ -amplitude = 0). The data is obtained from a total of 177 4 measurements and shown are mean values with the 1_s standard deviation. B) PreCon-GC 5 linearity (bottom x-axis); CO₂ sample size dependence for pure CO₂ working standard 6 7 directly injected to section B. The data is obtained from a total of 318 measurements 8 corrected for IRMS nonlinearity and blank; shown are mean values with the 1st standard 9 deviation. C) Air amount dependence (bottom x-axis); air sample size dependence for air standards/samples injected to section A. The data is obtained from a total of 46 measurements 10 corrected for IRMS nonlinearity, PreCon-GC linearity and system blank, shown are mean 11 values with the 1σ standard deviation. The grey bars indicate the typical procedural blank and 12 sample size range of air extracted from ice samples, respectively. 13



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Figure S4: Laboratory comparison measurements of Law Dome ice samples covering the recent past (1851–1969 AD). Shown are the δ^{18} O-CO₂ values measured at CIC (x-axis) and CSIRO (y-axis; Rubino M., pers. communication). Blue boxes indicate 1 σ uncertainties defined for each laboratory by the respective side length.



2 Figure S5: High resolution records of δ^{18} O-CO₂ with error bars (1 σ , left axis) and δ^{18} O-H₂O

3 (right axis) for an ice section from NGRIP. The sample in red has been defined as an outlier
4 (for details see Sect. 4.3 in the main manuscript).