Supplement for Reconstructing atmospheric H2 over the past century from bi-polar firn air records

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Text S1: Calibration of NEEM reconstructions from Petrenko et al., (2013)

The reconstructions published by Petrenko et al. (2013) were based on measurements made at NOAA/GML on the NOAA96 calibration scale. The NOAA96 calibration scale is known to have drifted over time due to increasing H_2 in most GML H_2 calibration standards stored in high pressure aluminum cylinders. As a part of the NEEM firn air sampling campaign (July 2008), matched flask pairs were filled at 12 unique depths. One flask of each pair was analyzed at NOAA/GML and the other was analyzed at CSIRO. On average, the CSIRO measurements were 23.8 ppb higher than the NOAA measurements made on the same samples. At that time, CSIRO was using the CSIRO94 calibration scale. Since then, CSIRO has formally revised their measurements to the MPI09 scale (Jordan & Steinberg, 2011, Section 2.2). On average, the revised measurements are 16.5 ppb higher than the original measurements. On the basis of these two empirical comparisons, we have added 40.3 ppb (i.e. 23.8 + 16.5 ppb) to the reconstructions published by Petrenko et al. (2013) to correct them to the modern MPI09 calibration. The corrected reconstructions are plotted in Figure 4a.

Figure S1: Modelled H_2 age distributions ("Green's functions") for several depths at NEEM (a) and Summit (b)

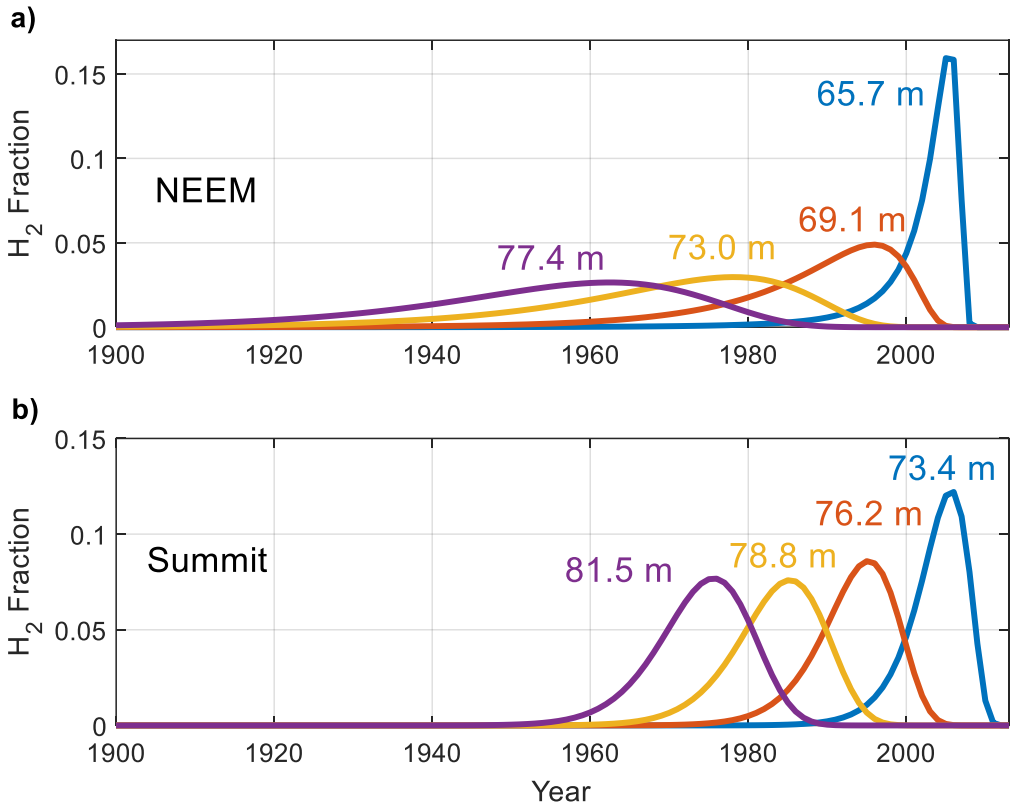


Figure S2: Atmospheric H_2 reconstructed from Summit firn air measurements; the reconstruction shows a more pronounced increase and maximum when the uncertainty on the firn air measurements is reduced. Orange line and shading- result from Summit and associated ±1σ uncertainty as in Figure 1; teal line and shading- result from Summit and associated ±1σ uncertainty with the uncertainty on the Summit firn air measurements arbitrarily reduced by 25%; black x's–annual mean synthetic Summit H_2 history (Section 5; Pétron et al., 2023, Langenfelds et al., 2002)

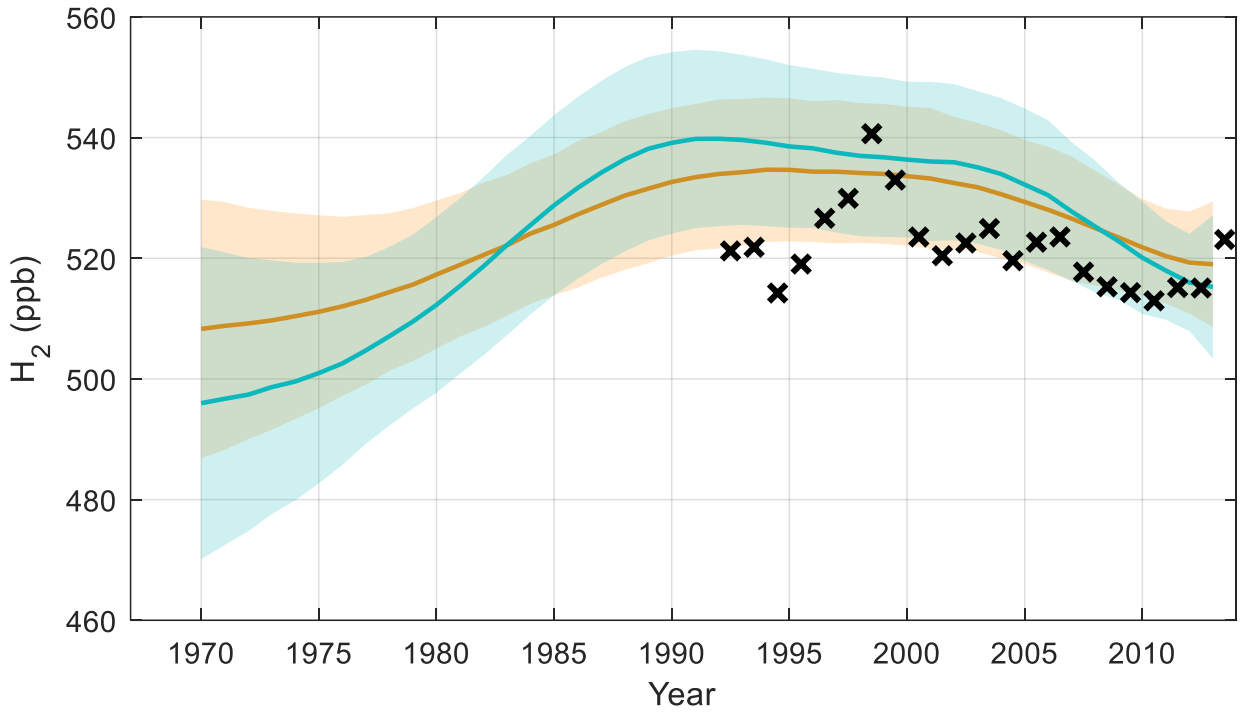


Figure S3: Atmospheric histories reconstructed independently from firn air profiles at three Greenland sites as in Figure 1. The larger non-linearity correction form Jordan & Steinberg (2011) has been applied to the firn air measurements from Tunu. For comparison, the original Tunu atmospheric history from Figure 1a is plotted as the dark red dashed line in a) and the measurements from Figure 1d have been plotted as green triangles in d). The same trends are observed in both Tunu histories, but the history resulting from the Jordan & Steinberg (2011) non-linearity correction is ~15 ppb higher than the history resulting from the NOAA/GML non-linearity correction. There is still an apparent calibration offset between the Tunu history and the histories reconstructed from the other two sites.

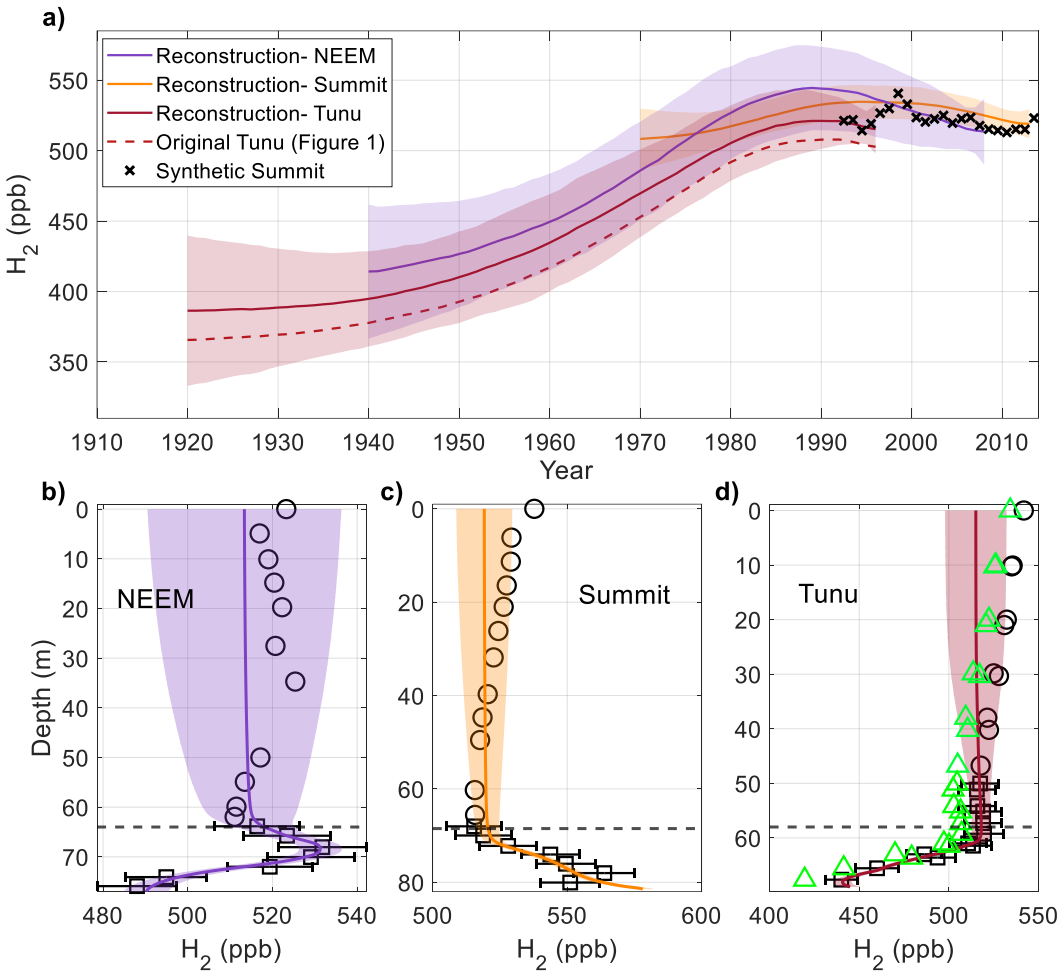


Figure S4: Joint atmospheric H_2 reconstruction using firn air from three Greenland sites (NEEM, Summit, and Tunu) as in Figure 2. The larger non-linearity correction form Jordan & Steinberg (2011) has been applied to the firn air measurements from Tunu. For comparison, the original joint atmospheric history from Figure 2 is plotted as the dashed magenta in a) and the measurements from Figure 2d have been plotted as green triangles in d). The differences between original joint reconstruction and the Jordan & Steinberg (2011) corrected reconstruction are minimal because of the inclusion of the calibration offset parameter in the inversion (γ). Optimized γ is 1.071 in the original reconstruction and 1.038 in the Jordan & Steinberg (2011) corrected reconstruction. The different γ's compensate for the different corrections.

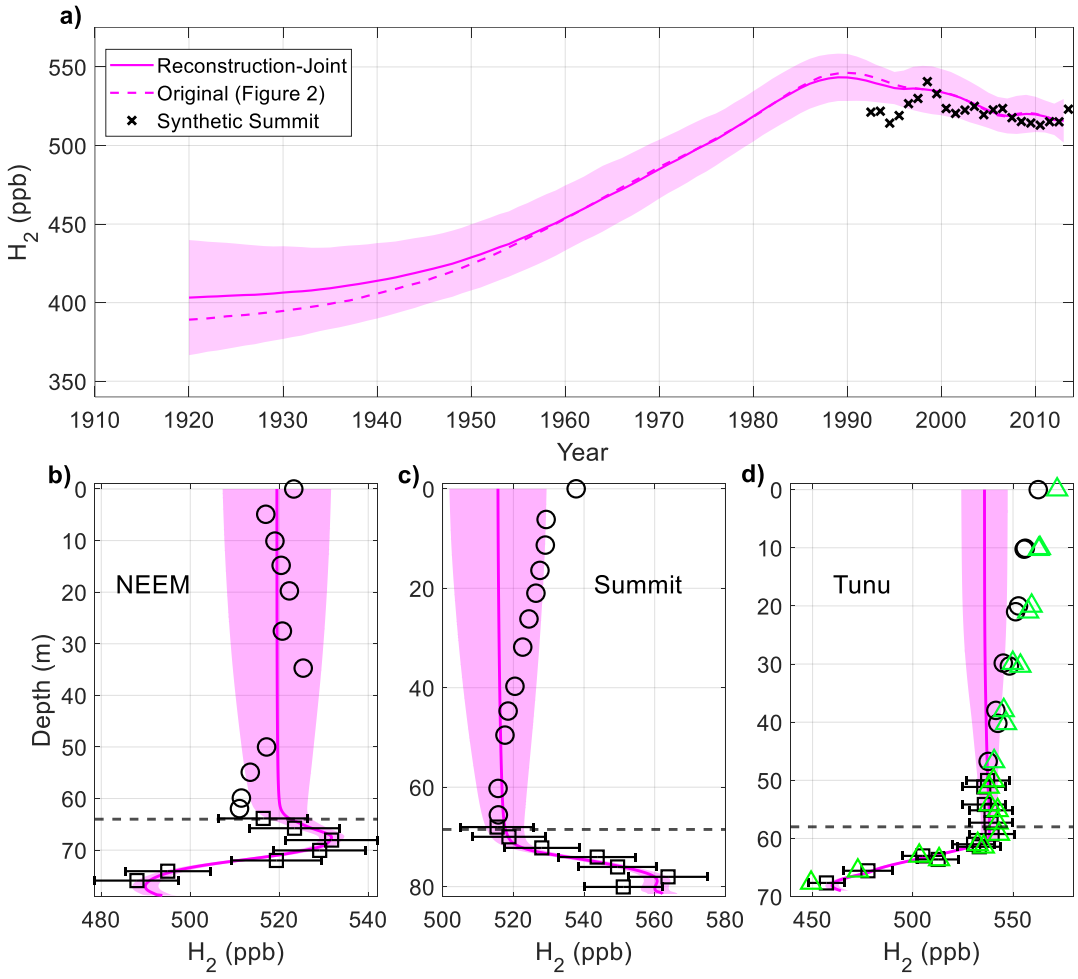


Figure S5: The synthetic history used to force the firn air model (blue line and shading in a) and depth profiles generated by the model (blue line and shading in b-d) as described in Section 5. Firn air measurements are plotted in b-d as in Figure 2. For comparison, the joint reconstruction and corresponding modeled depth profiles are plotted as dashed pink lines. The depth profiles modeled from the synthetic history show substantially poorer agreement with the measurements, particularly from 65-70 m at NEEM and 50-60 m at Tunu.

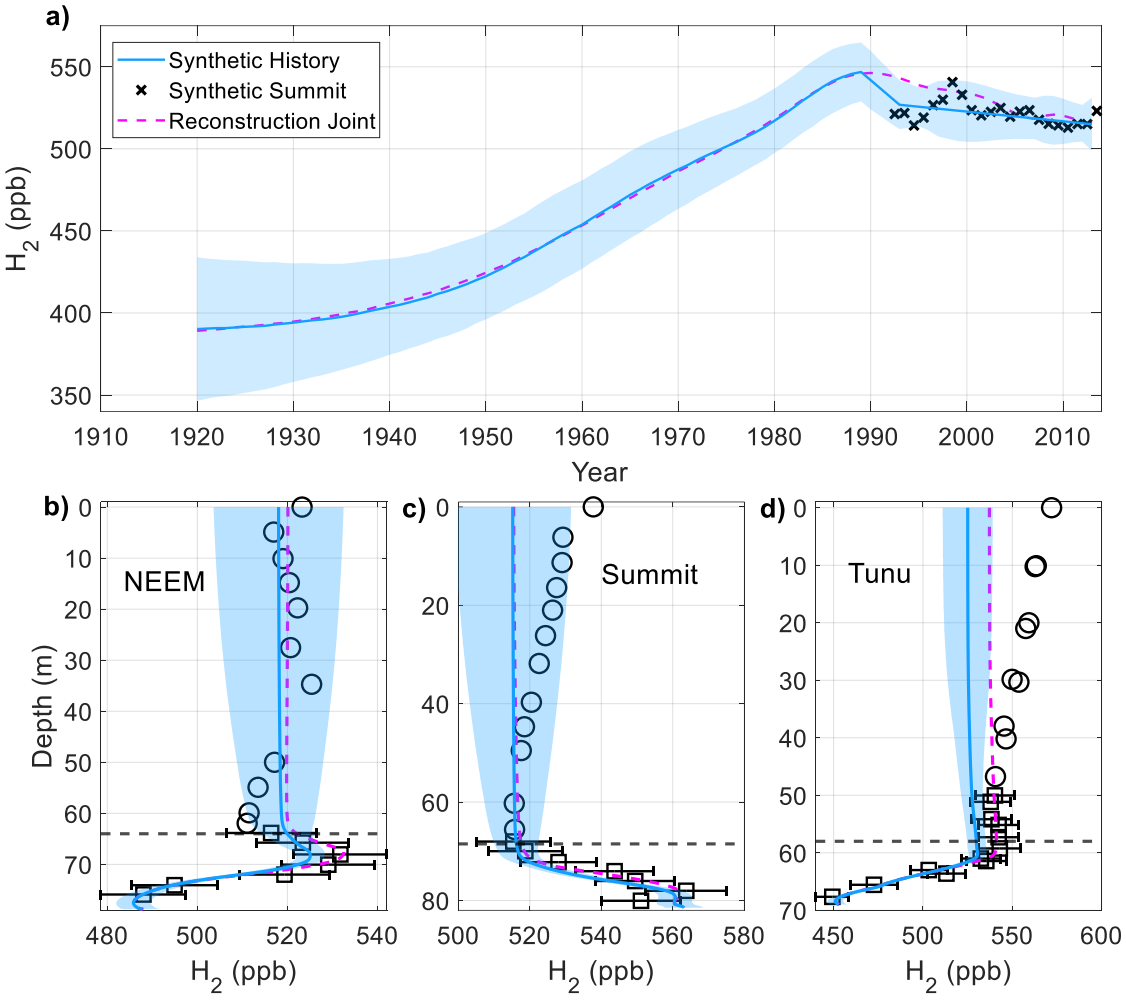


Figure S6: Density profiles used to model firn air at NEEM (a) and Summit (b). Annual mean density (black lines are based on measurements (Buizert et al., 2012; Adolph & Albert, 2014); Winter layer density (blue lines) and summer layer density (red lines) are estimated based on Fujita et al., 2014.

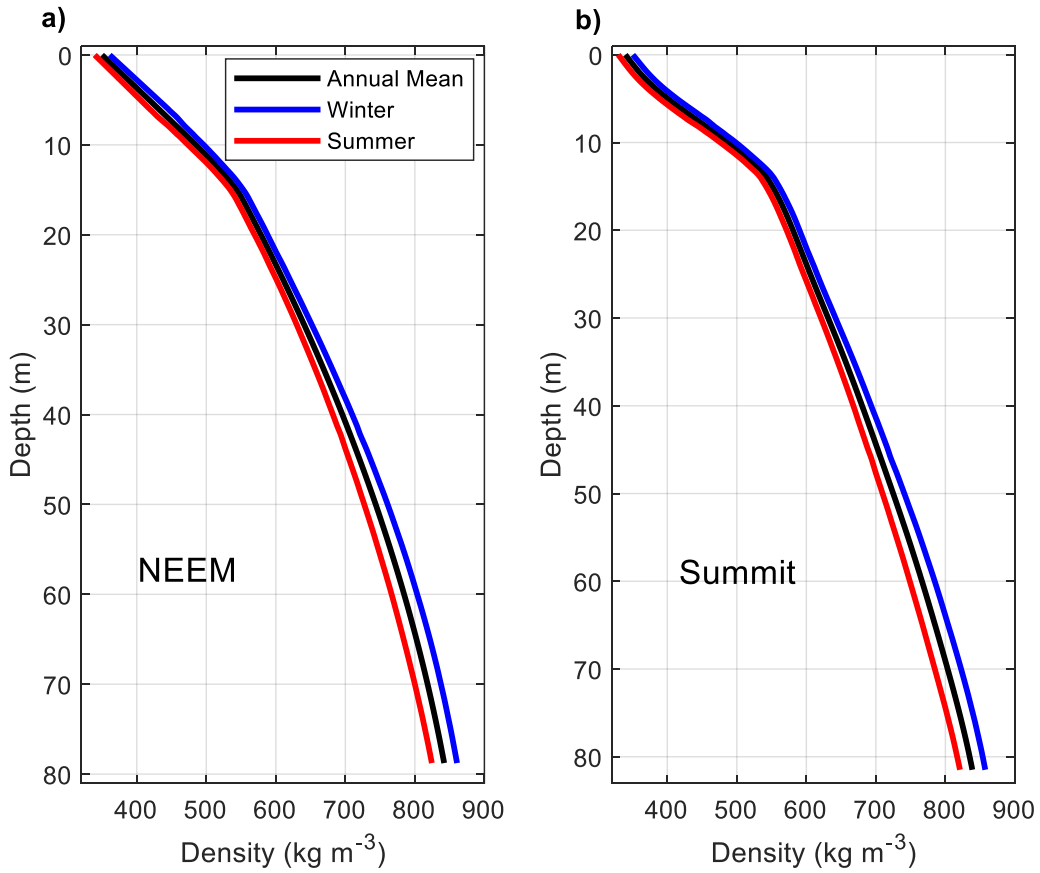
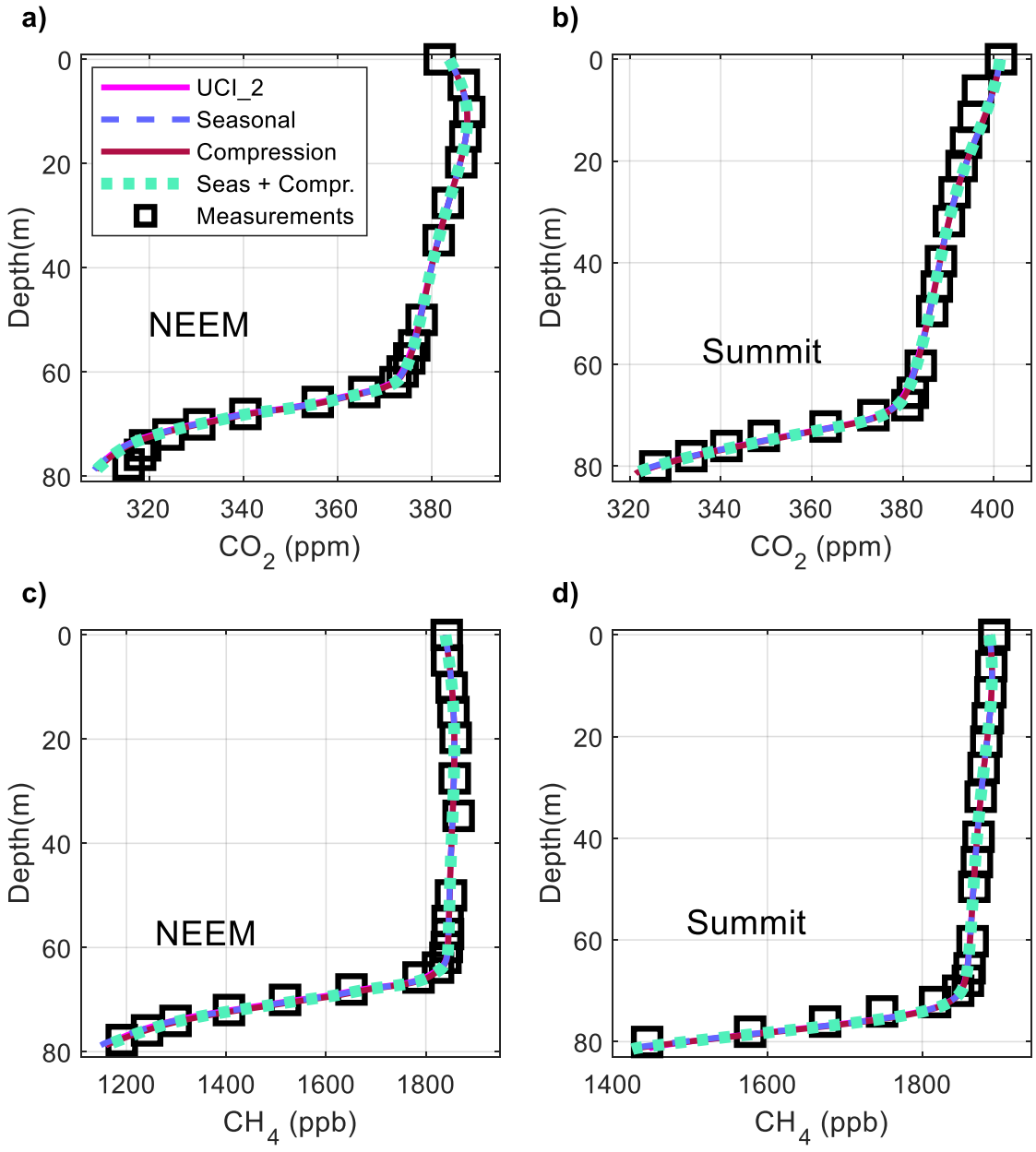


Figure S7: Measured and modelled CO_2 and CH_4 in the firn air at NEEM and Summit. Magenta lines- CO_2 and CH_4 levels generated by the original UCI_2 model; dashed lavender lines- CO_2 and CH_4 levels generated by the model with seasonal layering implemented (Section 7.1); maroon lines- CO_2 and CH_4 levels generated by the model with reduced bubble compression (Section 7.2); dotted cyan lines- CO_2 and CH_4 levels generated by the model with both seasonal layering and reduced bubble compression (Section 7.3); black squares- CO_2 and CH_4 measurements corrected for gravitational fractionation and depth-averaged. Modelled CO_2 and CH_4 are insensitive to the revisions described in Section 7 because they are not affected by pore close-off fractionation.



References

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