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Supplement of

Reconstructing atmospheric H_2 over the past century from bi-polar firn air records

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Supplement

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)

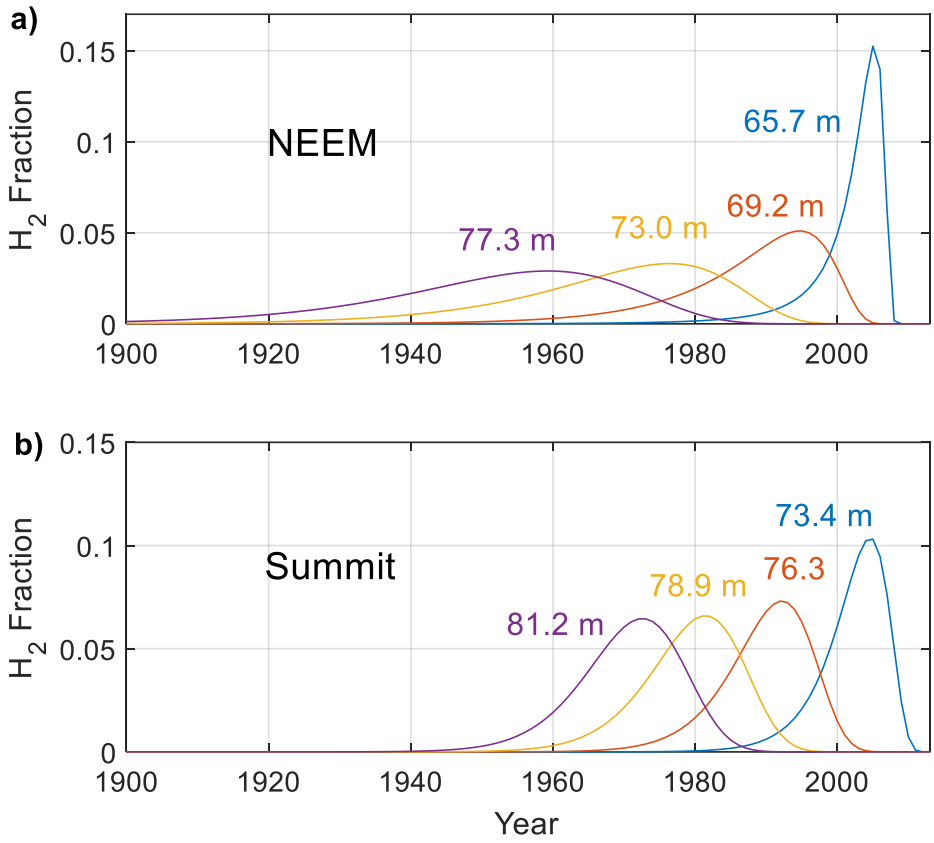


Figure S2: Atmospheric histories reconstructed independently from firn air profiles at the two Greenland sites using the *Mitchell_optimized* configuration. a) purple line and shading- result from NEEM and associated ±1σ uncertainty; orange line and shading- result from Summit with the uncertainty on the firn measurements reduced by 50% and associated ±1σ uncertainty; dashed black line- the "base-case" Summit reconstruction plotted in Figure 4a; black x's– annual mean synthetic Summit H_2 history (Section 5; Pétron et al., 2023; Langenfelds et al., 2002), purple crosses and orange triangles- firn data plotted against modeled mean age for NEEM and Summit respectively, the firn data have been adjusted for the effects of pore close-off fractionation; b) black markers- measured H_2 depth profile at NEEM; squares with error bars are measurements used in the reconstruction, and circles are measurements excluded from the reconstruction because of seasonality ; purple line and shading- modeled depth profile using the atmospheric history plotted in purple in a) with the propagated ±1σ uncertainty; the dashed black line indicates the top of lock-in zone; c) as in b) for Summit, with the measurement error reduced by 50%; Reducing the uncertainty on the Summit measurements yields H_2 levels 15-20 ppb lower prior to 1975 and very similar levels after 1975. The modeled depth profile in the reduced uncertainty case shows a decreasing trend in the bottom of the firn as is observed in the measurements.

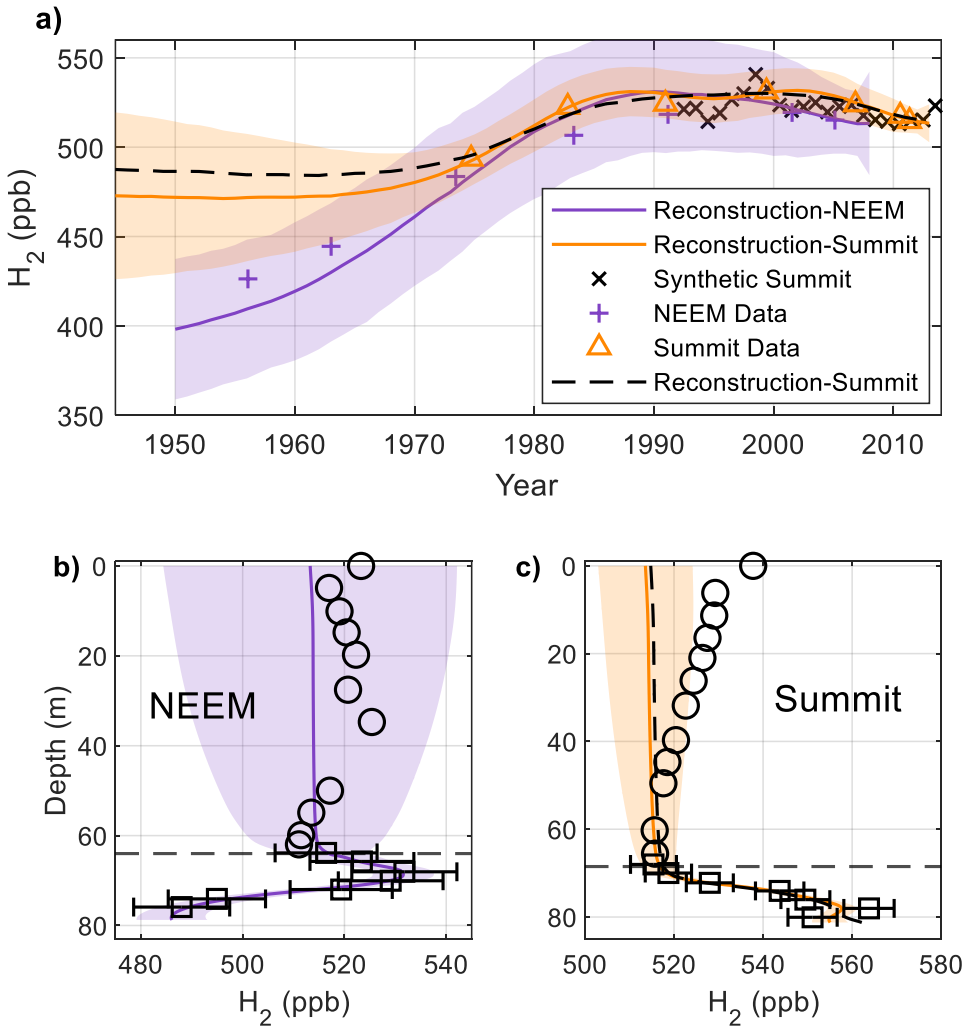


Figure S3: Age distribution (or Green's Function) for H_2 at Megadunes at a depth of 67.4 m calculated with (blue line) and without (magenta line) pore close-off fractionation enabled.

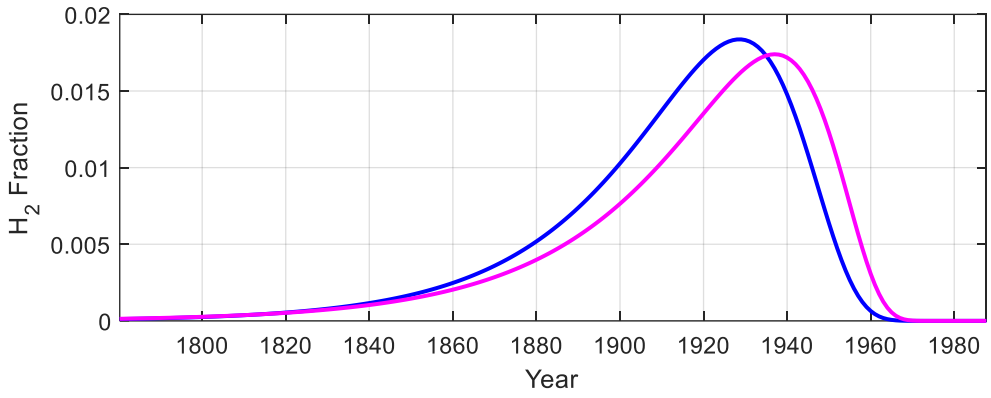


Figure S4: The synthetic history used to force the firn air model (blue line and shading in a) and depth profiles generated by the model (blue line and shading in b-c) as described in Section 4. Purple crosses and orange triangles are the firn data plotted against modelled mean age for NEEM and Summit respectively as in Figure 4. Firn air measurements are plotted in b-c as in Figure 4. For comparison, the joint reconstruction and corresponding modeled depth profiles are plotted as dashed green lines. The depth profiles modeled from the synthetic history show good agreement with the measurements.

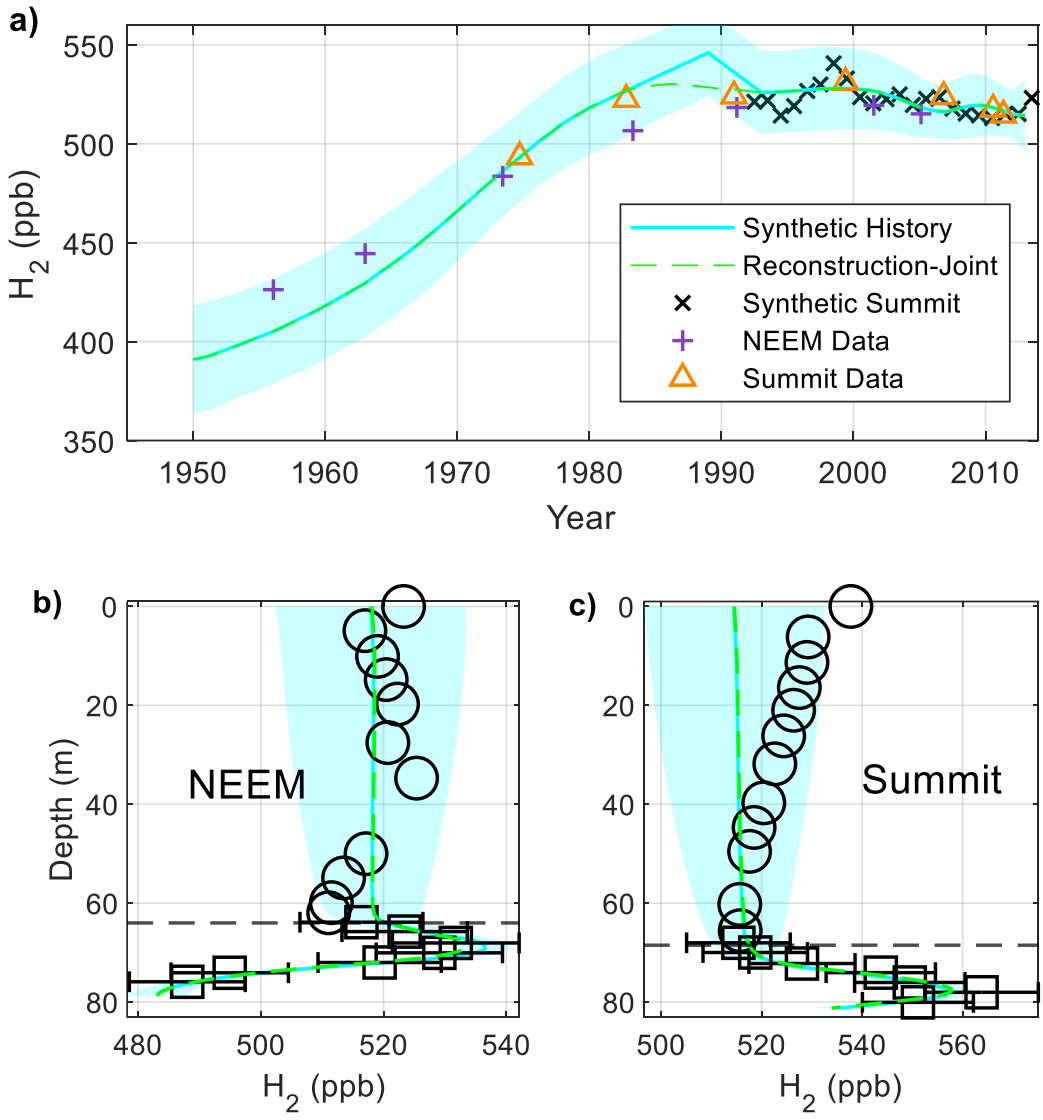
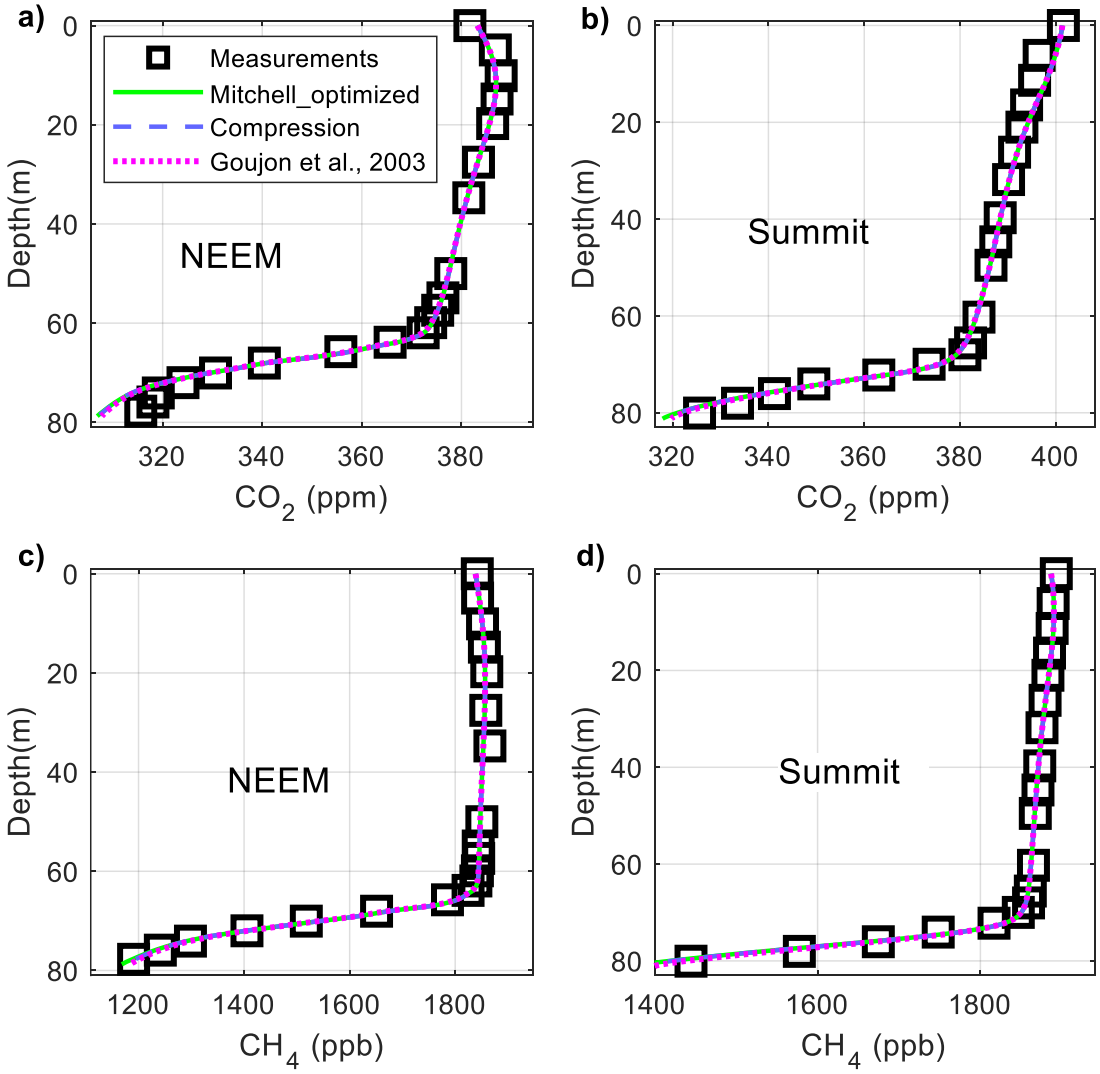


Figure S5: Measured and modeled CO_2 and CH_4 in the firn air at NEEM and Summit using the three model configurations described in Section 3.2: *Mitchell_optimized* (green lines), *Compression* (dashed purple lines), and Goujon et al. (2003; dotted magenta lines).



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