Low atmospheric CO2 during the Little Ice Age due to cooling-induced terrestrial uptake

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**Low atmospheric carbon dioxide (CO2) concentration1 during the Little Ice Age has been used to derive the global carbon cycle sensitivity to temperature2. Recent evidence3 confirms earlier indications4 that the low CO2 was caused by increased terrestrial carbon storage. It remains unknown whether the terrestrial biosphere responded to temperature variations, or there was vegetation re-growth on abandoned farmland5. Here we present a global numerical simulation of atmospheric carbonyl sulfide in the pre-industrial period. Carbonyl sulfide concentration is linked to changes in gross primary production6 and shows a positive anomaly7 during the Little Ice Age. We show that a decrease in gross primary production and a larger decrease in ecosystem respiration is the most likely explanation for the CO2 decrease and carbonyl sulfide increase. Therefore, temperature change, not vegetation re-growth, was the main cause for the increased terrestrial carbon storage. We address the inconsistency between ice core CO2 records from different sites8 measuring CO2 and 13CO2 in ice from Dronning Maud Land (Antarctica). Our interpretation allows us to derive the temperature sensitivity of pre-industrial CO2 fluxes for the terrestrial biosphere (L = -10 to -90 PgC K-1), implying a positive climate feedback and providing a benchmark to reduce model uncertainties9.**

Models of future carbon cycle-climate changes predict a large range in atmospheric carbon dioxide (CO2) concentrations, mainly because of uncertainties in the response of the terrestrial carbon cycle to the future temperature increase9. While the carbon cycle is currently dominated by the effect of anthropogenic CO2 ('fertilization'), pre-industrial records of temperature driven-CO2 changes provide a way to quantify the size of temperature-carbon cycle feedbacks. The Little Ice Age (LIA, 1500-1750) was a widespread10 cool period that coincided with low CO2 concentrations1 (Figure1a). The CO2 change made only a minor contribution to the cooling1, therefore the LIA is a suitable epoch from which to derive the carbon cycle sensitivity to temperature2.

It has recently been shown that changes in terrestrial organic carbon storage best explain the observed multi-decadal variations in CO2 concentrations over the past millennium3. However, there are open questions about the size of the atmospheric LIA CO2 decrease8 and whether it was caused predominantly by the temperature response of land4, or by land use change following pandemics5. To accurately determine the terrestrial carbon cycle's sensitivity to temperature (L) from the LIA records, it is crucial to clearly identify the cause of the LIA CO2 decrease and to precisely quantify its size.

The net terrestrial CO2 flux to/from the atmosphere depends on the difference between Net Primary Production (NPP) and Heterotrophic Respiration (Rh). Two hypotheses have been proposed to explain the low CO2 during the LIA: 1) global NPP increased due to widespread abandonment of farms caused by pandemic diseases11; 2) global NPP decreased due to the effect of temperature, but Rh reduced proportionately more due to its higher sensitivity to temperature4.

Carbonyl sulfide (COS) and CO2 are both removed from the atmosphere by plants through leaf stomata. Unlike CO2, however, COS is hydrolysed by the enzyme carbonic anhydrase and there are no major emissions of COS back to the atmosphere from the terrestrial biosphere at the global scale, other than from biomass burning12. Carbonyl sulfide has been used to investigate variations of the recent gross terrestrial carbon flux12, as the atmospheric COS concentration over land varies as a function of Gross Primary Production6 (NPP=GPP-Ra, Autotrophic Respiration). The record of COS from Siple Dome ice covering the last 350 years, merged with the more smoothed 2000 year record from SPRESSO ice7, shows a positive anomaly of COS concentration during the LIA compared to the preindustrial average (Figure 1a). We interpret the positive COS anomaly as an effect of a decrease in GPP at the global scale, assuming that COS emissions from the ocean did not significantly change during the LIA. To test our hypothesis, we quantify the perturbation of the pre-industrial COS budget due to a temperature decrease. We write a COS budget for present times12 with uncertainties associated with the fluxes13. We write the sinks to soil, canopy and chemical removal (mostly driven by hydroxyl radical, OH·) using first-order kinetics with coefficients (ksoil, kcanopy and kOH) derived from their modern values12:

Foc-COS + Foc-DMS + Foc-CS2 + Fant-COS + Fant-CS2 + Fant-DMS + Ffire-COS + Foc-phot-COS = [COS] \* (kOH + kcanopy + ksoil) (1)

where oc = ocean, ant = anthropogenic, and source terms are from left to right: the direct oceanic COS flux (photochemical); the indirect oceanic fluxes as dimethyl sulfide (DMS) and carbon disulfide (CS2), both quickly oxidised to COS; the direct anthropogenic COS flux; the indirect anthropogenic fluxes as CS2 and as DMS; biomass burning; an additional photochemical ocean flux previously used to balance the budget12. We then use the same terms and ks to write a pre-industrial COS budget, setting the anthropogenic COS emissions to zero and halving the biomass burning COS source (see Methods and Supplementary Table 1). To simulate the pre-industrial to LIA COS variation, we assume the same relative decrease in GPP and Rh as those given by the Q10 factor of the one-dimensional global carbon cycle model4 for an idealized temperature change of 1 °C (4.8 % for GPP corresponding to the canopy uptake sink, kcanopy, and 5.2 % for Rh, associated with the soil sink, ksoil). We calculate a pre-industrial to LIA COS increase of 18 ppt, which is in the same direction as (though smaller than) the measured anomaly7 (Figure 1a). To attribute a likelihood to the COS increase, we set uncertainties of the source terms at 20% of the modern values, assuming that most source processes will change relatively little, and uncertainty in the turn-over rates at 10% of preindustrial values. With this configuration, the calculated reduction in GPP is significant at the 95% level. In summary, the contemporaneous CO2 decrease and COS increase can be explained by the reduced temperature during the LIA, causing GPP, NPP and Rh to decrease, with the respiration reduction dominating due to its higher temperature dependence.

Figure 1

Different explanations are unlikely. A decline in farming activity during the LIA would have increased global GPP due to vegetation re-growth, thus decreasing atmospheric COS, and meaning that pandemic-induced abandonment of farms was not the main cause of the atmospheric CO2 decrease5,11. Our finding agrees with modelling results showing that the effect of anthropogenic land use change on atmospheric CO2 was negligible during the LIA14, and that there was a net flux of carbon into the European terrestrial biosphere due to increased soil carbon storage as a result of cooling15. The net long-term effect of the LIA biomass burning decline16 on CO2 is uncertain, due to vegetation re-growth after fire. However, a reduction in biomass burning would have decreased COS. Our interpretation supports the negative L found by CMIP517 (Coupled Model Intercomparison Project), that is, a positive climate feedback of terrestrial carbon.

These findings allow us to estimate L from the pre-industrial period. There are numerous regional, continental and global temperature reconstructions available over the last millennium (Figure 1b and c show those18,19,20,21 used in the following calculation of L). However, there are inconsistencies between different LIA CO2 records, including the high accumulation rate sites DSS (Law Dome, East Antarctica1) and WAIS Divide (West Antarctic Ice Sheet8), and the low accumulation rate sites South Pole and EDML (EPICA Dronning Maud Land22). The WAIS CO2 record is 3-6 ppmv higher than the DSS CO2 record8, and the cause of the offset remains elusive8.

To provide further insights into CO2 variations during the LIA, we have measured the CO2 concentration in air extracted from the medium resolution Antarctic ice core Dronning Maud Land (DML) covering the period 1300-1900 (Figure 2a). Figure 2b shows the records from DSS1,23 and WAIS8.

The gas age distribution of DML (68 % width = 65 years, Figure 2c) is wider than that of DSS (68 % width = 8 years) and WAIS24 (68 % width = 19 years). Therefore, DML provides a more smoothed record of atmospheric composition changes than DSS and WAIS.

Figure 2b shows the most likely (dotted blue line) atmospheric CO2 history providing the closest (see SI3.2 for details) reconstruction to the DSS observation once smoothed with the DSS age distribution (solid blue line). The DSS-derived atmospheric CO2 record smoothed with the DML age distribution closely reproduces the LIA CO2 decrease measured in DML ice (compare red line and red circles in Figure 2a), providing evidence that the CO2 records from DSS and DML are compatible (largest difference = 2.1 ppm). On the contrary, the WAIS-derived atmospheric CO2 history smoothed with the DML age distribution (dashed, red line in Figure 2a) shows higher values than the new DML CO2 record for all ages, confirming the CO2 offset in WAIS.

Figure 2

To partition the contribution from the terrestrial biosphere and the oceans to the total CO2 decrease, we have measured the 13C change between 1300 and 1900 in DML ice (Figure 3a). With improved methodology24, and using ice suitable for CO2 analyses (with low carbon monoxide levels, SI4.2), we have carried out reliable and high precision 13C measurements of CO2 extracted from ice bubbles (typical total uncertainty for DML: 0.05 ‰). A Kalman Filter Double Deconvolution (KFDD25) of the DML 13CO2 and CO2 changes confirms that the terrestrial biosphere was the main contributor to the atmospheric CO2 decrease (Figure 3b). The oceans response to the atmospheric change partially counters the terrestrial flux (Figure 3c).

Figure 3

Carbon cycle-climate model simulations of the LIA CO2 have often combined the data from different ice cores26, without consideration of the different air age resolution of the cores. We take advantage of the higher resolution information available from DSS to estimate L. It is likely that the LIA CO2 net flux was mostly driven by the high-latitude Northern Hemisphere terrestrial response to temperature because: 1) the Northern Hemisphere contains most of the world's terrestrial biosphere; 2) the LIA temperature reconstructions showing the best correlation with the CO2 decrease (Figure 1b) are from the high-northern latitude regions18,20 and, specifically, the Arctic3,21. Therefore, to derive L, we use a number of Northern Hemispheric temperature reconstructions18,19,20 (Fig 1b) together with the DSS CO2 record1,23.

We use a timescale-dependent characterisation27 of the response of the carbon cycle to estimate the strength of the temperature influence (Methods). This provides a coherent quantification of temperature-to-carbon feedbacks and reconciles previous studies2,3,26 with consistent use of L and appropriate recognition of time scales. The carbon cycle response is represented by a response function consisting of a sum of exponentials28. We parameterise the terrestrial response in terms of ' (Pg of C yr-1 K-1) with a re-adjustment on 100 year timescales. This can be related to  (Pg of C K-1) with the dependence on , the timescale of variation given by  = - '/(1/ + 1/100). Our fits are consistent with fitting timescales of 100 years so that  ≈ -50 '. We obtain ' for various regions, X, by fitting temperature records TX to give estimates 'X and applying scale factors that characterise the relation between global and regional changes. We derive a range of ' (see Supplementary Table 2) that corresponds to L in the range: -10 to -90 Pg of C K-1 when using a factor of 2/329 to convert NH L to global. This estimate of the temperature sensitivity of terrestrial carbon stores can be used to constrain model predictions of future CO2 and temperature in CMIP6.

The first model interpretation of the LIA COS increase demonstrates that cooling, rather than recovery from land use, was the main cause of the LIA CO2 uptake. Our finding argues against the recent suggestion that 1610 could mark the beginning of the Anthropocene30. COS concentration shows great potential as an independent measure of pre-industrial CO2 fluxes that will be improved with additional ice core data and reduced uncertainty in the source terms.

Methods

COS model

We divide the last 700 years into 3 time slices: Present (industrial), Pre-industrial and LIA. The magnitudes of terms (sources and sinks) in equation (1) for the three time slices are reported in Supplementary Table 1. The inverse residence times (rate coefficients) are calculated as the ratio of each sink to the atmospheric COS concentration (kOH= 101/484 = 0.21, kcanopy= 738/484 = 1.52, ksoil = 355/484 = 0.75) for time slice "Present", which is out of balance by 74.5 Gg of S/year. We write a preindustrial COS budget by setting the anthropogenic COS emissions to zero, halving the biomass burning flux31 and using the inverse residence times calculated for "Present". With an average preindustrial COS concentration of 330 ppt7, we derive a budget unbalanced by 132 Gg of S for the pre-industrial period (Table S1), meaning that an atmospheric COS concentration of 383.5 ppt would be required to balance the budget (with corresponding sinks of 80, 585 and 281 Gg of S/year). We associate the uptake of COS by canopy and soil to photosynthesis (GPP) and heterotrophic respiration (Rh), respectively12,32:

kcanopy = Kcanopy \* GPP; ksoil = Ksoil \* Rh

We simulate the effect of changes in GPP and Rh during the LIA by scaling kcanopy and ksoil to the same relative changes used by the one-dimensional global carbon cycle model4 (4.8 % and 5.2 % respectively) for an idealised temperature change of 1 °C (the maximum change for the Northern Hemisphere land, where the effect is most relevant). GPP is often assumed to be roughly twice NPP and it is reasonable to assume a similar Q10 value for both. kcanopy and ksoil become 1.45 [(1.52-1.45)/1.52\*100=4.8%] and 0.70 [(0.73-0.70)/0.70\*100=5.2%] respectively. Assuming a balanced budget, we calculate a COS concentration of 401.6 ppt for the LIA, corresponding to a pre-industrial-to-LIA atmospheric COS concentration increase of 18 ppt (401.6-383.5 ppt). Even with uncertainty in the source terms of 30% of modern values, GPP reduction is significant at the 90% level.

We note that autotrophic respiration (Ra) does not have an influence on the COS budget because COS is hydrolysed by plants. We also note that an anoxic soil source may have a strong temperature dependence33 suggesting that for some times and locations the soil source can overwhelm the soil sink. However, plant uptake generally dominates the COS budget over land. This observation allows us to assume that sources of COS from soils can be considered negligible on the global scale.

The reforestation assumed by the early anthropogenic hypothesis implies a significant shift from C4 to C3 productivity. Considering that Leaf Relative Uptake (LRU) is 60 % higher for C3 than C4 plants34 and that COS uptake can be approximated as GPP × LRU × (COS/CO2) mixing ratio, the C4 to C3 shift should have driven a decrease in COS, not the observed increase.

CO2 uptake responds to changes in CO2 concentration, the so-called “CO2 fertilisation effect”, which increased CO2 uptake over the industrial period. This has been hypothesised to contribute to an increase of COS concentration during the Industrial period31. A reverse effect of decreased CO2 on CO2 uptake probably occurred in the LIA, but it would have either not affected or have led to a small decrease in COS, as lower CO2 concentration would have opened more stomata and increased COS uptake. For a steady-state solution with fixed sources, the LIA CO2 decline of 1.5-2% (Fig. 2) and a corresponding GPP decline of 5% would result in a COS rise of 3%. This is assuming the LRU does not change and the soil sink is more or less in one-to-one correlation with the canopy sink.

To test the sensitivity of the COS result to changes in the photochemical ocean fluxes used previously to balance the budget12 (this is the main and most uncertain source term), we repeat the calculation described in the main text with a number of different photochemical ocean fluxes. In Supplementary Table 1, the case that would balance the preindustrial budget is shown in parentheses (469 GgS instead of 600 GgS). For this photochemical ocean flux we find a pre-industrial-to-LIA atmospheric COS concentration increase of 16 ppt (330 to 346 ppt, compared to 18 ppt found with a photochemical ocean flux of 600 GgS), suggesting that the simulated pre-industrial-to-LIA COS anomaly does not depend strongly on the magnitude of ocean emissions of COS. If we combine the direct and the additional ocean photochemical fluxes into one term in our analysis, our conclusions would not be affected.

It is worth noting that a number of mechanisms (photochemical and dark production, hydrolysis, air-sea gas exchange, and vertical mixing) contribute to the direct ocean-atmosphere flux of COS35,36, plus the indirect flux due to the conversion of carbon disulfide (CS2) and dimethylsulfide (DMS) to COS by atmospheric oxidation processes. Based on the complex nature of the relationship between climate and oceanic fluxes, it is unlikely that the processes contributing to the oceanic flux of COS would have all responded to a changing climate in the same direction during the LIA. It is thus difficult to estimate pre-industrial to LIA changes of the net ocean-atmosphere COS flux and use them in our simple approach. Finally, we have also tested the sensitivity of our result to changes in the biomass burning flux31 and we have not found any significant change (data not shown).

The positive LIA COS anomaly found in the LIA7 needs to be confirmed in order to constrain more sophisticated CO2/COS models. A recent study37 has focused on the last 8000 years and does not have the resolution required to look at the LIA in detail. A new high resolution record of COS is needed for further investigation of the change of atmospheric COS during the LIA.

The relationship between GPP, CO2 and COS is complicated and our simple model does not address all of the details of it. However, our analysis captures the main elements of the budget and consistently leads to our conclusion that cooling, rather than recovery from land use, was the main cause of the LIA CO2 uptake.

Antarctic sampling sites

The DML ice core was drilled dry with an electromechanical drill from Dronning Maud Land (77°S, 10°W; 2300m asl, Fig. S1) during the 1997/1998 austral summer38. The site has a mean annual temperature of -38 °C and a relatively high snow accumulation rate (70 kg m-2 yr-1) compared with the Antarctic plateau, though much lower than Law Dome. Eighteen firn air samples39 were taken starting from the surface to the firn-ice transition zone at 73.5 m and used to constrain the firn diffusion model40,41. The ice age scale for DML has been defined using a combination of layer counting, correction for densification, then a glaciological thinning model guided by several volcanic markers in the non-sea salt sulphate observed in the core and correlated across to other well-dated cores42.

A second high resolution core, DSS0506 from Law Dome, reaching back only to 1700 AD (gas age), is used to extend the new record from DML to more recent times, link with CO2 measurements over the industrial period (SI4.1), and show that the DML records are compatible with the CO2 and 13C-CO2 reconstructions over the last two centuries23. DSS0506 was thermally drilled in a dry hole during the 2005/2006 austral summer in the DSS region of Law Dome (66°46’S, 112°48’E; 1370 m asl, Supplementary Figure 1). The site has high snow accumulation rate (600 kg m-2 yr-1) and a mean annual temperature of -22°C. In the following, measurements from DML and DSS0506 are also compared to the results previously published from the DE08 core (Law Dome, 66°43’S, 113°12’E)1,23. The ice age scale for DSS0506 was matched through 18O-H2O measurements to the ice age scale assigned to previously sampled DSS cores42. Locations of the sites are shown in Supplementary figure 1.

Extraction of air from ice cores and analysis of CO2, 13C-CO2

The extraction of air from ice uses a dry grating technique in the Ice Core Extraction Laboratory (ICELAB) at the CSIRO Aspendale (Australia). The extraction procedure has recently been optimised for 13C-CO2 measurements23. Briefly, 0.7–1.0 kg of ice was cooled to –80 °C in a chest freezer for at least 24 h prior to extraction. The ice was then sealed in a stainless steel container containing a perforated inner cylinder and the vessel evacuated to less than 10–4 Torr for at least 25 min. The ice was grated by mechanically shaking the container for 10 min. This process yielded on average 70 mL of air at STP, estimated by the extraction line volume and pressure. The air was cryogenically collected in a stainless steel tube welded to a Swagelok valve and soldered to a copper base which was cooled to 23–24 K, after removing water at –100 °C. The sample tube (trap) was warmed in a water bath at room temperature for 5 min, before being connected to the gas chromatographs and split for manual injection and analyses of CO2, CH4, N2O and CO (within 1 h of the extraction) and to a MAT252 IRMS for 13C and 18O (within 12 h).

Firn modelling

We used the CSIRO firn model40,41 to date firn air, calculate the age distributions and provide corrections for gravity and diffusion fractionation.

Inputs to the firn model used for DML are mean annual temperature (-38°C), pressure (730mb), accumulation rate (70 kg m-2 yr-1), the depth profile of firn density (spline fit to density measurements) and profiles of closed and open porosity versus density (there are no closed porosity measurements for DML, so we use a spline fit based on closed porosity measurements at DE08-2 with a correction for cut bubbles40,41). We calibrated effective diffusivity (or, more accurately, inverse tortuosity) versus porosity to give optimum agreement between the modelled and measured concentration of eight trace gases (Supplementary Figure 2).

For DSS0506, there are no measurements of firn air to tune the firn model diffusivity, and no closed porosity measurements. Considering that DSS and DSS0506 are very close to each other (about 300 m), we assume that DSS0506 has the same characteristics as DSS, and use the same model inputs as used for DSS23.

Gas diffusion in firn causes the air trapped in ice to be younger then the surrounding ice. The gas-age of each sample can be obtained from the ice-age, considering an ice age-gas age difference. For DML, from the drilling and firn sampling records, the close-off depth, the depth at which it is no longer possible to withdraw air out of the firn with a vacuum pump, is around 72 m. The age of DML ice at 72 m is 664 years from the drilling date of January 1998, so the year 1334. From our firn modelling, the mean age of CO2 in air at close-off is 76 years, giving an age difference between ice and air of 588 years for CO2, which we apply to all samples.

For DSS0506, the ice-air age difference for CO2 used for DSS is used here (61 years). This number is consistent with previous work1,23 and provides the age for which measurements of CH4 concentration in DSS ice best overlap the measured CH4 at DE08 and DE08-2 ice, and the age which is most consistent with the measured 14C-CO2 bomb pulse44.

Double Deconvolution

A double deconvolution calculation uses CO2 and 13C to estimate the net fluxes of CO2 between the atmosphere and terrestrial biosphere and the atmosphere and oceans. We use the new DML CO2 and 13C records in the Kalman Filter Double Deconvolution25 (KFDD). This combines the statistical analysis of the Kalman Filter, which allows estimation of uncertainties in the fluxes, with CO2 and 13C mass balance from a (globally aggregated) carbon cycle model (needed to calculate the isotopic disequilibrium fluxes). The carbon cycle model we use consists of a two-box terrestrial model and a mixed layer pulse response function of a box diffusion model of the ocean. The KFDD is well suited to interpretation of ice core data with long gaps because it does not assume values for either CO2 or 13C in the data gaps.

Discrepancy between the 13C records at DML/DSS and at WAIS.

The difference between the 13C records at DML/DSS and at WAIS (Figure 3a) could be due to differences in the calibration scales used at CSIRO and at Oregon State University, or to the effect of *in-situ* production of CO2 on its 13C. An inter-comparison between CSIRO and Oregon State University8 has checked the calibration issue for CO2, but this has not been done for 13C (this is planned), so the reason for the difference is currently unknown. However, the CSIRO records link ice and firn data to well calibrated atmospheric data23, demonstrating their reliability.

Carbon cycle sensitivity to climate change

Our analysis of temperature sensitivity is based on representing the change in atmospheric carbon mass as:

 (SE1)

i.e. temperature influences carbon fluxes (characterised by response function ) and then the carbon cycle (characterised by response function ) responds to concentration changes. This is the same conceptual form as27:

 (SE2)

where and characterise responses to temperature change and and characterise responses to consequent atmospheric change. The mapping between (SE1) and (SE2) involves 3 steps:

- using the Laplace transform45 of (SE1);

- recognising the factor as the CO2 airborne fraction;

- using the general timescale-dependent form of the airborne fraction in terms of Laplace transforms46.

Thus the Laplace transform generalises (SE2) to include a dependence on the timescale47 expressing the response to a temperature perturbation, , as:

 (SE3)

with lower case symbols used for Laplace transforms45,46 and .

The approach of Bauska3 differs from our approach by taking the atmospheric response to the left side of equation (1) as a deconvolution (or in practice double deconvolution) operation. Our representation of is essentially the same as Bauska’s one-box model48. We parameterise it as

 (SE4)

whence . For the present we take = 100 years. The parameterisation used by Bauska48 seems (assuming that C refers to perturbations) to correspond to

 (SE5)

whence

 (SE6)

Thus although Bauska uses to denote the quantity we call it only corresponds to the definition27 of in the limit. Further analysis (to be presented elsewhere) suggests that the estimated for the northern hemisphere48 correspond to

 (SE7)

where the are the timescales of the exponential smoothing used in the estimation. The various values given by Bauska3 are consistent with -46 PgC/K at = 125 years, assuming our preferred values of = 100 years.

To construct our own estimates of the sensitivity, we extract as a factor, with . We use the associative property of convolutions to write (SE1) as

 (SE8)

where is the convolution of and . We express as a sum of exponentials28 and from the one-box model, so that is readily expressed as a sum of exponentials.

To account for our use of regional reconstructions of temperature we put:

 (SE9)

where we introduce factors to relate region X to global temperatures by whence . To provide global estimates we use29 and apply this for both the whole of the northern hemisphere and parts thereof.

The regressions were performed using the "lm" procedure in the programming language R, after calculating at annual time steps. The offset used in defining affects the intercept of the regression, but not the estimate of .

As explained in the main text, the values shown in Supplementary Table 2 can be converted to values simply multiplying them by -50 because our fits are consistent with fitting timescales of 100 years ( ≈ -50 '). Only the temperature reconstructions of the Northern Hemisphere18,19,20 have been used to derive values because we don't attempt a partitioning of the temperature signal into the continental21 contribution (disaggregation). Having shown that DSS and DML agree well (over the time period of DML measurements: 1300-1900), we now use the entire DSS record over the last millennium (pre-industrial) to derive the terrestrial CO2 sensitivity to temperature. In Supplementary Table 2, the CO2 sensitivity to temperature increases (that is, the range of values) becomes more negative going from the 500-1750 to the 1500-1800 time period. This is an effect of the increasing weight of the 1610 CO2 decrease on the total period. Since the 1610 event has not yet been clearly confirmed as a real atmospheric event, we exclude the 1500-1800 period (shown in Supplementary Table 2) from our calculation, because this is the period for which the 1610 event has the highest weight. For the remaining periods, is in the range: -11 to -33 PgC K-1 (500-1750), -15 to -48 PgC K-1 (1000-1750) and -31 to -87 PgC K-1 (1300-1750). As we do not find any reason to favour one of the time periods used, the range of values is approximated as -10 to -90 PgC K-1. The final estimate of  is attributed only to land (L) based on the finding from the double deconvolution that the ocean was not responsible for the CO2 change.

Data availability

The authors declare that the data supporting the findings of this study are available within the article and its supplementary information files.

Code availability

The code used to generate the carbonyl sulfide global numerical model can be accessed on-line.

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Author contributions

DME conceived the study. DME and MR planned the project. DME, AMS, MAJC, RM, and WTS sampled, dated and provided ice cores. MR, DME, CEA, RLL, and LPS carried out the measurements. CMT developed and run the firn modelling and the KFDD. PJR, MR, CMT and DME developed the COS model and interpreted the results. IE, MR, DME and CMT performed the carbon sensitivity to temperature analysis. All authors contributed to results interpretation and manuscript writing.



**Figure 1ǀ Carbon Cycle and temperature variability over the LIA**: Reconstructions of a) atmospheric CO2 (spline fit to Law Dome1, solid line) and COS anomaly (20 year aggregated data7 from the pre-industrial mean of 330 ppt) - the dotted line shows our modelled pre-industrial-to-LIA COS anomaly; b) Northern Hemisphere annual mean (black line is M200518 and red line is Mann9919) and 50 year-smoothed (green line is CL201220) temperature reconstructions; c) 30 year mean-Northern Hemispheric continental temperature reconstructions from the PAGES2k Network21. All temperature reconstructions are expressed as anomalies from the 1961-1990 reference period.



**Figure 2ǀ Comparison of CO2 records**: a) DML CO2 measurements; DSS-derived and WAIS-derived atmospheric reconstructions smoothed with DML age distribution. b) DSS and WAIS CO2 measurements; DSS-derived and WAIS-derived atmospheric CO2 reconstruction; DSS-derived and WAIS-derived atmospheric CO2 reconstruction smoothed with DSS and WAIS age distribution respectively; c) CO2 age distribution for DML, WAIS and DSS. Error bars are 1 uncertainties: they are typically 0.6 ppm (range 0.4-1.4 ppm)23 for DSS and DML CO2 measurements, whereas they are not reported here for WAIS CO2 measurements, but are typically 0.8 ppm (range 0.1-2 ppm)8.



**Figure 3ǀ Double Deconvolution of DML CO2 and 13C**: The new records for a) CO2 concentration and 13C from DML, together with the existing 13C measurements from DSS23 and WAIS3. Error bars are analytical uncertainties (typically 0.6 ppm and 0.05 ‰ for DML and 0.1 ‰ for DSS23). Error bars for WAIS have not been reported, but are typically around 0.04 ‰3. The solid green and blue lines represent CO2 fluxes and their 1 uncertainties for b) the terrestrial biosphere-atmosphere and (c) the ocean-atmosphere, calculated in the KFDD25 using only DML observations.