Dear Editor and referees,

Before providing our answers to the referees' comments, we need to make the Editor and the referees aware of a change in the manuscript we have decided to introduce because of a new article, which has just been published in Quaternary Science Reviews (Koch et al., 2019). We felt that it is important to mention the finding of that article in our paper because of the possible consequences on the interpretation of the greenhouse gas records. Therefore, we have added a sentence at page 15 line 13-16: "*Rubino et al. (2016) showed that the simultaneous COS increase during the LIA confirms that the LIA CO_2 decline was caused by net terrestrial uptake due to cooling (heterotrophic respiration declining more than Gross Primary Production, due to its higher sensitivity on temperature changes), though a very recent paper estimating the amount of carbon taken up by land use change following the colonisation of the Americas by the Europeans (Koch et al., 2019) provides a different view. Nonetheless, the multi-species approach used by Rubino et al. (2016, e.g. using trends of CO_2, $\delta^{13}C$-CO_2 and COS) can provide multiple constraints to help understand the biogeochemical processes behind atmospheric CO_2 variations over the recent past.*", and a sentence at page 17 lines 23-26: "*The emissions from anthropogenic land use change have also been quantified for each world region (Pongratz and Caldeira, 2012, see Fig. 6e), and can be used to subtract the human contribution from the total CO_2 change, even though there is a debate on the amount of land use change following the European colonisation of the Americas (Koch et al., 2019).*"

Referee #1

We thank Referee #1 to support publication of our paper. In the following, we address the referee's comments in the order of appearance in the annotated manuscript.

Page 2, line 1 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text "(GHGs, including halocarbons)" of the following sentence in the manuscript "The three well-mixed atmospheric greenhouse gases (GHGs, including halocarbons) that contribute the most to current global warming are CO_2, CH_4 and N_2O." and has commented: "**there is a contradiction here as the sentence refers to only three GHGs**."

Author's response: The sentence refers to only three GHGs, as the referee correctly points out, because our study does not include another group of well-mixed GHGs that is halocarbons. We agree with the referee that the sentence could be misleading. We believe there is no need to mention these "synthetic greenhouse gases", as the radiative forcing of even the largest one, CFC-12, was below that of N_2O for all but 1984-2008. CO_2, CH_4 and N_2O are the long lived GHGs that contribute most to "current" global warming.

Author's changes in manuscript: We have changed the sentence at page 2 lines 1-2 to: "*The three well-mixed (long-lived) atmospheric greenhouse gases (GHGs) that contribute the most to current global warming are CO_2, CH_4 and N_2O.*"

Page 5, line 2 (of the manuscript with no track changes revisions)

Comment from referee: "**This paragraph needs a map which depicts the different ice core sites, the accumulation distribution and the wind direction**"

Author's response: We agree with the referee that a map would help the reader, so we have produced a map of Law Dome, which is now figure 1. The other figures numbers have been changed accordingly.

Author's changes in manuscript: A reference to Figure 1 has been added at page 5 line 8 "*The ice cores used in this study, referred to as DE08, DE08-2, DSS and DSS0506, were drilled at Law Dome, East Antarctica (Fig. 1).*" Also, the figure caption for figure 1 describes the map: "*Figure 1: Map of the Law Dome region, slightly modified from Smith et al. (2000), showing the location of the drilling sites DE08, DE08-2, DSS, DSS0506 and DSSW20K discussed in the text. Dotted lines are accumulation isopleths (kg m^{-2} yr^{-1}) and unbroken lines are elevation contours (meters above sea level). The inset shows the location of the region in Antarctica*"

Page 5, line 8 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text "Re-working of the accumulated snow is minimal as high wind speeds are relatively infrequent and the snow surface is smooth." and has commented "**I question this statement, there is always wind re-working. You could, however, say that the wind re-working is not able to erase annual layers**"

Author's response: We agree with the referee that our sentence can be improved to describe wind conditions at Law Dome more accurately.

Author's changes in manuscript: We have modified the sentence at page 5 lines 11-13 to: "*Re-working of the accumulated snow is insufficient to erase annual layers as high wind speeds are*

relatively infrequent. The resulting annual layering is thick and regular and preserved for much of the ice thickness (van Ommen et al., 2005)"

Page 6, line 5 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text "ice grown with no visible bubbles in it" and has commented "**this is too vague, how exactly do you produce this ice?**"

Author's response: A detailed explanation of how BFI is produced has been provided in previously published article, such as Rubino et al. (2013). Here, we report a short explanation and introduce a reference to Rubino et al. (2013).

Author's changes in manuscript: We have added a sentence at page 6 lines 12-17 to explain how BFI is produced: "*BFI is grown in ICELAB by keeping a container filled with deionized water in thermal equilibrium, in order to grow ice as slowly as possible from the bottom to the top of the container. The container features Plexiglass sidewalls that are electrically heated. The water exchanges heat only through the metallic base and freezes from the bottom to the top. If the process is slow enough, the produced ice is free of visible bubbles. The results of the tests performed on ICELAB-BFI, as well as on other, externally grown BFI, have been extensively described by Rubino et al. (2013).*"

Page 6, line 25 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text "condensable gases and to extract CO_2 (plus N_2O) from air. The residual CO_2 (and N_2O) is injected into the MAT252 ion source via" and has commented "**you have to describe somewhere how you correct for the N_2O interference in the mass spec (chemical slope calibration)**"

Author's response: A detailed explanation of how the N_2O correction is performed has been provided in previously published article, such as Allison and Francey (2007). Here, we report a short explanation citing Allison and Francey (2007).

Author's changes in manuscript: We have added a sentence at page 7 lines 4-7 to explain how the N_2O correction is performed: "*Nitrous oxide (N_2O) has identical molecular masses to CO_2 and interferes with the isotopic analyses. To remove this interference, a correction is made to the IRMS output in GASLAB using the relative ionisation efficiency of N_2O and CO_2, the isotopic composition of N_2O and the measured N_2O and CO_2 concentration, as described in detail by Allison and Francey (2007)."*

Page 8, lines 17-21 and page 11, lines 12-15 (of the manuscript with no track changes revisions)

Comment from referee: At page 8, line 17-21, the referee has highlighted the text: "Francey et al. (1999) estimated statistical and systematic δ^{13}C-CO_2 biases between 0.025 and 0.07 ‰, and uncertainties of up to ±0.05 ‰, but found an unexplained discrepancy of up to 0.2 ‰ (Trudinger, 2000, section 3.8) around 1900 AD from the South Pole δ^{13}C-CO_2 firn record measured at NOAA-INSTAAR (National Oceanic and Atmospheric Administration-Institute of Arctic and Alpine Research, Boulder, Colorado)." and has commented "**is it worrysome that the Bauska data agree better with the uncorrected Francey data than with the revised data by Rubino (see below)? Note that the Bauska data for the last glacial termination also agree within error limits with the data by Schmitt et al., 2012. This needs more discussion**". At page 11, line 12-15, the referee has highlighted the text: "It is important to resolve the difference between the Law Dome and the WAIS d13C-CO2 records to establish a Pre-Industrial baseline and, thus, a Pre-Industrial-to-Industrial d13C-CO2 difference, as well as a Pre-Industrial to Last Glacial Maximum δ^{13}C-CO_2 difference. These could be

" and has added a comment which reminds to the comment at page 8, line 17-21: "**see comment above on the offsets between different d13C records**".

Author's response: We completely agree with the referee that it is worrisome that the Bauska δ^{13}C data do not agree with the Rubino et al. δ^{13}C dataset, which has revised the Francey et al. δ^{13}C dataset and resolved the discrepancy between the Law Dome and South Pole δ^{13}C records. Because of the way we have decided to structure our paper (section 3.1 shows the old Law Dome datasets, whereas section 3.2 shows the new Law Dome records and how they compare with records from other sites), we believe it is more appropriate to add the discussion suggested by the referee in section 3.2 at page 11 lines 24-32.

Author's changes in manuscript: We have modified the discussion at page 11 line 33 – page 12 line 10 to address the referee's comment: "*The Bauska et al. (2015) record agrees within uncertainties with the Francey et al. (1999) dataset. However, Rubino et al. (2013) is the only record to show consistency with all firn records and direct atmospheric measurements (see Fig.s 3c and 5a). This would suggest that the Rubino et al. (2013) is currently the most accurate record and should be used to set a pre-industrial baseline. However, no definite conclusion can be drawn until a thorough intercomparison study is carried out between the labs that have produced the WAIS and the Law Dome δ^{13}C-CO$_2$ datasets (Oregon State University-University of Colorado-Institute of Arctic and Alpine Research, INSTAAR and CSIRO). It is important to resolve the difference between the Law Dome and the WAIS δ^{13}C-CO$_2$ records in order to establish a Pre-Industrial baseline and, thus, a Pre-Industrial-to-Industrial δ^{13}C-CO$_2$ difference. Setting a Pre-Industrial baseline could have consequences on the Last Glacial Maximum-to-Pre-Industrial δ^{13}C-CO$_2$ difference as well (Schmitt et al., 2012). These values are useful for biogeochemical interpretation (Broecker and McGee, 2013; Krakauer et al., 2006).*"

Page 9, line 1-2 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "==In doing so, they resolved the 0.2 ‰ discrepancy found between the Law Dome δ^{13}C-CO$_2$ record and the South Pole δ^{13}C-CO$_2$ firn record==." and has commented: "**these d13C offsets are the most important discrepancies, it may be worthwhile to show the South Pole data**"

Author's response: We agree with the referee that the δ^{13}C difference between the Law Dome ice core record and the South Pole firn record was the most important discrepancy found between datasets from different sites. However, we feel that this issue has been extensively discussed in the Rubino et al. (2013) paper. Also, showing the South Pole firn data in figure 2 (where the only other firn record is shown, now figure 3) would be out of context, as the figure only shows ice and firn data from Law Dome. Therefore, we have added an extra plot (figure 5) with the South Pole firn data and a reference to the Rubino et al. (2013) paper for further details.

Author's changes in manuscript: We have added a line at page 9, line 16-18: "*In doing so, they resolved the 0.2 ‰ discrepancy found between the Law Dome δ^{13}C-CO$_2$ record and the South Pole δ^{13}C-CO$_2$ firn record (the South Pole firn records have been reported in Fig 5, but see Rubino et al., 2013, for more details)*"

Page 9, lines 14-23 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text:

"- To investigate changes in Pre-Industrial sources of CH_4, Ferretti et al. (2005) produced a record of $\delta^{13}C$-CH_4 in Law Dome ice covering the last 2000 years (not shown). They reported unexpected changes of the global CH_4 budget, mainly attributed to variations of biomass burning emissions during the Late Pre-Industrial Holocene (LPIH) through an atmospheric box model (Lassey et al., 2000). The $\delta^{13}C$-CH_4 record from Ferretti et al. (2005) has not been included in ICEBASE because the air samples extracted in ICELAB were measured on a mass spectrometer not maintained by CSIRO-GASLAB. Therefore, the $\delta^{13}C$-CH_4 data are not on a CSIRO calibration scale.

- Park et al. (2012) measured oxygen and intramolecular nitrogen isotopic compositions of N_2O (not shown) covering 1940 to 2005 in Law Dome firn air and archived air samples from Cape Grim (Tasmania). In doing so, they confirmed that the rise in atmospheric N_2O levels is largely the result of an increased reliance on nitrogen-based fertilizers. These measurements are not included in ICEBASE either." and has commented "**as this data base summarizes all gas results from Law Dome, it is really a pity that the Mischler and Park data are not accessible via this tool as well. It is clear that these data cannot be updated constantly, as they come from other labs, but the status quo of the data sets as published could be included in the data collection**"

Author's response: It is tempting to include the $\delta^{13}C$-CH_4 and $\delta^{15}N$-N_2O records in our database, but, as the referee has correctly points out, those data have not been produced in CSIRO GASLAB. Therefore, we have no control over them. We have written this paper to make the scientific community aware of the updates we have performed on our $CO_2/\delta^{13}C$-CO_2, CH_4 and N_2O dataset, and to explain how the dataset has been produced and revised. One of the main reasons to revise and publish these records was because our CO_2, CH_4 and N_2O data were used in the Meinshausen et al. (2017) compilation and $\delta^{13}CO_2$ in the Graven et al compilation for CMIP6 (we say this in the Introduction), whereas we are not aware of CH_4 or N_2O isotopes being used in CMIP6. The risk of introducing records that are not treated in the same way as the CSIRO data is that we raise confusion among people using the datasets. The Ferretti (not Mischler as the referee writes) and Park data can be downloaded from different repositories and will always be available to the scientific community, independently from the updates of the Law Dome datasets we will release from time to time.

Page 10, line 11 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "Comparison with records from other cores show general agreement, but also a number of unexplained discrepancies." and has commented "**too vague**"

Author's response: This sentence is vague because it is just an introduction to the following list of bullet points. We has replaced it with a clearer sentence.

Author's changes in manuscript: We have modified the sentence at page 10 line 27: "*The following list compares the new Law Dome records with records from other sites and discusses the main differences:*"

Page 10, lines 30-32 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "The difference is even more surprising when the tight agreement between the Law Dome CH_4 record and the WAIS CH_4 record (Mitchell et al., 2011) around this time is considered (compare red circles and grey squares in Fig. 3c)." and has commented "**I don't really understand this argument. The CO_2 and CH_4 measurements are independent and in case of Mitchell even the gas extraction is separate from that of CO2**"

Author's response: The CO_2 and CH_4 measurements are mostly independent from each other in terms of measurement technique, but their comparison allows us to test whether the two sites of Law Dome and WAIS are providing consistent records in terms of smoothing of the atmospheric signal. The fact that the CH_4 records are consistent, whereas the CO_2 records show significant differences points towards a problem with CO_2, rather than issues related to poor understanding of the site (dating, firn smoothing, etc…). In other words, the consistency between the Law Dome and the WAIS CH_4 records is evidence of

1. Consistent dating (ice age and gas age)
2. Similar smoothing of the atmospheric signals at the two sites ([ice age-gas age and gas age distribution).

Therefore, the differences found in the CO_2 records are hard to explain with issues of dating uncertainty, as partly claimed by Ahn et al. (2012), or differences in smoothing of the atmospheric signals between the two sites. This support a chemical origin of the discrepancies (in-situ production), which is more likely to occur for CO_2 than for CH_4.

That said, the comment of the reviewer has alerted us that the way we have phrased our explanation is not very clear. Therefore, we have modified the text to make it easier to understand.

Author's changes in manuscript: We have modified the sentence a line at page 11 lines 16-18, by adding: "*The consistency between the Law Dome and the WAIS CH_4 record rules out dating issues or large differences in smoothing of the atmospheric signals between the two sites. This suggests a chemical origin (in-situ production) of the CO_2 discrepancies, which is more likely to occur for CO_2 than for CH_4.*"

Page 11, lines 18-21 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "Interestingly, the LIA CH_4 decrease measured at NEEM appears to start before the CH_4 decrease measured at Law Dome/WAIS, suggesting that the LIA event had an effect on the Northern Hemisphere CH_4 concentration first, and then propagated to the Southern Hemisphere." and has commented "**Is such a multidecadal lag really possible from a CH_4 cycle/atmospheric mixing point of view? You could check this using a multi-box model. It looks more like an age scale issue as the Mitchell record is shifted to younger ages compared to Law Dome in this time interval.**"

Author's response: We thank the referee for this important comment, which has compelled us to think about this issue carefully. We have updated the original NEEM CH_4 gas age scale published in Rhodes et al. (2013), with the new NEEM ice age scale published in Sigl et al. (2015) and the revised delta_age (gas age-ice age) after Buizert et al. (2014). The different timing is now partially resolved (15 years now, instead of 30 years). Having added the CH_4 GISP2 record (as suggested by reviewer 2), we have commented on how the Northern (GISP2) and Southern (WAIS) records have been synchronised by Mitchell et al. (2013) based on the reasoning that "The multidecadal events observed in both ice core records must have occurred simultaneously since the durations of the events were much larger than the atmospheric mixing time (~1 year)." There are multiple possible reasons, associated with the differences of the sites and/or the sampling resolution of the records, to explain the discrepancy found between Northern (NEEM) vs Southern (Law Dome/WAIS) Hemisphere CH_4 records, as discussed in the following:

- Age scale issues, as suggested by the referee. Usually, age scale issues are not very significant for the last centuries. Over such a short time scale, the age of the ice is

established through annual layer counting. However, there can be significant uncertainty associated with the Δage (ice age-gas age).

- Smoothing of the atmospheric signals due to air diffusion in the firn open porosity. As shown for the Law Dome CO_2 record smoothed through the gas age distribution of DML in Figure 2 of Rubino et al. (2016), the smoothing causes a shift in age of the max and min values of the LIA CO_2 decrease. For the Law Dome vs DML comparison, the shift amounts to a few years. NEEM has higher accumulation than DML, so firn smoothing should cause an even smaller shift.
- Inadequate sampling resolution. The NEEM CH_4 records plotted in figure 3 (now figure 4) is a 5 year average of the high resolution record published in Rhodes et al. (2013). The Law Dome CH_4 record has a lower sampling resolution (5 datapoint over a 30-year period of decreasing CH_4 concentration, so on average 1 datapoint every 6 years). By increasing the sampling resolution, it is possible that the time shift between the NEEM and the Law Dome CH_4 event decreases.

A thorough investigation of the cause of the differences in the LIA CH_4 event in the Northern (as recorded in NEEM) and the Southern (as recorded in Law Dome/WAIS) Hemisphere is out of the scope of our paper. However, in the future, this discrepancy should be resolved to obtain a precise synchronisation of all ice core records available over the LIA.

Author's changes in manuscript: We have modified the discussion at page 12 lines 18-27 (now page 12, lines 10-20): "*The age scale of the NEEM CH_4 record published in Rhodes et al. (2013) has been revised with the updated ice age scale published in Sigl et al. (2015) and the new estimate of Δage provided by Buizert et al. (Buizert et al., 2014). Mitchell et al. (2013) have synchronised the GISP2 CH_4 record with the WAIS CH_4 record to investigate changes of the Inter Polar Difference in the Pre-Industrial based on the reasoning that "the multidecadal events observed in both ice core records must have occurred simultaneously since the durations of the events were much larger than the atmospheric mixing time (~1 year)" (Mitchell et al., 2013). The NEEM CH_4 record has not been synchronised with the others, and there are multiple possible reasons, including age scale issues, different smoothing of the atmospheric signals at the different sites and inadequate sampling resolution, to explain the discrepancy found between the NEEM and the GISP2/Law Dome/WAIS CH_4 records during the LIA. A thorough investigation is out of the scope of this paper, but, in the future, this discrepancy should be resolved to obtain a precise synchronisation of all ice core records available over the LIA.*".

Page 12, lines 20-25 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "Considering that:

- All GHG records in ice cores are a smoothed representation of the real atmospheric history;

- DSS is the highest accumulation rate site ever sampled in Antarctica recording the LIA CO_2 event;

- There is the risk that the WAIS core is affected by in-situ production of CO_2;

- Accurate CO2 record have not been derived from Greenland ice cores

we suggest that there is a need to sample a new, clean and deep ice core from Law Dome, to recover the real atmospheric LIA CO_2 decrease and other rapid changes in atmospheric composition during Pre-Industrial millennia." and has commented "**this would fit better into the conclusions**"

Author's response: We agree with the referee.

Author's changes in manuscript: We have moved the sentence from page 12 lines 20-25 to page 18 lines 16-23.

Page 13, lines 2-3 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "processes removing GHGs from the atmosphere (sinks)." and has commented "**typically we do not talk about sinks in the case of CO₂ as for the carbon cycle there is not really a destruction of the molecule but a constant exchange of carbon between different reservoirs**"

Author's response: We agree with the referee that since there is no destruction of CO_2 in the atmosphere, then, strictly speaking, there is no "sink" in the case of CO_2. However, the general biogeochemical literature uses the word "sink" to signify a process removing GHGs, including CO_2, from the atmosphere (e.g. information from the Global Carbon Project https://www.globalcarbonproject.org/). Thus, we have decided to leave the sentence unaltered.

Page 13, line 29 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "recent" and has commented "**unclear**"

Author's response: To clarify, the word "recent" here means over the last decades, as opposed to the records from ice cores covering the last centuries/millennia.

Author's changes in manuscript: We have replace the word "recent" now at page 15 line 4 with "*over the last decades*".

Page 14, lines 21-22 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "tropospheric species [OH], oxidation by stratospheric species [OH, Cl and O(1D)], and oxidation in soils are the main sinks." and has commented "**marine boundary layer Cl sink**"

Author's response: We thank the reviewer to have reminded us of this sink.

Author's changes in manuscript: We have added the text "*and reactive chlorine in the marine boundary layer*" at page 15 line 33.

Page 14, line 33 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "hypothesis of an early anthropogenic influence." and has commented "**the use of this expression is misleading here, as the "early anthropogenic influence hypothesis" by Ruddiman refers to a much earlier increase. Please change the wording.**"

Author's response: Generally, the "early anthropogenic hypothesis" refers to the explanation of an influence on the changes of atmospheric CO_2 and CH_4 concentration during the Holocene, originally suggested by Ruddiman. In some of his papers, Ruddiman also discusses the influence of human activities on the atmospheric CO_2 and CH_4 concentration during the Little Ice Age. Therefore, the "early anthropogenic hypothesis" can also refer to any pre-industrial alteration of the atmospheric chemical composition caused by human activities. However, to avoid confusion, we follow the referee's suggestion.

Author's changes in manuscript: We have modified the text at page 16 line 11 to "*supporting the hypothesis of a pre-industrial anthropogenic influence on atmospheric CH₄*".

Page 15, lines 9-10 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "==As already mentioned, the Pre-Industrial inter-hemispheric N₂O difference is also poorly constrained==." and has commented "**I doubt this can be resolved, as it is extremely small due to the long life-time of N₂O**"

Author's response: We agree with the referee that the Inter-hemispheric N₂O difference is small and we would need very high precision ice core measurements to resolve it. However, with the development of new analytical techniques, it could become feasible. Therefore, we have decided to leave the sentence unaltered

Page 16, lines 1-4 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "==There are regional (Mann et al., 2008), continental (Pages2k, 2013) and hemispheric (Neukom et al., 2014) temperature reconstructions that can be used in Coupled Carbon Cycle-Climate Models to quantify the contribution from each region to the total CO₂ decrease (Fig. 4b).==" and has commented "**the wording is weird. It is not clear how the reconstructions could be "Used in Coupled Climate Models", the provide a benchmark**"

Author's response: We are just suggesting that regional temperature reconstructions could be used as "forcing" for models describing the relationship between climate and carbon cycle to quantify the regional contribution to the total CO₂ change recorded through the LIA

Author's changes in manuscript: We have modified the sentence at page 17 line 17: "*There are regional (Mann et al., 2008), continental (Pages2k, 2013) and hemispheric (Neukom et al., 2014) temperature reconstructions that can be used to drive models describing the relationship between climate and carbon cycle to quantify the contribution from each region to the total CO₂ decrease*".

Page 16, lines 11-13 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "==The consequences of the LIA climatic changes on contemporary societal development are important for understanding why different communities were more or less vulnerable, resilient or even adaptive (Degroot, 2018), and plan future choices accordingly==." and has commented "**This is a little far fetched as all societies today have technical means that were not available during the LIA. So it can be questioned, whether we really learn something from the LIA about societal resilience.**"

Author's response: We agree with the referee that current societies have more advanced technical means than in the LIA. However, the ability of a society to adapt to climate change will not depend on technical means only. Political and socio-economic factors will influence how efficiently our society will adapt to future climate change. So, being able to quantify which regions have been more vulnerable to past climate change, also in terms of the response of the natural carbon cycle, could help plan future adaptation strategies.

Author's changes in manuscript: To put our statement into perspective, we have modified the sentence at page 17 lines 29-31: "*The consequences of the LIA climatic changes on societal development are important for understanding why different communities were more or less vulnerable, resilient or even adaptive (Degroot, 2018). Being able to quantify which regions have*

been more vulnerable to past climate change, also in terms of the response of the natural carbon cycle, could help plan future adaptation strategies".

Page 16, lines 15-16 (of the manuscript with no track changes revisions)

Comment from referee: The referee has highlighted the text: "(δ^{13}C-CO$_2$, δ^{13}C-CH$_4$, δD-CH$_4$, δ^{15}N-N$_2$O, δ^{18}O-N2O)" and has commented "**here you refer to the isotopes of all greenhouse gases, but you only store δ^{13}CO$_2$ in your data base (see comment above).**"

Author's response: A few lines below (page 16, lines 17-18) we have clearly stated that, of all the isotopic records, only the δ^{13}C-CO$_2$ is constantly being updated and revised. However, to avoid confusion, we have removed the records that are not stored in the database.

Author's changes in manuscript: We have modified the sentence at page 18, lines 2-3: "*The records of GHG (CO$_2$, CH$_4$, N$_2$O) concentrations and the isotopic composition of CO$_2$ (δ^{13}C-CO$_2$) from the Law Dome ice cores are one of the most important sources of information for models trying to predict the future behaviour of biogeochemical cycles and their influence on the climate system.*"

Supplement page 2

Comment from referee: The referee has highlighted the text: "derive the gas-age from the ice-age-vs-gas-age difference for ice samples and gas-age vs depth for firn samples" and has commented "**it is not clear how this is done (firn modeling). Please elaborate on this somewhere in the supplement**"

Author's response: An extensive description of how gas age is attributed to ice and firn samples has been provided in past papers. For firn, the dating is based on the firn model, but for ice samples the gas-age – ice age is based on a number of factors, including firn modelling.

Author's changes in the Supplement: We have added the following line to the text at page 2: "*For firn samples, the dating is based on the firn air diffusion model, whereas for ice samples it is based on a number of factors, including firn model (Trudinger et al., 2013)*".

Supplement page 4

Comment from referee: The referee has highlighted the text: "The blank correction is quantified by the average deviation of replicated BFI/Blanks measured concentration and isotopic composition from the expected value (i.e.: the value associated with the reference gas used). A blank correction is calculated for each period when the conditions of preparation/storage/extraction are the same. In other words, a new blank correction is calculated each time any of the factors (operator, freezer, temperature of cold room, duration of extraction, etc...) that are believed to influence preparation/storage/extraction changes. The blank correction has an uncertainty associated with it, given by the standard deviations of differences from the expected value." and has commented: "**how large is this blank correction typically for the different measured species**"

Author's response: We agree with the referee that it is useful for the reader to have an idea of the size of the blank correction, so we have added the best estimate for each species.

Author's changes in the Supplement: We have added a sentence at page 4: "*The blank correction can vary significantly depending on the conditions of the extraction line and on how experienced the line operator is. Typical values are within the following ranges: 0.5-1.5 ppm (uncertainty 0.5-2 ppm, 1σ) for CO$_2$, 3-10 ppb (uncertainty 3-15 ppb, 1σ) for CH$_4$, 0.5-3 ppb (uncertainty 0.5-4 ppb, 1σ) for N$_2$O and 0.03-0.1 ‰ (uncertainty 0.04-0.13 ‰, 1σ) for δ^{13}C-CO$_2$.*"

Supplement page 4

Comment from referee: The referee has highlighted the text: "The gravity correction: Gravitational enrichment of heavier species in air in the firn open porosity (Craig et al., 1988; Schwander et al., 1988) has different effects depending on the difference between the mass of the measured species and the average mass of air: [X]corr = 10-3 × d15N × (MX - Mair) × [X]meas, where X is the measured species (i.e.: CH_4, CO_2 and N_2O), "corr" and "meas" stands for corrected and measured respectively, and $\delta^{15}N$ is the isotopic ratio of molecular nitrogen (N_2) in firn. For $\delta^{13}C$ measurements, the gravity corrected $\delta^{13}C$ equals the sum of a correction factor (very close to the $\delta^{15}N-N_2$) and the measured $\delta^{13}C$ (see Rubino et al., 2013 for details)." and has commented: "**how large is this gravity correction typically for the different species? Here you refer to $\delta^{15}N_2$ values. Where do they come from? Are these values also stored in the database (they should)? How do you correct iff you do not have $\delta^{15}N_2$ values?**"

Author's response: The questions of the referee are all very relevant and we have included a few lines to answer them in the Supplement.

Author's changes in the Supplement: We have added a few lines at page 4: "*The values of $\delta^{15}N$ are often measured in firn to constrain the firn diffusion model. In case of missing $\delta^{15}N$ measurements, the firn model is constrained with other measurements and then used to simulate the $\delta^{15}N$ profile. Our database stores all measured and modelled $\delta^{15}N$ values for firn sites at Law Dome. The gravity correction is typically 1-1.5 ppm for CO_2, 2-6 ppb for CH_4, 1-1.4 ppb for N_2O and 0.25-0.3 ‰ for $\delta^{13}C$-CO_2.*"

Supplement page 4

Comment from referee: The referee has highlighted the text: "The diffusion correction (only for measurements of isotopic composition): For measurements of isotopic ratios in firn and ice air samples, a so-called diffusion correction is needed (Trudinger et al., 1997). This correction arises from the fact that an isotope ratio is the ratio of two isotopes with slightly different diffusion coefficients and therefore slightly different effective ages (Trudinger, 2000, section 3.6). For hypothetical species with constant isotopic ratio, but changing atmospheric concentrations, the isotopic ratio in the firn can be significantly different from the atmospheric ratio. For $\delta^{13}C$, the diffusion correction is proportional to the rate of change of CO_2 concentration, which makes the $\delta^{13}C$ diffusion correction insignificant in the LHPI, and a very significant term in the Industrial Period." and has commented "**how large is this correction typically? How do you do the correction (firn modeling)?this needs more detail**"

Author's response: The questions of the referee are all very relevant and we have included a few lines to answer them in the Supplement.

Author's changes in the Supplement: We have added a few lines at page 4: "*The diffusion correction is estimated using the CSIRO firn diffusion model and, at Law Dome, can range from around 0 in the Pre-Industrial to 0.13 ‰ in the Industrial Period.*"

Referee #2

We thank Referee #2 to support publication of our paper. In the following, we address the referee's comments in the order of appearance.

Page 2, line 15-16 (of the manuscript with no track changes revisions)

Comment from referee: **I suggest to rephrase "it is extremely difficult to separate the impacts of anthropogenic increases in CO_2 on carbon sinks from the impacts of global warming or increased CO_2 concentration on these sinks.". This statement was unclear for me**

Author's response: We have change the statement to make it clear.

Author's changes in manuscript: We have modified the sentence at page 2 lines 15-17 to: "*Additionally, temperature and CO_2 have both increased almost continuously through the 20th century, making it difficult to separate the impacts of CO_2 on carbon sinks from the impacts of temperature increase on these sinks.*"

Page 3, line 7 (of the manuscript with no track changes revisions)

Comment from referee: **Rhodes et al., 2016 (Climate of the Past) include more CH4 data from Greenland.**

Author's response: We thank the referee for this important comment, which has helped us address an important weakness of our study when comparing the Law Dome CH_4 records with CH_4 records from other sites. As the referee points out, Rhodes et al. (2013) shows the GISP2 CH_4 record as well, published in Mitchell et al. (2013). We have added this record to figure 3c (now 4c) and have cited Mitchell et al. (2013).

Author's changes in manuscript: We have modified the sentence at page 3 lines 8 adding "… and from GISP2 (Mitchell et al., 2013)…" and have added the GISP2 CH_4 record to figure 3c (now 4c).

Page 5, section 2.1

Comment from referee: **use the same unit for all accumulation data, for homogeneity**.

Author's response: We agree with the reviewer that it is better to have all accumulation rates expressed with the same units. We have decided to convert all accumulation rates to kg m^{-2} yr^{-1}, which is also consistent with the units used in Figure 1. We have also left the accumulation rate at DE08/DE08-2 as meters of ice equivalent per year in brackets, as it is nice to give a better feel to the non-specialist reader for what the accumulation looks like.

Author's changes in manuscript: We have expressed all units of accumulation rate at page 5 in kg m^{-2} yr^{-1}.

Page 6, line 23 (of the manuscript with no track changes revisions)

Comment from referee: typo "I think".

Author's response: fixed

Page 11, line 20 (of the manuscript with no track changes revisions)

Author's response: We thank the reviewer for this important comment, which, together with a similar comment of reviewer 1, and has helped us improve this part of the manuscript. We have updated the original NEEM CH_4 gas age scale published in Rhodes et al. (2013), with the new NEEM ice age scale published in Sigl et al. (2015) and the revised Δage (gas age-ice age) after Buizert et al. (2014). The different timing is now partially resolved (15 years now, instead of 30 years). Having added the CH_4 GISP2 record, we have commented on how the Northern (GISP2) and Southern (WAIS) records have been synchronised by Mitchell et al. (2013) based on the following reasoning: "The multidecadal events observed in both ice core records must have occurred simultaneously since the durations of the events were much larger than the atmospheric mixing time (~1 year).". As already written above, there are multiple possible reasons, associated with the differences of the sites and/or the sampling resolution of the records, to explain the discrepancy found between Northern (NEEM) vs Southern (Law Dome/WAIS) Hemisphere CH4 records, as discussed in the following:

- Age scale issues, as suggested by the referee. Usually, age scale issues are not very significant for the last centuries. Over such a short time scale, the age of the ice is established through annual layer counting. However, there can be significant uncertainty associated with the delta_age (ice age-gas age).
- Smoothing of the atmospheric signals due to air diffusion in the firn open porosity. As shown for the Law Dome CO2 record smoothed through the gas age distribution of DML in Figure 2 of Rubino et al. (2016), the smoothing causes a shift in age of the max and min values of the LIA CO2 decrease. For the Law Dome vs DML comparison, the shift amounts to a few years. NEEM has higher accumulation than DML, so firn smoothing should cause an even smaller shift.
- Inadequate sampling resolution. The NEEM CH4 records plotted in figure 3 (now figure 4) is a 5 year average of the high resolution record published in Rhodes et al. (2013). The Law Dome CH4 record has a lower sampling resolution (5 datapoint over a 30-year period of decreasing CH4 concentration, so on average 1 datapoint every 6 years). By increasing the sampling resolution, it is possible that the time shift between the NEEM and the Law Dome CH4 event decreases.

A thorough investigation of the cause of the differences in the LIA CH4 event in the Northern (as recorded in NEEM) and the Southern (as recorded in Law Dome/WAIS) Hemisphere is out of the scope of our paper. However, in the future, this discrepancy should be resolved to obtain a precise synchronisation of all ice core records available over the LIA.

Author's changes in manuscript: We have modified the discussion at page 12 line 18-27: "*The age scale of the NEEM CH_4 record published in Rhodes et al. (2013) has been revised with the updated ice age scale published in Sigl et al. (2015) and the new estimate of Δage provided by Buizert et al. (Buizert et al., 2014). Mitchell et al. (2013) have synchronised the GISP2 CH_4 record with the WAIS CH_4 record to investigate changes of the Inter Polar Difference in the Pre-Industrial based on the reasoning that "the multidecadal events observed in both ice core records must have occurred simultaneously since the durations of the events were much larger than the atmospheric mixing time (~1 year)" (Mitchell et al., 2013). The NEEM CH_4 record has not been synchronised with the others,*

and there are multiple possible reasons, including age scale issues, different smoothing of the atmospheric signals at the different sites and inadequate sampling resolution, to explain the discrepancy found between the NEEM and the GISP2/Law Dome/WAIS CH$_4$ records during the LIA. A thorough investigation is out of the scope of this paper, but, in the future, this discrepancy should be resolved to obtain a precise synchronisation of all ice core records available over the LIA.".

Figures:

Comment from referee: **I find the figures difficult to read: I would advise to increase size for labels and titles.**

Author's response: We have chosen the size for labels and titles based on the font size in the template provided for ESDD articles for consistency. We would be happy to increase the size if the editorial office allows us to do so.

Author's changes in manuscript: We have not changed the size because we need approval from the ESDD editorial office.

Figure 4:

Comment from referee: **this figure highlight two important past findings (Rubino et al., 2016 ; Ferreti et al., 2005). It also includes data that can potentially be relevant for further studies and interpretations. I am not sure these data (b, d, and e) need to be plotted; likely description in the manuscript is enough. If the authors want to keep these data as part of plot 4, I would recommend to clarify the figure, e.g. the panel b and c can be shifted, so the figure reports first ice core data, and second complementary climatic data**.

Author's response: We agree with the reviewer that swapping figures 4b and 4 c (now 5b and 5c) makes sense for clarity of presentation, but also under the point of view of citation order.

Author's changes in manuscript: We have modified figure 4 (now figure 5) by swapping figure 4b and 4c (now 5b and 5c). We have modified the figure caption and the citation to figure 5b and 5c in the text accordingly.

Technical comments related to Supplement:

Comment from referee: **My main concern is about the way uncertainties are calculated by multiplying the blank uncertainty with a factor u.f. I find this process complex, not fully understandable for data users, and maybe operator-dependent. To me, the blank uncertainty is independent from other sources of uncertainties (e.g., dispersion of results observed for replicated measurements on of the same sample). Independent uncertainties when propagated do not multiply each others**.

Author's response: We thank the referee for the detailed comments provided on the way we calculate the uncertainty associated with the results we produce. We agree with the referee that the process we have developed is quite complex. Unfortunately, our rule-based selection procedure needs to take into account all the little pieces of information that are normally evaluated by an operator based on the experience matured over 20+ years at ICELAB-GASLAB. Our aim, though, was to develop an automatic system, which would minimise operator-dependent judgements, to make it consistent in time and between different operators. We understand that it is very difficult for an external data user to understand the details of the procedure we have developed. We have tried to make the description of it as clear as possible.

As the referee states, the blank uncertainty is independent from other sources of uncertainties, such as those mentioned by the referee. We have propagated the uncertainty using the guidelines from the Joint Committee for Guides in Metrology (2008). The uncertainty associated with the blank correction dominates over the other sources of uncertainty.

Author's changes in the Supplement: We have added a citation to the Joint Committee for Guides in Metrology (2008), Evaluation of measurement data—Guide to the expression of uncertainty in measurement, Bur.Int. des Poids et Mesures Pavillon de Breteuil, France, at page 5. We have also added a couple of sentences at page 4: "*The uncertainty associated with gravity and the diffusion corrections are negligible compared to the uncertainty associated with the blank correction*" and at page 5 "*However, the variability associated with replicates of the same sample is negligible compared with the uncertainty associated with the blank correction.*" to explain that the blank uncertainty dominates over the other sources of uncertainty.

Comment from referee: **We can observe here that for a sample where u.f. = 1 (i.e., qf and mq = fair or good), the data uncertainty is reduced to only the blank uncertainty, ignoring for example that different replicated measurements of the same sample will likely not be exactly all the same**.

Author's response: The referee is right: different replicated measurements of the same sample will not show the same result. However, the variability associated with replicates of the same sample is negligible compared to the uncertainty associated with the blank correction, which quantifies the variability associated with multiple tests run together with the samples. Additionally, because of the way the ICELAB-GASLAB system has been conceived (measurements of different species on the same ice sample), replicates of the same sample measured for the same species are so rare that there is no uncertainty associated with replicates for the vast majority of the samples analysed.

Author's changes in the Supplement: We have modified a sentence at page 3: "*Only a few measurements of concentration have been replicated. For isotopes, there has never been enough air to measure replicates*". We have also modified a sentence at page 4 of the Supplement: "*Because of the small size of ice core samples generally available and the need for large air volume to measure multiple species, the vast majority of samples have no replicated measurements.*" and another sentence at page 5: "*However, the variability associated with replicates of the same sample is negligible compared with the uncertainty associated with the blank correction.*"

Comment from referee: **The u.f. factor includes many parameters (flags, and criteria associated to weights), and some of them are not related to uncertainty. As an example, the first parameter is "melt layer". A melt layer can, e.g., results in high methane concentration (due to in situ production), but the measurement uncertainty of such high concentration should not be different from a regular sample. Just higher concentration will be measured. A melt layer sample does not have the quality required for reconstructing past CH$_4$, but its measurement could be of great quality! Overall, I would advise that the authors identify more clearly what causes uncertainties, instead of considering everything.**

Author's response: Our database is in constant development and it is possible that we will find better ways of including factors affecting the total uncertainty in the future. However, for now, when a melt layer is found, a sample is rejected because, as the referee suggests, melt layers are known to alter the concentration of the species we measure.

Author's changes in the Supplement: We have added a sentence at page 3: "*For example, a melt layer is classified as evidence of a fatal problem of sample quality and provides a q.s. = 3 and a q.f. = "reject".*"

Comment from referee: **Some of the flags and criteria associated to weights seem subjective, and maybe operator-dependent in their evaluation (at least this is what I feel when reading the Supplement).**

Author's response: The thresholds for flags and weights have been decided based on a "calibration". The idea was to replicate with an automatic procedure what had been done in the past manually. The aim was to make the procedure consistent over time and as independent from the operator as possible.

Author's changes in Supplement: We have added a line at page 3: "*The flagging and weighting thresholds are tuned by calibrating the rule-based selection on the manual selection used before the database was conceived. The idea was to replicate with an automatic procedure what had been done in the past manually. The aim was to make the procedure consistent over time and as independent from the operator as possible. In summary, the rule-based selection converts qualitative judgments on the robustness of sample preparation, extraction and analysis into quantitative scores in order to consistently select/reject the results and quantify uncertainty.*"

Comment from referee: **When all criteria reports "reject" (i.e., u.f. = 4), the data is not rejected, but the uncertainty is increased more. It seems to me that these data should be excluded (as suggested by the wording "fatal problem").**

Author's response: When q.f. = "reject", the sample is marked with a rejection flag. However, the result of that sample is retained in the database and a u.f. = 4 is associated with it. The reason why we have decided to do that is to give enough flexibility for the operator to overrule the automatic selection, providing a convincing justification that the operator's choice is appropriate. If a data user wants to use that sample, the uncertainty associated with the results is very high (4 × the blank uncertainty and then propagated as explained).

Author's changes in the Supplement: We have added a line at page 5: "*When q.f. = "reject", the sample is marked with a rejection flag. However, the result of that sample is retained in the database and a u.f. = 4 is associated with it. The reason why we have decided to do that is to provide enough flexibility for the operator to overrule the automatic selection when there is a strong reason (e.g. new insight developed over time). If a data user wants to use that sample, the uncertainty associated with the results is very high (4 × the blank uncertainty and then propagated as explained below).*"

Comment from referee: **What are the typical blanks observed, and typical blank uncertainties observed?**

Author's response: This comment, together with a similar comment from referee 1, has helped us provide important information, which was missing from the previous version of the manuscript. We thank the referees for that.

Author's changes in the Supplement: We have added a line at page 5: "*The blank correction can vary significantly depending on the conditions of the extraction line and on how experienced the line operator is. Typical values are within the following ranges: 0.5-1.5 ppm (uncertainty 0.5-2 ppm, 1σ) for CO_2, 3-10 ppb (uncertainty 3-15 ppb, 1σ) for CH_4, 0.5-3 ppb (uncertainty 0.5-4 ppb, 1σ) for N_2O and 0.03-0.1 ‰ (uncertainty 0.04-0.13 ‰, 1σ) for $\delta^{13}C\text{-}CO_2$.*" and a sentence at the end of page 4 of the Supplement: "*The uncertainty associated with gravity and the diffusion corrections are negligible compared to the uncertainty associated with the blank correction*"

Comment from referee: **I am not convinced that CO concentration is a good tool to evaluate the quality of a measurement (similarly to "melt layer", see before), or the quality of a sample. CO can**

be produced by chemical processes (the authors mention biological production of CO, citation is missing for that), but to my knowledge no collocated productions of CO and, e.g. CO$_2$, CH$_4$ or N$_2$O have been reported so far in ice cores. The processes involved could be different, and a sample compromised for CO can be of good quality for others analyses. Ambient CO is often higher than what is in ice core bubbles, but this is also clear with CH$_4$.

Author's response: High CO is quite a reliable indicator of contamination by the ingress of lab/storage facility air into the sample, or by leaks during processing the sample. High CO has also been reported together with high CO$_2$ and low δ^{13}C-CO$_2$ values in a study of Antarctica vs Greenland CO$_2$ by Francey et al. (1997).

Author's changes in the Supplement: At page 2, we have cited Francey et al. (1997) showing evidence of in-situ production of CO in Greenland ice. We have modified the associated sentence: "*High CO values have been measured in Greenland ice (Francey et al., 1997) together with high CO$_2$ and low δ^{13}C-CO$_2$, suggesting in situ oxidation of organic material deposited on the Greenland icecap (Francey et al., 1997)*".

Revised records of atmospheric trace gases CO$_2$, CH$_4$, N$_2$O and δ^{13}C-CO$_2$ over the last 2000 years from Law Dome, Antarctica

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Abstract. Ice core records of the major atmospheric greenhouse gases (CO$_2$, CH$_4$, N$_2$O) and their isotopologues covering recent centuries provide evidence of biogeochemical variations during the Late-Holocene and Pre-Industrial Periods and over the transition to the Industrial Period. These records come from a number of ice core and firn air sites, and have been measured in several laboratories around the world and show common features, but also unresolved differences. Here we present revised records, including new measurements, performed at the CSIRO Ice Core Extraction LABoratory (ICELAB) on air samples from ice obtained at the high accumulation site of Law Dome (East Antarctica). We are motivated by the increasing use of the records by the scientific community and by recent data-handling developments at CSIRO-ICELAB. A number of cores and firn air samples have been collected at Law Dome to provide high-resolution records overlapping recent, direct atmospheric observations. The records have been updated through a dynamic link to the calibration scales used in the Global Atmospheric Sampling LABoratory (GASLAB) at CSIRO, which are periodically revised with information from the latest calibration experiments. The gas-age scales have been revised based on new ice-age scales, and the information derived from a new version of the CSIRO firn diffusion model. Additionally, the records have been revised with new, rule-based selection criteria and updated corrections for biases associated with the extraction procedure, and the effects of gravity and diffusion in the firn. All measurements carried out in ICELAB-GASLAB over the last 25 years are now managed through a database (the ICElab dataBASE or ICEBASE) which provides consistent data management, automatic corrections and selection of measurements, and a web-based user interface for data extraction. We present the new records, discuss their strengths and limitations and summarise their main features. The records reveal changes in the carbon cycle and atmospheric chemistry over the last two millennia, including the major changes of the anthropogenic era and the smaller,

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mainly natural variations beforehand. They provide the historical data to calibrate and test the next inter-comparison of models used to predict future climate change (Coupled Model Inter-comparison Project - phase 6, CMIP6). The datasets described in this paper, including spline fits, are available at https://doi.org/10.25919/5bfe29ff807fb (Rubino et al., 2018).

1 Introduction

The three well-mixed (long-lived) atmospheric greenhouse gases (GHGs, including halocarbons) that contribute the most to current global warming are CO_2, CH_4 and N_2O. Their concentrations have been increasing since the beginning of the Industrial Period, causing most of the current ~1 °C temperature increase above the average global temperature in the period 1861-1880 (Stocker et al., 2013). The temperature increase limit of 2 °C set by the Paris Agreement for 2100 requires substantial reduction of GHG emissions in the next decades, and, consequently, significant reductions in the rates of GHG concentration increases. Predicting how GHG concentrations will vary in the future requires a clear understanding of the biogeochemical processes responsible for their variations. However, models of future long-term climate changes predict a large range in GHG concentrations for a given scenario of emissions (Friedlingstein et al., 2014), and one of the key uncertainties is associated with feedbacks in the coupled carbon-climate system (Arora et al., 2013). Climate modellers have analysed and compared results from state-of-the-art climate model simulations to gain insights into the processes of climate variability, change and feedbacks through the Coupled Model Inter-comparison Project (CMIP). In CMIP, records of GHGs can be used either as forcing or as a diagnostic (Graven et al., 2017; Meinshausen et al., 2017). However, real-time records of GHGs started in a period when anthropogenic forcing was already very significant, and the atmosphere and the Earth system were in strong disequilibrium, and therefore do to not provide a balanced state for model spin-up. Additionally, temperature and CO_2 have both increased almost continuously through the 20th century, making it difficult to separate the impacts of CO_2 on carbon sinks from the impacts of temperature increase on these sinks. Also, it is extremely difficult to separate the impacts of anthropogenic increases in CO_2 on carbon sinks from the impacts of global warming or increased CO_2 concentration on these sinks. Furthermore, real-time records are often too short to draw strong conclusions on multi-decadal variability. To provide a balanced system for model spin-up, and evaluate the ability of models to capture observed variability on multi-decadal and longer time-scales, a branch of CMIP ('Historical Simulations') starts in 1850 (Eyring et al., 2016), while another branch (the 'Paleoclimate Modelling Intercomparison Project', PMIP) focuses on paleo-climate simulations (Schmidt et al., 2014). Yet, policymakers need short-term predictions of global warming (next decades to century), and the Intergovernmental Panel on Climate Change has very recently provided a special report on the impacts of global warming of 1.5 °C above Pre-Industrial levels. The last millennium is a very suitable period to support these types of investigations since the Earth system was much closer to its current state than e.g. previous periods of glacial-interglacial transition.

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Ice cores are exceptional archives of factors influencing past climate change because they contain a large range of substances, including water (H_2O) in the ice itself, as well as ionic species, organic molecules and atmospheric gases sealed in bubbles (Barbante et al., 2010). They can span from polar (Antarctica and Greenland mostly) to tropical (high altitude) sites (Thompson et al., 2013), and extend several hundred thousands ~~of~~ years back in time (Higgins et al., 2015; Wolff et al.,
5 2010). Ice cores from different locations have different accumulation rates and temperatures, which translate into differences in time resolution, the age of the deepest layers and ~~archival~~ archive suitability. Focusing on the last millennium, multiple ice core records of GHG concentration and isotopic composition are available:

- CO_2 from EDML (EPICA Dronning Maud Land, Antarctica) and South Pole (Siegenthaler et al., 2005), Law Dome, East Antarctica (Etheridge et al., 1996; MacFarling Meure et al., 2006; Rubino et al., 2013), DML (Dronning Maud Land, Rubino
10 et al., 2016) and WAIS (West Antarctic Ice Sheet, Ahn et al., 2012);

- $\delta^{13}C$-CO_2 from Law Dome (Francey et al., 1999; Rubino et al., 2013), WAIS (Bauska et al., 2015) and DML (Rubino et al., 2016);

- CH_4 from NEEM (Rhodes et al., 2013) and from GISP2 (Mitchell et al., 2013) in Greenland, Law Dome (Etheridge et al., 1998; MacFarling Meure et al., 2006) and WAIS (Mitchell et al., 2011) in Antarctica;

15 - N_2O from EUROCORE and GRIP in Greenland (Flückiger et al., 1999), Dome C (Flückiger et al., 2002), and Law Dome (MacFarling Meure et al., 2006) in Antarctica.

There are other records focusing on periods other than the last centuries, but also covering the whole or part of the Industrial and the Pre-Industrial Periods (i.e. for N_2O: H15 by Machida et al., 1995; Styx glacier by Ryu et al., 2018; Talos Dome by Schilt et al., 2010). We have decided not to include them in our comparison because their temporal resolution (Schilt et al.,
20 2010) and/or coverage (Machida et al., 1995; Ryu et al., 2018) limits their value for comparison with the records focusing on the last centuries.

There are real differences between records of the same GHG from different sites caused by atmospheric features, such as the inter-hemispheric gradient (North-South or Greenland vs Antarctica). The inter-hemispheric gradient is different from one GHG to another, depending on the balance between, and the distribution of, sources and sinks for that specific GHG in the
25 two hemispheres, as well as on the atmospheric circulation and the ~~gases'~~ atmospheric lifetimes of the gases. There are also differences which do not reflect atmospheric changes, due, for example, to the characteristics of the sites where the ice is sampled. Ice core site characteristics influence the measured gas records due to the gaseous diffusion through the upper-most layers of porous, compacting snow, the 'firn' (Schwander et al., 1993). Together, diffusion in firn and gradual bubble close-off result in a smoothed representation of the atmospheric history in ice core gas records. The smoothing process depends on
30 the depth of the firn layer and on how quickly bubbles close off and trap air during firn to ice transition. Ice cores sites in Greenland generally have higher accumulation rates and temperatures than in Antarctica. ~~As a consequence~~Consequently, GHG records from many Antarctic sites are usually a more smoothed representation of the atmospheric history.

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Unfortunately, there is no reliable CO_2 record available from Greenland because there is evidence of *in-situ* production of CO_2 (Anklin et al., 1995; Barnola et al., 1995). The most likely explanation for this is a high levels of impurities in Greenland ice reacting with acidity and/or hydrogen peroxide (Jenk et al., 2012; Tschumi and Stauffer, 2000). Law Dome, Antarctica, provides the best time-resolved ice core records due to the very high accumulation rate at this site (Etheridge et al., 1996; Goodwin, 1990), even more so than Greenland. Also, records from multiple Law Dome sites show no evidence of *in-situ* production because they agree with records from colder sites in Antarctica (Rubino et al., 2016; Siegenthaler et al., 2005), and compare closely with each other, with air extracted from the firn, and with modern atmospheric records (Rubino et al., 2013).

However, there are unexplained differences between records of the same GHG, particularly for CO_2. For example, while the CO_2 records of South Pole and EDML over the last centuries are consistent with Law Dome when their broader age smoothing is taken into account (Rubino et al., 2016; Siegenthaler et al., 2005), the WAIS CO_2 record is on average 3 ppm higher than the Law Dome CO_2 record (Ahn et al., 2012). The similarity between the high frequency variations of the CH_4 records from Law Dome and WAIS (Mitchell et al., 2011) suggests that the two sites (Law Dome and WAIS) introduce similar smoothing of the atmospheric signals. However, the Law Dome CO_2 minimum measured around 1610 AD CE does not have a corresponding feature at WAIS (Ahn et al., 2012). Considering that a comparison between the two laboratories where Law Dome and WAIS samples were measured has shown no significant offset (Ahn et al., 2012), the differences between the WAIS and the Law Dome CO_2 records could be explained by a small effect of *in-situ* production at WAIS. Additionally, there is a significant difference in the mean Pre-Industrial level of $\delta^{13}C$-CO_2 measured at WAIS and Law Dome (Bauska et al., 2015; Rubino et al., 2016). These differences need to be resolved with inter-calibration campaigns between different laboratories, using ice cores from different sites (including new high accumulation cores) and accurate modelling of gas-age (both the mean value and spread) at each site.

To provide the most consistent datasets possible for the past centuries, we have previously compared the Law Dome records of CO_2, CH_4, N_2O and $\delta^{13}C$-CO_2 to firn and modern atmospheric measurements (MacFarling Meure et al., 2006; Rubino et al., 2013). The consistency between these measurements is evidence of our ability to extend current atmospheric records back in time using ice and firn. However, because of the emissions during the Industrial Revolution, our measurements of modern and old (Pre-Industrial) air samples lie in different concentration ranges and the calibrations used for measurements of modern air samples are, therefore, in a concentration range rather different from that used for measurements of old air samples. The measurements performed in ICELAB-GASLAB at CSIRO have the advantage of being calibrated across the range of concentrations of old and modern air sample measurements. Also, ice core gas extractions and analyses are technically challenging, and different people at CSIRO-ICELAB have produced those measurements over almost three decades. Thus, it is possible that the extraction/analysis procedures have introduced different biases over time, influencing the measurements by variable amounts. However, except for minor developments over time (Etheridge et al., 1996; Francey

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et al., 1999; MacFarling Meure et al., 2006; Rubino et al., 2013, 2016) the equipment used for extraction and analysis has not fundamentally changed.

In this study, we describe the procedure recently developed at CSIRO ICELAB-GASLAB to ~~automatically~~ perform calibration scale updates and data selection and correction automatically and in a consistent way for all measurements made over the last 25 years. In the Supplement, we provide a detailed explanation of the database recently created to store, process and extract the information about the samples analysed, the measurements performed and the results obtained. We present updated records of CO_2, CH_4, N_2O and $\delta^{13}C$-CO_2 measured in ice and firn air from Law Dome (Rubino et al., 2018). After merging them with other relevant records, they will be used to run models participating at CMIP6 (Graven et al., 2017; Meinshausen et al., 2017). We discuss the strengths and limitations of the Law Dome GHG records and compare our records with other records from different sites to show similarities and unresolved discrepancies. Finally, we discuss the main features of those records, their implications for biogeochemical, atmospheric and climatic studies, and possible future lines of research.

2 Methods

2.1 Law Dome

The ice cores used in this study, referred to as DE08, DE08-2, DSS and DSS0506, were drilled at Law Dome, East Antarctica (Fig. 1). Law Dome is a relatively small (~150 km diameter and 1390 m high) ice sheet on the coast of Wilkes Land. It receives large and regular snowfall mainly from the east, and the surface rarely melts in the colder central regions. The ice flow is mainly independent of the flow of the main East Antarctic ice sheet because of the drainage around Law Dome by two glacier systems (the Totten and the Vanderford). Re-working of the accumulated snow is ~~minimal~~ insufficient to erase annual layers as high wind speeds are relatively infrequent ~~and the snow surface is smooth~~. The resulting annual layering is thick and regular and preserved for much of the ice thickness (van Ommen et al., 2005).

DE08 and DE08-2 were drilled in 1987 and 1993, respectively, only 300 m apart and 16 km east of the summit of Law Dome (66°44'S, 112°50'E, 1390 m above mean annual sea level), and have an accumulation rate of approximately 1100 kg m^{-2} yr^{-1} (equivalent to 1.4 m of ice ~~equivalent~~ per year). DSS (Dome Summit South) was drilled between 1988 and 1993, 4.6 km south-south west of the summit, and has an accumulation rate of about 600 kg m^{-2} yr^{-1} ~~0.7 m ice equivalent per year~~ (Etheridge et al., 1996; Goodwin, 1990; van Ommen et al., 2005). In January-February 1993, air was sampled from the firn layer at DE08-2, providing air with mean ages back to 1976 A.D. (Etheridge et al., 1996). Another firn campaign was carried out at DSSW20K (accumulation rate of approximately 150 kg m^{-2} yr^{-1} ~~0.17 m ice equivalent per year~~), 20 km west of DSS in December 1997 (Sturrock et al., 2002), which provided air dating back to about 1940 A.D. (Trudinger et al., 2002b). DSS0506 was thermally drilled in a dry hole (Burn-Nunes et al., 2011) during the 2005/2006 austral summer near the Law

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Dome summit (66°46'S, 112°48'E, 1370 masl). The site has ~~high snow~~an accumulation rate ~~(of about~~ 600 kg m^{-2} yr^{-1}~~)~~ and a mean annual temperature of -22 °C.

2.2 ICELAB extraction

Measurement of the composition of air in ice core bubbles requires an extraction step to release the air from ice. The dry extraction technique used at ICELAB has been described in detail in previous publications (Etheridge et al., 1996; MacFarling Meure et al., 2006), with recent minor alterations to optimise extraction and measurement of δ^{13}C-CO$_2$ analyses (Rubino et al., 2013). Briefly, after ice sample selection and preparation (removing the outer 5–20 mm with a band saw), typically 0.7–1.3 kg of ice is placed in a polyethylene bag (Layflat, USP®) and cooled down to -80 °C in a chest freezer for at least 24 h prior to extraction. The ice is then placed inside a perforated inner cylinder ('cheese grater') fixed inside an internally electropolished stainless steel container which is then evacuated to less than 10^{-4} Torr and maintained at that pressure for at least 25 min. The ice is then grated by mechanically shaking the container for 10 minutes, which releases the trapped air. The process yields on average 70 mL (range 50-90 mL) of air, estimated from the pressure in the extraction line (whose volume has been previously calibrated). The air is passed through a water vapour trap (~-100 °C) and then cryogenically collected in an electropolished and preconditioned stainless steel trap at around 20 K (~~-250~~-253 °C). The sample trap is warmed in a water bath at room temperature (~25 °C) for 5 min to vaporise and mix the gases before being transported into the instrument laboratory. Samples are analysed on gas chromatographs (GCs) for CO$_2$, CH$_4$, CO, H$_2$, and N$_2$O within 24 h after extraction, and on the isotope ratio mass spectrometer (IRMS) for δ^{13}C and δ^{18}O within 12 h.

To estimate the uncertainty ~~associated with~~ and any possible bias introduced by the extraction procedure (called the blank correction), test samples are run together with the real ice samples. The test samples can either be reference air samples of known composition processed with no ice present (named 'blanks'), or reference air samples injected over ice grown with no visible bubbles in it and grated as for an actual ice core sample (the so called bubble free ice, or BFI). BFI is grown in ICELAB by keeping a container filled with deionized water in thermal equilibrium, in order to grow ice as slowly as possible from the bottom to the top of the container. The container features Plexiglass sidewalls that are electrically heated. The water exchanges heat only through the metallic base and freezes from the bottom to the top. If the process is slow enough, the produced ice is free of visible bubbles. The results of the tests performed on ICELAB-BFI, as well as on other, externally grown BFI, have been extensively described by Rubino et al. (2013).

2.3 GASLAB analysis

Each extracted air sample is analysed for trace gas concentrations (defined as mole fractions in parts per million (ppm) or parts per billion (ppb) in dry air) using several GCs in GASLAB. A Series 400 CARLE/EG&G (Tulsa, Oklahoma, USA) GC equipped with flame ionization detector is used to measure CH$_4$ and CO$_2$ (the latter converted, after column separation, to

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CH$_4$ using a nickel catalyst at 400 °C). A Trace AnalyticalRGA3 (Menlo Park, California, USA) GC, equipped with a mercuric oxide reduction gas detector, is used to measure CO and H$_2$, which reduces HgO to gaseous Hg for detection by UV absorption. N$_2$O is measured on a Shimadzu GC-8AIE (Kyoto, Japan) equipped with an electron capture detector. In normal GASLAB operation, air samples (including those sampled from firn) in low-pressure flasks and high-pressure

5 cylinders are injected and analysed on the GCs using automated inlet systems to ensure reproducibility and minimum sample consumption (Francey et al., 2003). Because of the limited amount of air available, a semi-automated procedure is used to inject the small volume of ice core air into the GCs inlet systems. Approximately 15-20 mL are used to measure CO$_2$, CH$_4$, CO and H$_2$, and 12-15 mL are used to measure N$_2$O. The remaining air (typically 40 mL) is used for δ^{13}C and δ^{18}O measurements. The volumes indicated are total volume used for flushing gas transfer lines as well as for analysis.

10 The δ^{13}C and δ^{18}O of the CO$_2$ in the residual air are measured using the MAT252 (Finnigan MAT GmbH, Bremen) IRMS located in GASLAB. Low pressure, large volume whole air samples from flasks (atmospheric or firn air samples) and the small volume, high pressure, whole air samples from ICELAB are introduced into the IRMS through a common inlet (multiport) equipped with an all stainless steel mass flow controller (Brooks 5950 5850I think) to ensure constant mass flow conditions for all samples. The IRMS uses two cryogenic traps (MT Box C, Finnigan) to retain water vapour and other

15 condensable gases and to extract CO$_2$ (plus N$_2$O) from air. The residual CO$_2$ (and N$_2$O) is injected into the MAT252 ion source via a dedicated micro-volume and crimped capillary. Nitrous oxide (N$_2$O) has identical molecular masses to CO$_2$ and interferes with the isotopic analyses. To remove this interference, a correction is made to the IRMS output in GASLAB using the relative ionisation efficiency of N$_2$O and CO$_2$, the isotopic composition of N$_2$O and the measured N$_2$O and CO$_2$ concentration, as described in detail by Allison and Francey (2007). High precision isotopic ratios are determined by

20 alternating sample CO$_2$ and reference CO$_2$ injected via matched crimped capillaries. The carbon isotopic ratio of the sample (sa) is expressed relative to the reference (ref) following Eq. (1):

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sa}}{(^{13}C/^{12}C)_{ref}} - 1 \right] \times 1000 \qquad (1).$$

When comparing measurements performed more than 20 years apart, rigorous traceability in the propagation of calibration scales becomes an important factor. This is obtained with a long-term, continuous comparison of standard cylinders for both

25 GC (Francey et al., 2003) and IRMS (Allison and Francey, 2007) analyses. The current calibration scales used are WMO X2004A for CH$_4$, WMO X2007 for CO$_2$, NOAA 2006A for N$_2$O and CSIRO2005 for CO$_2$ isotopes (CO$_2$-in-air scale, which is linked to the VPDB-CO$_2$ scale).

2.4 ICELAB database

A new database allows storage, selection, correction, updating and extraction of the data produced in ICELAB-GASLAB. It

30 allows results to be dynamically updated if changes in analytical methods or calibration scales are implemented, keeping ice,

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firn and atmospheric measurements consistent with each other. Data are stored in tables where the information associated with each specific sample is linked via a Universal Analysis Number (UAN) that acts as the index for combining all information. The structure of the database and its tables are described in detail in the Supplement. The database includes procedures, which automatically perform sample selection, correct results and estimate uncertainty, and provide a routine for data extraction (see Supplement for details).

3 Results and discussions

3.1 Development of the Law Dome GHG records, internal consistency, unexplained discrepancies and limitations

The first Pre-Industrial record of CO_2 from Law Dome covering the whole last millennium was published by Etheridge et al. (1996, reported here with red squares in Fig. 2a and 3a). It was one of the first ice core records to show the overlap with firn (Fig. 2a3a) and contemporary atmospheric measurements. The overlap of ice core and contemporary atmospheric measurements is one of the main advantages of the Law Dome ice core sites, due to their high snow accumulation rates and the resultant relatively quick bubble close-off time and recently enclosed air. This feature has been described extensively in previous papers (Etheridge et al., 1996; MacFarling Meure et al., 2006; Rubino et al., 2013) and used, together with the overlap between different cores, to demonstrate our confidence in extending contemporary GHG concentration measurements back in time. Based on replicate analyses of test samples (blanks and BFI) over time periods of several months, on ice samples within an annual layer, and the overlap mentioned above, Etheridge et al. (1996) estimated that the uncertainty of the CO_2 measurements was 1.2 ppm (1σ). The major biogeochemical events discussed in Etheridge et al. (1996) were the LIA (Little Ice Age) CO_2 decline between 1550 and 1750 ~~AD~~ CE with the subsequent recovery from the LIA perturbation between 1750 and 1800 ~~AD~~ CE in the Pre-Industrial Period, and the 1940s stabilisation of atmospheric CO_2 concentration (Fig. 3a) which ended just before the Mauna Loa and South Pole atmospheric records began.

A few years later, the same authors published the Law Dome Pre-Industrial record of CH_4 covering the last millennium (Etheridge et al., 1998, red squares in Fig. 2b and 3b) ~~covering the last millennium~~. The tight overlap for the first time between ice, firn and contemporary atmospheric CH_4 measurements that began more than 20 years later than for CO_2, confirmed that the ice core air record is a faithful representation of the past atmospheric CH_4 concentration (Fig. 2b3b). The estimated uncertainty was 5 ppb. The major features discussed in Etheridge et al. (1998) were the LIA CH_4 decline, supporting a terrestrial origin for the synchronous CH_4/CO_2 decrease, and the rapid increase in CH_4 growth rates after 1945 ~~AD~~ CE which peaked in 1981 ~~AD~~CE, just as atmospheric monitoring began. It was also possible to determine the Pre-Industrial inter-hemispheric difference in CH_4 (24-58 $\pm$ 10 ppb), based on comparison with CH_4 measurements from Greenland (Eurocore and GISP2), also made in ICELAB/GASLAB, and supporting evidence from Blunier et al. (1993) and Chappellaz et al. (1997). The variability over time of the CH_4 Pre-Industrial inter-hemispheric gradient provides a constraint

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to quantify variations of sources and sinks of CH$_4$ (Mitchell et al., 2013). The same is not possible for CO$_2$ because of the above-mentioned *in-situ* production in Greenland ice.

To quantify variations of the sources and sinks of CO$_2$, Francey et al. (1999) measured its isotopic ratio (δ^{13}C, red squares in Fig. 1c2c and 3c) in Law Dome ice. This record provided a means to quantify the relative CO$_2$ uptake from ofby the land and the ocean to the total atmospheric CO$_2$ change (Trudinger et al., 2002a), when the emissions from fossil fuel and land use change were taken into account for the Industrial Period, and assuming that, in the Pre-Industrial Period, there was no significant influence of anthropogenic activities on the atmospheric δ^{13}C-CO$_2$ (Pongratz and Caldeira, 2012; Stocker et al., 2011), and also assuming no significant changes in inter-hemispheric CO$_2$ exchange times (Francey and Frederiksen, 2016; Frederiksen and Francey, 2018). The δ^{13}C-CO$_2$ decrease measured by Francey et al. (1999) in the last two centuries (Fig. 2c3c) is mainly due to ^{13}C-depleted CO$_2$ derived from fossil fuel CO$_2$ emissions, and is important evidence of the prominent role of anthropogenic emissions on the Industrial Period CO$_2$ increase. Francey et al.(1999) also discussed the increase of δ^{13}C-CO$_2$ during the LIA, supporting the interpretation of a terrestrial origin for the synchronous CH$_4$/CO$_2$ decrease (Trudinger et al., 1999), though with lower sampling resolution compared to the CO$_2$ in Etheridge et al. (1996). Francey et al. (1999) estimated statistical and systematic δ^{13}C-CO$_2$ biases between 0.025 and 0.07 ‰, and uncertainties of up to ±0.05 ‰, but found an unexplained discrepancy of up to 0.2 ‰ (Trudinger, 2000, section 3.8) around 1900 AD CE from the South Pole δ^{13}C-CO$_2$ firn record measured at NOAA-INSTAAR (National Oceanic and Atmospheric Administration-Institute of Arctic and Alpine Research, Boulder, Colorado).

The early Law Dome GHG records have been revised and extended over time as follows.

- MacFarling-Meure et al. (2006) extended the CO$_2$ and CH$_4$ records back through the last two millennia (green diamonds in Figs. 1a 2a and b), and increased sample density in the Industrial Period (green diamonds in Figs. 2a 3a and b). They also confirmed the LIA CO$_2$/CH$_4$ decrease as well as the 1940s CO$_2$ stabilisation, and produced a record of N$_2$O (green diamonds in Fig. 1d2d) which, in turn, overlaps with firn N$_2$O measurements (green diamonds in Fig. 2d3d). The authors interpreted the N$_2$O decrease of about 5 ppb during the LIA as additional evidence for the terrestrial origin of the LIA GHG decrease. The measurement uncertainty remained the same for CO$_2$ (1.2 ppm) as for Etheridge et al. (1996), but decreased slightly for CH$_4$ (from 5 ppb in Etheridge et al., 1998; to 4 ppb in MacFarling Meure et al., 2006). The uncertainty of the N$_2$O measurements was 6.5 ppb. The authors also found an increase of N$_2$O concentration of about 10 ppb between 675 and 800 ADCE, which does not seem to be related to any known climatic featureevent.

- Rubino et al.(2013) revised the δ^{13}C-CO$_2$ record (see yellow triangles in Figs. 1c2c and 3c) by updating the calibration scale and revisiting the corrections applied in Francey et al. (1999) for blank, gravity and diffusion effects, using the revised CSIRO firn model (Trudinger et al., 2013) for the gravity and diffusion corrections (Trudinger et al., 1997). In doing so, they resolved the 0.2 ‰ discrepancy found between the Law Dome δ^{13}C-CO$_2$ record and the South Pole δ^{13}C-CO$_2$ firn record (the South Pole firn records have been reported in Fig 5, but see Rubino et al., 2013, for more details). They also increased

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sample density during the Industrial Period and applied the new chronology available for Law Dome ice (Plummer et al., 2012), which caused a shift of about 150 years for samples that are 2000 years old (see difference between the ages of green diamonds and yellow triangles in Fig. ~~1a~~2a). The age difference becomes negligible in the last millennium, as evident by comparing red squares and yellow triangles in Fig. ~~1c~~2c.

5 - Rubino et al. (2016) carried out additional CO_2 and $\delta^{13}C$-CO_2 measurements (see blue circles in Fig.s ~~2a~~ 2-3 a and c) from ice cores sampled at the Law Dome site of DSS0506 (Pedro et al., 2011). The data extended back to 1700 ~~AD~~ CE effective air age and provided additional evidence of consistent results between different ice cores and firn records where they overlapped. However, the increasing CO_2 trend measured in DSS0506 between 1700 and 1850 ~~AD~~ CE does not tightly match that previously attributed to recovery from the LIA (Etheridge et al., 1996).

10 It is also worth mentioning the results of two other studies performed using Law Dome ice and firn, which were sampled but not measured using CSIRO-GASLAB instruments.

- To investigate changes in Pre-Industrial sources of CH_4, Ferretti et al. (2005) produced a record of $\delta^{13}C$-CH_4 in Law Dome ice covering the last 2000 years (not shown). They reported unexpected changes of the global CH_4 budget, mainly attributed to variations of biomass burning emissions during the Late Pre-Industrial Holocene (LPIH) through an atmospheric box model (Lassey et al., 2000). The $\delta^{13}C$-CH_4 record from Ferretti et al. (2005) has not been included in ICEBASE because the air samples extracted in ICELAB were measured on a mass spectrometer not maintained by CSIRO-GASLAB. Therefore, the $\delta^{13}C$-CH_4 data are not on a CSIRO calibration scale and have not been included in ICEBASE.

- Park et al. (2012) measured oxygen and intramolecular nitrogen isotopic compositions of N_2O (not shown) covering 1940 to 2005 in Law Dome firn air and archived air samples from Cape Grim (Tasmania). In doing so, they confirmed that the rise

20 in atmospheric N_2O levels is largely the result of an increased reliance on nitrogen-based fertilizers. These isotopic measurements are also not included in ICEBASE ~~either~~.

3.2 The new Law Dome GHG records and comparison with records from other sites.

Figures ~~3~~ 4-5 shows the newly revised Law Dome GHG records (red circles). Following the rule-based selection described in the Supplementary Material, there are 299 ice core measurements for CO_2, 307 for CH_4 and 147 for N_2O (compared to

25 212, 228 and 103 respectively in MacFarling Meure et al., 2006), and 86 for $\delta^{13}C$-CO_2 (compared to 58 in Francey et al., 1999; and 69 in Rubino et al., 2013). All of the major features described in previous publications are retained. However, the differences mentioned above can potentially influence the biogeochemical and climatic interpretation of these records. Given that the Law Dome GHG records are a major source of information for models used to predict the future behaviour of the Earth System (Graven et al., 2017; Köhler et al., 2017b; Meinshausen et al., 2017), in the following paragraphs we provide

30 an explanation of the main reasons for these differences.

- Changes to the calibration scale result in small, mostly negligible, differences.

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- All records (except the δ^{13}C-CO$_2$) start in 154 ~~AD~~ CE (effective age for CO$_2$) rather than 0 ~~AD~~CE. This causes a revision of air ages towards more recent times for all events recorded in the second last millennium (e.g. the 10 ppb increase of N$_2$O between 675 and 800 ~~AD~~ CE discussed in MacFarling-Meure et al. (2006) is now dated 701-822 ~~AD~~CE, Fig. ~~3d~~4d), but less than 2 year change in dating after about 1000 ~~AD~~CE.

5   - Each data point has an uncertainty, which is independently calculated based on the weighting and flagging systems described in the Supplementary Material. The uncertainty does not include any additional uncertainty associated with inter-core variability. For example, based on comparisons between samples of the same ages, the discrepancy found between DSS0506 and other Law Dome cores in the period 1700-1850 ~~AD~~ CE suggests that the inter-core variability can potentially add a random, extra-uncertainty of up to 5 ppm. Further research is needed to precisely quantify the inter-core variability.

10   ~~Comparison with records from other cores show general agreement, but also a number of unexplained discrepancies.~~The following list compares the new Law Dome records with records from other sites and discusses the main differences:

- There is good agreement between the revised CO$_2$/δ^{13}C-CO$_2$ Law Dome records and the CO$_2$/δ^{13}C-CO$_2$ records from DML produced in ICELAB-GASLAB (blue triangles in Fig. ~~3a~~ 4-5 a and b). Once the different gas age distributions of the ice cores are taken into account, the two records are in very good agreement, with difference of less than 2 ppm for CO$_2$, and

15   differences within error bars for δ^{13}C-CO$_2$ (Rubino et al., 2016). Given that both records have been produced at CSIRO-ICELAB/GASLAB, we can exclude any possible inter-laboratory offset.

- There is also acceptable agreement (random differences up to 4 ppm) between the CO$_2$ Law Dome record and the CO$_2$ records from EDML and South Pole (Siegenthaler et al., 2005, white and green squares in Fig. 4b). Considering that the records have been produced in different laboratories (CSIRO-ICELAB/GASLAB and University of Bern), it is possible that

20   part of the difference is explained by an inter-laboratory offset.

- There is a systematic difference (3 ppm on average) between the Law Dome CO$_2$ record and the WAIS CO$_2$ record in the Pre-Industrial (Ahn et al., 2012, see gray squares in Fig. 4b). Though small, the difference is of concern because it is systematic throughout the whole record. The two laboratories (CSIRO-ICELAB/GASLAB and Oregon State University) that produced these records have also run a comparison experiment to quantify the contribution of a possible inter-laboratory

25   offset to the total discrepancy (Ahn et al., 2012). The good agreement (measurements from the two laboratories were consistent within the 1σ analytical uncertainty) found by the inter-comparison experiment suggests that the discrepancy is mostly due to an inter-core difference.

- There is an increase in this difference to >8 ppm between the Law Dome CO$_2$ dip around 1610 ~~AD~~ CE and the WAIS CO$_2$ decrease during the LIA (Ahn et al., 2012, compare gray squares and red circles in Fig. 4b). WAIS is considered a high

30   accumulation site and should retain the same events as those recorded at Law Dome. The difference is even more surprising when the tight agreement between the Law Dome CH$_4$ record and the WAIS CH$_4$ record (Mitchell et al., 2011) around this time is considered (compare red circles and grey squares in Fig. ~~3c~~4c). The consistency between the Law Dome and the

WAIS CH_4 record rules out dating issues or large differences in smoothing of the atmospheric signals between the two sites. This suggests a chemical origin (in-situ production) of the CO_2 discrepancy, which is more likely to occur for CO_2 than for CH_4. Clearly, the two sites record the same CH_4 events, but not the same CO_2 events, which suggests a small *in situ* production of CO_2 in WAIS ice. This interpretation is supported by additional evidence of 6 ppm discrepancy (Köhler et al., 2017b) during the Last Glacial Maximum, Last Termination and Early Holocene between the EDC CO_2 record (Monnin et al., 2001, 2004) and the WAIS CO_2 record (Marcott et al., 2014).

- There is a difference of up to 0.15 ‰ (compare gray squares and red circles in Fig. 4a) between the Law Dome $\delta^{13}C$-CO_2 record (Rubino et al., 2013) and the WAIS $\delta^{13}C$-CO_2 record (Bauska et al., 2015). This difference is most likely due to an inter-laboratory offset, but may also indicate a contribution from the CO_2 discrepancy on to its $\delta^{13}C$, or by a combination of the two. It is not possible to quantify the inter-laboratory offset without running an inter-comparison study. However, it is possible to calculate a maximum effect of the *in-situ* CO_2 production on the $\delta^{13}C$ measured at WAIS, assuming that the 3 ppm extra-CO_2 measured in WAIS (compared to an average Pre-Industrial CO_2 concentration of 280 ppm measured at Law Dome) is totally due to the *in-situ* production, and that it all comes from carbonate-carbon ($\delta^{13}C$ = 0‰), because organic-carbon with $\delta^{13}C$ = -27 ‰, would make the WAIS $\delta^{13}C$-CO_2 at WAIS more negative than the Law Dome $\delta^{13}C$-CO_2. Under this assumption, we calculate a possible shift of 0.07 ‰ through an isotope mass balance (=[0-(-6.55)]*3/283). This is enough tocan only explain only part of the discrepancy, but can go up to 0.14 ‰ if an extra amount of 6 ppm is assumed (Ahn et al., 2012; Köhler et al., 2017b). The Bauska et al. (2015) record agrees within uncertainties with the Francey et al. (1999) dataset. However, Rubino et al. (2013) is the only record to show consistency with all firn records and direct atmospheric measurements (see Fig.s 3c and 5a). This would suggest that the Rubino et al. (2013) is currently the most accurate record and should be used to set a pre-industrial baseline. However, no definite conclusion can be drawn until a thorough intercomparison study is carried out between the labs that have produced the WAIS and the Law Dome $\delta^{13}C$-CO_2 datasets (Oregon State University-University of Colorado-Institute of Arctic and Alpine Research, INSTAAR and CSIRO). It is important to resolve the difference between the Law Dome and the WAIS $\delta^{13}C$-CO_2 records in order to establish a Pre-Industrial baseline and, thus, a Pre-Industrial-to-Industrial $\delta^{13}C$-CO_2 difference,. as well as a Pre Industrial to Last Glacial Maximum $\delta^{13}C$-CO_2 difference Setting a Pre-Industrial baseline could have consequences on the Last Glacial Maximum-to-Pre-Industrial $\delta^{13}C$-CO_2 difference as well (Schmitt et al., 2012). These could be useful valuesThese values are useful for biogeochemical interpretation (Broecker and McGee, 2013; Krakauer et al., 2006).

- As expected, the Law Dome/WAIS CH_4 concentrations are lower than the NEEM high resolution CH_4 record (Rhodes et al., 2013, the white squares in Fig. 4c show the median CH_4 concentrations for 5 year time slices, after data outliers have been removed) by an amount which is consistent with an inter-hemispheric CH_4 difference of 40-60 ppb (Mitchell et al., 2013). Interestingly, the LIA CH_4 decrease measured at NEEM appears to start before the CH_4 decrease measured at Law

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Dome/WAIS, suggesting that the LIA event had an effect on the Northern Hemisphere CH₄ concentration first, and then propagated to the Southern Hemisphere. Given that the global distribution of the terrestrial biosphere is skewed towards the Northern Hemisphere, this may be further evidence that the LIA atmospheric GHG decrease was caused mostly by land sequestration. The age scale of the NEEM CH_4 record published in Rhodes et al. (2013) has been revised with the updated

5   ice age scale published in Sigl et al. (2015) and the new estimate of Δage provided by Buizert et al. (Buizert et al., 2014). Mitchell et al. (2013) have synchronised the GISP2 CH_4 record with the WAIS CH_4 record to investigate changes of the Inter Polar Difference in the Pre-Industrial based on the reasoning that "the multidecadal events observed in both ice core records must have occurred simultaneously since the durations of the events were much larger than the atmospheric mixing time (~1 year)" (Mitchell et al., 2013). The NEEM CH_4 record has not been synchronised with the others, and there are multiple

10   possible reasons, including age scale issues, different smoothing of the atmospheric signals at the different sites and inadequate sampling resolution, to explain the discrepancy found between the NEEM and the GISP2/Law Dome/WAIS CH_4 records during the LIA. A thorough investigation is out of the scope of this paper, but, in the future, this discrepancy should be resolved to obtain a precise synchronisation of all ice core records available over the LIA.

- The N_2O records from Greenland (Flückiger et al., 1999, Eurocore and GRIP, gray and white squares in Fig. 4d,

15   respectively) and from EDC (Flückiger et al., 2002, green squares in figure 4d) show higher scatter than the Law Dome N_2O record. All records need higher sampling resolution to investigate changes of atmospheric N_2O concentration over the last centuries with more confidence. A new N_2O record from a high resolution site is required to explore the real variations of N_2O in the Pre-Industrial Period (Ryu et al., 2018).

3.3 The LIA and the 1610 AD CE CO_2 minimum in DSS (Law Dome).

20   In an attempt to produce $\delta^{13}C$ data around the Law Dome 1610 AD CE CO_2 minimum (inadequately sampled by Francey et al., 1999) and confirm the interpretation of its terrestrial origin (Rubino et al., 2016; Trudinger et al., 1999), in 2012 we measured 18 samples from DSS, the only core at Law Dome covering the whole LPIH. The results both for CO_2 and for $\delta^{13}C$ are significantly lower than the spline fit to the revised records from Law Dome (results not shown). On the contrary, the CH_4 concentration measured is very consistent with the spline fit to the revised CH_4 record. In the past, abnormally low CO_2

25   concentration was interpreted as a sign of post coring melting (PCM), CO_2 being much more soluble than CH_4. With PCM, the N_2O concentration is usually low as well. However, in 7 of the 18 DSS samples that provided enough air to measure N_2O, the N_2O concentration was, on average, not significantly lower than the spline fit to the revised Law Dome record. This argues against the hypothesis of PCM. Another possibility is the effect of clathrate formation which could alter CO_2 and $\delta^{13}C$, but issues due to clathrate can be ruled out because none of the ice cores in this study reached depths or temperatures

30   sufficient for clathrate formation which can affect the extraction and measurement of enclosed gases and $^{13}C-CO_2$ in particular (e.g. Schaefer et al., 2011). We do not have a definite explanation for the low CO_2 and $\delta^{13}C$ measured, but the
30

results suggest that the DSS core may no longer be a reliable archive for CO_2. This experiment was conducted while we were measuring the DSS0506 CO_2 samples published in Rubino et al. (2016). During that survey, we also found a similar behaviour for 6 of the 34 DSS0506 samples measured. Since the two cores - DSS0506 and DSS - were stored in the same freezer in Hobart (Tasmania, Australia), with DSS0506 stored for a shorter period of time, we suggest the low CO_2 may be a recent effect of storage (see Supplement to Rubino et al., 2016).

The LIA, and particularly the 1610 ~~AD~~ CE CO_2 event, is important for our understanding of the carbon cycle dynamics and the carbon-climate system in the past. It has been used to derive the CO_2 sensitivity to temperature (Cox and Jones, 2008; Rubino et al., 2016), it is the most prominent biogeochemical event during the LPIH, and it has even been suggested as the beginning of the new geologic era called the Anthropocene (Lewis and Maslin, 2015). Therefore, it is of fundamental importance that we understand the amplitude of the minimum as recorded by the ice and the timing and likely size of the original atmospheric decrease before smoothing during firn diffusion and enclosure into bubbles. ~~Considering that:~~

~~- All GHG records in ice cores are a smoothed representation of the real atmospheric history;~~

~~- DSS is the highest accumulation rate site ever sampled in Antarctica recording the LIA CO_2 event;~~

~~- There is the risk that the WAIS core is affected by *in situ* production of CO_2;~~

~~- Accurate CO_2 record have not been derived from Greenland ice cores~~

~~we suggest that there is a need to sample a new, clean and deep ice core from Law Dome, to recover the real atmospheric LIA CO_2 decrease and other rapid changes in atmospheric composition during Pre-Industrial millennia.~~

3.4 Biogeochemical and climatic interpretation of the Law Dome GHG records

The Law Dome GHG records have been used for biogeochemical and climatic interpretation of changes in CO_2 (Joos et al., 1999; Joos and Bruno, 1998; Rubino et al., 2013; Trudinger et al., 2002a), CH_4 (Ferretti et al., 2005; Ghosh et al., 2015), and N_2O (Park et al., 2012) over the past decades to millennia. They are also used as reference atmospheric GHG records for model simulations of the carbon-climate system of the LPIH (Graven et al., 2017; Köhler et al., 2017b; Meinshausen et al., 2017). Here we present an overview of the insight obtained through interpretation of the Law Dome GHG records, and provide some perspective on the challenges we will have to face to obtain a deeper understanding of the carbon-climate system during the LPIH and the Industrial Period.

The biogeochemical interpretation of GHG variations depends on quantifying their sources and sinks. The concentration of GHGs in the atmosphere is the net result of the processes releasing GHGs to the atmosphere (sources) and processes removing GHGs from the atmosphere (sinks). The atmospheric circulation, then, redistributes GHGs assuming consistency in the reasonably well known patterns of air movement. Measuring the atmospheric concentration of GHGs provides one constraint on the net sources vs sinks. However, generally, multiple sources and sinks act simultaneously. Therefore, multiple constraints are necessary to partition the contribution of each source or sink. Measuring the isotopic composition of

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each GHG provides an additional constraint (albeit usually with additional complexity), but there are also other independent constraints, such as the inter-hemispheric difference or evidence coming from other species, that help quantify the contribution of sources and sinks. Additionally, the net GHG emission strength is reflected in the rate of change of atmospheric concentration. So, ice core records that track rapid changes (i.e. high resolution) are best to infer budgets and hence biogeochemical information before direct atmospheric observations. The Law Dome records provide the highest resolution among existing Antarctic ice cores. There have been recent studies looking into the effects of firn microstructure (including density layers) on bubble trapping (Burr et al., 2018; Fourteau et al., 2017; Gregory et al., 2014; Mitchell et al., 2015). Improved understanding of these processes, how they affect smoothing of atmospheric GHG signals, and their incorporation into numerical models may lead to a more accurate quantification of the relationship between ice core GHG measurements at different sites and the original atmospheric variations.

CO_2: There are two major reservoirs that can change atmospheric concentrations over years to millennia are the terrestrial biosphere (land) and the oceans. Fossil fuel and land use emissions have added to these over recent centuries. Measurements of $\delta^{13}C\text{-}CO_2$ have been used to quantify the contribution of land and ocean to the atmospheric CO_2 variations measured (Joos et al., 1999; Joos and Bruno, 1998; Trudinger et al., 2002a). For example, the interpretation of CO_2 and $\delta^{13}C\text{-}CO_2$ variations through a Double Deconvolution (Fig. 4a6a) has identified the terrestrial biosphere as the main contributor to the LIA CO_2 decline (Rubino et al., 2013, 2016; Trudinger et al., 2002a). This agrees with the findings of Bauska et al. (2015) who used the WAIS CO_2 and $\delta^{13}C\text{-}CO_2$ records to suggest that changes in terrestrial organic carbon stores best explain the observed multi-decadal variations in the $\delta^{13}C\text{-}CO_2$ and in CO_2 concentrations from 755 to 1850 ADCE. This agreement of interpretation from the DSS and WAIS records shows that what matters for the biogeochemical interpretation is the change in concentration over time, rather than the absolute concentration measured in different ice cores. The above studies assume consistency in the inter-hemispheric transport of Northern Hemisphere terrestrial emissions over multiple decades. Preliminary examination suggests Southern Hemisphere $\delta^{13}C\text{-}CO_2$ recent records over the last decades are more susceptible to multi-year changes in the ratio of eddy to mean advective interhemispheric transport (Francey and Frederiksen, 2016; Frederiksen and Francey, 2018) than is the case for CO_2 concentration, as a result of differences in isotopic equilibration that occur for the two transport modes.

An additional constraint for the biogeochemical interpretation of the LIA CO_2 decrease has recently come from the new interpretation (Rubino et al., 2016) of the record of carbonyl sulfide (COS, Aydin et al., 2008) from the SPRESSO ice core (South Pole Remote Earth Science and Seismological Observatory) and modelling of its increase over the LIA (Rubino et al., 2016). Rubino et al. (2016) showed that the simultaneous COS increase during the LIA confirms that the LIA CO_2 decline was caused by net terrestrial uptake due to cooling (heterotrophic respiration declining more than Gross Primary Production, due to its higher dependence sensitivity on temperature changes). Clearly, though a very recent paper estimating the amount

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of carbon taken up by land use change following the colonisation of the Americas by the Europeans (Koch et al., 2019) provides a different view., Nonetheless, a the multi-species approach used by Rubino et al. (2016, e.g. using trends of CO_2, $\delta^{13}C$-CO_2 and COS)(e.g. using trends of CO_2, $\delta^{13}C$-CO_2 and COS) can provide multiple constraints to help understand the biogeochemical processes behind atmospheric CO_2 variations over the recent past.

The 1940s CO_2 plateau is a prominent feature in the Industrial part of the Law Dome CO_2 record, and occurs at a time of continued fossil fuel emissions. Taking into consideration the smoothing effects of firn diffusion and bubble trapping on the rate of change of potential atmospheric signals, an uptake of around 2-3 GtC/yr between 1942-49 would be required to explain the observed plateau. The Law Dome $\delta^{13}C$-CO_2 measurements suggest that the oceans were responsible for at least two thirds of this uptake (Rubino et al., 2013; Trudinger, 2000, section 6.4; Trudinger et al., 2002a). Bastos et al. (2016) used the latest estimates of fossil-fuel and land-use change emissions, ocean uptake reconstructions and terrestrial models, but was not able to explain the plateau, although they did not consider decadal variability in the ocean carbon sink that may have been important. Better understanding of the 1940s feature is needed to quantify how variable ocean and land carbon exchange can be on multi-year to decadal timescales, and how this variability relates to climate variability. Improved understanding is expected to come from more high-precision, high-time-resolution ice core measurements to confirm $\delta^{13}C$-CO_2 variation through the Industrial Period, additional constraints such as COS, better understanding of the smoothing effects on trapped air along with improved modelling of other influences on atmospheric $\delta^{13}C$-CO_2 such as the effect of climate on isotopic discrimination (Randerson et al., 2002; Scholze et al., 2003).

CH_4: There are multiple natural sources/sinks: geological, wetlands, wildfires, termites, and ocean sediments are the main sources, while oxidation by tropospheric species [OH], oxidation by stratospheric species [OH, Cl and O(1D)], and oxidation in soils and reactive chlorine in the marine boundary layer are the main sinks. Also for CH_4, measurements of its isotopic composition ($\delta^{13}C$-CH_4 and δD-CH_4) have helped quantify the contribution of land vs ocean to the measured atmospheric CH_4 variations (Ferretti et al., 2005; Mischler et al., 2009; Sapart et al., 2012). However, because there are more distinct CH_4 source types than isotopic tracers, and more spatially distributed sources than can be resolved by the geographically restricted suite of ice cores (despite the fact that the ice cores of Antarctica and Greenland are both known to provide reliable CH_4 records), a unique solution for the history of CH_4 sources is not possible. Nonetheless, the full suite of isotopic tracers and bipolar ice core data provides important boundary conditions for testing hypothetical CH_4 source/sink histories, allowing elimination of large classes of scenarios. By measuring $\delta^{13}C$-CH_4 in Law Dome ice, Ferretti et al. (2005) provided evidence of a remarkable decrease of pyrogenic CH_4 during the last millennium (Fig. 4c6b). This interpretation was confirmed by Mischler et al. (2009) and Sapart et al. (2012), who measured both $\delta^{13}C$-CH_4 and δD-CH_4 in ice cores from Antarctica and Greenland respectively. They also found an increasing agricultural source of CH_4 throughout the last millennium, with most of the change between the 1500s and the 1600s, supporting the hypothesis of an early a pre-industrial anthropogenic influence on atmospheric CH_4. Additional source information is provided by measurements of carbon monoxide (CO) and its
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isotopes (δ^{13}C-CO and δ^{18}O-CO, Wang et al., 2010), through evidence of variations of biomass burning, and ^{14}CH$_4$, which identifies CH$_4$ emissions from fossil sources., However, the measurement of ^{14}CH$_4$which is limited so far to large air samples extracted from firn (Lassey et al., 2007b, 2007a) or from large ice samples collected where glacial-age ice outcrops at the surface (Petrenko et al., 2009, 2017).

5   N$_2$O: There are also multiple natural sources and sinks of N$_2$O, both on land and in the ocean. The main sources are microbiological processes, especially in tropical soils, while the main sinks are photochemical reactions in the atmosphere. To the best of our knowledge, there are only two attempts to use δ^{15}N-N$_2$O and δ^{18}O-N$_2$O records to better constrain the land vs ocean sources of N$_2$O over the last century (Park et al., 2012; Prokopiou et al., 2017), and these used the larger volumes of air available in firn. No study has extended the investigation to the last millennia, but there is an analysis covering the Last

10   Deglaciation by Schilt et al.(2014). As already mentioned, the Pre-Industrial inter-hemispheric N$_2$O difference is also poorly constrained. Thus, there is room for vast improvement to understand the N cycle from measurements of N$_2$O concentration and its isotopes in ice cores (Schilt et al., 2014). However, there is a risk of *in-situ* production of N$_2$O, especially in Greenland ice (Flückiger et al., 2002). More records, with high sampling resolution, from both hemispheres are needed to confirm the features found in Law Dome (MacFarling Meure et al., 2006) and understand the causes of the changes in N$_2$O

15   concentration over time (Ryu et al., 2018).

The climatic interpretation of the Law Dome GHG records has generally been carried out by comparing the timing of GHG variations and temperature changes, and testing hypotheses of mechanistic relationships between the two with coupled carbon cycle-climate models.

Medieval Climate Anomaly: An important climatic event of the LPIH is the Medieval Climate Anomaly (MCA, roughly

20   950–1250 ADCE), which showed higher temperature in some regions (Goosse et al., 2005; Mann et al., 2009). During the MCA, there are generally higher levels of GHGs, but the timings of increase vary from one gas to another, with N$_2$O showing a rise between 701 and 822 AD CE (well before the start of the MCA), CO$_2$ increasing between 950 and 1200 ADCE, and CH$_4$ showing some variability superimposed on a long-term increasing trend (Fig. 3b4b-d).

Little Ice Age: The main climatic event of the last two millennia is the LIA (roughly 1400-1700 CE, Mann et al., 2008;

25   Neukom et al., 2014; Pages2k, 2013). There is a clear decrease of all GHG during the LIA, which, together with the other evidence mentioned above, suggests that all processes releasing GHG from land slowed down during the cold phase (Fig. 3 4 b-d). However, as for the MCA, the change in concentration is not simultaneous for all GHG. While both CO$_2$ and N$_2$O seem to decrease starting around 1550 AD CE (but N$_2$O would need higher sampling resolution to confirm this), CH$_4$ has a later decline, starting around 1580 ADCE. Also, the CH$_4$ decrease seems to last for a shorter period of time, ending around 1610

30   ADCE, whereas the CO$_2$ low is maintained longer, ending about 1750 ADCE. At the same time, there was a significant decrease of biomass burning (Ferretti et al., 2005; Mischler et al., 2009; Sapart et al., 2012; Wang et al., 2010), interpreted to be mostly a consequence of decreased fire emissions. While the relationship between CO$_2$ and temperature variation has

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been used to infer the sensitivity of CO_2 to temperature (Cox and Jones, 2008; Rubino et al., 2016), confirming and quantifying a positive feedback of terrestrial carbon with temperature (Rubino et al., 2016), it is now time to investigate the regional contribution to the total CO_2 change, as attempted by Bauska et al. (2015), and the contribution from different processes within the terrestrial biosphere, such as net primary production, heterotrophic respiration and biomass burning.

5 There are regional (Mann et al., 2008), continental (Pages2k, 2013) and hemispheric (Neukom et al., 2014) temperature reconstructions that can be used ~~in~~ to drive ~~Coupled Carbon Cycle Climate Models~~ models describing the relationship between climate and carbon cycle to quantify the contribution from each region to the total CO_2 decrease (Fig. ~~4b~~6c). There are also hydro-climatic reconstructions (Cook et al., 2009, 2010, 2015) providing evidence of dry and wet periods over the LPIH (Fig. ~~4d~~6d), which can be used, together with records of charcoal (Marlon et al., 2013, 2016) and biomass burning

10 tracers in ice cores (Grieman et al., 2017) to quantify the contribution of declining biomass burning in each region to the total CO_2 decrease. The emissions from anthropogenic land use change have also been quantified for each world region (Pongratz and Caldeira, 2012, see Fig. 6e), and can be used to subtract the human contribution from the total CO_2 change, even though there is a debate on the amount of land use change following the European colonisation of the Americas (Koch et al., 2019). ~~Therefore, we~~We suggest that the LIA provides a suitable epoch to further study carbon cycle-climate

15 feedbacks, for predictions of the future carbon-climate system, particularly to understand the role of different regions of the world on changes of atmospheric chemistry and biogeochemical fluxes and carbon pools. The consequences of the LIA climatic changes on ~~contemporary~~ societal development are important for understanding why different communities were more or less vulnerable, resilient or even adaptive (Degroot, 2018)~~.,~~ Being able to quantify which regions have been more vulnerable to past climate change, also in terms of the response of the natural carbon cycle, could help plan future adaptation

20 strategies~~and plan future choices accordingly~~.

4 Conclusions

The records of GHG (CO_2, CH_4, N_2O) concentrations and the~~ir~~ isotopic composition of CO_2 (δ^{13}C-CO_2,~~δ^{13}C-CH_4, δD-CH_4, δ^{15}N-N_2O, δ^{18}O-N_2O~~) from the Law Dome ice cores are ~~one of~~ among the most important sources of information for models trying to predict the future behaviour of biogeochemical cycles and their influence on the climate system. The records of

25 CO_2, CH_4, N_2O and δ^{13}C-CO_2 are constantly being updated with new measurements, and revised for changes in calibration scales and corrections for the effects of laboratory extractions and those of gravity and diffusion in firn. This paper has provided an in-depth explanation of the procedures used to extract and measure the samples in CSIRO-ICELAB, and store, correct and select the results obtained. Given the widespread use of the datasets produced at CSIRO ICELAB-GASLAB, it is important to provide a track record of the reasons for changes carried out over time, and keep the records open to the

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scientific community. This should help with their use in modelling and avoid misinterpretation (for example, the mistake spotted by Köhler et al., 2017a, in the paper from Machado and Froehner, 2017).

The GHG records from Law Dome have already provided significant insight into biogeochemical and climatic feature over the last centuries. However, there is room for deeper understanding, for example studying the influence of different regions
on variations in atmospheric chemistry. Also, there are unresolved discrepancies (e.g. the LIA CO_2 decrease) which need to be resolved and Law Dome appears to provide the most suitable ice cores for high resolution investigation of atmospheric changes over the last centuries. Considering that:

- All GHG records in ice cores are a smoothed representation of the real atmospheric history;

- DSS is the highest accumulation rate site ever sampled in Antarctica recording the LIA CO_2 event;

- There is the risk that the WAIS core is affected by *in-situ* production of CO_2;

- Accurate CO_2 record have not been derived from Greenland ice cores

we suggest that there is a need to sample a new, clean and deep ice core from Law Dome, to ~~recover the real~~confirm or improve our knowledge of the atmospheric LIA CO_2 decrease and other rapid changes in atmospheric composition during Pre-Industrial millennia.

Finally, there are open questions about the real size of past atmospheric variations of some species, such as N_2O and COS, and the reasons for those variations, which, once resolved with new measurements, could provide additional understanding and insights, useful to better predict the future behaviour of biogeochemical cycles and their influence on the climate system.

Author contribution

MR conceived the database structure, performed measurements between 2009-2013 and ~~wrote~~led writing of the paper. DME supervised the process, performed measurements ~~between 1992-2003~~ and collected samples. RH wrote the database queries and procedures in Microsoft SQL server and developed the web-based user interface with Microsoft Visual Studio. DPT, CEA, RJF, RLL, ~~PLS~~LPS and DAS carried out measurements of samples and standards in GASLAB, and performed calibration scale updates. CMT carried out the numerical modelling~~interpretation~~, including the CSIRO firn model, the ~~D~~double ~~D~~deconvolution and the Spline fit to the data. MAJC, TDVO and AMS collected, stored and distributed samples and contributed to ice dating.

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Data Availability

Data connected with this paper are available in the CSIRO Data Access Portal (https://doi.org/10.25919/5bfe29ff807fb). Each species has been ordered by core and by age. In detail, for each species and each record the following fields are available (Rubino et al., 2018):

- Sample ID
- Ice Age
- Gas age
- Value
- Uncertainty

For each species, the calculated spline fit with time steps of 1 year and growth rate are also given. The spline fits attenuate variations with periods of less than 20 years by 50% for CO_2 and CH_4, 100 years for N_2O and 50 years for $\delta^{13}CO_2$. When using these data please consider citing the original publications from which the data underlying this compilation have been taken

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Figure captions

Figure 1: Map of the Law Dome region, slightly modified from Smith et al. (2000), showing the location of the drilling sites DE08, DE08-2, DSS, DSS0506 and DSSW20K discussed in the text. Dotted lines are accumulation isopleths (kg m^{-2} yr^{-1}) and unbroken lines are elevation contours (meters above sea level). The inset shows the location of the region in Antarctica

Figure 2: Published Pre-Industrial Period (1-1900 AD) GHG records from Law Dome ice extracted and measured at CSIRO ICELAB-GASLAB. (a) CO_2; (b) CH_4; (c) $\delta^{13}C$-CO_2 and (d) N_2O

Figure 23: Published and unpublished Industrial Period (1750-2000) GHG records from Law Dome ice and firn, extracted and measured at CSIRO ICELAB-GASLAB. (a) CO_2; (b) CH_4; (c) $\delta^{13}C$-CO_2 and (d) N_2O

Figure 34: Revised records (100-1900 AD) of (a) $\delta^{13}C$-CO_2; (b) CO_2; (c) CH_4 and (d) N_2O from Law Dome ice compared to published records from other sites: WAIS-$\delta^{13}C$-CO_2 from Bauska et al. (2015), WAIS-CO_2 from Ahn et al. (2012), DML-CO_2 and -$\delta^{13}C$-CO_2 from Rubino et al. (2016), EDML- and South Pole-CO_2 from Siegenthaler et al. (2005), WAIS-CH_4 from Mitchell et al. (2011), NEEM-CH4 from Rhodes et al. (2013) and GISP2-CH_4 from Mitchell et al. (2013), Eurocore- and GRIP-N_2O from Flückiger et al. (1999), EDC-N_2O from Flückiger et al. (2002).

Figure 5: Revised records (1750-2010 AD) of (a) $\delta^{13}C$-CO_2; (b) CO_2; (c) CH_4 and (d) N_2O from Law Dome ice and firn compared to the South Pole firn records of $\delta^{13}C$-CO_2, CO_2, N_2O and to published records from other sites: WAIS-$\delta^{13}C$-CO_2 from Bauska et al. (2015), WAIS-CO_2 from Ahn et al. (2012), DML-CO_2 and -$\delta^{13}C$-CO_2 from Rubino et al. (2016), EDML- and South Pole-CO_2 from Siegenthaler et al. (2005), WAIS-CH_4 from Mitchell et al. (2011), NEEM-CH4 from Rhodes et al. (2013) and GISP2-CH_4 from Mitchell et al. (2013), Eurocore-N_2O from Flückiger et al. (1999).

Figure 46: Biogeochemical and climatic interpretation of the Law Dome GHG records: (a) atmospheric CO_2 fluxes from (negative values on the y axis) and to (positive values on the y axis) the terrestrial biosphere (land: green line) and the ocean (blue line), resulting from the Double Deconvolution of CO_2 and $\delta^{13}C$-CO_2 (Rubino et al., 2016). (b) Temperature variations of different continents in the Northern Hemisphere (Asia: yellow line, Europe: blue line; North America: red line) from Pages2k (2013); (eb) Flux of atmospheric CH_4 from biomass burning (Ferretti et al., 2005); (c) Temperature variations of different continents in the Northern Hemisphere (Asia: yellow line, Europe: blue line; North America: red line) from Pages2k (2013); (d) Palmer Drought Severity Index (PSDI) of different continents in the Northern Hemisphere (Asia: yellow line, Europe: blue line; North America: red line) from Cook et al. (2009, 2010, 2015) (d) Atmospheric CO_2 fluxes from different continents in the Northern Hemisphere (Asia: yellow line, Europe: blue line; North America: red line) due to Pre-Industrial land use change from Pongratz et al. (2012).
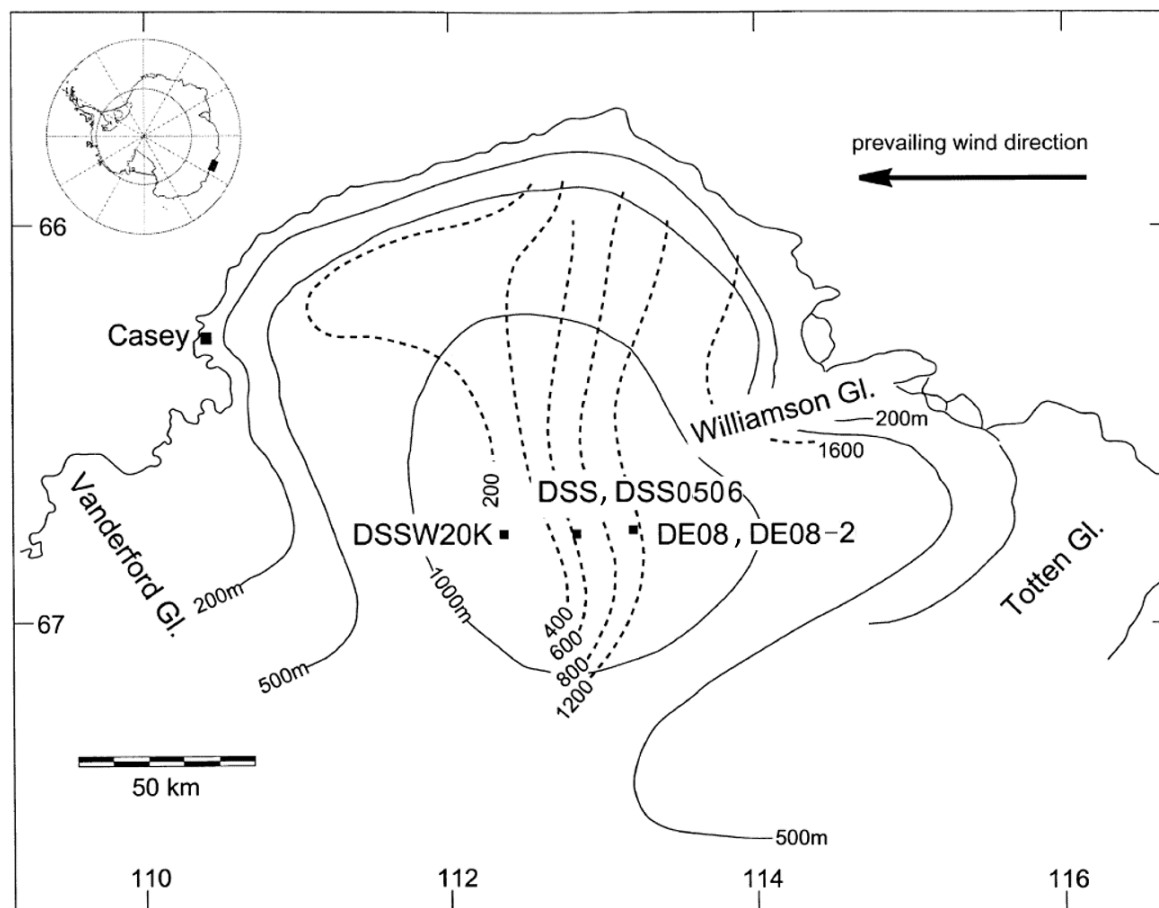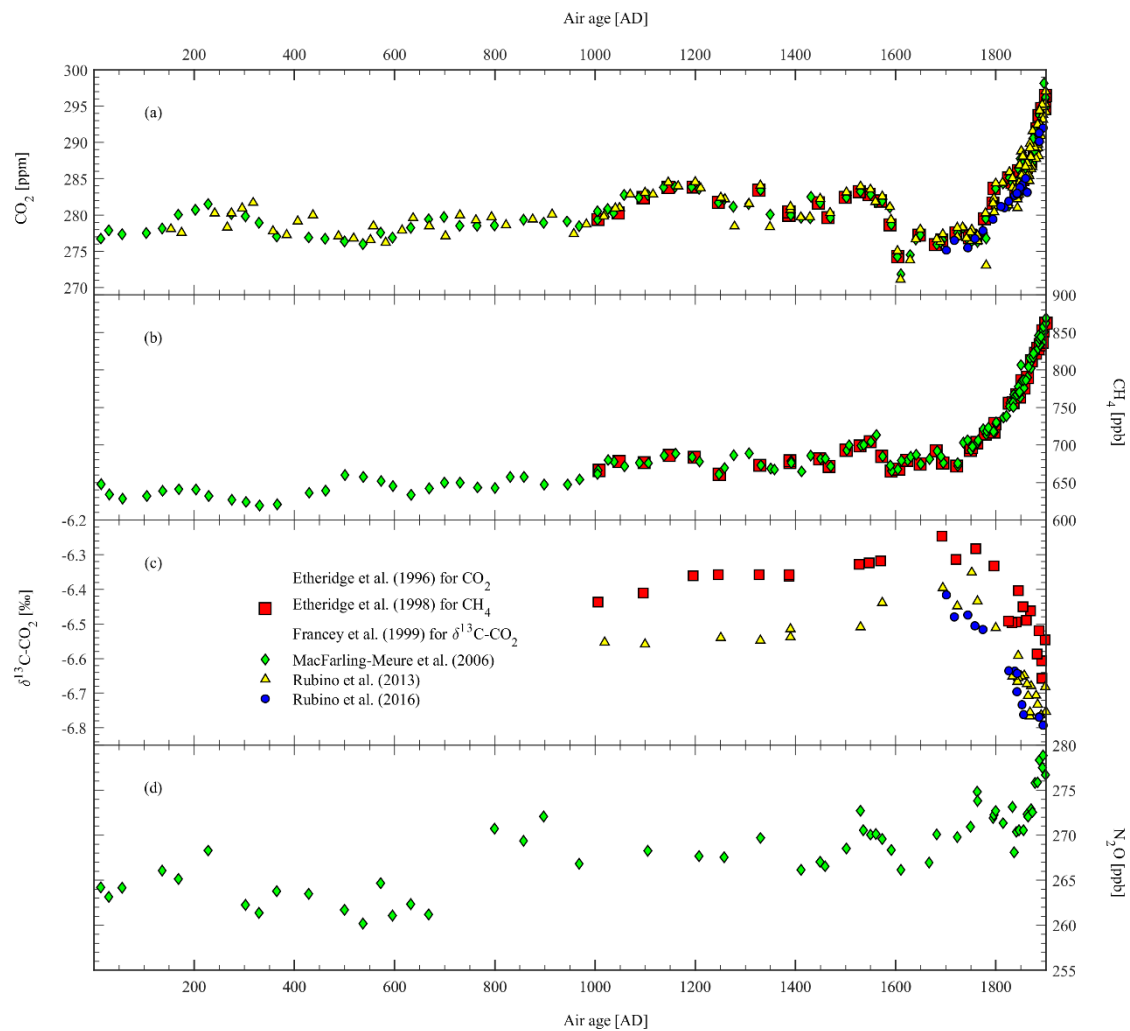
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Figure 1: Map of the Law Dome region, slightly modified from Smith et al. (2000), showing the location of the drilling sites DE08, DE08-2, DSS, DSS0506 and DSSW20K discussed in the text. Dotted lines are accumulation isopleths (kg m^{-2} yr^{-1}) and unbroken lines are elevation contours (meters above sea level). The inset shows the location of the region in Antarctica

85   Figure ~~1~~2: Published Pre-Industrial Period (1-1900 AD) GHG records from Law Dome ice extracted and measured at CSIRO ICELAB-GASLAB. (a) CO_2; (b) CH_4; (c) $\delta^{13}C\text{-}CO_2$ and (d) N_2O

90

95

100

105

110

Air age [AD]

1760 1780 1800 1820 1840 1860 1880 1900 1920 1940 1960 1980 2000

CO_2 [ppm]

355
335
315
295
275

(a)

(b)

Etheridge et al. (1996), for CO_2
Etheridge et al. (1998) for CH_4
Francey et al. (1999) for δ^{13}C-CO_2
MacFarling-Meure et al. (2006)
Rubino et al. (2013)
Rubino et al. (2016)

CH_4 [ppb]

1700
1500
1300
1100
900
700

δ^{13}C-CO_2 [‰]

-6.3
-6.7
-7.1
-7.5
-7.9

(c)

DE08-2 firn in Etheridge et al. (1996) for CO_2, Etheridge et al. (1998) for CH_4,
Francey et al. (1999) for δ^{13}C-CO_2, unpublished for N_2O
DSSW20K firn in MacFarling-Meure et al. (2006) for CO_2, CH_4, and N_2O,
Rubino et al. (2013) for δ^{13}C-CO_2

(d)

N_2O [ppb]

310
300
290
280
270

1760 1780 1800 1820 1840 1860 1880 1900 1920 1940 1960 1980 2000
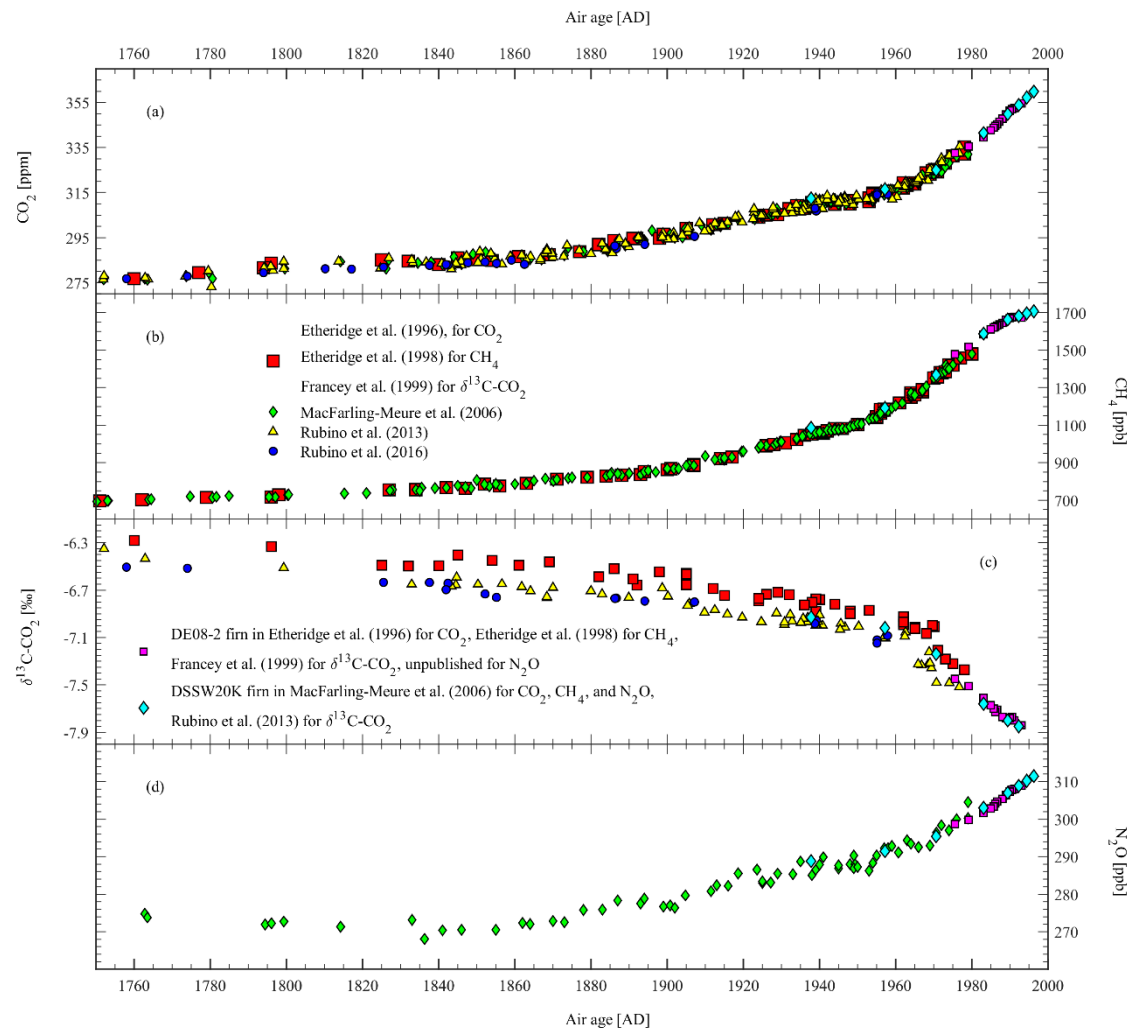
Air age [AD]

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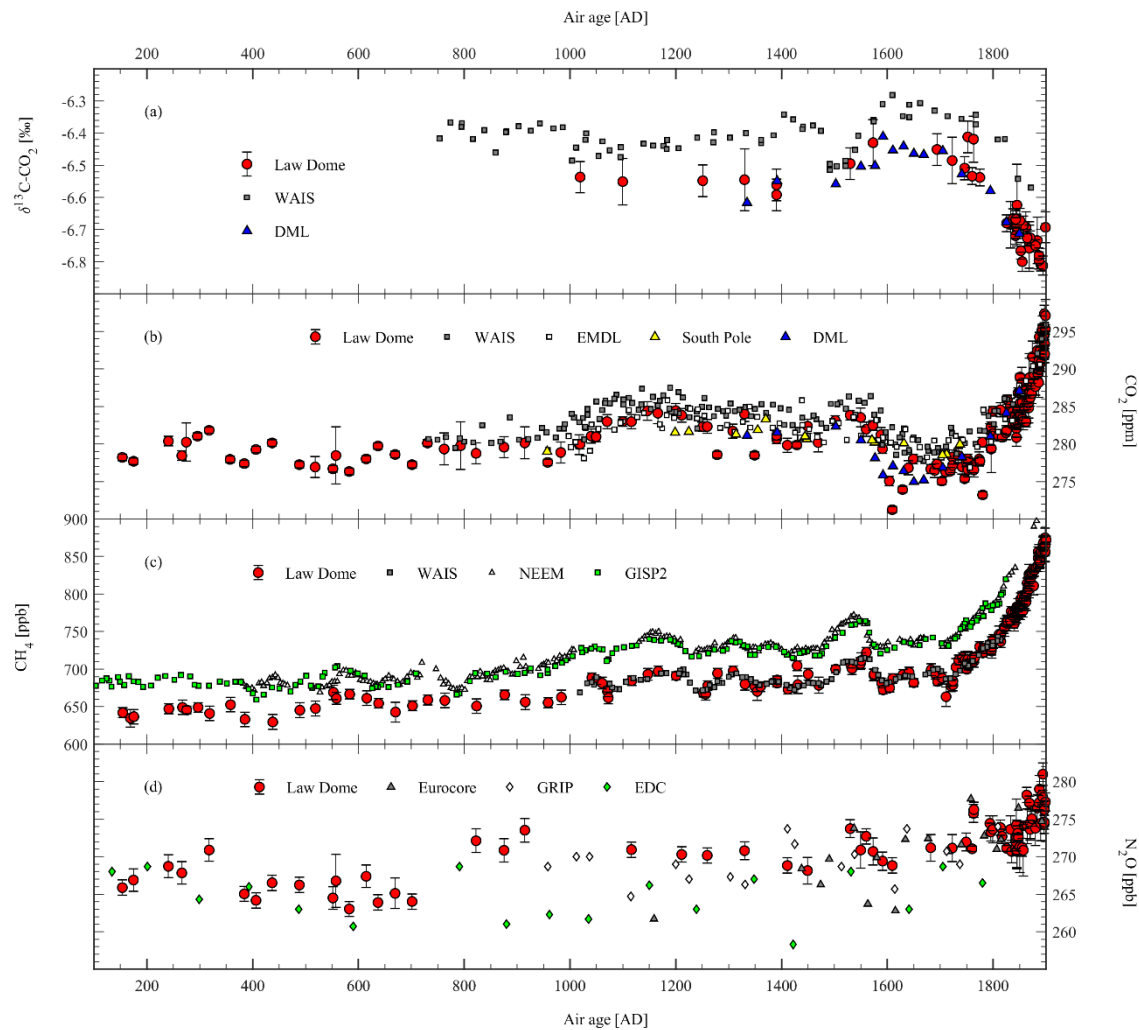
Figure 3̶4: Revised records (100-1900 AD) of (a) δ^{13}C-CO_2; (b) CO_2; (c) CH_4 and (d) N_2O from Law Dome ice compared to published records from other sites: WAIS-δ^{13}C-CO_2 from Bauska et al. (2015), WAIS-CO_2 from Ahn et al. (2012), DML-CO_2 and -δ^{13}C-CO_2 from Rubino et al.

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140   (2016), EDML- and South Pole-CO_2 from Siegenthaler et al. (2005), WAIS-CH_4 from Mitchell et al. (2011), NEEM-CH4 from Rhodes et al. (2013) and GISP2-CH_4 from Mitchell et al. (2013), Eurocore- and GRIP-N_2O from Flückiger et al. (1999), EDC-N2O from Flückiger et al. (2002).
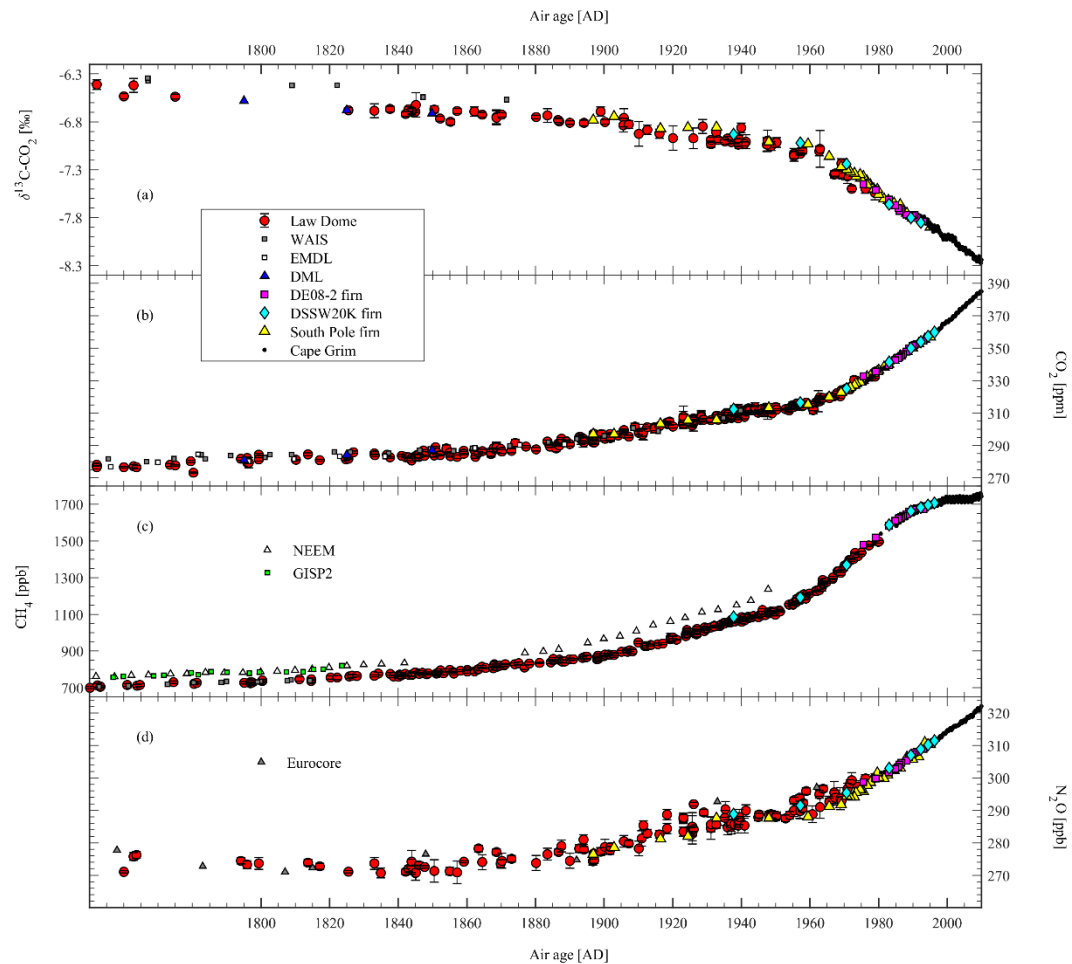
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Figure 5: Revised records (1750-2010 AD) of (a) δ^{13}C-CO$_2$; (b) CO$_2$; (c) CH$_4$ and (d) N$_2$O from Law Dome ice and firn compared to the South Pole firn records of δ^{13}C-CO$_2$, CO$_2$, N$_2$O and to published records from other sites: WAIS-δ^{13}C-CO$_2$ from Bauska et al. (2015), WAIS-CO$_2$ from Ahn et al. (2012), DML-CO$_2$ and -δ^{13}C-CO$_2$ from Rubino et al. (2016), EDML- and South Pole-CO$_2$ from Siegenthaler et al. (2005), WAIS-CH$_4$

170 from Mitchell et al. (2011), NEEM-CH4 from Rhodes et al. (2013) and GISP2-CH$_4$ from Mitchell et al. (2013), Eurocore-N$_2$O from Flückiger et al. (1999).
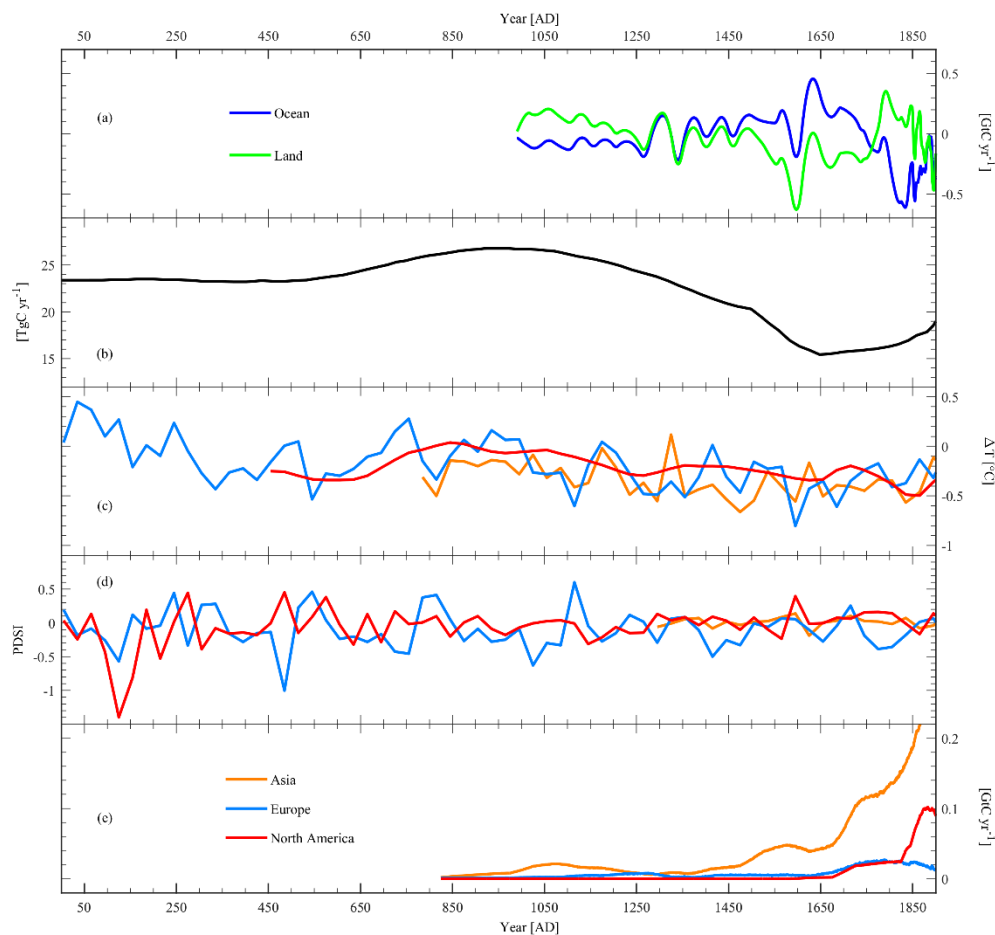
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S1 ICELAB database

The ICELAB-GASLAB is a Microsoft SQL Server that consists of numerous tables linked together by a Universal Analysis Number (UAN) that is assigned to each sample prior to analysis. The UAN is contained in every table and serves as the index connecting all information about the sample. The structure of the database, ie hierarchy of tables, reflects the chronological sequence of steps involved in collecting a sample (ice-core, firn-air), preparing an ice sample, extracting air from that sample and analysing the concentration and isotopic composition of the extracted air (only the ICE-relevant tables and procedures are described here). The web-interface to the ICELAB database, developed with Microsoft Visual Studio, is shown in Fig. S1. It indicates the general structure and relationships crucial to the database, as described below.

Samples are divided into three categories (ICE, Tests and FIRN), and data pertaining to these categories are stored in separate tables. Whenever a unique air sample is prepared (ICE, Test or FIRN) a unique UAN is created and stored in the relevant table.

"ICE" contains the ice sample ID (e.g.: "DE08-256", or "DSS-144"), ice collection parameters, depth, age, mass and volume (calculated using an average ice density), along with comments pertaining to the visual, glaciological characteristics (such as "crusts", "melt layers", "cracks", etc.). Also included are the operator's initials and the preparation date.

"TEST" contains information about the type of test ("Blanks" and "BFI") and a sample comment (e.g.: "BFI no shaking", that is without shaking the ice grater, or "BFI Ar-sparged", that is BFI grown under a flow of Argon), reference gas used (that is the reference tank or flask of known composition used for the test), and physical parameters such as mass and volume. This also contains the operator's initials and the preparation date.

"FIRN" contains information about the sample collection (depth, age, volume of gas pumped, sampling date and time, pressure of the sample after sampling and the type of firn air sampling device used).

Further tables store information about the sample preparation and combine information that is stored in other tables, such as in the GASLAB database, to collect relevant information in a central location, as described below.

"EXTRACTION" contains information about the extraction procedure, and is therefore relevant only for ice and test samples (firn samples need no extraction). This table includes extraction date and time, storage period (i.e. time between preparation and extraction), storage temperature, the ID number of the "grater" used, the composition of the material used to seal the grater (either "Indium" or "Copper"), ID number of the sample trap, a number of fields recording the various pressure levels measured at each step of the extraction procedure (e.g.: "Pressure in the extraction line before water trap cooling", "Pressure in the extraction line after water trap cooling", "Pressure after sample grating", etc.), the volume of air extracted (calculated from the "pressure after sample grating" and the "volume of the extraction line"), the residual mass of uncrushed ice, the calculated extraction efficiency (from the air released and the mass of ice crushed).

"Analysis Data" contains information for ice, firn and test samples, including the number of replicate measurements, the analysis date and time, the sample storage period (time between extraction and analysis) and the volume injected in each instrument. "Analysis Data" is linked to other tables, named after the species analysed ("CH$_4$", "CO$_2$", "CO", "H$_2$"

and "N_2O") and these are generated by importing the results of the GC measurements (the concentration measured both from the area and from the height of the GC peak) from the GASLAB database.

"Average Analysis Info" stores the averaged results for each measured species. This includes the arithmetic average for repeat measurements (or single value), the weighted (if applicable) average (calculated using the criteria described in the section Selection Criteria below), the difference between arithmetic and weighted averages, range of measured values (for replicates only) and the difference between the measured and the expected value (for test samples).

"ICE 13C" and "FIRN 13C" import and store the information from a separate database, ISOBASE, that contains the results of the isotopic analyses. The information stored includes the analysis date, the sample storage period (between extraction and analyses), the signal measured for the most abundant isotopomer (at m/e 44), the raw isotopic delta values with respect to the working standard used ($\delta^{45}CO_2$ and $\delta^{46}CO_2$) and the corrected delta values on the VPDB scale ($\delta^{13}C$ and $\delta^{18}O$). Both sets of delta values are provided with combined uncertainty estimates for the entire analysis and calculation procedure.

"Ice/FirnCorrected" contains information for ice and firn samples that have been corrected using Tests information. ICE samples are corrected for extraction procedure effects, whereas both ICE and FIRN samples are corrected for gravity and diffusion effects in the firn. Corrections are applied in the following order:

"Blank corrected average": the "Weighted average" corrected for effects of the extraction procedure, estimated through the test samples, and with an associated uncertainty estimate.

"Gravity corrected average": the "Blank corrected average" corrected for the effect of gravity in the firn, estimated from firn diffusion model (Trudinger et al., 1997, 2013), and with an associated uncertainty estimate

"Diffusion corrected average": the "Gravity corrected average" corrected for the effect of diffusion in the firn. This is only applied to measurements of the CO_2 isotopic composition (Trudinger et al., 1997), and with an associated uncertainty estimate

A final quality assessment (selection tick) is assigned after the corrections based on the criteria described below.

Every table allows comments to be added so that one can assess each stage of the correction procedure.

"Reference and Lookup" tables contain information that is used for correction and assessment procedures. The information allows us to:

a. derive the ice age from the depth at which the ice sample was collected,

b. derive the gas-age from the ice-age-vs-gas-age difference for ice samples and gas-age vs depth for firn samples. For firn samples, the dating is based on the firn air diffusion model, whereas for ice samples it is based on a number of factors, including firn model (Trudinger et al., 2013),

c. apply blank, gravity and diffusion corrections to measurements,

d. store and access information available from different types of measurements that are not part of the usual GASLAB/ICELAB analytical procedures (e.g $\delta^{18}O$, H_2O_2, etc...).

Finally, "Ice/Tests/Firn Output" are web-based interfaces that allow data extract based on multiple criteria.

S1.1 Sample selection

A rule-based method has been developed to allow for consistent and automatic sample flagging. The method separately considers the two parts where biases can be introduced:

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1. <u>Sample storage/preparation/extraction</u>: flags have been associated with any possible source of uncertainty or bias. The diagnostic fields that have an associated flag are:

    a. Fields describing visual characteristics, such as "crusts", "melt layers", "cracks", etc…

    b. Fields recording the main factors influencing the extraction procedure, e.g.: "Pressure in the extraction line before water trap cooling", "Pressure in the extraction line after water trap cooling", "Temperature of cryogenic trapping", etc…

    c. The measured CO concentration: carbon monoxide is used as a diagnostic tool. High CO values have been measured in Greenland ice (Francey et al., 1997) together with high CO_2 and low $\delta^{13}C$-CO_2, suggesting in situ oxidation of organic material deposited on the Greenland icecap (Francey et al., 1997)~~as it can be produced in situ by chemical/biological reactions and is an indication of the quality of the sample~~. High CO concentrations can also indicate contamination during sample storage/preparation/extraction as the ambient CO concentration is often higher than what it is in ice core bubbles.

    d. Fields having comments typed in by the operator. For these, the operator types in the flag value as well.

The flags are assigned integer values between 0 and 3, with 0 being no problem and 3 being evidence of a fatal problem. All flags are averages to provide a "quality score" (q.s.) and this number is used to set a "quality flag" (q.f.), according to the following thresholds:

- q.f.="reject" if q.s. = 3
- q.f.="poor" if q.s. > 0.5
- q.f.="fair" if $0.3 \leq$ q.s. ≤ 0.5
- q.f.="good" if q.s. < 0.3

For example, a melt layer is classified as evidence of a fatal problem of sample quality and provides a q.s. = 3 and a q.f. = "reject".

2. <u>Sample analysis</u>: a weighting system has been used to attribute weights (w) to different replicated measurements of the same sample and to calculate a weighted average. ~~(only for~~Only a few measurements of concentration have been replicated.~~, not f~~ For isotopes, ~~for which~~ there ~~is normally~~has never been~~ not~~ enough air to measure replicates~~)~~. The weights are associated with:

    a. The volume injected into the instruments

    b. Any issue arising from the integration of the GC peak (baseline, shape, etc...)

    c. The difference between the results derived from peak area vs peak height integration.

The weights can get a value between 0 and 1 (0, 0.3, 0.5, 1), with zero being evidence of a fatal problem. A summary weight takes the minimum value of all weights, allowing us to be as conservative as possible, albeit at the cost of losing samples. A "measurement score" (m.s.) averages the summary weights of all replicates, providing one number which is then converted into a "measurements quality" (m.q.):

    - m.q.="poor" if m.s.< 0.4

    - m.q.="fair" if $0.4 \leq$ m.s. < 0.7

    - m.q.="good" if m.s. ≥ 0.7.

The weighted average is calculated from the measured concentration (x_i) of each replicate and the corresponding summary weight (w_i) as: $x_w = \Sigma_i(x_i * w_i)/\Sigma_i w_i$ and provides the best estimate of the concentration measured for each sample. The difference between the average and the weighted average shows the impact of the weights on the

averaging. In case the summary weight of a sample equals zero, only the arithmetic average is calculated (m.q.="reject").

While the flagging system refers to the quality of a sample, the weighting system refers to the quality of a measurement. Given that multiple (partially or totally) independent measurements can be performed on a sample (for different species such as CH_4, CO_2, CO and N_2O), there is a summary weight associated with each type of measurement carried out (m.s.$_{CH4}$, m.s.$_{CO2}$, etc...).

The flagging and weighting thresholds are tuned by calibrating the rule-based selection on the manual selection used before the database was conceived. The idea was to replicate with an automatic procedure what had been done in the past manually. The aim was to make the procedure consistent over time and as independent from the operator as possible. In summary, the rule-based selection converts qualitative judgments on the robustness of sample preparation, extraction and analysis into quantitative scores in order to consistently select/reject the results and quantify uncertainty.

S1.2 Results corrections

A number of corrections are applied to the measured concentrations and isotopic composition of trace gases. They are, following the order in which they are applied:

- The blank correction: this is related to any effect arising during sample storage/preparation/extraction. To quantify these effects, tests are run with (BFI) or without ice (Blanks). There is no reference ice core material, with known concentration and isotopic composition of trace gases available. We have chosen to simulate the extraction procedure is by growing gas-free ice (that is ice with no visible bubbles and is thus assumed to be gas-free) and inject a reference gas in the extraction line before starting the extraction procedure. This is in part also simulating the storage and the preparation because the BFI is trimmed at the same stage of processing and with the same band saw used for ice core samples, and is stored between preparation and extraction in the same conditions as ice core samples. The blank correction is quantified by the average deviation of replicated BFI/Blanks measured concentration and isotopic composition from the expected value (i.e.: the value associated with the reference gas used). A blank correction is calculated for each period when the conditions of preparation/storage/extraction are the same. In other words, a new blank correction is calculated each time any of the factors (operator, freezer, temperature of cold room, duration of extraction, etc...) that are believed to influence preparation/storage/extraction changes. The blank correction has an uncertainty associated with it, given by the standard deviations of differences from the expected value. The blank correction can vary significantly depending on the conditions of the extraction line and on how experienced the line operator is. Typical values are within the following ranges: 0.5-1.5 ppm (uncertainty 0.5-2 ppm, 1σ) for CO_2, 3-10 ppb (uncertainty 3-15 ppb, 1σ) for CH_4, 0.5-3 ppb (uncertainty 0.5-4 ppb, 1σ) for N_2O and 0.03-0.1 ‰ (uncertainty 0.04-0.13 ‰, 1σ) for $\delta^{13}C$-CO_2.

- The gravity correction: Gravitational enrichment of heavier species in air in the firn open porosity (Craig et al., 1988; Schwander et al., 1988) has different effects depending on the difference between the mass of the measured species and the average mass of air. It can be evaluated as: $[X]_{corr} = 10^{-3} \times \delta^{15}N \times (M_X - M_{air}) \times [X]_{meas}$, where X is the measured species (i.e.: CH_4, CO_2 and N_2O), "corr" and "meas" stands for corrected and measured respectively, and $\delta^{15}N$ is the isotopic ratio of molecular nitrogen (N_2) in firn. For $\delta^{13}C$ measurements, the gravity corrected $\delta^{13}C$ equals the sum of a correction factor (very close to the $\delta^{15}N$-N_2) and the measured $\delta^{13}C$ (see Rubino et al., 2013 for details). The values of $\delta^{15}N$ are often measured in firn to constrain the firn diffusion model. In case of missing $\delta^{15}N$ measurements, the firn

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model is constrained with other measurements and then used to simulate the $\delta^{15}N$ profile. Our database stores all measured and modelled $\delta^{15}N$ values for firn sites at Law Dome. At Law Dome, the gravity correction is typically 1-1.5 ppm for CO_2, 2-6 ppb for CH_4, 1-1.4 ppb for N_2O and 0.25-0.3 ‰ for $\delta^{13}C$-CO_2.

- The diffusion correction (only for measurements of isotopic composition): For measurements of isotopic ratios in firn and ice air samples, a so-called diffusion correction is needed (Trudinger et al., 1997). This correction arises from the fact that an isotope ratio is the ratio of two isotopes with slightly different diffusion coefficients and therefore slightly different effective ages (Trudinger, 2000, section 3.6). For hypothetical species with constant isotopic ratio, but changing atmospheric concentrations, the isotopic ratio in the firn can be significantly different ~~than~~ from the atmospheric ratio. For $\delta^{13}C$, the diffusion correction is proportional to the rate of change of CO_2 concentration, which makes the $\delta^{13}C$ diffusion correction insignificant in the LHPI, and a very significant term in the Industrial Period. The diffusion correction is estimated using the CSIRO firn diffusion model and, at Law Dome, can range from around 0 in the Pre-Industrial to 0.13 ‰ in the Industrial Period.

We estimated the uncertainty in the gravity and diffusion corrections with the ensemble of diffusivity parameters (Trudinger et al., 2013), including among our parameter sets the possibility of dispersive mixing in the lock-in zone, which may arise from a non-uniform velocity distribution and viscous flow in the firn open porosity (Buizert et al., 2012). The uncertainty associated with gravity and the diffusion corrections are negligible compared to the uncertainty associated with the blank correction.

S1.3 Uncertainty estimation

Because of the small size of ice core samples generally available and the need for large air volume to measure multiple species, ~~it is uncommon to have enough air to perform~~ the vast majority of samples have no replicated measurements. It is, therefore, essential to be able to estimate the uncertainty associated with each one single measurement. The flagging system described above provides a way to attribute an uncertainty to each sample. When replicates are available for one sample, it is important to properly quantify the reliability of each replicate and the contribution it should give to the average and the associated uncertainty. However, the variability associated with replicates of the same sample is negligible compared with the uncertainty associated with the blank correction. The weighting system described above provides a tool to estimate how reliable each replicate is, and, consequently, the impact it should have on the final average and the final uncertainty.

The uncertainty is estimated as the product of the uncertainty associated with the blank correction times an amplification factor which is derived from considerations of the q.s. and the m.s. combined together. This "uncertainty factor" (u.f.) is in the range 1-4:

- u.f.=4 if both q.f.= "reject" and m.q.="reject"
- u.f.=3 if either q.f.= "reject" or m.q.="reject"
- u.f.=2 if both q.f.= "poor" and m.q.="poor"
- u.f.=1.5 if either q.f.= "poor" or m.q.="poor"
- u.f.=1 if both q.f.= "fair/good" and m.q.="fair/good".

In other words, the blank uncertainty is multiplied by 1, 1.5, 2,3 or 4, depending on the q.f. and the m.q. values, to get a modified blank uncertainty. When q.f. = "reject", the sample is marked with a rejection flag. However, the result of that sample is retained in the database and a u.f. = 4 is associated with it. The reason why we have decided to do that is to

provide enough flexibility for the operator to overrule the automatic selection when there is a strong reason (e.g. new insight developed over time). If a data user wants to use that sample, the uncertainty associated with the results is very high (4 × the blank uncertainty and then propagated as explained below). The final uncertainty is then calculated as the square root of the sum of the modified blank uncertainty squared, plus the uncertainty associated with the gravity correction squared, plus (but only for measurements of isotopic composition) the uncertainty associated with the diffusion correction squared (Joint Committee for Guides in Metrology, 2008).

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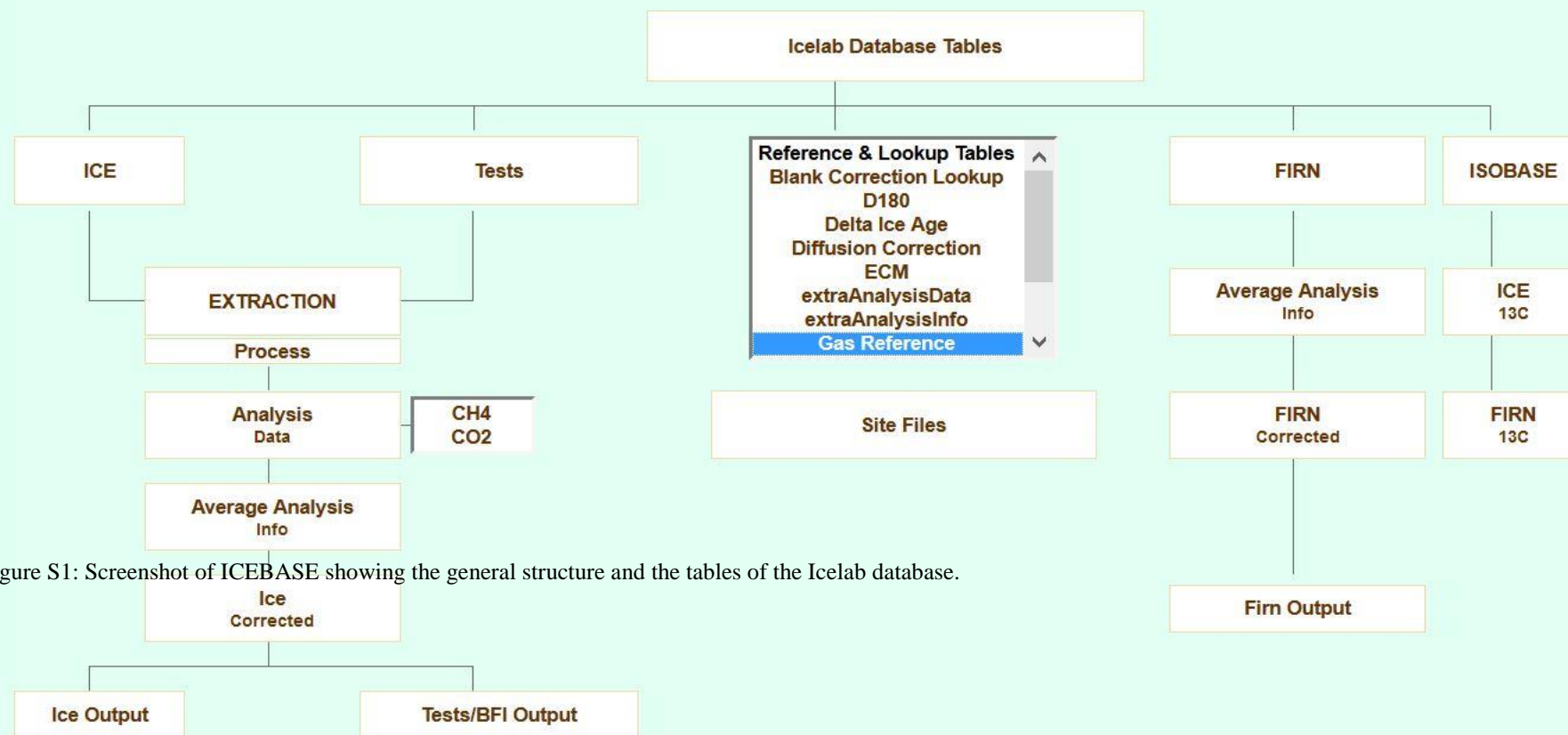
Figure S1: Screenshot of ICEBASE showing the general structure and the tables of the Icelab database.