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Revised records of atmospheric trace gases CO_2, CH_4, N_2O and $\delta^{13}C$-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_2O) 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, 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).

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1 Introduction

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. 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 provide a balanced state for model spin-up. 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.

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 thousands of years back in time (Higgins et al., 2015; Wolff et al., 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 suitability. Focusing on the last millennium, multiple ice core records of GHG concentration and isotopic composition are available:

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-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 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) in Greenland, Law Dome (Etheridge et al., 1998; MacFarling Meure et al., 2006) and WAIS (Mitchell et al., 2011) in Antarctica;

-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 N2O: 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., 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 two hemispheres, as well as on the atmospheric circulation and the gases' atmospheric lifetimes. 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 the depth of the firn layer and 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, GHG records from many Antarctic sites are usually a more smoothed representation of the atmospheric history. 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 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

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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 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 $\delta^{13}C\text{-}CO_2$ 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 $\delta^{13}C\text{-}CO_2$ 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 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 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 $\delta^{13}C\text{-}CO_2$ 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.

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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. 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 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 1.4 m 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 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 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 Dome summit (66°46'S, 112°48'E, 1370 masl). The site has high snow accumulation rate (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 $\delta^{13}C\text{-}CO_2$ 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 °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

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transported into the instrument laboratory. Samples are analysed on gas chromatographs (GCs) for CO_2, CH_4, CO, H_2, and N_2O within 24 h after extraction, and on the isotope ratio mass spectrometer (IRMS) for $\delta^{13}C$ and $\delta^{18}O$ within 12 h.

To estimate the uncertainty associated with and any possible bias introduced by the extraction procedure, 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).

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 to 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 Hg for detection by UV absorption. N_2O 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 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_2O. The remaining air (typically 40 mL) is used for $\delta^{13}C$ and $\delta^{18}O$ measurements. The volumes indicated are total volume used for flushing gas transfer lines as well as for analysis.

The $\delta^{13}C$ and $\delta^{18}O$ 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 I 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 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 a dedicated micro-volume and crimped capillary. High precision isotopic ratios are determined by 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):

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

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

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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_2O 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 allows results to be dynamically updated if changes in analytical methods or calibration scales are implemented, keeping ice, 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, red squares in Fig. 1a). It was one of the first ice core records to show the overlap with firn (Fig. 2a) 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 with the subsequent recovery from the LIA perturbation between 1750 and 1800 AD in the Pre-Industrial Period, and the 1940s stabilisation of atmospheric CO_2 concentration 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 (Etheridge et al., 1998, red squares in Fig. 1b) 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. 2b). 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

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CH_4/CO_2 decrease, and the rapid increase in CH_4 growth rates after 1945 AD which peaked in 1981 AD, just as atmospheric monitoring began. It was also possible to determine the Pre-Industrial inter-hemispheric difference in CH_4 (24-58 ± 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 to quantify variations of sources and sinks of CH_4. 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 ($\delta^{13}C$, red squares in Fig. 1c) in Law Dome ice. This record provided a means to quantify the relative CO_2 uptake from of 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 $\delta^{13}C$-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 $\delta^{13}C$-CO_2 decrease measured by Francey et al. (1999) in the last two centuries (Fig. 2c) 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 $\delta^{13}C$-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 $\delta^{13}C$-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 $\delta^{13}C$-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 Fig.s 1a and b), and increased sample density in the Industrial Period (green diamonds in Fig.s 2a 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_2O (green diamonds in Fig. 1d) which, in turn, overlaps with firn N_2O measurements (green diamonds in Fig. 2d). The authors interpreted the N_2O 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_2O measurements was 6.5 ppb. The authors also found an increase of N_2O concentration of about 10 ppb between 675 and 800 AD, which does not seem to be related to any known climatic feature.

- Rubino et al.(2013) revised the $\delta^{13}C$-CO_2 record (see yellow triangles in Fig.s 1c) 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

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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 $\delta^{13}C\text{-}CO_2$ record and the South Pole $\delta^{13}C\text{-}CO_2$ firn record. They also increased 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). The age difference becomes negligible in the last millennium, as evident by comparing red squares and yellow triangles in Fig. 1c.

- Rubino et al.(2016) carried out additional CO_2 and $\delta^{13}C\text{-}CO_2$ measurements (see blue circles in Fig.s 2a and c) from ice cores sampled at the Law Dome site of DSS0506 (Pedro et al., 2011). The data extended back to 1700 AD 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 does not tightly match that previously attributed to recovery from the LIA (Etheridge et al., 1996).

It is also worth mentioning the results of two studies performed using Law Dome ice and firn, 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 $\delta^{13}C\text{-}CH_4$ 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 $\delta^{13}C\text{-}CH_4$ 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 $\delta^{13}C\text{-}CH_4$ 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.

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

Figure 3 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 212, 228 and 103 respectively in MacFarling Meure et al., 2006), and 86 for $\delta^{13}C\text{-}CO_2$ (compared to 58 in Francey et al., 1999; and 69 in Rubino et al., 2013). All 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 an explanation of the main reasons for these differences.

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

- All records (except the $\delta^{13}C\text{-}CO_2$) start in 154 AD (effective age for CO_2) rather than 0 AD. 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_2O between 675 and 800 AD discussed in MacFarling-Meure et al. (2006) is now dated 701-822 AD, Fig. 3d), but less than 2 year change in dating after about 1000 AD.

- 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 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.

Comparison with records from other cores show general agreement, but also a number of unexplained discrepancies.

- There is good agreement between the revised $CO_2/\delta^{13}C\text{-}CO_2$ Law Dome records and the $CO_2/\delta^{13}C\text{-}CO_2$ records from DML produced in ICELAB-GASLAB (blue triangles in Fig. 3a 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 differences within error bars for $\delta^{13}C\text{-}CO_2$ (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. 3b). Considering that the records have been produced in different laboratories (CSIRO-ICELAB/GASLAB and University of Bern), it is possible that 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 (Ahn et al., 2012, see gray squares in Fig. 3b). 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 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 and the WAIS CO_2 decrease during the LIA (Ahn et al., 2012, see gray squares in Fig. 3b). WAIS is considered a high 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). 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

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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 ‰ between the Law Dome $\delta^{13}C$-CO_2 record and the WAIS $\delta^{13}C$-CO_2 record (Bauska et al., 2015, see gray squares in Fig. 3a). This difference is most likely due to an inter-laboratory offset, but may also indicate a contribution from the CO_2 discrepancy on 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 $\delta^{13}C$-CO_2 at WAIS more negative than Law Dome. Under this assumption, we calculate a possible shift of 0.07 ‰ through an isotope mass balance (=[0-(-6.55)]*3/283). This is enough to 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). It is important to resolve the difference between the Law Dome and the WAIS $\delta^{13}C$-CO_2 records 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. These could be useful values 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. 3c show the median CH4 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. 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. 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 N_2O records from Greenland (Flückiger et al., 1999, Eurocore and GRIP, gray and white squares in Fig. 3d, respectively) and from EDC (Flückiger et al., 2002, green squares in Fig. 3d) 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 CO_2 minimum in DSS (Law Dome).

In an attempt to produce $\delta^{13}C$ data around the Law Dome 1610 AD 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

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CH_4 concentration measured is very consistent with the spline fit to the revised CH_4 record. In the past, abnormally low CO_2 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 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 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 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 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.

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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 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 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 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. 4a) 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 AD. 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 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

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(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 on temperature changes). Clearly, a multi-species approach (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 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. 4c). 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 anthropogenic influence on atmospheric CH_4. Additional source information is

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provided by $^{14}CH_4$, which identifies CH_4 emissions from fossil sources, the measurement of 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).

N_2O: There are also multiple natural sources and sinks of N_2O, 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 $\delta^{15}N\text{-}N_2O$ and $\delta^{18}O\text{-}N_2O$ records to better constrain the land vs ocean sources of N_2O 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 Deglaciation by Schilt et al.(2014). As already mentioned, the Pre-Industrial inter-hemispheric N_2O difference is also poorly constrained. Thus, there is room for vast improvement to understand the N cycle from measurements of N_2O concentration and its isotopes in ice cores (Schilt et al., 2014). However, there is a risk of *in-situ* production of N_2O, 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_2O 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 950–1250 AD), 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_2O showing a rise between 701 and 822 AD (well before the start of the MCA), CO_2 increasing between 950 and 1200 AD, and CH_4 showing some variability superimposed on a long-term increasing trend (Fig. 3b-d).

Little Ice Age: The main climatic event of the last two millennia is the LIA (roughly 1400-1700 AD, Mann et al., 2008; 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 b-d). However, as for the MCA, the change in concentration is not simultaneous for all GHG. While both CO_2 and N_2O seem to decrease starting around 1550 AD (but N_2O would need higher sampling resolution to confirm this), CH_4 has a later decline, stating around 1580 AD. Also, the CH_4 decrease seems to last for a shorter period of time, ending around 1610 AD, whereas the CO_2 low is maintained longer, ending about 1750 AD. 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 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

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terrestrial biosphere, such as net primary production, heterotrophic respiration and biomass burning. 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 CO_2 decrease (Fig. 4b). There are also hydro-climatic reconstructions (Cook et al., 2009, 2010, 2015) providing evidence of dry and wet periods over the LPIH (Fig. 4d), which can be used, together with records of charcoal (Marlon et al., 2013, 2016) and biomass burning 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. 4e), and can be used to subtract the human contribution from the total CO_2 change. Therefore, we suggest that the LIA provides a suitable epoch to further study carbon cycle-climate 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), and plan future choices accordingly.

4 Conclusions

The records of GHG (CO_2, CH_4, N_2O) concentrations and their isotopic composition ($\delta^{13}C$-CO_2,$\delta^{13}C$-CH_4, δD-CH_4, $\delta^{15}N$-N_2O, $\delta^{18}O$-N_2O) 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. The records of CO_2, CH_4, N_2O and $\delta^{13}C$-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 scientific community. This should help with their use in modelling and avoid misinterpretation (Köhler et al., 2017a; 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. 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, could provide additional understanding and insights, useful to better predict the future behaviour of biogeochemical cycles and their influence on the climate system.

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Author contribution

MR conceived the database structure, performed measurements between 2009-2013 and wrote 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 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 Double Deconvolution and the Spline fit to the data. MAJC, TDVO and AMS collected, stored and distributed samples.

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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. 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: Published Pre-Industrial 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

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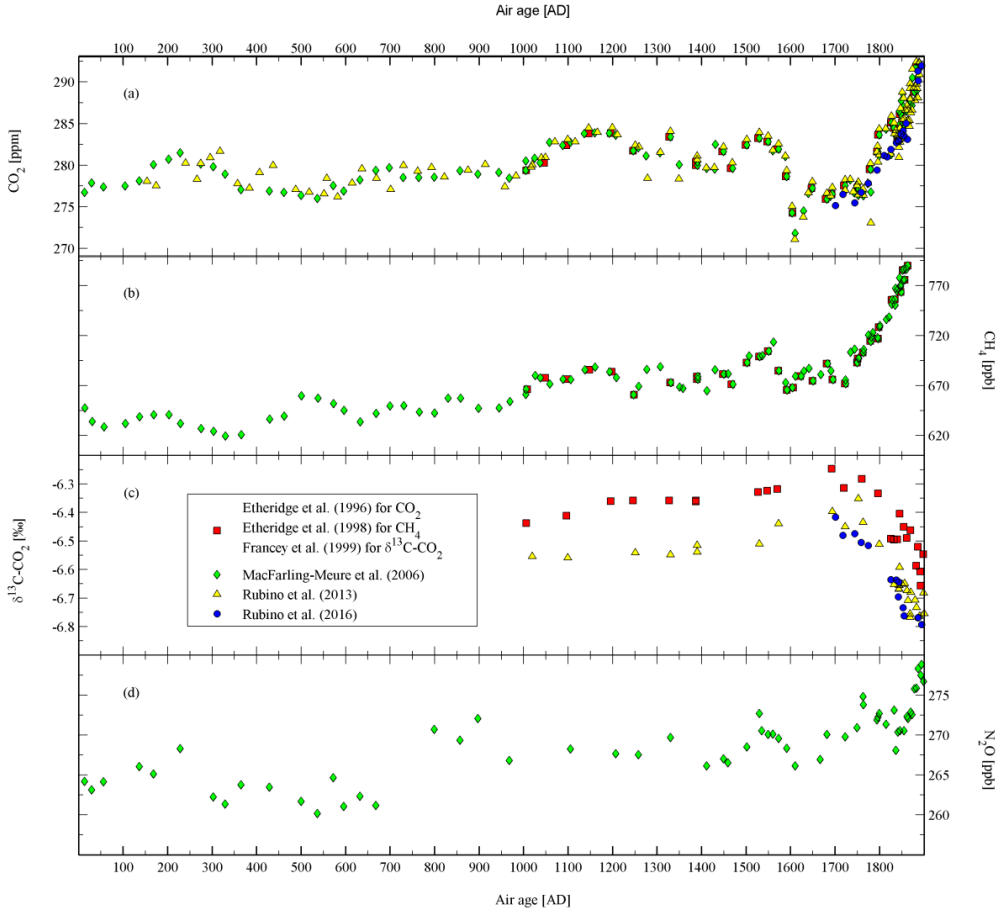

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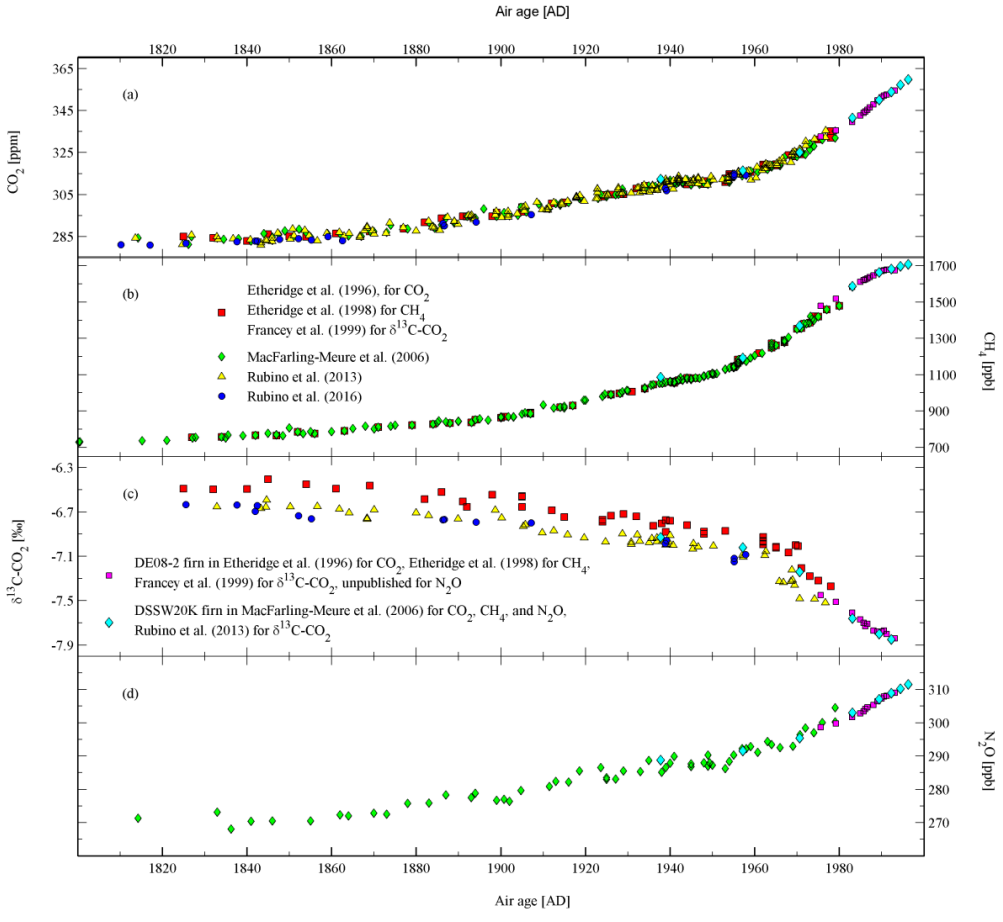

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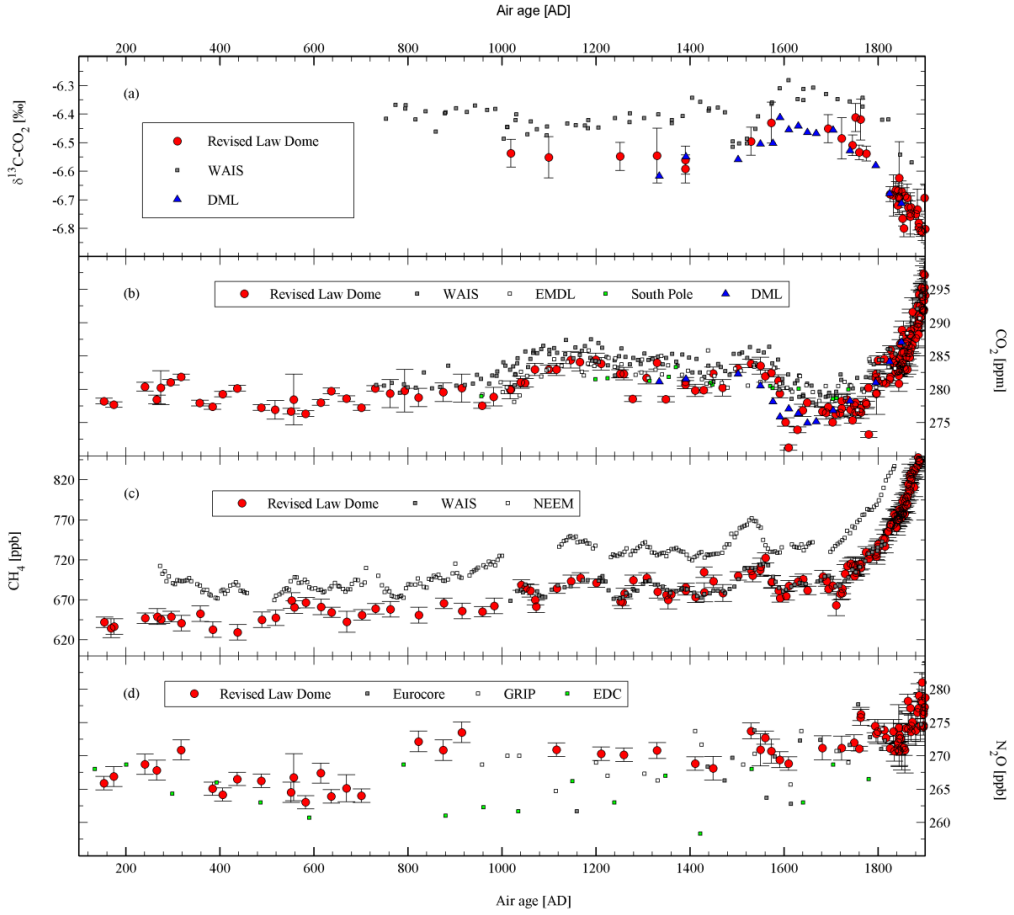

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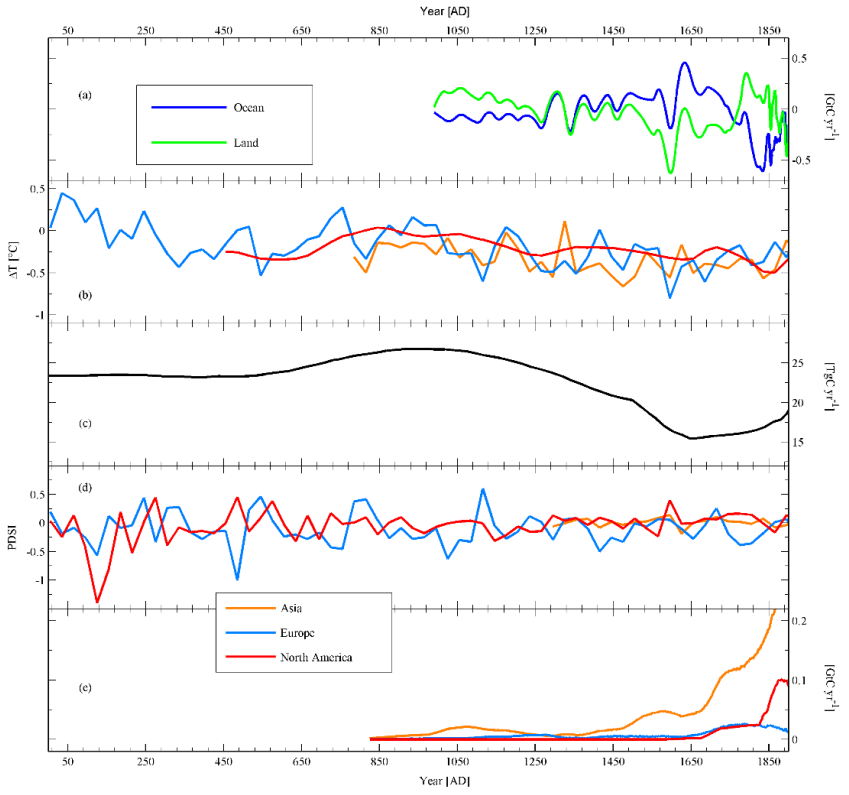

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