# Law Dome $CO_2$, $CH_4$ and $N_2O$ ice core records extended to 2000 years BP

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[1] New measurements of atmospheric greenhouse gas concentrations in ice from Law Dome, Antarctica reproduce published Law Dome $CO_2$ and $CH_4$ records, extend them back to 2000 years BP, and include $N_2O$. They have very high air age resolution, data density and measurement precision. Firn air measurements span the past 65 years and overlap with the ice core and direct atmospheric observations. Major increases in $CO_2$, $CH_4$ and $N_2O$ concentrations during the past 200 years followed a period of relative stability beforehand. Decadal variations during the industrial period include the stabilization of $CO_2$ and slowing of $CH_4$ and $N_2O$ growth in the 1940s and 1950s. Variations of up to 10 ppm $CO_2$, 40 ppb $CH_4$ and 10 ppb $N_2O$ occurred throughout the preindustrial period. Methane concentrations grew by 100 ppb from AD 0 to 1800, possibly due to early anthropogenic emissions. **Citation:** MacFarling Meure, C., D. Etheridge, C. Trudinger, P. Steele, R. Langenfelds, T. van Ommen, A. Smith, and J. Elkins (2006), Law Dome $CO_2$, $CH_4$ and $N_2O$ ice core records extended to 2000 years BP, *Geophys. Res. Lett.*, *33*, L14810, doi:10.1029/2006GL026152.

## 1. Introduction

[2] Changes in atmospheric composition before contemporary observations began are best found from measurements of air occluded in polar ice, either in bubbles in impermeable ice or channels in the overlying firn layer. Records of the past millennium have revealed substantial increases in the concentrations of greenhouse gases during the past 200 years [*Etheridge et al.*, 1996, 1998; *Sowers*, 2001] due to anthropogenic emissions. Records of trace gas concentrations and their isotopic ratios have been used to constrain biogeochemical models [*Trudinger et al.*, 2002a; *Ferretti et al.*, 2005], force global climate model simulations [*Crowley*, 2000; *Bauer et al.*, 2003], and as proxies of past global temperature changes [*Gerber et al.*, 2003].

[3] Measurements of ice core and firn air from the Law Dome ice sheet (East Antarctica: 66°46′08″E, 112°48′28″S) have already provided records of $CO_2$, $CH_4$ and their $\delta^{13}C$ isotopes over the past 1000 years with high precision and

unparalleled temporal resolution [*Etheridge et al.*, 1996, 1998; *Francey et al.*, 1999; *Ferretti et al.*, 2005]. The trends found in the Law Dome $CH_4$ and $CO_2$ records are broadly consistent with those observed in other records [*Stauffer et al.*, 2002; *Siegenthaler et al.*, 2005]. However, different records show concentration differences between AD1000 and 1500 and need further investigation to determine whether they are artifacts of the ice samples or measurement technique or due to the different ice core age resolutions. Also, the $CO_2$ stabilization found during the 1940s implies atmosphere-land-ocean fluxes of carbon that are beyond the range deduced from the direct atmospheric record of the past decades [*Trudinger et al.*, 2002a]. Here we further investigate these variations by re-measuring and extending the $CO_2$ and $CH_4$ Law Dome records to 2000 years BP and produce a new Law Dome $N_2O$ record.

## 2. Methods

[4] Air samples were extracted from the Law Dome DE08, DE08-2 and DSS ice cores [*Etheridge et al.*, 1996; *Morgan et al.*, 1997] and from the DSSW20K firn air site [*Sturrock et al.*, 2002]. Air samples were dated following the methods described by *Etheridge et al.* [1996, 1998] *Trudinger et al.* [2002b] and *MacFarling Meure* [2004]. Air was extracted from the ice core samples using a dry extraction "cheese grater" and cryogenic trapping technique developed by *Etheridge et al.* [1996], with only minor alterations [*MacFarling Meure*, 2004]. Air from the firn layer was pumped into containers using techniques described by *Sturrock et al.* [2002]. The trapped air samples were analyzed by gas chromatography (GC) and the trace gas concentrations are reported on the calibration scales maintained by CSIRO GASLAB [*Francey et al.*, 2003].

[5] Regular testing (described in Auxiliary Material[1]) showed that the ice core air measurements were not systematically influenced by the extraction system or measurement technique. For example, simulations of the extraction procedure using standard air samples found mean enhancements of $1.1 \pm 0.8$ ppm for $CO_2$, $4.1 \pm 4.0$ ppb for $CH_4$, and $1.8 \pm 0.9$ ppb for $N_2O$. The measurements have been corrected by these amounts. Also, replicates at 15 depths showed a spread of less than 1.1 ppm $CO_2$, 4.1 ppb $CH_4$, and 6.5 ppb $N_2O$ from the mean concentration, defined as the 1-$\sigma$ measurement precision. This shows a small improvement over our previous $CH_4$ and $CO_2$ measurements [*Etheridge et al.*, 1996, 1998] and substantial improvement for $N_2O$ [*Etheridge et al.*, 1988]. Measurements were

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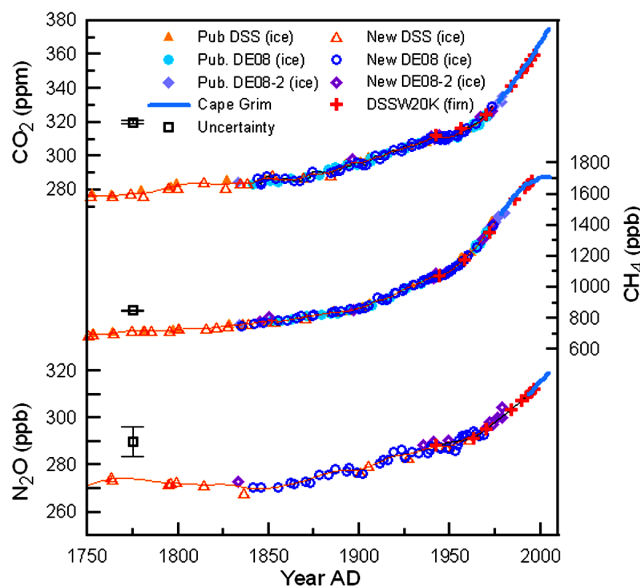
**Figure 1.** The Law Dome ice core and firn air records: AD 1800 to Present. (top) $CO_2$, (middle) $CH_4$ and (bottom) $N_2O$. Also shown are published Law Dome records and contemporary records from Cape Grim (deseasonalized flask, archive and in situ). Thin lines are spline fits (*Enting*, 1987): 20 year smoothing for $CO_2$ and $CH_4$, and 40 year smoothing for $N_2O$. Uncertainties associated with ice core air samples are graphically shown, firn air uncertainties are described in text.

rejected when there was evidence of post coring melting (4 samples), leaks (5), insufficient air sample for a reliable measurement of $N_2O$ (7), significant open pore spaces in shallow cores (3) and equipment failures (3). All measurements rejected from the records were attributed to a known cause.

[6] Air preserved in the shallowest Law Dome ice overlaps with contemporary, air archive and firn air records (Figure 1) and is used to test the effects of air enclosure and storage in ice, and the extraction and measurement processes, on the air composition. The contemporary and archive records are measured on similar instruments and the same calibration scales as the ice data, and are expected to have concentrations similar to the Law Dome ice and firn air records, as they were obtained from mid-high latitudes of the Southern Hemisphere. The ice core records compare well (within 1-σ uncertainty) to the deseasonalized air archive, in situ and flask records from Cape Grim, Tasmania [*Francey et al.*, 2003, and references therein] from the mid-1970s. The DSSW20K firn air measurements overlap both the contemporary and ice core records (within the 1-σ uncertainty) for all gases. Firn air samples are not exposed to the processes of bubble enclosure, ice core drilling, or air extraction by crushing and large volumes of air can be collected for analysis. Therefore, the uncertainty associated with each of these steps is removed. The 1-σ measurement precision of the firn air samples is 0.1 ppm $CO_2$, 2 ppb $CH_4$ and 0.3 ppb $N_2O$.

[7] The records of the last 200 years are composed of measurements from three Law Dome ice cores, so measurements of similar age from the different cores were com-

pared. The cores were drilled at different times using different methods and have been stored at different locations during the last 10 years. The measurements of $CO_2$, $CH_4$ and $N_2O$ from the three ice cores do not differ by more than the analytical uncertainty during common periods, nor is there evidence of contamination of the isotopic ratios of $\delta^{13}CO_2$ [*Francey et al.*, 1999] or $\delta^{13}CH_4$ [*Ferretti et al.*, 2005]. Also, concentrations of recently emitted gases, such as $SF_6$, $C_2F_6$ and halons are negligible or zero in deeper ice samples (W. Sturges, personal communication, 2005). Therefore, we conclude there has been no detectable contamination of the gases in the ice cores during storage.

## 3. Results and Discussion

[8] The new Law Dome ice core and firn air results (see Auxiliary Material) extend the existing Law Dome records by 1000 years to AD 0 and increase the data density between AD 1000 and 1980. Additionally, new $N_2O$ measurements have been made for this period. The results show significant atmospheric variability on decadal, centennial and millennial timescales.

### 3.1. Industrial Period Trace Gas Variations (AD 1800 to Present)

[9] The trace gas records show significant increases in atmospheric concentrations during the last 200 years (29% $CO_2$, 150% $CH_4$ and 21% $N_2O$), most of which occurred during the 20th century (Figure 1). The increased data density adds definition to the observed variations during this period.

[10] The stabilization of atmospheric $CO_2$ concentration during the 1940s and 1950s is a notable feature in the ice core record. The new high density measurements confirm this result and show that $CO_2$ concentrations stabilized at 310–312 ppm from ~1940–1955. The $CH_4$ and $N_2O$ growth rates also decreased during this period, although the $N_2O$ variation is comparable to the measurement uncertainty. Smoothing due to enclosure of air in the ice (about 10 years at DE08) removes high frequency variations from the record, so the true atmospheric variation may have been larger than represented in the ice core air record. Even a decrease in the atmospheric $CO_2$ concentration during the mid-1940s is consistent with the Law Dome record and the air enclosure smoothing, suggesting a large additional sink of ~3.0 PgC yr$^{-1}$ [*Trudinger et al.*, 2002a]. The $\delta^{13}CO_2$ record during this time suggests that this additional sink was mostly oceanic and not caused by lower fossil emissions or the terrestrial biosphere [*Etheridge et al.*, 1996; *Trudinger et al.*, 2002a]. The processes that could cause this response are still unknown.

[11] The $CO_2$ stabilization occurred during a shift from persistent El Niño to La Niña conditions [*Allan and D'Arrigo*, 1999]. This coincided with a warm-cool phase change of the Pacific Decadal Oscillation [*Mantua et al.*, 1997], cooling temperatures [*Moberg et al.*, 2005] and progressively weakening North Atlantic thermohaline circulation [*Latif et al.*, 2004]. The combined effect of these factors on the trace gas budgets is not presently well understood. They may be significant for the atmospheric $CO_2$ concentration if fluxes in areas of carbon uptake, such as the North Pacific Ocean, are enhanced, or if efflux from the tropics is suppressed.
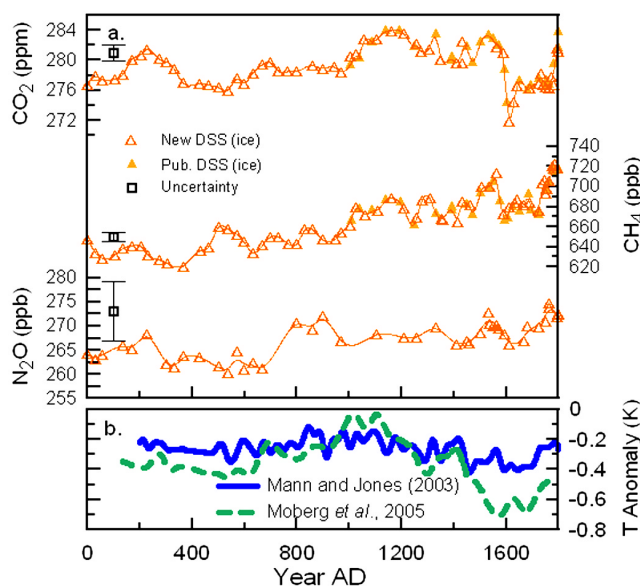
**Figure 2.** The Law Dome trace gas records: AD 0 to 1800. (a) $CO_2$, $CH_4$ and $N_2O$ records shown with published Law Dome records. Spline fits (40 year smoothing for $CO_2$ and $CH_4$, 100 year smoothing for $N_2O$) and uncertainties are graphically shown. (b) Northern Hemispheric temperature anomalies [*Mann and Jones*, 2003; *Moberg et al.*, 2005].

## 3.2. Late Preindustrial Holocene (LPIH) Changes (0 to 1800 AD)

[12] One of the most notable features in the records is the abrupt decrease in concentrations during the 16th and 17th centuries. Following AD 1550 gas concentrations decreased by 10 ppm $CO_2$, 40 ppb $CH_4$ and ~5 ppb $N_2O$, with minima at ~AD 1600 (Figure 2a). The lower concentrations coincide with a period of generally cooler Northern Hemisphere temperatures commonly termed the Little Ice Age, LIA (AD 1300–1850 [e.g., *Jones and Mann*, 2004]). Several reconstructions of northern hemisphere temperature anomalies of the last 2000 years [e.g., *Mann and Jones*, 2003; *Moberg et al.*, 2005] show their coldest periods around AD 1600 (Figure 2b).

[13] Previous interpretations of the Law Dome $CO_2$, $CH_4$ and the $\delta^{13}C$ isotope records suggests that reduced emissions from the terrestrial biosphere were the likely cause of the lower gas concentrations during the LIA [*Francey et al.*, 1999; *Trudinger et al.*, 2002a; *Ferretti et al.*, 2005]. We note that there are no Law Dome $\delta^{13}CO_2$ measurements at AD 1600, so it is unclear whether the initial $CO_2$ decrease was driven by the terrestrial biosphere, and some changes to oceanic carbon exchange are possible. Also, a temperature-dependent terrestrial plant $CH_4$ source recently identified by *Keppler et al.* [2006] could help explain lower LIA emissions. However, the total pre-industrial $CH_4$ source (~200 Tg yr$^{-1}$) does not support a plant source in the range estimated by *Keppler et al.* [2006] (62–236 Tg yr$^{-1}$) without a major revision of the other known sources (wetlands, biomass burning, fossil, animals) or of the sink strength. We can also add information about the LIA using the $N_2O$ record. Emissions of $N_2O$ from soils under natural vegetation (the largest natural source) would decrease under the cold, and possibly

dry [*Jones and Mann*, 2004, and references therein], conditions dominating in the northern hemisphere during the LIA. Changing sea surface temperatures may also affect $N_2O$ emissions by changing the biogeochemical cycle of nitrogen or the solubility of $N_2O$ in the surface water column (0.04 ppb for 1°C change in the surface 100m [*Flückiger et al.*, 2002]), although this is not expected to be significant during the LIA. Therefore, we conclude that the lower gas concentrations during the LIA were dominantly driven by changes in emissions from the terrestrial biosphere due to colder temperatures.

[14] Previous studies have also shown that trace gas concentrations responded to changes in the climate system during the LPIH causing small climate feedbacks [*Etheridge et al.*, 1996; *Crowley*, 2000; *Bauer et al.*, 2003], rather than being a significant climate driver [*Ruddiman*, 2003]. *Gerber et al.* [2003] calculated that a change of 1°C in Northern Hemisphere temperature during the LPIH would result in a global $CO_2$ change of 12 ppm. The quality of previous $CO_2$ data and an assumption of unchanging ocean circulation are uncertainties in this relationship. The new measurements increase the certainty of the $CO_2$ changes in the Law Dome record and as previously mentioned, the $\delta^{13}CO_2$ suggests that the gas response during the LIA is mainly the result of a cooling of the terrestrial biosphere rather than of the ocean. We apply the *Gerber* relationship to the Law Dome $CO_2$ record through the LIA, and calculate an overall Northern Hemispheric cooling of 0.4°C between AD 1550 and 1700. Similarly, the abrupt 10 ppm $CO_2$ decrease between AD 1550 and 1610, if driven by the terrestrial biosphere, would indicate a temperature decrease of 0.8°C. This is larger than the temperature change derived by *Mann and Jones* [2003] but more comparable to that derived by *Moberg et al.* [2005]. The temperature proxies evident in the combined trace gas records could be further exploited. We find no evidence for the 30 ppm variation during the 13th century indicated by the stomatal $CO_2$ proxy of *van Hoof et al.* (2005).

[15] The $CH_4$ concentration increased by ~100 ppb between AD 0 and 1800 (Figure 2a). We discuss this increase in terms of $CH_4$ sources, as changes to the $CH_4$ sink are unlikely during the LPIH [*Thompson*, 1992]. The LPIH $CH_4$ budget was largely composed of emissions from natural sources (wetlands and natural biomass burning). Emissions from these sources are dependent on climatic factors, particularly temperature and precipitation. Warm, wet conditions enhance emissions from wetlands, while warm, dry conditions enhance emissions from biomass burning. Northern Hemisphere temperature records (Figure 2b) show long term cooling during this period, which does not support increased natural emissions. Smaller contributions to the $CH_4$ budget come from anthropogenic sources, including rice agriculture, ruminant livestock, domestic waste, wood-fuel and biomass burning. The anthropogenic sources are strongly linked to human population, which increased by over 400% during the LPIH [*McEvedy and Jones*, 1979], making it plausible that anthropogenic emissions contributed to the $CH_4$ rise before 1800.

[16] The most notable $N_2O$ preindustrial variation was a 10 ppb increase between AD 670 and 810. There is some evidence of this change in the Dome C $N_2O$ record [*Flückiger et al.*, 2002], but more measurements are needed

to verify and resolve it. There is no evidence of changes in the other trace gases or climate proxies at this time. It appears that the change in $N_2O$ was not caused by changes in climate (or that the hemisphere-scale climate proxies did not record a climate event at the time) or by changes in biogeochemical factors that also affect $CO_2$ or $CH_4$.

## 4. Conclusions

[17] New measurements of $CO_2$, $CH_4$ and $N_2O$ over the past 2000 years confirm the large increases during the last 200 years and more precisely define variability during the LPIH. LPIH changes are mainly a response to changing climate, with small contributions from human activities. Previously-noted variations in the published records are confirmed, particularly during the LIA period and the 1940s. New $N_2O$ measurements show an increase of almost 10 ppb between AD 675 and 800, and a decrease in the $N_2O$ concentration between AD 1770 and 1840. More $N_2O$ measurements during this period will validate and define these variations.

## References

Allan, R. J., and R. D. D'Arrigo (1999), Persistent ENSO sequences: How unusual was the 1990–1995 El Nino?, *Holocene*, 9, 101–118.

Bauer, E., M. Claussen, V. Brovkin, and A. Huenerbein (2003), Assessing climate forcings of the Earth system for the past millennium, *Geophys. Res. Lett.*, 30(6), 1276, doi:10.1029/2002GL016639.

Crowley, T. J. (2000), Causes of climate change over the past 1000 years, *Science*, 289, 270–277.

Enting, I. G. (1987), On the use of smoothing splines to filter $CO_2$ data, *J. Geophys. Res.*, 92, 10,977–10,984.

Etheridge, D. M., G. I. Pearman, and F. R. De Silva (1988), Atmospheric trace gas variations as revealed by air trapped in an ice core from Law Dome, Antarctica, *Ann. Glaciol.*, 10, 28–33.

Etheridge, D. M., L. P. Steele, R. L. Langenfelds, R. J. Francey, J.-M. Barnola, and V. I. Morgan (1996), Natural and anthropogenic changes in atmospheric $CO_2$ over the last 1000 years from air in Antarctic ice and firn, *J. Geophys. Res.*, 101, 4115–4128.

Etheridge, D. M., L. P. Steele, R. J. Francey, and R. L. Langenfelds (1998), Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions and climatic variability, *J. Geophys. Res.*, 103, 15,979–15,996.

Ferretti, D. F., J. B. Miller, J. W. C. White, D. M. Etheridge, K. R. Lassey, D. C. Lowe, C. MacFarling Meure, M. F. Dreier, C. M. Trudinger, and T. D. van Ommen (2005), Unexpected changes to the global methane budget over the last 2,000 years, *Science*, 309, 1714–1717.

Flückiger, J., E. Monnin, B. Stauffer, J. Schwander, T. F. Stocker, J. Chappellaz, D. Raynaud, and J. Barnola (2002), High-resolution Holocene $N_2O$ ice core record and its relationship with $CH_4$ and $CO_2$, *Global Biogeochem. Cycles*, 16(1), 1010, doi:10.1029/2001GB001417.

Francey, R. J., C. E. Allison, D. M. Etheridge, C. M. Trudinger, I. G. Enting, M. L. Leuenberger, R. L. Langenfelds, E. Michel, and L. P. Steele (1999), A 1000-year high precision record of $\delta^{13}C$ in atmospheric $CO_2$, *Tellus*, 51, 170–193.

Francey, R. J., et al. (2003), The CSIRO measurement of greenhouse gases in the global atmosphere, in *Baseline Atmospheric Program (Australia), 1999–2000*, edited by N. W. Tindale, N. Derek, and P. J. Fraser, pp. 42–53, Bur. of Meteorol. and CSIRO Atmos. Res., Melbourne, Vic., Australia.

Gerber, S., F. Joos, P. Brugger, T. F. Stocker, M. E. Mann, S. Sitch, and M. Scholze (2003), Constraining temperature variations over the last millennium by comparing simulated and observed atmospheric $CO_2$, *Clim. Dyn.*, 20, 281–299.

Jones, P. D., and M. E. Mann (2004), Climate over past millennia, *Rev. Geophys.*, 42, RG2002, doi:10.1029/2003RG000143.

Keppler, F., J. Hamilton, M. Braß, and T. Rockman (2006), Methane emissions from terrestrial plants under aerobic conditions, *Nature*, 439, 187–191.

Latif, M., et al. (2004), Reconstructing, monitoring and predicting multi-decadal-scale changes in the North Atlantic thermohaline circulation with sea surface temperature, *J. Clim.*, 17, 1605–1614.

MacFarling Meure, C. (2004), The variation of atmospheric carbon dioxide, methane and nitrous oxide during the Holocene from ice core analysis, Ph.D. thesis, Univ. of Melbourne, Melbourne, Vic., Australia.

Mann, M. E., and P. D. Jones (2003), Global surface temperatures over the past two millennia, *Geophys. Res. Lett.*, 30(15), 1820, doi:10.1029/2003GL017814.

Mantua, N. J., S. R. Hare, Y. Zhang, J. M. Wallace, and R. C. Francis (1997), A Pacific interdecadal climate oscillation with impacts on salmon production, *Bull. Am. Meteorol. Soc.*, 78, 1069–1079.

McEvedy, C., and R. Jones (1979), *Atlas of World Population History*, Penguin Group, New York.

Moberg, A., D. M. Sonechkin, K. Holmgren, N. M. Datsenko, and W. Karlen (2005), Highly variable Northern Hemisphere temperatures reconstructed from low- and high- resolution proxy data, *Nature*, 433, 613–617.

Morgan, V. I., C. W. Wookey, J. Li, T. D. van Ommen, W. Skinner, and M. F. Fitzpatrick (1997), Site information and initial results from deep ice drilling on Law Dome, Antarctica, *J. Glaciol.*, 43, 3–10.

Ruddiman, W. F. (2003), The anthropogenic greenhouse era began thousands of years ago, *Clim. Change*, 61, 261–293.

Siegenthaler, U., E. Monnin, K. Kawamura, R. Spahni, J. Schwander, B. Stauffer, T. Stocker, J.-M. Barnola, and H. Fischer (2005), Supporting evidence from the EPICA Dronning Maud Land ice core for atmospheric $CO_2$ changes during the past millennium, *Tellus, Ser. B*, 57, 51–57.

Sowers, T. (2001), $N_2O$ record spanning the penultimate deglaciation from Vostok ice core, *J. Geophys. Res.*, 106(D23), 31,903–31,914.

Stauffer, B., J. Flückiger, E. Monnin, J. Schwander, J.-M. Barnola, and J. Chappellaz (2002), Atmospheric $CO_2$, $CH_4$ and $N_2O$ records over the past 60,000 years based on the comparison of different polar ice cores, *Ann. Glaciol.*, 35, 202–208.

Sturrock, G. A., D. M. Etheridge, C. M. Trudinger, P. J. Fraser, and A. M. Smith (2002), Atmospheric histories of halocarbons from analysis of Antarctic firn air: Major Montreal Protocol species, *J. Geophys. Res.*, 107(D24), 4765, doi:10.1029/2002JD002548.

Thompson, A. M. (1992), The oxidizing capacity of the Earth's atmosphere: Probable past and future changes, *Science*, 256, 1157–1169.

Trudinger, C. M., I. G. Enting, P. J. Rayner, and R. J. Francey (2002a), Kalman filter analysis of ice core data 2. Double deconvolution of $CO_2$ and $\delta^{13}C$ measurements, *J. Geophys. Res.*, 107(D20), 4423, doi:10.1029/2001JD001112.

Trudinger, C. M., D. M. Etheridge, P. J. Rayner, I. G. Enting, G. A. Sturrock, R. L. Langenfelds, and A. M. Smith (2002b), Reconstructing atmospheric histories from measurements of air composition in firn, *J. Geophys. Res.*, 107(D24), 4780, doi:10.1029/2002JD002545.

van Hoof, T. B., K. A. Kaspers, F. Wagner, R. S. W. van de Wal, W. M. Kürschner, and H. Visscher (2005), Atmospheric CO2 during the 13th century AD: reconciliation of data from ice core measurements and stomatal frequency analysis, *Tellus, Ser. B*, 57, 351–355.

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