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

C. MacFarling Meure,[1] D. Etheridge,[1] C. Trudinger,[1] P. Steele,[1] R. Langenfelds,[1] T. van Ommen,[2] A. Smith,[3] and J. Elkins[4]

Received 26 February 2006; revised 30 April 2006; accepted 16 May 2006; published 21 July 2006.

[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 ± 0.8 ppm for CO_2, 4.1 ± 4.0 ppb for CH_4, and 1.8 ± 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-σ 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

[1]Marine and Atmospheric Research, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Victoria, Australia.
[2]Department of the Environment and Heritage, Australian Antarctic Division, and Antarctic Climate and Ecosystems CRC, Hobart, Tasmania, Australia.
[3]Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia.
[4]NOAA, Earth System Research Laboratory, Boulder, Colorado, USA.

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2006gl026152.

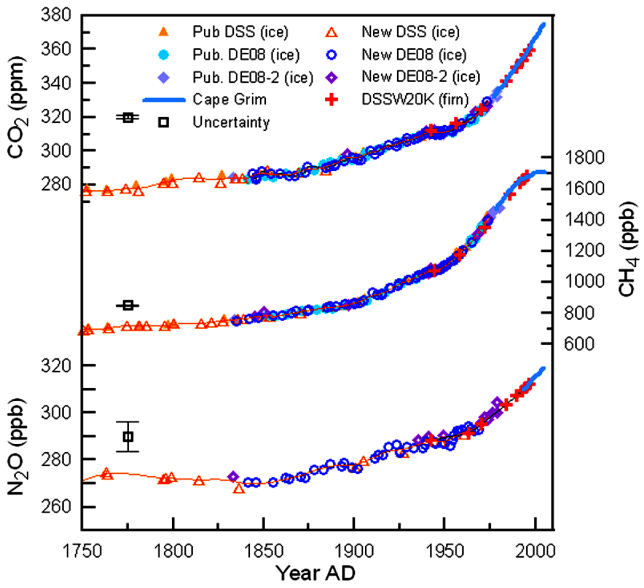

Figure 1. The Law Dome ice core and firn air records: AD 1800 to Present. (top) CO_2, (middle) CH_4 and (bottom) N_2O. Also shown are published Law Dome records and contemporary records from Cape Grim (deseasonalized flask, archive and in situ). Thin lines are spline fits (*Enting*, 1987): 20 year smoothing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

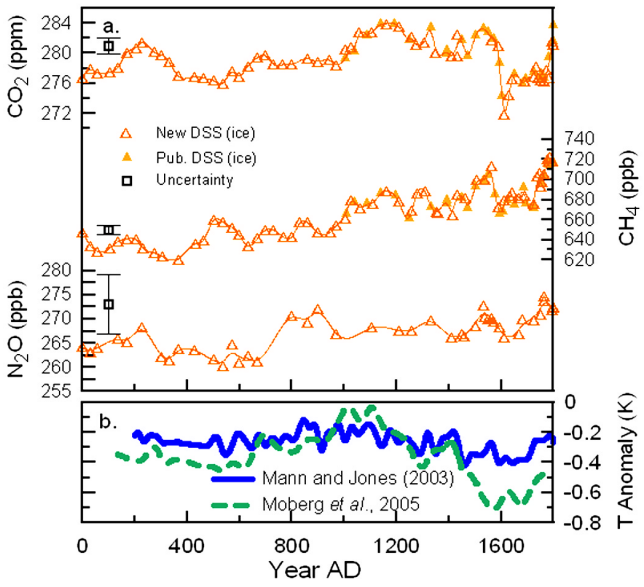

Figure 2. The Law Dome trace gas records: AD 0 to 1800. (a) CO_2, CH_4 and N_2O records shown with published Law Dome records. Spline fits (40 year smoothing for CO_2 and CH_4, 100 year smoothing for N_2O) and uncertainties are graphically shown. (b) Northern Hemispheric temperature anomalies [*Mann 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 CO2 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 multidecadal-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.

J. Elkins, NOAA, Earth System Research Laboratory, Boulder, CO 80305, USA.

D. Etheridge, R. Langenfelds, C. MacFarling Meure, P. Steele, and C. Trudinger, Marine and Atmospheric Research, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Vic 3195, Australia. (cec@bluep.com)

A. Smith, Australian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia.

T. van Ommen, Department of the Environment and Heritage, Australian Antarctic Division, and Antarctic Climate and Ecosystems CRC, Hobart, Tas 7001, Australia.