Atmospheric carbon dioxide occluded in the Siple Dome ice core, ...
Ahn, Jinho
ProQuest Dissertations and Theses; 2005; ProQuest Dissertations & Theses Full Text
pg. n/a

UNIVERSITY OF CALIFORNIA, SAN DIEGO

Atmospheric CO_2 occluded in the Siple Dome ice core, Antarctica, and its application to climate change

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy in Earth Sciences

By

Jinho Ahn

Committee in charge:

Professor Martin Wahlen, Chair
Professor Christopher Charles
Professor Joel Norris
Professor Jeff Severinghaus
Professor William Trogler

2005

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

The dissertation of Jinho Ahn is approved, and it is acceptable in quality and form for publication on microfilm:

Joel Norris

William C. Trogler

Jeff Severinghaus

Martin Wahlen

Chair

University of California, San Diego

2005

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

I would like to thank my advisor, Martin Wahlen, for his guidance and support. He encouraged me to start working on ice core research. His sincere attitude in science influenced my research. Jeff Severinghaus gave me invaluable insights and guidance in application of noble gases to CO_2 study. Also I want to express my gratitude to the rest of my committee, William Trogler, Joel Norris, and Chris Charles, for generously sharing their time and for taking the time to give thoughtful consideration to this work.

Many people assisted in my experiments. Bruce Deck gave indispensable technical advice; Alane Bollenbacher kindly prepared air standards; the National Ice Core Laboratory assisted with core processing; Jackson Kwong, Sharon Sneed, and Ross Beaudette provided valuable time and efforts with experimental assistance.

The studies were performed in collaboration with Ed Brook at Oregon State University, Kendrick C. Taylor at Desert Research Institute, James W. C. White at Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Paul Mayewski at Climate Change Institute, University of Maine, and Sarah Das at Woods Hole Oceanographic Institution (WHOI).

Invaluable scientific advice improved this work. Thanks to Bernhard Stauffer, Richard Alley, Joe McConnell, Kenji Kawamura, Joan Fitzpatrick and Tomoko Ikeda-Fukazawa.

Financial support was provided by the National Science Foundation, Office of Polar Program (99-80619) and Scripps Institution of Oceanograhpy Graduate Department.

All the researchers, teachers, students, and staff at the Scripps Institution of Oceanography have made my experience here a pleasure. In particular, classmates in the Paleoclimatology Seminar, especially, the students in Jeff Severinghaus's lab, Alexi Grachev, Takuro Kobashi, Melissa Headly and Vas Petrenko. They shared their invaluable experiences, insights and perspectives. Myrl Hendershott, the graduate department chair, and Anne Cressey of the Geoscience Research Division listened compassionately to my difficulties. Yongjae Yu and Gabrielle Ayres, Center of Excellence-LTPDP, provided heartfelt writing and presentation support. The Korean community gave me much joy during my academic endeavor at the Scripps Institution of Oceanography.

I am greatly indebted to my Mother and Father for their immeasurable love and support. Also, I give thanks to my Father and Mother in-law for their help through prayer and babysitting. My spiritual siblings in the East County Bible Fellowship, L.A.-Fullerton Korean Church, Yongdong Church in Seoul, Korea must be acknowledged for their precious and continuous prayer and love.

Finally, I thank my lovely wife Hannah (Sung-In), and daughter Serena (Song-eun), who came into my life during this research. They have truly made my life complete.

VITA

Jinho Ahn

Education

1995, B.Sc. Geological Sciences and Chemistry, Seoul National University
1999, M.S. Geology, Seoul National University
Thesis: Regional metamorphism of pelitic schists in the Yeoncheon area, Imjingang Belt, Korea: Application of cathodoluminescence to metapelites
2005, Ph.D. Earth Sciences, SIO, Univ. of Calif., San Diego
Dissertation: Atmospheric CO_2 *occluded in the Siple Dome ice core, Antarctica, and its application to climate change*

Employment History

2000-2005	Graduate Student Researcher, SIO, Univ. of Calif., San Diego
1998-1999	Graduate Student Researcher, Seoul National University, Seoul, Korea
1996-1998	Military services, Yang-Gu, South Korea

Teaching Assistant

1995	Introduction to Petrology, Seoul National University
1998	Minerals and rocks, Seoul National University

Peer-reviewed Publications

Ahn, J. and Cho, M. Application of cathodoluminescence to fine-grained pelitic schists of the Imjingang Belt, Korea. *Eur. J. Min.*, 12, 1057-1062 (2000)

Ahn, J., Wahlen, M., Deck, B.L., Brook, E.J., Mayewski, P.A., Taylor, K.C., and J.W.C. White, A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica Ice core, *J. Geophys. Res.*, 109, D13305, doi:10.1029/2003JD004415 (2004)

Ahn, J., Severinghaus, J., Hadly, M., Wahlen, M., Brook, E.J., Mayewski, P.A., and Taylor, K.C., CO_2 diffusion in the polar ice: Observations from the Siple Dome, Antarctic ice core (submitted for publication)

Ahn, J., Wahlen, M., Mayewski, P.A., Taylor, K.C., Brook, E.J., Deck, B.L. and J.W.C. White, Excess CO_2 in the Antarctic Siple Dome ice core record (submitted for publication)

Ahn, J. Wahlen, M. and Deck, B., Stable isotopic study of the atmospheric CO_2 trapped in Antarctic ice cores (in preparation for publication)

Data Repository

Ahn, J., M. Wahlen, and B. Deck, Atmospheric CO_2 Trapped in the Ice Core from Siple Dome, Antarctica. *Boulder, CO: National Snow and Ice Data Center. Digital media. http://nsidc.org/data/docs/agdc/nsidc0202_wahlen/* (2003)

Conference Presentation

Ahn, J., Wahlen, M., Deck, B.L., Brook, E.J., Mayewski, P.A., Taylor, K.C., and J.W.C. White, A record of atmospheric CO_2 from the Siple Dome, Antarctica ice core, *The 12th International Symposium on Polar Sciences, Korea Polar Research Institute, Ansan, Korea, May 17-19* (2005)

Ahn, J., Wahlen, M., Deck, B.L., Brook, E.J., Mayewski, P.A., Taylor, K.C., J.W.C. White and J. Fitzpatrick, Excess CO_2 in the Antarctic Siple Dome ice core record, *AGU Fall Meeting (2004)*

Ahn, J., Wahlen, M., Deck, B.L., Brook, E.J., Mayewski, P.A., Taylor, K.C., and J.W.C. White, A record of atmospheric CO_2 in the Siple Dome Core A, Antarctic Ice Core, *Siple Dome Science Meeting, Reno, Nevada* (2004)

Ahn, J., Wahlen, M., Deck, B.L., Brook, E.J., Mayewski, P.A., Taylor, K.C., and J.W.C. White, A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica Ice core, *AGU Fall Meeting* (2003)

Suwa, M., J. Ahn, B. Barnett, M. Bender, E. Brook, M. Wahlen, and J. White, The age reconstruction of the bottom part of the Siple Dome Ice Core, *Tenth Annual WAIS (The West Antarctic Ice Sheet Initiative) Workshop, Sterling, Virginia, USA, September 17-20,* (2003)

Ahn, J., Wahlen, M. and Deck, B., Measurement of Atmospheric CO_2 Trapped in the Siple Dome Ice Core, *AGU Fall meeting* (2001)

Cho, M. and Ahn, J., Park, H. and Kim, Y., Tectonometamorphic evolution of the Imjingang Belt, Central Korea, *Sixth International Eclogite Conference, Ehime Prefectural Science Museum, Niihama, Japan, September 1-7* (2001)

Ahn, J. and Cho, M., Application of cathodoluminescence microscopy in metapelites: Plagioclase growth model in a staurolite-zone schist, Imjingang Belt, Korea. *Annual Meeting of the Petrological Society of Korea* (1999)

Ahn, J., Yi, K., and Cho, M., Application of cathodoluminescence to metamorphic petrology. *Annual Meeting of the Geological Society of Korea* (1998)

ABSTRACT OF THE DISSERTATION

Atmospheric CO_2 occluded in Siple Dome ice core, Antarctica, and its application to climate change

By

Jinho Ahn

Doctor of Philosophy in Earth Science

University of California, San Diego, 2005

Professor Martin Wahlen, Chair

Understanding how the atmospheric concentration of CO_2 changed in the past in response to other changes in the climate system provides us with a better understanding of how current and future changes in the carbon cycle will influence our future climate.

This study found that the general trend of the CO_2 concentration from the Siple Dome ice follows the temperature and is mostly in agreement with other Antarctic ice core CO_2 records. During the last glacial termination, a lag of CO_2 versus Siple Dome isotopic temperature is suggested. These results strongly support previous suggestions of a close link between Antarctic temperature and CO_2 change during the last deglaciation.

Studying melt layers contained in the core provided unique information on CO_2 diffusion in ice. On the basis of a combined study of noble gases (Xe/Ar and Kr/Ar), electrical conductivity, and Ca^{2+} ion content, for the first time it was

confirmed that substantial CO_2 diffusion through the ice occurs on timescales of thousands of years. The product of the diffusion constant and the solubility was obtained as 4.3 (± 2.1) × 10^{-21} m^2s^{-1} $molCO_2$ $m^{-3}ice$ $(PaCO_2)^{-1}$ at –23 °C. This work shows that the smoothing of the CO_2 record in the core by diffusion is one to two orders of magnitude smaller than the smoothing induced by the gas age distribution at the depth of 287 m (gas age = 2.74 kyrBP, thousand years before 1950) in the Siple Dome ice.

Further results of this research found that Siple Dome CO_2 concentrations during the last deglaciation and in the Holocene are at certain times greater than those in other Antarctic ice cores by up to 20 ppm (μmol CO_2 / mol air). Snow melting/refreezing is suggested as the main cause of the excess CO_2. These results show that Antarctic ice samples from relatively warm sites are not an accurate proxy for paleoatmospheric CO_2.

Finally, carbon isotope studies on CO_2 for the Siple Dome (last 40 kyr) and Vostok (160-110 kyr) ice cores from Antarctica, extend and confirm the previous results from the Taylor Dome ice core covering the last 28 kyr. However, the data are scattered and depleted on average compared to those from the Taylor Dome ice core, and are not considered a reliable atmospheric record. Future studies should include a sublimation method for bubble-free ice in order to avoid isotopic fractionation during gas extraction from the ice.

CHAPTER I

Introduction

1. Background

Continuous and precise atmospheric CO_2 concentration measurements were initiated in 1958 at Mauna Loa, Hawaii, and show a continuous increase of CO_2 concentration from 315 ppm (uatm/atm) to 377 ppm through 2004, with an average annual increase of 1.4 ppm [*Keeling and Whorf,* 2005]. This increase of the most important greenhouse gas, after water vapor, is caused by human activity, such as, combustion of fossil fuels, cement production and deforestation. To predict our future climate, the understanding of carbon cycling is a prerequisite. Therefore, understanding how the atmospheric concentration of CO_2 changed in the past, in response to other changes in the climate system, provides us with a better understanding of how current and future changes in the carbon cycle will influence our future climate.

The paleoatmospheric history before 1958 can only be investigated reliably by analysing air trapped in polar ice. Earlier work revealed that the CO_2 concentration is increasing rapidly since the industrial revolution, from 280 ppm [*Neftel et al.,* 1985; *Etheridge et al.*, 1996]. Moreover, Antarctic ice core CO_2 records of the past hundred thousands years show that atmospheric CO_2 concentration changed [e.g., *Delmas et al.*, 1980; *Neftel et al.,* 1982; *Fischer et al.*, 1999; *Petit et al.*, 1999; *Kawamura et al.*, 2003; *EPICA Community members*, 2005]. During the glacial periods CO_2 concentration was 180-200 ppm. During the warm interglacial times the CO_2 concentration was 260-280 ppm. However, the causes of the atmospheric CO_2 change and its relationship with other climate factors are not well known. Possible causes are discussed in *Sigman and Boyle* [2000] and *Kohfeld et al.* [2005].

Carbon isotopes of atmospheric CO_2 can be used to better characterize the global carbon cycle [*Keeling*, 1989]. The sources and sinks of CO_2, including the major carbon reservoirs, produce isotopically distinct CO_2. Therefore, comparison to the atmospheric inventory can yield constraints for the global budgets. Direct and continuous measurements on $^{13}C/^{12}C$ of CO_2 started in 1978 later than the CO_2 concentration measurements [*Keeling et al.*, in press]. Thus, the $^{13}C/^{12}C$ of CO_2 before 1978 depend on trapped air in polar ice cores [e.g., *Leuenberger et al.*, 1992; *Smith et al.*, 1999; *Francey et al.*, 1999]. Although the demand of paleoatmospheric $\delta^{13}C$ of CO_2 has been increased to constrain the carbon cycle models [*Broecker and Henderson*, 1998; *Sigman and Boyle*, 2000], only a few $\delta^{13}C$ ice core data are known in air prior to the Holocene period [e.g., *Leuenberger et al.*, 1992; *Smith et al.*, 1999].

Successful reconstruction of paleoatmospheric CO_2 levels from ice cores were conducted since the late 1970s and early 1980s [*Delmas et al.*, 1980; *Barnola et al.*, 1983]. Melting of ice samples should be avoided as CO_2 can be produced by the reaction of carbonate ($CaCO_3$ and $MgCO_3$) with acid in the ice. CO_2 records from Antarctic ice cores are considered to be representative of paleoatmospheric CO_2 concentrations. However, Greenland ice cores are not useful for determining the paleoatmospheric concentration because of in situ production of CO_2 due to high dust content [*Barnola et al.*, 1995; *Anklin et al.*, 1995, 1997, *Smith et al.*, 1997a, 1997b, *Tschumi and Stauffer*, 2000]. The preservation of atmospheric CO_2 in polar ice is a critical issue and it is assumed that the diffusion of CO_2 in the ice is negligible.

2. Siple Dome ice core

The Siple Dome ice core from West Antarctica was drilled from 1997 to 1999. The site is at 81.66° S, 148.82° W, at an altitude of 621 meters asl, with an annual mean temperature of -25.4 °C, and an accumulation rate of 12.4 g $cm^{-2} yr^{-1}$ as water equivalent (Figure 1 and Table 1). The total depth of the core is 1003.8 m. The high accumulation rate at Siple Dome allows rapid climate changes to be more accurately preserved, and permits a more accurate assessment of the relative timing between ice-isotopic variations and variations in occluded gases compared to the low accumulation rate sites like Vostok, Dome C, or Dome Fuji (Table 1). The mean annual temperature is far below the freezing point of water, but occasionally the surface temperature can reach slightly over 2 °C during austral summer, and, thus, causes snow melting [*Das*, 2003]. Once the snow melt percolates down from the surface, it re-freezes in a high density layer (crust formed in austral winter) due to a strong capillary force. The refozen melt in the crust forms melt layers in the ice core, and is defined by the reduced bubble size [*Das*, 2003]. CO_2 is enriched considerably in melt layers due to the high solubility of CO_2 gas in the melt [*Neftel et al.*, 1983]. At the present surface pressure condition at the Siple Dome, we can expect 16,230 μmol CO_2 / mol air in melt water at 0 °C in equilibrium with atmospheric air (Andrew Dickson, personal communication).

On the other hand, the CO_2 spike, due to snow melting/refreezing, may diffuse through the ice matrix for thousands of years [*Neftel et al.*, 1983]. Therefore, the melt layer in the ice potentially provides information about CO_2 diffusion in polar ice as a natural laboratory. The study of CO_2 diffusion in ice has been hampered by a diffusion coefficient that is too small to be precisely measured in the laboratory [*Hondoh*, 1996] and a lack of evidence of CO_2 diffusion in polar ice.

3. The Goal and content of this work

The work performed for this dissertation investigates (1) the atmospheric CO_2 change and its relationship with the southern ocean temperature change; (2) the validity of ice core derived data for the paleoatmospheric CO_2 records, and measuring the permeation coefficient of CO_2 in the ice; (3) the possible mechanisms of the in situ production of CO_2 in the Siple Dome ice core; and (4) a stable isotopic study of $\delta^{13}C$ of CO_2.

Chapter two discusses the atmospheric CO_2 records in the Siple Dome ice core and their implications for carbon cycle changes during the last Termination.

Chapter three reports the observed CO_2 diffusion in the Siple Dome ice core and suggests a quantitative permeation coefficient of the CO_2 in the polar ice and its implications for paleoclimate studies.

Chapter four investigates excess CO_2 in the Siple Dome ice core. It is suggested that the main mechanism is the snow melting/refreezing on the surface at Siple Dome.

Chapter five reports $\delta^{13}C$ of CO_2 in the Siple Dome ice core for the last 40 kyrs, and in the Vostok ice core for the Termination II (150-110 kyrBP). The results are compared to the Taylor Dome ice core records, and the carbon cycle changes during the Terminations are discussed.

References

Anklin, M., J.-M. Barnola, J.Schwander, B. Stauffer, and D. Raynaud, Processes affecting the CO_2 concentrations measured in Greenland ice, *Tellus*, *B47*, 461-470, 1995.

Anklin, M., J. Schwander, B. Stauffer, J. Tschumi, A. Fuchs, J.-M. Barnola, and D. Raynaud, CO_2 record between 40 and 8 kyr B.P. from the Greenland Ice Core Project ice core, *J. Geophys. Res., 102*, 26,539-26,545, 1997.

Barnola, J.M., D. Raynaud, A. Neftel, and H. Oeschger, Comparison of CO_2 measurements by two laboratories on air from bubbles in polar ice, *Nature, 303*, 410-413, 1983.

Barnola, J. M., M. Anklin, J. Porcheron, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 evolution during the last millennium as recorded by Antarctic and Greenland ice, *Tellus, 47B*, 264-272, 1995.

Broecker, W.S., and G.M. Henderson, The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes, *Paleoceanography*, *13*, 352-364, 1998.

Das, S. West Antarctic ice sheet surface melting and Holocene Variability. Ph.D. thesis. Pennsylvania State University, 2003.

Delmas, R. J., J. M. Ascencio, and M. Legrand, Polar ice evidence that atmospheric CO_2 20,000yr BP was 50% of present, *Nature, 284,* 155-157, 1980.

EPICA Community members, Eight glacial cycles from an Antarctic ice core, *Nature*, *429*, 623-628, 2004.

Etheridge, D.M., L.P. Steele, R.L. Langenfelds, R.J. Francey, J.M. Barnola, and V.I. Morgan, 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, 1996.

Fischer, H., M. Wahlen, J. Smith, D. Mastroianni, and B. Deck, Ice core records of atmospheric CO_2 around the last three glacial terminations, *Science, 283,* 1712-1714, 1999.

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

Hondoh, T., *Clathrate Hydrates in Polar Ice Sheets*, 41-48 pp., 1996.

Kawamura, K., T. Nakazawa, S. Aoki, S. Sugawara, Y. Fujii, and O. Watanabe, Atmospheric CO_2 variations over the last three glacial-interglacial climate cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique, *Tellus, 55B*, 126-137, 2003.

Keeling, C.D., Bacastow, R.B., Carter, A.F., Piper, S.C., Whorf, T.P., Heimann, M., Mook, W.G., Roeloffzen, H., A three-dimensional model of atmospheric CO2 transport based on observed winds: 1. Analysis of observed data, in *AGU Monograph 55*, 165-236, American Geophysical Union, Washington, 1989.

Keeling, C.D. and T.P. Whorf, Atmospheric CO_2 records from sites in the SIO air sampling network. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A., 2005.

Keeling, C.D., S. C. Piper, R. B. Bacastow, M. Wahlen, T. P. Whorf, M. Heimann, and H. A. Meijer, Atmospheric CO_2 and $^{13}CO_2$ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications, in "A History of Atmospheric CO_2 and its effects on Plants, Animals, and Ecosystems", editors, Ehleringer, J. R., T. E. Cerling, M. D. Dearing, Springer Verlag, New York, in press, 2005.

Kohfeld, K.E., C.L. Quéré, S.P. Harrison, and R.F. Anderson, Role of marine biology in glacial-interglacial CO_2 cycles, *Science, 308*, 74-78, 2005.

Leuenberger, M., U. Siegenthaler, and C.C. Langway, Carbon isotope composition of atmospheric CO_2 during the last ice age from an Antarctic ice core, *Nature, 357*, 488-490, 1992.

Neftel, A., H. Oeschger, J. Schwander, B. Stauffer, and R. Zumbrunn, Ice core sample measurements give atmospheric CO_2 content during the past 40,000 yr, *Nature, 259*, 220-223, 1982.

Neftel, A., H. Oeschger, J. Schwander, and B. Stauffer, Carbon Dioxide Concentration in Bubbles of Natural Cold Ice, *J. Phys. Chem.*, *87*, 4116-4120, 1983.

Neftel, A., E. Moor, H. Oeschger, and B. Stauffer, Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries, *Nature, 315*, 45-47, 1985.

Petit, J. R., J. Jouzel, D. Raynaud, N. I. Barkov, J.-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M.

Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature, 399*, 429-436, 1999.

Sigman, D.M. and E.A. Boyle, Glacial/interglacial variations in atmospheric carbon dioxide, *Nature, 407*, 859-869, 2000.

Smith, H. J., M. Wahlen, D. Mastroianni, and K. Taylor, The CO_2 concentration of air trapped in GISP2 ice from the Last Glacial Maximum-Holocene transition, *Geophys. Res. Lett., 24*, 1-4, 1997a.

Smith, H. J., M. Wahlen, D. Mastroianni, K. Taylor, and P. Mayewski, The CO_2 concentration of air trapped in Greenland Ice Sheet Project 2 ice formed during periods of rapid climate change, *J. Geophys. Res., 102*, 26,577-26,582, 1997b.

Smith, H.J., H.Fischer, M. Wahlen, D. Mastroianni and B. Deck, Dual modes of the carbon cycle since the last glacial maximum, *Nature, 400*, 248-250, 1999.

Tschumi, J. and B. Stauffer, Reconstructing past atmospheric CO_2 concentration based on ice-core analyses: open questions due to in situ production of CO_2 in the ice, *J. Glaciol., 46*, 45-53, 2000.

CHAPTER II

A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica ice core

Abstract. We have measured the CO_2 concentration of air occluded during the last 40,000 years in the deep Siple Dome A (hereafter Siple Dome) ice core, Antarctica. The general trend of CO_2 concentration from Siple Dome ice follows the temperature inferred from the isotopic composition of the ice and is mostly in agreement with other Antarctic ice core CO_2 records. CO_2 rose initially at ~ 17.5 kyrBP (thousand years before 1950), decreased slowly during the Antarctic Cold Reversal, rose during the Younger Dryas, fell to a local minimum at around 8 kyrBP, and rose continuously since then. The CO_2 concentration never reached steady state during the Holocene, as also found in the Taylor Dome and EPICA Dome C (hereafter Dome C) records. During the last glacial termination, a lag of CO_2 versus Siple Dome isotopic temperature is probable. The Siple Dome CO_2 concentrations during the last glacial termination and in the Holocene are at certain times greater than in other Antarctic ice cores by up to 20 ppm (μmol CO_2 / mol air). While in situ production of CO_2 is one possible cause of the sporadic elevated levels, the mechanism leading to the enrichment is not yet clear.

1. Introduction

Understanding how the atmospheric concentration of CO_2 changed in the past in response to other changes in the climate system provides us with a better understanding of how current and future changes in the carbon cycle will influence our future climate. The concentration of CO_2 in the atmosphere during previous times can be determined by measurements made on the air trapped in ice cores [e.g., *Delmas* *et al.*, 1980; *Neftel et al.*, 1982; *Fischer et al.*, 1999; *Petit et al.*, 1999]. CO_2 records from Antarctic ice cores are considered to be representative of paleoatmospheric concentrations. Greenland ice cores are not useful for determining the paleoatmospheric concentration because of in situ production of CO_2 due to high dust content [*Barnola et al.*, 1995; *Anklin et al.*, 1995, 1997, *Smith et al.*, 1997a, 1997b, *Tschumi and Stauffer*, 2000].

The Siple Dome ice core from West Antarctica was drilled from 1997 to 1999. The site is at 81.66° S, 148.82° W, at an altitude of 621 meters asl, with an annual mean temperature of -25.4 °C and an accumulation rate of 12.4 g $cm^{-2}\,yr^{-1}$ as water equivalent (Figure 1 and Table 1). The total depth of the core is 1003.8 m. The high accumulation rate at Siple Dome allows rapid climate changes to be more accurately preserved and permits more accurate assessment of the relative timing between ice-isotopic variations and of variations in occluded gases compared to the low accumulation rate sites like Vostok, Dome C, or Dome Fuji (Table 1). In this study, we compare the CO_2 record from the Siple Dome ice core for the last 40,000 years with CO_2 records from other Antarctic ice cores using common time scales based on the GISP2 gas age and correlation to Antarctica using CH_4 concentrations variations. We also examine the relative timing of the CO_2 increase and temperature change. The highest resolution CO_2 record from Law Dome covering only the last thousand years [Etheridge et al., 1996], and the recent Dome Fuji CO_2 record over the last 320 kyrs [Kawamura et al., 2003] measured by the wet extraction method are not discussed.

2. Method and Time Scales

Measurements were made on 462 samples from 86 depths in the top 832 meters in the Siple Dome ice core. These measurements span over the last 40,000 years. The ice core has a diameter of 13 cm. The outer 0.5 to 2 cm of the samples was removed with a band saw to reduce the possibility of contamination from present atmospheric CO_2 or post-drilling chemical reactions. The Siple Dome core samples contain bubbles and did not contain clathrates. Post collection temperature monitoring confirmed that the ice was kept below -15 °C from the time it was removed from the drill site to arrival at Scripps Institution of Oceanography (SIO). The storing, cutting, and loading of samples into a mechanical crusher at SIO was done at –25 °C. At most depths four to six ice samples, taken from a depth interval spanning 1 to 3 cm (mostly less than several years in ice age), were analyzed for each reported data point. At some depths samples of 6 to 12 cm depth intervals were used because of poor quality (extensive fracturing in the ice). Many fractures were observed below 500 m and the samples were more extensively trimmed in this region to assure sampling of unfractured ice. Contamination through undetected fractures results in higher CO_2 values due to high CO_2 concentration in the ambient air.

For outliers in a group of samples cut from the same depth interval, we applied Grubb's test at the 95% confidence level to the suspected data. In this test a ratio of the difference between the outlier and the mean and the standard deviation of the data for the group was compared to a critical value [*Iglewicz and Hoaglin,* 1993]. We rejected results from 12 individual ice samples (usually the highest values) out of the total of 462 analyzed.

The gas extraction and IR spectroscopic methods used are well established [*Wahlen et al.,* 1991; *Smith et al.,*1997a and b; *Fischer et a*l., 1999]. Occluded air was dry extracted by mechanical crushing of samples in a double walled crusher cooled using an ethanol-liquid nitrogen mixture at about -50 °C. The liberated air was collected in cold traps chilled by closed cycle He refrigerators to a temperature of about 32 K. The frozen air samples held in the cold traps were liberated by heating and transferred to an IR absorption cell held at a constant pressure and temperature. IR absorption measurements were made several times on each gas sample with a tunable diode laser by scanning a single vibrational-rotational CO_2 absorption line at Doppler resolution in the R-branch of the 4.3 μm CO_2 absorption band. To calibrate the instrumentation, measurements were made with three air standards of precisely known CO_2 concentrations of 163, 240, and 330 ppm (± 0.01 ppm, *C. D. Keeling,* pers. comm.) that were introduced over three of the crushed ice samples, thus duplicating the crushing procedure. This calibration procedure was performed each day. A group of samples from the same depth interval were measured on the same day. The average standard deviation of the data of the samples from the same depth interval measured on the same day (5.9 ppm) is greater than the daily internal precision (1.7 ppm) measured on crushed ice samples with reference gas added. Considering the daily uncertainty in calibration and the reproducibility, we expect the internal precision to be better than 2 ppm when measured on different days for a group of samples from the same depth interval with constant CO_2 concentration among the samples. Directly introduced standards (not over ice) were run to check laser linearity and performance.

The gas age dating of the Siple Dome core over the time period of 40 to 8.2 kyrBP is established by correlation of CH_4 data with those of the GISP2 ice core [*Taylor et al.*, 2004b; *Brook et al.*, 2005]. The methods for CH_4 measurements are described in *Brook et al.* [2000, 2005]. For ice younger than 8.2 kyrBP the age of the ice was determined by counting annual layers and the corresponding gas ages were assigned by subtracting the ice age – gas age difference (Δage) from the ice ages [*Taylor et al.*, 2004a]. The Δage was calculated with a firn densification model [*Brook et al.*, 2005]. The Δage is about 280 ± 80 years in the early Holocene, increasing to about 750 ± 220 years during the Last Glacial Maximum (LGM). The gas age of bubble ice varies according to ice bubble close-off depth. We estimate that the width of the age distribution is on the order of 10% of the Δage value [*Goujon et al.*, 2003].

3. Results

3.1. Data quality

Measurements were made over a period of 2.5 years at random depth intervals to eliminate the possibility that unnoticed analytical changes would create trends in the data. Measurements of Siple Dome CO_2 made in 2001 (black open squares) at SIO agree well with those made in 2002 and early 2003 (solid circles) as shown in Figure 2b.

The results can be compared to other Antarctic ice cores as shown in Figure 2b. The CO_2 concentration of Dome C, Taylor Dome and Byrd cores were measured in

Bern [*Monnin et al.*, 2001; *Flückiger et al.*, 2002; *Indermühle et al.*, 1999, 2000; *Neftel et al.*, 1988; *Staffelbach et al.*, 1991] and compare well with the SIO data. This is expected because Bern's gas extraction method (dry crushing) is similar to that at SIO.

High accumulation rate provides a small width of gas age distribution and therefore a record of high temporal resolution. Similarly, the use of small pieces of ice potentially also improves temporal resolution. On the other hand, this potentially increases the scatter in the data since inhomogeneities are not smoothed out as they are in larger samples covering longer intervals of time [*Smith et al.*, 1997a]. The accumulation rate at Siple Dome is two and five times larger than that at Taylor Dome and Dome C, respectively. Thus, the high accumulation rate at Siple Dome (Table 1) and the small sample size (4 to 6 cm^3) used in the measurement at SIO may increase the scattering of the Siple Dome data. Sample sizes used in the Siple Dome CO_2 study at SIO are half of those used for Taylor Dome and Dome C at Bern. Some Taylor Dome samples were also measured at SIO (Figure 2b) and there is good agreement between the SIO and the Bern results, even though the volume of samples for a depth interval used at SIO was about one fourth of what was used at Bern, where calibration was routinely done using reference gases from SIO at 251.7 ppm and 321.06 ppm [*Indermühle et al.*,1999].

3.2. The trend of the Siple Dome CO_2 record

In general, the trends in the Siple Dome CO_2 record (solid circles and open squares in Figure 2b) follow temperature trends, indicated by δD_{ice} (Figure 2a), which is taken as a proxy for local temperature. The general time series of Siple Dome CO_2 concentration confirms previous studies in Antarctic ice cores (Figures 2 and 3). The Siple Dome CO_2 record shows a continuous decrease from 214 ppm at 38 kyrBP to 186 ppm at LGM (~ 18 kyrBP) and then a rapid increase up to 247 ppm during the early part of the last termination. It is important to note that the CO_2 increase is reversed during the Antarctic Cold Reversal (15 to 13 kyrBP) reaching a local minimum of 239 ppm, which has been observed in the Dome C, Taylor Dome and Byrd records. After the Antarctic Cold Reversal, Siple Dome CO_2 increases again reaching up to 284 ppm at the beginning of the Holocene (11.5 kyrBP). This increase occurs during the Younger Dryas interval as shown in the Dome C record [*Monnin et al.*, 2001]. During the Holocene, the Siple Dome CO_2 concentrations decrease to a local minimum of 261 ppm at about 8 kyrBP, and then increase to 285 ppm in the late Holocene (mean of the scattered values). There is good agreement of this local minimum at about 8 kyrBP between the different Antarctic cores from Siple Dome, Taylor Dome, Dome C and Vostok. The CO_2 concentration never reaches steady state during the Holocene after the end of the last termination as was also found in the Taylor Dome and Dome C records [*Indermühle et al.*, 1999; *Flückiger et al.*, 2000].

Figure 3 shows an enlarged portion of Figure 2 covering the last termination. Again, Siple Dome CO_2 follows the temperature proxy (δD_{ice}) as seen in other Antarctic ice cores. For most of the record, the Siple Dome CO_2 time trend is almost the same as that of the high resolution Dome C record.

However, at the depth (677.61 m) corresponding to around 15 kyrBP, CO_2 in Siple Dome is higher than in Dome C by about 21 ppm. We believe that this anomalous CO_2 value is suspecious as an atmospheric CO_2 record because of the following two reasons. First, near the depth of the anomalously high CO_2 value (~ 20cm apart in depth), the $\delta^{40}Ar$ and $\delta^{15}N$ of N_2 values reach atmospheric values, indicating there was no diffusive column and a possible hiatus in deposition [*Severinghaus et al.*, 2003]. Second, the difference of 21 ppm is too large to be explained by age uncertainties. The anomaly occurs at a greater depth than that corresponding to the beginning of Antarctic Cold Reversal (defined by the rapid increase in CH_4 concentration from Siple Dome ice, as defined in the Dome C ice core, where abrupt CO_2 and CH_4 increases happened [*Monnin et al.*, 2001]). Thus the age uncertainty at this depth does not affect the CO_2 difference between Siple Dome and Dome C significantly (<5ppm).

Except for this anomalous period, we calculate the rates of CO_2 change and time lag of CO_2 compared to temperature. During the last termination, CO_2 changed at the rate of 19.1 ppm/kyr from 17.7 to 15 kyrBP, -5.2 ppm/kyr during the Antarctic Cold Reversal (15 to 13 kyrBP) and 26.8 ppm/kyr from 13.0 to 11.3 kyrBP, respectively. These values are similar to CO_2 changes in the Dome C record [*Monnin et al.*, 2001].

3.3 Phase relationship between changes in CO_2 and Siple Dome temperature

To compare the phasing of changes in CO_2 and surface temperature (using δD_{ice} as a temperature proxy), we interpolated the CO_2 and δD_{ice} data on a 10-year spacing. We calculated the change in CO_2 and δD_{ice} (dCO_2/dt and $d(\delta D_{ice})/dt$) for 10-year intervals and smoothed them by averaging over time windows ranging from 0 to

500 years. The correlation coefficient between the dCO_2/dt and $d(\delta D_{ice})/dt$ was then calculated for different lag times and for different degrees of smoothing. The maximum correlation coefficients were obtained with a 210 ~ 330 year lag of dCO_2/dt behind $d(\delta D_{ice})/dt$ with a smoothing of 200 ~ 500 years as shown in Figure 4a. Several maxima in correlation coefficients for different time lags are observed over less than 200-year windows, possibly due to the average spacing of 230 years in the CO_2 data. To check the sensitivity of the time lag by the uncertainties in CO_2 concentration and Δage, we carried out Monte Carlo simulations for CO_2 concentrations in two conditions, namely maximum Δage (estimated Δage + uncertainty) and minimum Δage (estimated Δage - uncertainty). For each situation, we produced 3000 different sets of CO_2 concentrations, which vary randomly with Gaussian propagation in their uncertainties. After interpolation and smoothing both dCO_2/dt and $d(\delta D_{ice})/dt$ with 500-year window, maximum correlation coefficients were obtained with a 369 ± 23 years lag (mean ± 1σ) for maximum Δage and 196 ± 25 (mean ± 1σ) for minimum Δage as seen in Figure 4b. The time lags for CO_2 behind temperature are greater than the uncertainty of the Δage of 80 years at the end of the last termination but close to 220 years at LGM. The time lags roughly agree with *Fischer et al.* [1999] (600 ± 400 years during the last three terminations in Byrd, Taylor Dome and Vostok records) and are slightly less than the value proposed by *Monnin et al.* [2001] (410 years during the last termination in Dome C record). *Indermühle et al.* [2000] found higher values (1200 ± 700 years) for the period 60 to 20 kyrBP in the Taylor Dome record, as did

Caillon et al. [2003] (800 ± 200 years) across termination III in the Vostok record. Although the correlation method discussed above suggests that changes in surface temperature at Siple Dome could lead changes in the concentration of atmospheric CO_2 by ~300 years, this lead is small relative to both our sampling interval and possible systematic error in Δage, for example due to inaccuracies in estimating past accumulation rates, which are derived from a thermodynamic model employing temperatures calculated from the δD_{ice} record [*Brook et al.*, 2005]. Our main conclusion is therefore that a lead of CO_2 versus Siple Dome temperature is unlikely, a lag of CO_2 versus Siple Dome temperature is likely, and that our results provide strong support for previous suggestions of a close link between Antarctic temperature and CO_2 change during the deglaciation.

4. Possible Mechanisms for In Situ CO_2 Production

In some depth intervals the CO_2 concentrations in Siple Dome ice are higher than in the Vostok, Taylor Dome and Dome C cores (Figure 2 and 3). These differences are up to 20 ppm greater (e.g., at around 11 kyrBP). One possible explanation for these differences is uncertainty in the age scales, particularly at times when CO_2 was changing. For example, during the two periods of rapid CO_2 increase during the last termination, an offset of 300 years between otherwise identical records would produce a CO_2 difference of 10 ppm. This effect may explain the differences between the Siple Dome versus the Dome C and Siple Dome versus the Taylor Dome cores (Figure 5c). The low CO_2 values of the Byrd ice core at about 39 kyrBP can be compared to low values in Taylor Dome at about 42 kyrBP (not shown in the Figure 2) on the GISP2 age scale [*Indermühle et al.*, 2000]. However, elevated CO_2 levels in the Siple Dome at times of relatively little change in CO_2 (for example, during the Antarctic Cold Reversal or in the earliest Holocene) cannot be attributed to time scale uncertainties. Interestingly, most of the cold period (40 ~ 23 kyrBP) CO_2 data from the Siple Dome ice shows little difference in CO_2 when compared to other cores.

As mentioned above, large variations of atmospheric CO_2 concentrations between Antarctic ice core sites are unlikely, prompting us to search for another explanation for the differences between the Siple Dome CO_2 and other records. To examine the possibility and the mechanisms of CO_2 production, we check the CO_2 difference between Siple Dome and Taylor Dome or Dome C (Figure 5c). We call this "excess CO_2" although we cannot rule out the possibility of CO_2 consumption in other ice cores by the interaction between CO_2 in the bubbles and the carbonates in the ice (i.e., $CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$) [*Neftel et al.*, 1982].

The excess CO_2 is high at depth of 100 to 330 m (0.4 to 3.5 kyrBP) and 560 to 640 m (9.5 to 12.5 kyrBP) but is within the experimental uncertainty at depths > 708 m (17.5 kyrBP). The Siple Dome ice samples are more fractured than Taylor Dome samples below about 500 m (about 8 kyr). One possibility is that the CO_2 in the core might be compromised by air entering fractures in the core that reseal after the ice reaches the surface, during transportation and storage. However, there are high excess CO_2 values in the late Holocene Siple Dome ice where fracturing is minor, and low excess CO_2 in glacial ice where Siple Dome ice is highly fractured. Moreover, correlations between the scattering of data from adjacent samples and excess CO_2 does not support the possibility of ambient air contamination. The above observations imply the possibility that some of the artifacts in Siple Dome CO_2 records are related to in situ CO_2 production in the ice.

Possible CO_2 production mechanisms include (1) carbonate-acid reaction [*Delmas*, 1993; *Anklin et al.*, 1995 and 1997; *Barnola et al.*, 1995; *Smith et al.*, 1997a, b], (2) oxidation of organic compounds abiologically [*Tschumi and Stauffer,* 2000], or biologically [*Campen et al.,* 2003], and (3) snow melting-refreezing [*Neftel et al.*, 1983; *Stauffer et al.*, 1985].

We have calculated the potential CO_2 produced by the carbonate-acid reaction between $CaCO_3$ and H^+ [*Neftel et al.,* 1988], as shown in Figure 5e, using the non-sea salt Ca (nssCa) ion content assuming all of the nssCa is from $CaCO_3$ and that all $CaCO_3$ reacts to produce CO_2. This source of potential CO_2 is too low to produce the excess CO_2 observed during the Holocene and shows little correlation with the excess CO_2 data (Figure 5c). Moreover, electric conductivity measurements (ECM, proxy for H^+) do not show any significant change at the depth intervals of high excess CO_2 in Figure 5c. Thus, it is unlikely that a carbonate-acid reaction has affected the Siple Dome CO_2 record.

Oxidation of organic compounds has been proposed to be at least as important as acid-carbonate reactions for CO_2 production (e.g., $2H_2O_2 + HCHO \rightarrow 3H_2O + CO_2$) [*Tschumi and Stauffer,* 2000]. Organic acid concentrations in Siple Dome ice core have not yet been reported. H_2O_2 is one of the important oxidants of organics in ice. The top 100 m of Siple Dome ice core shows concentrations near or below the detection limits of ~ 0.02 μM H_2O_2 except at the 0 to 2.5 m depth [*McConnell*, 1997]. This H_2O_2 concentration corresponds to a potential CO_2 production of less than 5 ppm assuming an adequate supply of organic acids, which does not easily explain the 20 ppm excess CO_2. CH_3COO^- and $HCOO^-$ can act as other oxidants [*Tschumi and Stauffer,* 2000]. Another possible CO_2 production mechanism is respiration of microorganisms (consuming organic acids and producing CO_2) within the ice [*Campen et al.,* 2003]. Natural organic acids and other organic materials have much lower values of $\delta^{13}CO_2$, approximately -25 ‰, compared to atmospheric $\delta^{13}CO_2$ (preindustrial value of about -6.5 ‰) and $CaCO_3$ (0 ~ 4 ‰). Thus, precise $^{13}CO_2$ values could be used to investigate the sources of excess CO_2. For example if the early Holocene CO_2 record has excess CO_2 values of 20 ppm derived from organic materials, it would reduce the $\delta^{13}CO_2$ value by about 1 ‰. However, $^{13}CO_2$ analyses in the Siple Dome ice core have been hampered by the contamination of the ice by drilling fluid, n-butyl acetate, which in the mass spectrometer lead to fragmentation interference with m/z = 45 [*Ahn et al.*, 2001].

CO_2 can be considerably enriched in frozen melt layers due to the high solubility of CO_2 in melt water [*Neftel et al.*, 1983]. At Dye 3, Greenland, melt layers contribute about 7 % by volume at today's climate conditions and show mean CO_2 concentration as much as 1500 ppm [*Stauffer et al.*, 1985]. The annual mean snow temperature of Siple Dome is –25.4 °C, the highest among the Antarctic ice cores discussed in this paper [*Severinghaus et al.*, 2001], and occasional surface melting occurs during the summer, resulting in thin bubble free layers in the ice core. These melt layers can be detected visually, see arrows in Figures 3c and bars in Figure 5d [*Das*, 2003]. The ice samples measured for the Siple Dome CO_2 did not include visible melt layers. However, it is likely that small melt layers would not be detected visually, particularly deeper in the core where ice flow has thinned the layering. The mode of excess CO_2 is only weakly associated with that of melt layers (Figure 5c and 5d). Alternative possibilities beside warm temperature and the coastal location of the Siple Dome (Figure 1 and Table 1) include higher ambient temperatures during the austral summer (often being substantially higher than the mean annual temperature of -25.4 ^{o}C), combined with high sea salt concent, resulting in CO_2 contamination.

5. Conclusion

We present the CO_2 record of air occluded over the last 40,000 years in the Siple Dome ice core, Antarctica. The general time series of Siple Dome CO_2 concentration is similar to previous studies in other Antarctic ice core CO_2 records. Siple Dome ice also shows that surface temperature inferred from δD_{ice} correlates well with CO_2 concentration as shown in other Antarctic ice cores. During the last termination, it is likely that the change of the Siple Dome CO_2 concentrations lags the Siple Dome temperature change. Despite similarities with other Antarctic ice cores, the Siple Dome ice shows higher CO_2 concentrations than those in other Antarctic ice cores at some depth intervals, which may be due to in situ production in the ice. The cause of these elevated concentrations is not known with certainty. CO_2 production due to surface melting is the leading hypothesis, but the evidence is not definitive.

Acknowledgments. We wish to thank Jeff Severinghaus, Sarah Das, Richard Alley, Joe McConnell and Jihong Cole-Dai for advice and for providing unpublished data. Anonymous reviewers provided constructive comments. Staff at the National Ice Core Laboratory is thanked for the assistance with core processing. This work was supported by the Office of Polar Program of the NSF (NSF OPP 99-80619). This chapter is reproduced fully, with permission from: Ahn, J., M. Wahlen, B.L. Deck, E.J. Brook, P.A. Mayewski, K.C. Taylor, and J.W.C. White (2004) "A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica ice core". Journal of Geophysical Research, vol. 109, doi:10.1029/2003JD004415.

References

Ahn, J., M. Wahlen, and B. Deck, Measurement of atmospheric CO_2 trapped in the Siple Dome ice core (abstract), *Eos Trans. AGU,*87, F122, 2001.

Alley, R., E.J. Brook, and S. Anandakrishnan, Timing of deglacial events during termination I, *Quat. Sci. Rev., 2,* 431, 2002.

Anklin, M., J.-M. Barnola, J.Schwander, B. Stauffer, and D. Raynaud, Processes affecting the CO_2 concentrations measured in Greenland ice, *Tellus*, *B47*, 461-470, 1995.

Anklin, M., J. Schwander, B. Stauffer, J. Tschumi, A. Fuchs, J.-M. Barnola, and D. Raynaud, CO_2 record between 40 and 8 kyr B.P. from the Greenland Ice Core Project ice core, *J. Geophys. Res., 102*, 26,539-26,545, 1997.

Barnola, J. M., M. Anklin, J. Porcheron, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 evolution during the last millennium as recorded by Antarctic and Greenland ice, *Tellus, 47B*, 264-272, 1995.

Blunier, T., and E.J. Brook, Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period, *Science, 291*, 109-112, 2001.

Blunier, T., J. Chappellaz, J. Schwander, A. Dallenbach, B. Stauffer, T. F. Stocker, D. Raynaud, J. Jouzel, H. B. Clausen, C. U. Hammer, and S. J. Johnsen, Asynchrony of Antarctic and Greenland climate change during the last glacial period, *Nature, 394*, 739-743, 1998.

Brook, E. J., S. Harder, J. P. Severinghaus, E. J. Steig, and C. M. Sucher, On the origin and timing of rapid changes in atmospheric methane during the last glacial period, *Global Biogeochem. Cycles*, *14*, 559-572, 2000.

Brook, E. J., J. W. C. White, A. S. M. Schilla, M. L. Bender, J. P. Severinghaus, K. C. Taylor and R. B. Alley, Timing of millennial-scale climate change at Siple Dome, west Antarctica, during the last glacial period, *Quat. Sci. Rev., 24*, 1333-1343, 2005.

Caillon, N., J.P. Severinghaus, J. Jouzel, J.-M. Barnola, J. Kang, and V.Y. Lipenkov, Timing of Atmospheric CO_2 and Antarctic Temperature Changes Across Termination III, *Science, 299*, 1728-1731, 2003.

Campen, R.K., T. Sowers, and R.B. Alley, Evidence of microbial consortia metabolizing within a low-latitude mountain glacier, *Geology, 31,* 231-234, 2003.

Das, S. West Antarctic ice sheet surface melting and Holocene Variability. Ph.D. thesis. Pennsylvania State University, 2003.

Delmas, R. J., J. M. Ascencio, and M. Legrand, Polar ice evidence that atmospheric CO_2 20,000yr BP was 50% of present, *Nature, 284,* 155-157, 1980.

Delmas, R. J. A natural artifact in Greenland ice-core CO_2 measurement. *Tellus, 45B,* 391-396, 1993.

Dome-F Deep Coring Group, Deep ice-core drilling at Dome Fuji and glaciological studies in east Dronning Maud Land, Antarctica. *Ann. Glaciol., 27,* 333-337, 1998.

Etheridge, D. M. and C. W. Wookey, Ice core drilling at a high accumulation area of Law Dome, Antarctica, in Ice Core Drilling, edited by C. Rado and D. Beaudoing, pp. 86-96, *Proceedings of the Third International Workshop on Ice Core Drilling Technology,* Grenoble, France, October 10-14, 1988, CNRS, Grenoble, 1989.

Etheridge, D. M., L. P. Steele, R. L. Langenfelds, R. J. Francey, J.-M. Barnola and V. I. Morgan, 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, 1996.

Fischer, H., M. Wahlen, J. Smith, D. Mastroianni, and B. Deck, Ice core records of atmospheric CO_2 around the last three glacial terminations, *Science, 283,* 1712-1714, 1999.

Flückiger, J., E. Monnin, B. Stauffer, J. Schwander, and T. F. Stocker, High-resolution Holocene N_2O ice core record and its relationship with CH_4 and CO_2, *Global Biogeochem. Cycles*, 16, 10.29/2001GB001417, 2002.

Gildor, H., E. Tziperman, and J.R. Toggweiler, Sea ice switch mechanism and glacial-interglacial CO_2 variations, *Global Biogeochem. Cycles, 16(3)* 10.1029/2001GB001446, 2002.

Goujon, C., J.-M. Barnola, C. Ritz, Modeling the densification of polar firn including heat diffusion: Application to close-off characteristics and gas isotopic fractionation for Antarctica and Greenland sites, *J. Geophys. Res., 108*(D24), 4792, doi:10.1029/2002JD003319, 2003.

Hamilton, G.S. Mass balance and accumulation rate across Siple Dome, West Antarctica. *Annals of Glaciol., 35,* 102-106, 2002.

Iglewicz, B., and D.C. Hoaglin, How to detect and Handle outliers (Asqc basic references in quality control, Vol. 16), p87, American Society for Quality, 1993.

Indermühle A., T. F. Stocker, F. Joos, H. Fisher, H. J. Smith, M. Wahlen, B. L. Deck, D. Mastroianni, J. Tschumi, T. Blunier, R. Meyer and B. Stauffer, Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica, *Nature, 398*, 121-126, 1999.

Indermühle, A., E. Monnin, B. Stauffer, T. F. Stocker and M. Wahlen, Atmospheric CO_2 concentration from 60-20 kyr BP from the Taylor Dome ice core, Antarctica, *Geophys. Res. Lett., 27*, 735-738, 2000.

Kawamura, K., T. Nakazawa, S. Aoki, S. Sugawara, Y. Fujii, and O. Watanabe, Atmospheric CO_2 variations over the last three glacial-interglacial climate cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique, *Tellus, 55B*, 126-137, 2003.

McConnell, J. R., Investigation of the atmosphere-snow transfer process for hydrogen peroxide, Ph.D. Dissertation, Department of Hydrology and Water Resources, University of Arizona, 1997.

Monnin, E., A. Indermühle, A. Daellenbach, J. Flückiger, B. Stauffer, T. F. Stocker, D. Raynaud, and J.-M. Barnola, Atmospheric CO_2 concentrations over the Last Glacial Termination, *Science, 291*, 112-114, 2001.

Neftel, A., H. Oeschger, J. Schwander, B. Stauffer, and R. Zumbrunn, Ice core sample measurements give atmospheric CO_2 content during the past 40,000 yr, *Nature, 259,* 220-223, 1982.

Neftel, A., H. Oeschger, J. Achvander, and B. Stauffer, Carbon dioxide concentration in bubbles of natural cold ice. *J. Phys. Chem., 87*, 4116-4120. 1983.

Neftel, A., H. Oeschger, T. Stauffelbach, and B. Stauffer, CO_2 record in the Byrd ice core 50,000-5000 years BP, *Nature, 331*, 609-611, 1988.

Petit, J. R., J. Jouzel, D. Raynaud, N. I. Barkov, J.-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature, 399*, 429-436, 1999.

Raynaud, D., J. Jouzel, J. M. Barnola, J. Chappellaz, R. J. Delmas, and C. Lorius, The ice record of greenhouse gases, *Science, 259,* 926-934, 1993.

Schwander, J., J. Jouzel, C. U. Hammer, J.-R. Petit, R. Udisti, and E. Wolff, A tentative chronology for the EPICA Dome Concordia ice core, *Geophys. Res. Lett., 28,* 4243-4246, 2001.

Severinghaus, J.P., A. Grachev, and M. Battle, Thermal fractionation of air in polar firn by seasonal temperature gradients, *Geochem. Geophys. Geosys., 2,* 2000GC000146 JUL 31, 2001.

Severinghaus, J.P., A. Grachev, B. Luz and N. Caillon, A method for precise measurement of argon 40/36 and krypton/argon ratios in trapped air in polar ice with applications to past firn thickness and abrupt climate change in Greenland and at Siple Dome, Antarctica, *Geochim Cosmochim. Acta.*, 67, 325-343, 2003.

Smith, H. J., M. Wahlen, D. Mastroianni, and K. Taylor, The CO_2 concentration of air trapped in GISP2 ice from the Last Glacial Maximum-Holocene transition, *Geophys. Res. Lett., 24,* 1-4, 1997a.

Smith, H. J., M. Wahlen, D. Mastroianni, K. Taylor, and P. Mayewski, The CO_2 concentration of air trapped in Greenland Ice Sheet Project 2 ice formed during periods of rapid climate change, *J. Geophys. Res., 102,* 26,577-26,582, 1997b.

Smith, H.J., H.Fischer, M. Wahlen, D. Mastroianni and B. Deck, Dual modes of the carbon cycle since the last glacial maximum, *Nature, 400,* 248-250, 1999.

Stauffer, B., A. Neftel, H. Oeschger, and J. Schwander, CO_2 concentration in air extracted from Greenland ice samples, in *Greenland Ice Core: Geophysics, Geochemistry and the Environment*, edited by C.C. Langway, Jr. et al., pp. 85-89, Geophysical Monograph 33: Washington, D.C., America Geophysical Union, 1985.

Staffelbach, T., B. Stauffer, A. Sigg, and H. Oeschger, CO_2 measurements from polar ice cores: more data from different sites, *Tellus, 43B,* 91-96, 1991.

Steig, E. J., D. L. Morse, E. D. Waddington and P. J. Polissar, Using the sunspot cycle to date ice cores, *Geophys. Res. Lett., 25,* 163-166, 1998.

Stevens, B and R. Keeling, The influence of Antarctic sea ice on glacial-interglacial CO_2 variations, *Nature, 404,* 171-174, 2000.

Tabacco, I. E., A. Passerini, F. Corbelli, and M. Gorman, Determination of the surface and bed topography at Dome C, East Antarctica, *J. Glaciol., 44,* 185-191, 1988.

Taylor, K.C., R.B. Alley, D.A. Meese, M.K. Spencer, E.J. Brook, N.W. Dunbar, R.C. Finkle, A.J. Gow, A.V. Kurbatov, G.W. Lamorey, P.A. Mayewski, E.A.

Meyerson, K. Nishiizumi and G.A. Zielinski, Dating the Siple Dome (Antarctica) ice core by manual and computer interpretation of annual layering, *J. Glaciol., 50*, 453-461, 2004a.

Taylor, K. C., J. W. C. White, J. P. Severinghaus, E. J. Brook, P. A. Mayewski, R. B. Alley, E. J. Steig, M. K. Spencer, E. Meyerson, D. A. Meese, G. W. Lamorey, A. Grachev, A. J. Gow and B. A. Barnett, Abrupt climate change around 22 ka on the Siple Coast of Antarctica, *Quaternary Sci. Rev.*, 23, 7-15, 2004b.

The EPICA Dome C 2001-02 Science and drilling teams, Extending The Ice Core Record Beyond Half a Million Years, *EOS, 83,* 509-517, 2002.

Toggweiler, R., Variation of atmospheric CO_2 by ventilation of the ocean's deepest water, *Paleoceanography, 14*, 571-588, 1999.

Tschumi, J. and B. Stauffer, Reconstructing past atmospheric CO_2 concentration based on ice-core analyses: open questions due to in situ production of CO_2 in the ice, *J. Glaciology, 46*, 45-53, 2000.

Waddington, E. D. and D. L. Morse, Spatial variations of local climate at Taylor Dome, Antarctica: Implications for paleoclimate from ice cores. *Ann. Glaciol., 20,* 219-225, 1994.

Wahlen, M., D. Allen, B. Deck, and A. Herchenroder, Initial measurement of CO_2 concentrations (1530 to 1940 AD) in air occluded in the GISP2 ice core form central Greenland, *Geophys. Res. Lett. 18*, 1457-1460, 1991.

Table 1. Characteristics of the Antarctic ice cores from which CO_2 gases have been measured.

Core name	Mean annual temperature (°C)	Mean accumulation rate as water equivalent $(\mathrm{g\ cm^{-2}\ yr^{-1}})$	Elevation (m)
Law Dome	-22 ~ -19[a,b]	60 ~ 110[b]	1390[b]
Siple Dome	**-25.4[c]**	**12.4[d]**	**621[e]**
Byrd[f]	-28	16	1530
Taylor Dome	-42[g]	7[h]	2374[h]
EPICA Dome C	-54[I]	3[j]	3233[k]
Vostok[f]	-55.5	2.3	3490
Dome Fuji[l]	-58	3.2	3810

[a][*Etheridge and Wookey*, 1989]; [b][*Etheridge et al.*, 1996]; [c][*Severinghaus et al.*, 2001]; [d][*Hamilton*, 2002]; [e][*Taylor et al.*, 2004b]; [f][*Raynaud et al.*, 1993]; [g][*Waddington and Morse*, 1994]; [h] as unit of cm ice equivalent per year [*Steig et al.*, 1998]; [i][*Schwander et al.*, 2001]; [j][*The EPICA Dome C 2001-02 science and drilling teams*, 2002]; [k][*Tabacco et al.*, 1998]; [l][*Dome-F Deep Coring Group*, 1998]

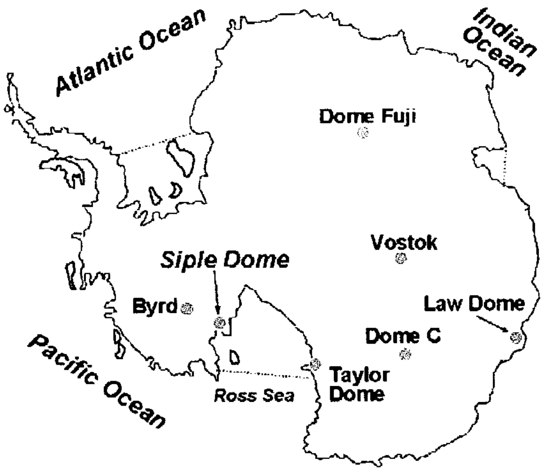


Figure 1. Location map of Antarctic ice cores referred to in the text.

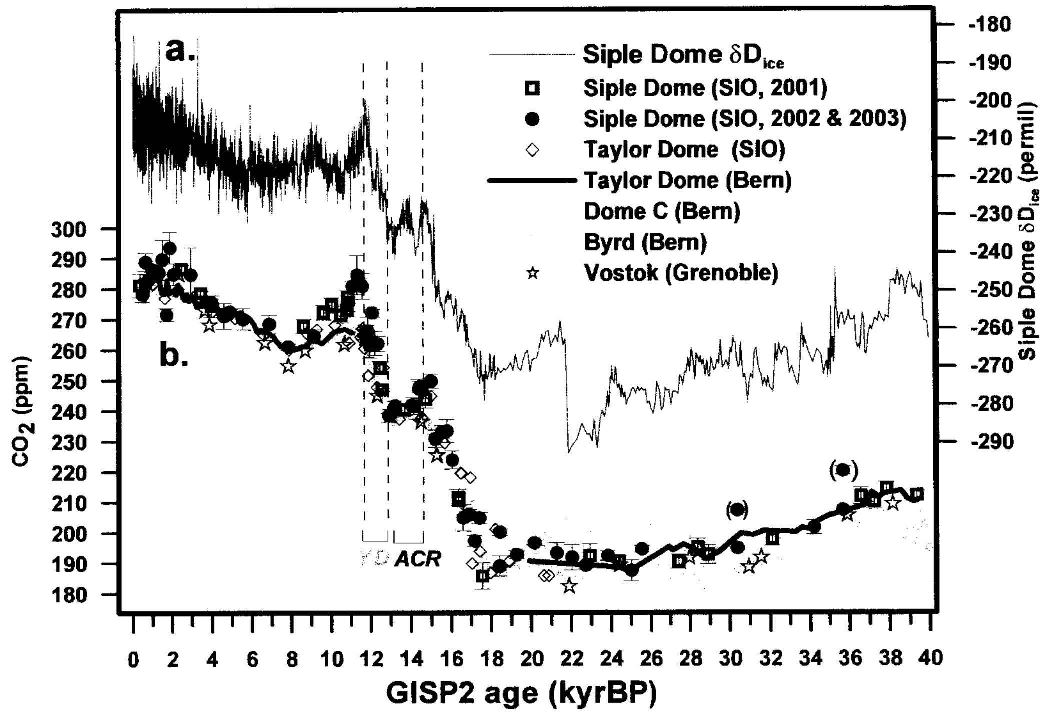


Figure 2. Antarctic ice core CO$_2$ plotted on GISP2 gas age scale. YD, Younger Dryas; ACR, Antarctic Cold Reversal. (a) Siple Dome δD$_{ice}$ on ice age scale. (b) Ice core CO$_2$ records on synchronized gas age scale with GISP2 via CH$_4$. Vostok data [*Petit et al.*, 1999], EPICA Dome C [*Monnin et al.*, 2001; *Flückiger et al.*, 2002], Taylor Dome [*Indermühle et al.*, 1999, 2000; *Smith et al.*, 1999] and Byrd [*Neftel et al.*, 1988; *Staffelbach et al.*, 1991] and Siple Dome [this study]. Error bars represent one standard error deviation of the replicate measurements at the same depth interval. The brackets indicate averages of two anomalously high values of the six samples from the same depth intervals. Taylor Dome gas ages of 40 to 20 kyrBP [*Brook et al.*, 2000]; Byrd gas ages [*Blunier et al.*, 2001]; Vostok gas ages for 40 to 10 kyrBP [*Blunier et al.*, 1998]. The Vostok GT4 time scales [*Petit et al.*, 1999] are younger than those of GISP2 by about 1 kyr for the latter of the last Termination and by up to 5 kyr during 40 to 20 kyrBP. The Holocene depth-gas age scales of the Vostok and Dome C are linearly interpolated between the youngest age points and synchronized gas age points in the early Holocene. Dome C gas ages for 17.2 to 11 kyrBP are synchronized with GISP2 in this study and for 22.5 to 17.2 kyrBP are extended from the synchronized gas age at 17.2 kyrBP by adding the depth-gas age intervals of the original paper [*Monnin et al.*, 2001].

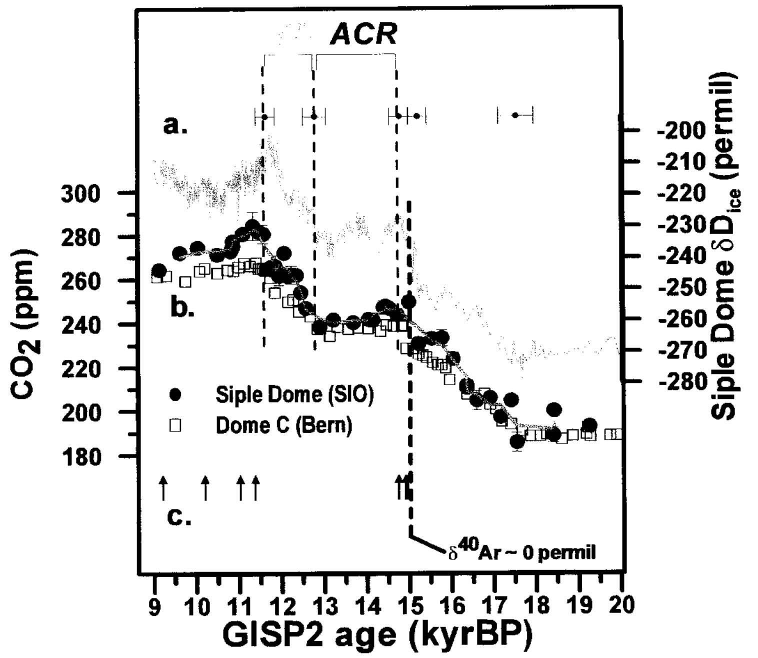


Figure 3. CO_2 change during the last Termination. YD, Younger Dryas; ACR, Antarctic Cold Reversal. (a) Siple Dome δD_{ice} on ice age scale. (b) CO_2 records from Siple Dome (solid circles) and Dome C (open squares) [*Monnin et al.*, 2001]. The line between Siple Dome CO_2 is the running average of three adjacent points. (c) Melt layers (vertical arrows) [*Das*, 2003]. The horizontal bars at top are gas age ranges around age tie points based on CH_4 records between Siple Dome and GISP2. The thick vertical dashed bar indicates where the argon and nitrogen isotopic anomaly occurs [*Severinghaus et al.*, 2003].

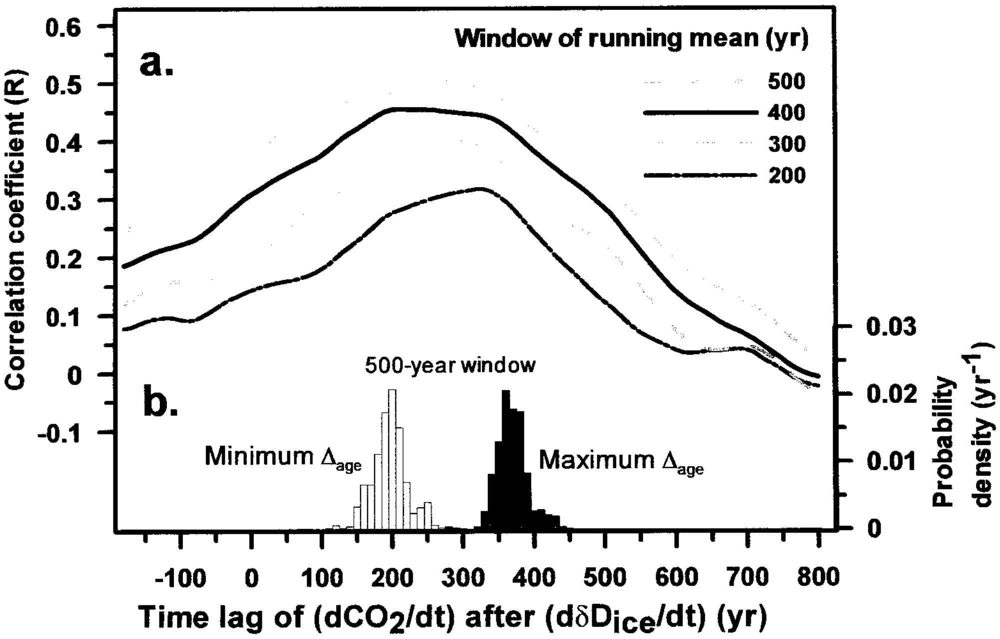


Figure 4. Time lag analysis of (dCO_2/dt) after ($d\delta D_{ice}/dt$) in the Siple Dome ice core during the last termination. (a) Correlation coefficients for different time lags after averaging data with windows of 200 ~ 500 years. (b) Histograms of the time lags after Monte Carlo simulation for CO_2 concentrations in two situations, maximum Δage and minimum Δage. For each situation, 3000 different sets of CO_2 concentrations were generated and used. The derived dCO_2/dt and $d(\delta D_{ice})/dt$ were smoothed with 500-year window for each data set.

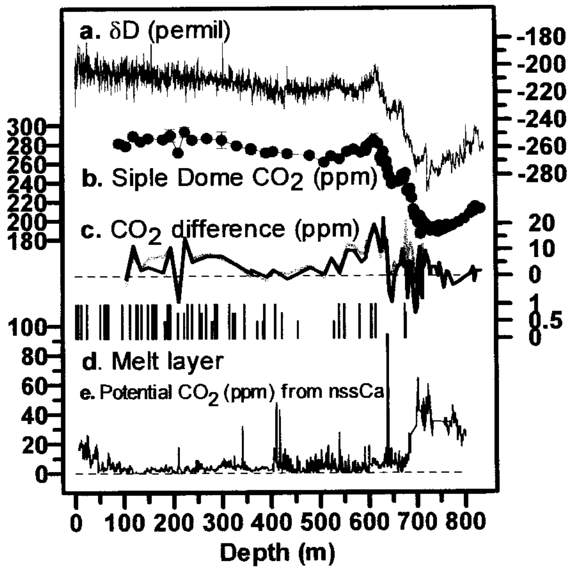


Figure 5. Comparison of possible processes of the excess CO_2 in Siple Dome ice cores on depth scale. (a) Siple Dome δD_{ice}. (b) Siple Dome CO_2. (c) CO_2 difference between Siple Dome and Taylor Dome (black line) or Dome C (gray line). The dashed horizontal line represents 0. (d) Melt layers [*Das,* 2003]. The lengths of bars indicate the confidence level. 1 = sure, 0.75 = probable, 0.5 = possible. (e) Potential CO_2 from acid-carbonate reaction. The dashed horizontal line represents 0. Non-sea-salt Ca (nssCa) was assumed to have been in the form of $CaCO_3$ and totally reacted with excess H^+. Considering total gas content in the unit gram of ice [Severinghaus, 2003], the CO_2 produced by the reaction was converted to a concentration change of CO_2.

CHAPTER III

CO_2 diffusion in polar ice:

Observations from the Siple Dome, Antarctic ice core

Abstract. Ancient atmospheric CO_2 trapped in polar ice cores has been used as a paleoatmospheric proxy. One assumption in doing so is that diffusion of CO_2 in the ice does not impact the concentration profile. However, CO_2 diffusion in polar ice is inadequately understood because the diffusion coefficient is too small to be accurately determined in the laboratory. We observe a gradual decrease of CO_2 concentration away from the melt-refrozen layers in the ice core from Siple Dome, Antarctica. On the basis of a combined study of noble gases (Xe/Ar and Kr/Ar), electric conductivity, and Ca^{2+} ion concentration, we confirm that substantial CO_2 diffusion occurs through the ice. This diffusion smoothes rapid changes of the CO_2 record. However, the smoothing of the CO_2 record by diffusion is one or two orders of magnitude smaller than the smoothing produced by the gas age distribution in our samples. Our modeling yields an estimate of the permeation coefficient (product of the diffusion constant and the solubility) as $4.3\ (\pm\ 2.1) \times 10^{-21}\ m^2s^{-1}$ mol CO_2 m^{-3} ice Pa^{-1} CO_2 at -23 °C.

Keywords: ice core; atmospheric CO_2; molecular diffusion; paleoclimate

1. Introduction

Paleoatmospheric CO_2 record reconstructed from ice cores helps us to understand the carbon cycle in different climatic periods over hundreds of thousand years [*Fischer et al.*, 1999; *Petit et al.*, 1999; *Kawamura et al.*, 2003; *EPICA Community members*, 2004]. Preservation of an atmospheric signal depends on the integrity of the ice core as an archive. In particular, CO_2 diffusion in polar ice is a key process, that may affect sample integrity, but is poorly understood. The study of CO_2

diffusion in ice has been hampered because the diffusion coefficient is too small to be precisely measured in the laboratory [*Hondoh*, 1996] and because of a lack of evidence concerning CO_2 diffusion in polar ice. A natural CO_2 spike can be formed at a refrozen melt layer (hereafter melt layer) due to the relatively high solubility of CO_2 in melt water, and this may diffuse through the ice during ice flow [*Neftel et al.*, 1983]. Therefore, the ice adjacent to a melt layer potentially acts as a natural laboratory and provides information about CO_2 diffusion in polar ice. In this regard, the Antarctic Siple Dome ice core provides valuable information because we observed a gradual increase of CO_2 concentration toward distinct melt layers (Figures 1 and 2). The Dye 3 ice core from Greenland also shows a CO_2 spike around a melt layer with ~ 2300 ppm at the depth of 124 m [*Stauffer et al.*, 1985]. However, at greater depth melt layers are not visible but CO_2 varies dramatically in a 50-cm core segment [*Neftel et al.*, 1983; *Stauffer et al.*, 1985].

We provide the first evidence of CO_2 diffusion in polar ice from high-resolution analyses on CO_2, Ca^{2+} ion, ECM (Electric Conductivity Measurement), and Xe/Ar and Kr/Ar of trapped air. Based on the observations, we also model the CO_2 diffusion in the ice and provide an estimate of the CO_2 permeation coefficient in the ice (see Appendix). Finally, implications of the results related to the polar ice cores are discussed.

2. Materials and Methods

CO_2 measurements were made on bubble ice that included some of the significant melted layers in the Siple Dome A Core (Figure 1), at Scripps Institution of

Oceanography (SIO). In each 1-cm depth interval of ice samples of 4 to 6 grams were used, and the outer 0.5 cm of the samples was removed with a band saw to reduce the possibility of contamination from present atmospheric CO_2 or post drilling chemical reactions. The gas extraction and IR spectroscopic methods used are well established [*Wahlen et al.*, 1991; *Smith et al.*, 1997a; *Smith et al.*, 1997b; *Fischer et al.*, 1999; *Ahn et al.*, 2004]. Trapped air is dry extracted by mechanical crushing of samples in a double walled crusher cooled to about –50 °C using flowing cold ethanol. The liberated air is collected in small cold traps chilled by closed cycle helium refrigerators to a temperature of about 32 K. The frozen air samples held in the cold traps were liberated by heating and then transferred to an IR absorption cell held at constant pressure and temperature. IR absorption measurements were made several times on each gas sample with a tunable diode laser. The single mode IR laser output was scanned across a single vibrational-rotational molecular absorption line of CO_2 at Doppler resolution. To calibrate the instrumentation, measurements were made with three air standards of precisely known CO_2 concentrations of 163, 240, and 330 ppm (±0.01 ppm, C. D. Keeling, personal communication). The standards were introduced over three of the crushed ice samples, thus mimicking the crushing procedure. This calibration procedure was performed each day. The internal precision is better than 2 ppm in the concentration range of 163 - 330 ppm.

Noble gas ratios were analyzed on a dual viscous-inlet Finnigan MAT 252 mass spectrometer at SIO. The $\delta^{132}Xe/^{36}Ar$, $\delta^{84}Kr/^{36}Ar$, and $\delta^{40}Ar/^{36}Ar$ are normalized to the clean marine air outside the laboratory. Gas from 40 - 60 grams of ice is extracted and gettered following the laboratory protocol developed by [*Severinghaus et al.*, 2003]. The pooled standard errors of the triplicate measurements for the GISP2 ice core of the Holocene, are 3.77 ‰ and 1.56 ‰ for $\delta^{132}Xe/^{36}Ar$ and $\delta^{84}Kr/^{36}Ar$, respectively, for the measurement conditions.

For Ca^{2+} ion concentration measurements, we used about 5 grams of ice from the same depth, where neighboring samples were used for CO_2 concentration measurements. Ice was prepared at SIO and measured at the Climate Change Institute of the University of Maine using Dionex-500 Ion Chromatography where calcium is measured on a CS12A Cation-exchange column with 25 mM methanesulfonic acid eluent, a self regenerating suppressor, and a conductivity detector. Sample size was 500 μL.

3. The excess CO_2 around the melt layers

The annual mean temperature at Siple Dome is –25.4 °C [*Severinghaus et al.*, 2001]. However, the ice has experienced occasional melting during austral summer (0 - 2 melt events per century during the Holocene) at warm surface temperatures (>2 °C) [*Das*, 2003]. The melt water percolates to greater depth in the firn (snow pack) and re-freezes at some depth (0 - 0.2 m), where the snow is in the form of a fine-crystal size crust and has a strong capillary force [*Das*, 2003]. Melt layers preserved in the Siple Dome ice core have lower gas content with reduced bubble size compared to normally sintered bubble ice and are easily identified visually (Figure1).

A 30-cm long ice sample from the depth of 286.7 – 287.0 m was intensively studied (Figure 1). The age of the ice is ~ 3.04 kyrBP (thousand years before 1950 C.E.), and the gas age is ~ 2.74 kyrBP [*Tayler et al.*, 2004]. Annual layers are about 5 to 9 cm thick at this depth [*Taylor et al.*, 2004]. Two melt layers (~ 1 cm thick) in this sample have smaller bubble sizes than does ice in a normal non-melt layer. In addition, melt layers have lower bubble-gas contents (10 - 20 % of that in a normal layer;

estimation by measurements of bubble size and number density). The upper (left) melt layer M1 is thicker than the lower (right) melt layer M2 (Figure 1). Some features between the two distinct melt layers seem to indicate partial melting.

Due to the high solubility of CO_2 in the melt water (Table 1), CO_2 may have an elevated concentration in the ice formed from a melt layer compared to that in the air. Considering the atmospheric CO_2 concentration of 278 ppm (μatm/atm) [*Indermühle et al.*, 1999] at the gas age of 2.74 kyrBP and the present surface pressure condition at the Siple Dome (937 hPa), we can expect 16,230 μmol CO_2 / mol total air dissolved in the 0 °C melt water in equilibrium (Andrew Dickson, personal communication), which is 58 times greater than that in the atmosphere (Table 1). If a thin film of snow melt has enough time to come to solubility equilibrium with the atmospheric air at the surface, and then refreezes rapidly at some greater depth, the excess CO_2 in the melt water can be trapped and preserved in small bubbles in the melt layer. These bubbles can be preserved through the firn metamorphism process and incorporated in mature ice, due to being surrounded by a layer of ice. The CO_2 concentration gradient between the melt layer and the neighboring "normal" bubble ice induces diffusion through the ice during periods of time greater than thousands of years. On the other hand, excess CO_2 would not be preserved in the melt layer, if degassing occurs during the refreeze of the melt. However, degassing requires that the freezing occur very slowly, so is unlikely.

Our high-resolution (depth interval of 1 cm) study shows that the CO_2 concentration gradually decreases from 750 to 285 ppm away from M1. Another smaller peak is also found around M2 (Figure 2). In comparison to other CO_2 records

(278 ppm) from colder Antarctic ice core sites, the CO_2 concentrations in the Siple Dome samples are greater by up to 470 ppm (excess CO_2), and clearly do not record atmospheric values.

In order to quantitatively determine the excess CO_2, resulting from the refrozen melt, we use other melt-sensitive gases. $^{132}Xe/^{36}Ar$ and $^{84}Kr/^{36}Ar$ in glacial ice are useful indicators of extensive snow melting and refreezing, as Xe and Kr are about four and two times as soluble in liquid water as Ar, respectively [*Severinghaus et al.*, 2003]. Considering the solubility of the noble gases at 0 °C, the gravitational fractionation in the firn layer, and Ar loss from the bubbles during sample handling or bubble close-off, our calculation using the Xe/Ar and Kr/Ar data gives the volume ratio of liquid water to pore air. This is accomplished by solving three equations for three unknowns with three observed quantities: Xe/Ar, Kr/Ar, and $^{40}Ar/^{36}Ar$. This allows us to estimate the volume percentage of the refrozen melt water in the sample used. By comparing by visual observation of volume of melt (defined by ice with small bubbles) to the estimated volume of melt from Xe/Ar and Kr/Ar, we estimate that about 50 % of M1 originated from re-freezing of melt, that filled open pore spaces in the firn layer. This number is comparable to the porosity of snow at the surface, 56% (ice density within top 20 cm of snow = 0.40 g cm^{-3}, Joan Fitzpatrick, 2003, personal communication), and suggests that most of the Xe, Kr and Ar were nearly equilibrated with the ancient atmosphere and trapped in M1. Therefore, we can also expect that the melt at the surface was nearly equilibrated with the ancient atmospheric CO_2 and was trapped in M1. We assume that diffusion of Xe, Kr and Ar in the ice is negligible compared to that of CO_2 (this is validated in the next section). By the volume of refrozen melt in M1, solubility of CO_2, and average ice-thinning factor of 0.714 (see Appendix), we calculate that the total CO_2 trapped in M1 at the snow surface is between 11.2 (± 3.4) × 10^{-9} mol CO_2 cm^{-2} (without thinning) and 15.7 (± 4.8) × 10^{-9} mol CO_2 cm^{-2} (with thinning). The thinning in the melt layer is expected to be less than in a normal layer due to the smaller porosity and higher rheological competence in the refrozen melt layer. The accuracy of the above estimation of excess CO_2 is limited by the possibly different degrees of equilibration of different gases in the melt water. For example, Xe should approach equilibrium more slowly than CO_2 due to its lower diffusivity. Thus, this estimation should be considered as complimentary to other independent estimations. However, this estimation supports the hypothesis that significant excess CO_2 is induced by the melting/refreezing process. Our modeling described in the next section does not require full equilibrium of atmo spheric CO_2 with the melt water.

4. CO_2 diffusion in the ice

In this section, we decipher the process causing the observed CO_2 distribution in the ice adjacent to the melt layers. The gradual decrease in CO_2 away from the melt layers is consistent with the hypothesis that CO_2 has diffused away from the melt layer over the 2.8 thousand years, and agrees with our results from a molecular volume diffusion model (Figure 3) [*Neftel et al.*, 1983; see Appendix for details]. In this model, we assume constant total gas content in the ice, although this is not completely realistic due to the fact that the melt layers contain lower total gas content than normal ice. Thinning of vertical layers with increasing depth due to the flow of the ice is taken into account. A time-dependent diffusion constant was used to correct for the thinning of the ice and to keep the initial vertical intervals. The same value of the diffusion constant of CO_2 in ice was applied for the two melt layers. The good fit of the model and data supports our proposition that the CO_2 originally trapped in the melt layer has diffused through the ice for thousands of years. For additional confirmation, we also integrate the observed excess CO_2 in the upper part of M1 (including upper half of M1), resulting in 5.4×10^{-9} mol CO_2 cm^{-2}. This is in agreement with the value found from the volume of refrozen melt (half volume of M1) as calculated in the previous section (3.9 to 10.2×10^{-9} mol CO_2 cm^{-2}). The baseline CO_2 levels far from the melt layers are higher than in the Taylor Dome and Dome C ice records by 11 ppm on average. A possible mechanism for this minor baseline excess CO_2 will be discussed in another paper.

Other potential alternative mechanisms for the excess CO_2 in the ice adjacent to the melt layers include: (1) invisible snow melting-refreezing micro-melt layers, (2) carbonate-acid reaction [*Anklin et al.*, 1995; *Anklin et al.*, 1997; *Barnola et al.*, 1995; *Delmas*, 1993; *Smith et al.*, 1997a; *Smith et al.*, 1997b], and (3) oxidation of organic compounds abiologically [*Tschumi and Stauffer*, 2000], or biologically [*Campen et al.*, 2003].

If the excess CO_2 outside M1 and M2 was formed by an invisible distribution of refrozen melt water, we would observe the same characteristics in the excess Xe/Ar and Kr/Ar as in the excess CO_2. However, we cannot detect any significantly elevated Xe/Ar and Kr/Ar outside the two melt layers where we see the significant excess CO_2 (Figure 2). Thus, a melt-refreezing process cannot explain the excess CO_2 distribution around the melt layers. It is important to note that diffusion of Xe, Kr, and Ar in the ice appears from this data to be negligible compared to that of CO_2. One possible issue to be considered is that Ar may diffuse more rapidly in the ice than Kr and Xe [*Severinghaus and Battle*, submitted]. If so, then the Kr/Ar and Xe/Ar ratios in adjacent ice to a melt layer would be lowered by the preferential migration of Ar. However, the good agreement of two noble gas data sets in all layers other than melt layers would have to be fortuitous if this were the case. For this reason this scenario is considered unlikely.

Total Ca^{2+} concentration indicates the upper limit of the amount of $CaCO_3$ that potentially could have reacted with H^+. There is no significant correlation between the excess CO_2 and the total Ca^{2+} or ECM (Electric conductivity measurements, a proxy for H^+) as shown in Figure 2. Moreover, assuming that all the Ca^{2+} is produced from the reaction between $CaCO_3$ and H^+, the potential excess CO_2 is ~17 ppm on average. This amount of Ca^{2+} is too small to explain our observations (excess CO_2 ~ up to 470 ppm). 1 μg Ca^{2+} per kg ice corresponds to 7 ppm of excess CO_2 for a normal ice layer.

Oxidation of organic compounds has been proposed to be at least as important as acid-carbonate reactions for CO_2 production (e.g., $2H_2O_2 + HCHO \rightarrow 3H_2O + CO_2$) [*Tschumi and Stauffer*, 2000]. However, excess CO_2 by oxidation of organic compounds could not likely produce 30 ppm excess CO_2, which is the CO_2 difference between Greenland and Antarctic ice core records for the Holocene [*Anklin et al.*, 1995; *Barnola et al.*, 1995]. Greenland ice cores have excess CO_2 related to various in situ production due to high dust content, whereas Antarctic ice cores are considered to be more representative of the paleoatmospheric CO_2 concentration [*Anklin et al.*, 1995; *Barnola et al.*, 1995; *Anklin et al.*, 1997; *Smith et al.*, 1997a; *Smith et al.*, 1997b; *Tschumi and Stauffer*, 2000]. Moreover, the top 100 m of the Siple Dome ice core show H_2O_2 concentrations near or below the detection limit of ~ 0.02 μM, except at 0 to 2.5 m depth [*McConnell*, 1997]. H_2O_2 is one of the major oxidants in snow. The H_2O_2 concentration at Siple Dome is much lower than that of other Antarctic ice cores. Thus, oxidation of organic compounds cannot explain the high excess CO_2 of up to 470 ppm.

Therefore we can safely exclude the possibilities of all 3 alternative explanations. In summary, we conclude that excess CO_2 distribution around the melt layers was formed by the diffusion of CO_2 through the ice matrix from the refrozen melt (M1, M2 and partial melt layers).

5. Smoothing of the CO_2 record in the polar ice

Significant diffusion for thousands of years in the ice sheet may smooth any local atmospheric rapid changes. We calculated the smoothing of the excess CO_2 concentration in a melt layer using a molecular volume diffusion process [*Neftel et al.*, 1983; see Appendix for details]. We estimate that the amplitudes of the CO_2 variation in the measured core segment are around 19 ~ 29 % and 13 ~20 % of the initial amplitude (c_0) for M1 and M2, respectively (Figure 3). The initial CO_2 concentration in M2 is estimated to be smaller than in M1 by a factor of about 0.6. We find higher CO_2 concentrations in the samples that include melt layers or partial melt layers than in the modeling because the former have lower gas content than the normal bubble ice. From the best-fit calculation, the permeation coefficient of CO_2 (the product of the diffusion constant and the solubility) is 4.3 (± 2.1) × 10^{-21} m^2s^{-1} mol CO_2 m^{-3} ice Pa^{-1} CO_2 at –23 °C (time-averaged temperature). This is one to two orders of magnitude greater than that estimated from the Dye 3 ice core (1.3×10^{-22} m^2s^{-1} mol m^{-3} Pa^{-1} at -20 °C) [*Neftel et al.*, 1983], but similar to the estimation (4.35×10^{-21} m^2s^{-1} mol m^{-3} Pa^{-1} at -23 °C) from a simulation of molecular dynamics in ice lattices [*Ikeda-Fukazawa et al.*, 2004; *Ikeda-Fukazawa and Fukumizu*, 2005]. Our result for the permeation coefficient of CO_2 is independent of the Xe/Ar and Kr/Ar data, but dependent on constant parameters such as time-averaged porosity and initial thickness of melt layers (see Appendix).

The gradual bubble close-off at the bottom of the firn layer (snowpack) effectively smoothes any rapid change in the atmosphere, and its effect can be roughly approximated by a Gaussian filter corresponding to the gas age distribution. The smoothing of the CO_2 concentration by diffusion in the ice is of the order of a few cm in our samples and thus is negligible compared to the smoothing by the gas age distribution at that depth (~ 30 years, corresponding to the diffusion in the depth interval of ~ 100 cm). However, at greater depths the smoothing by the diffusion may become larger. A 40-year pulse of atmospheric CO_2 is modeled with the calculated permeation coefficient. Compared to the smoothing of the CO_2 record by the gas age distribution, the range of smoothing by diffusion in the ice is rather small for the 10 kyr-old ice but it becomes similar in order of magnitude for 40 kyr-old ice. Our extension of the modeling results at a shallow depth (corresponding to 2.74 kyrBP) to greater depths is limited and requires further study. For example, the assumption of Henry's law for the CO_2 solubility in ice may not be valid through all the pressure ranges.

Our experience with Taylor Dome ice, which is all bubble ice, does not show evidence for significant smoothing of the CO_2 record on a millennial scale at least for 120 kyr (unpublished data). The formation of clathrate ice (bubble free ice) at depths from 500 to 1200 m (corresponding to the age of 25 ~ 65 kyr) at Antarctic cold drilling sites (Vostok, Dome Fuji, and EPICA Dome C), is expected to change gas diffusion. Considering the glacial-interglacial CO_2 records from the recent EPICA Dome C ice core [*EPICA Community members*, 2004] for >400 kyr, the diffusion of CO_2 in the clathrate ice is perhaps too small to smooth the CO_2 record on a millennial time scale.

Dividing the permeation coefficient by the solubility gives the diffusion coefficient. Unfortunately, the solubility of CO_2 in ice is not well known at present. We calculate the CO_2 diffusion coefficient in the ice matrix at $-23\,^{\circ}C$ to be $> 9.6\ (\pm 4.7) \times 10^{-14}\ m^2\ s^{-1}$ for a solubility of $<4.5\times10^{-8}$ mol $CO_2\ m^{-3}$ ice (Pa $CO_2)^{-1}$ [*Neftel et al.*, 1983] and $7.6\ (\pm 3.7) \times 10^{-11}\ m^2\ s^{-1}$ for a solubility of 5.7×10^{-11} mol $CO_2\ m^{-3}$ ice (Pa $CO_2)^{-1}$ [*Ikeda-Fukazawa and Fukumizu*, 2005]. At present, the solubility of CO_2 in ice is too small to be measured precisely [*Hondoh*, 1996]. Improved measurement on CO_2 solubility in ice in the future would allow a better estimate of the diffusion coefficient of CO_2 in polar ice. Further studies should include estimation of the change of CO_2 mixing ratio during storage with permeation coefficients for the main air gases such as O_2 and N_2.

6. Conclusion

The refrozen melt layers in the Siple Dome ice core have excess CO_2 due to the high solubility of CO_2 in the melt water. Our analyses of samples from the Siple Dome ice core show a gradual increase of CO_2 toward the refrozen melt layers. Combined with the noble gas study (Xe/Ar, Kr/Ar) and chemical and electric properties of the ice, we conclude that the CO_2 spike diffused throughout the ice. Comparing this observation to modeling of CO_2 diffusion, we calculate the product of solubility and the diffusion coefficient of CO_2 to be $4.3\ (\pm\ 2.1) \times 10^{-21}\ m^2s^{-1}\ molCO_2\ m^{-3}ice\ Pa^{-1}CO_2$ at $-23\ ^{o}C$. The smoothing of the CO_2 record by diffusion is one to two orders of magnitude smaller than the smoothing by gas age distribution at the depth of 287 m (gas age = 2.74 kyrBP) in the Siple Dome ice and so does not degrade the record.

Acknowledgments. We wish to thank Sharon Sneed at the Climate Change Institute for the major ion concentration measurements. We also thank to Sarah Das, Bruce Deck, Tomoko Ikeda-Fukazawa for invaluable advice and Alane Bollenbacher for the preparation of the CO_2 air standard. Bernhard Stauffer and Kenji Kawamura kindly reviewed and improved this paper. Ice cores were kindly cut by John Rhoades at the National Ice Core Laboratory. The early work was supported by the Office of Polar Program of the NSF (NSF OPP 99-80619). This chapter is reproduced fully, with permission from: Ahn, Jinho; Severinghaus, Jeff; Headly, Melissa; Wahlen, Martin; Brook, Ed J.; Mayewski, Paul A.; Taylor, Kendrick C. "CO_2 diffusion in polar ice:

Observation from the Siple Dome ice core, Antarctica", Earth and Planetary Science Letters, 2005 (submitted).

Appendix

Elevated CO_2 diffuses from a melt layer to bubbles within a normal layer through ice. The smoothing of the CO_2 concentration is calculated from molecular volume diffusion with constant concentration c_0 in a melt layer of width *2h* [6]. The diffusion equation is:

$$j = -D_0 \frac{dc_E}{dx_{eff}} \qquad (1)$$

where j is the flux of CO_2 by diffusion with the diffusion constant (D_0), c_E is the CO_2 concentration dissolved in the ice, and x_{eff} is the effective vertical distance by thinning by ice flow.

The c_E is related to CO_2 concentration in the bubbles (c_B), bubble pressure (p) as function of time ($p(z(t))$) and CO_2 solubility in ice according to Henry's law (L):

$$c_E = c_B p(z(t))L \qquad (2)$$

The total CO_2 concentration per unit volume of ice with the porosity of the ice (V_L) is:

$$c_{tot} = c_B V_L + c_E \, . \qquad (3)$$

Then, the diffusion equation becomes:

$$\frac{\partial c_{tot}}{\partial t} = \frac{\partial (c_B V_L)}{\partial t} + \frac{\partial c_E}{\partial t} = -\frac{\partial j}{\partial x_{eff}} \qquad (4)$$

where x_{eff} is related to the original distance x:

$$x_{eff} = \alpha(t)x \qquad (5)$$

If V_L is assumed to be constant, eqn (4) can be expressed as

$$\frac{\partial c_B}{\partial t}(V_L + p(t)L) = \frac{D_0}{\alpha(t)^2} p(t)L \frac{\partial^2 c_B}{\partial x^2} - Lc_B \frac{\partial p}{\partial t} \qquad (6)$$

When the solubility of CO_2 in ice is less than10^{-9} m^3 CO_2 STP m^{-3} ice Pa^{-1} CO_2 (4.5×10^{-8} mol CO_2 m^{-3} ice Pa^{-1} CO_2), $p(t)L$ is less than $0.025V_L$ at 144 m below the surface (half depth of the sample studied). The $p(t)L$ term can be omitted because $p(t)L \ll V_L$.

$$\frac{\partial c_B}{\partial t} = \frac{D_0}{\alpha(t)^2} p(t) \frac{L}{V_L} \frac{\partial^2 c_B}{\partial x^2} - \frac{L c_B}{V_L} \frac{\partial p}{\partial t} \tag{7}$$

The thinning factor $\alpha(t)$ is related to H (thickness of the ice sheet) and β (mean annual accumulation), and $p(t)$ to ρ (density of bubble ice) and $z(t)$ (depth below the surface):

$$\alpha(t) = \frac{H - z(t)}{H} \tag{8}$$

$$z(t) = H\left\{1 - \exp\left(-\frac{\beta t}{H}\right)\right\} \tag{9}$$

$$p(t) = \rho g z(t) \tag{10}$$

The final solution of the diffusion equation (eqn 7) is

$$c(x,T) = \frac{c_0}{2}\left\{erf\left(\frac{h-x}{2T^{1/2}}\right) + erf\left(\frac{h+x}{2T^{1/2}}\right)\right\} \exp\left(\frac{-L\rho}{V_L} gH\left\{1 - \frac{1}{1+(2\lambda T/D')^{1/2}}\right\}\right) \tag{11}$$

Where $T(t) = D_0 \frac{L}{V_L} \rho g H \left\{\frac{1}{2\lambda}\exp(2\lambda t) - \frac{1}{\lambda}\exp(\lambda t) + \frac{1}{2\lambda}\right\}$ (12)

$$\lambda = \frac{\beta}{H} \tag{13}$$

$$D' = D_0 \frac{L}{V_L} \rho g H \tag{14}$$

The constant parameters used for the Siple Dome ice studied are,

H	thickness of the ice sheet	1003.8 m
ρ	density of bubble ice	870 (± 20) kg m^{-3}

g	gravitational acceleration	9.8 m s^{-2}
β	mean annual accumulation	0.11 m yr^{-1}
V_L	porosity	0.05 (± 0.02)
h	half the width of a melt layer	0.00750 (± 0.00125) m for M1
		0.00510 (± 0.00085) m for M2
t	bubble gas age	8.80×10^{10} sec (2790 yr)

References

Ahn, J., M. Wahlen, B.L. Deck, E.J. Brook, P.A. Mayewski, K.C. Taylor, and J.W.C. White, A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica ice core, *J. Geophys. Res.*, *109, doi:10.1029/2003JD004415,* 2004.

Anklin, M., J.M. Barnola, J. Schwander, B. Stauffer, and D. Raynaud, Processes Affecting the CO_2 Concentrations Measured in Greenland Ice, *Tellus*, *47B*, 461-470, 1995.

Anklin, M., J. Schwander, B. Stauffer, J. Tschumi, A. Fuchs, J.M. Barnola, and D. Raynaud, CO_2 record between 40 and 8 kyr BP from the Greenland Ice Core Project ice core, *J. Geophys. Res.*, *102*, 26539-26545, 1997.

Barnola, J.M., M. Anklin, J. Porcheron, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 Evolution During the Last Millennium as Recorded by Antarctic and Greenland Ice, *Tellus*, *47B*, 264-272, 1995.

Campen, R.K., T. Sowers, and R.B. Alley, Evidence of microbial consortia metabolizing within a low-latitude mountain glacier, *Geology*, *31*, 231-234, 2003.

Das, S., West Antarctic ice sheet surface melting and Holocene Variability, Ph.D. thesis, Pennsylvania State University, 2003.

Delmas, R.J., A Natural Artifact in Greenland Ice-Core CO_2 Measurements, *Tellus*, *45B*, 391-396, 1993.

EPICA Community members, Eight glacial cycles from an Antarctic ice core, *Nature*, *429*, 623-628, 2004.

Fischer, H., M. Wahlen, J. Smith, D. Mastroianni, and B. Deck, Ice core records of atmospheric CO_2 around the last three glacial terminations, *Science*, *283*, 1712-1714, 1999.

Hondoh, T., *Clathrate Hydrates in Polar Ice Sheets*, 41-48 pp., 1996.

Ikeda-Fukazawa, T., K. Kawamura, and T. Hondoh, Mechanism of molecular diffusion in ice crystals, *Molecular Simulation*, *30*, 973-979, 2004.

Ikeda-Fukazawa, T., and K. Fukumizu, Solubility of gas molecules in ice crystals, *(submitted for publication)*, 2005.

Indermühle, A., T.F. Stocker, F. Joos, H. Fischer, H.J. Smith, M. Wahlen, B. Deck, D. Mastroianni, J. Tschumi, T. Blunier, R. Meyer, and B. Stauffer, Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica, *Nature*, *398*, 121-126, 1999.

Kawamura, K., T. Nakazawa, S. Aoki, S. Sugawara, Y. Fujii, and O. Watanabe, Atmospheric CO_2 variations over the last three glacial-interglacial climatic cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique, *Tellus*, *55B*, 126-137, 2003.

McConnell, J.R., Investigation of the atmosphere-snow transfer process for hydrogen peroxide, Ph.D. thesis, University of Arizona, Tucson, 1997.

Neftel, A., H. Oeschger, J. Schwander, and B. Stauffer, Carbon Dioxide Concentration in Bubbles of Natural Cold Ice, *J. Phys. Chem.*, *87*, 4116-4120, 1983.

Petit, J.R., J. Jouzel, D. Raynaud, N.I. Barkov, J.M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429-436, 1999.

Severinghaus, J.P., A. Grachev, and M. Battle, Thermal fractionation of air in polar firn by seasonal temperature gradients, *Geochem. Geophys. Geosys.*, *2*, 2000GC000146, 2001.

Severinghaus, J.P., A. Grachev, B. Luz, and N. Caillon, A method for precise measurement of argon 40/36 and krypton/argon ratios in trapped air in polar ice with applications to past firn thickness and abrupt climate change in Greenland and at Siple Dome, Antarctica, *Geochim. Cosmochim. Acta*, *67*, 325-343, 2003.

Severinghaus, J.P. and M. Battle, Fractionation of gases in polar ice during bubble close-off: new constraints from firn air Ne, Kr, and Xe, *Earth. Planet. Sci. Lett.*, (submitted), 2005.

Smith, H.J., M. Wahlen, D. Mastroianni, K. Taylor, and P. Mayewski, The CO_2 concentration of air trapped in Greenland Ice Sheet Project 2 ice formed during periods of rapid climate change, *J. Geophys. Res.*, *102*, 26577-26582, 1997a.

Smith, H.J., M. Wahlen, D. Mastroianni, and K.C. Taylor, The CO_2 concentration of air trapped in GISP2 ice from the last glacial maximum-holocene transition, *Geophys. Res. Lett.*, *24*, 1-4, 1997b.

Stauffer, B., A. Neftel, H. Oeschger, and J. Schwander, CO_2 concentration in air extracted from Greenland ice samples, in *Greenland Ice Core: Geophysics, Geochemistry and the Environment*, edited by C.C.Langway et al., pp. 85-89, AGU, Washington, D.C., 1985.

Taylor, K.C., R.B. Alley, D.A. Meese, M.K. Spencer, E.J. Brook, N.W. Dunbar, R.C. Finkle, A.J. Gow, A.V. Kurbatov, G.W. Lamorey, P.A. Mayewski, E.A. Meyerson, K. Nishiizumi and G.A. Zielinski, Dating the Siple Dome (Antarctica) ice core by manual and computer interpretation of annual layering, *J. Glaciol.*, *50*, 453-461, 2004.

Tschumi, J., and B. Stauffer, Reconstructing past atmospheric CO_2 concentration based on ice-core analyses: open questions due to in situ production of CO_2 in the ice, *J. Glaciol.*, *46*, 45-53, 2000.

Wahlen, M., D. Allen, B. Deck, and A. Herchenroder, Initial measurements of CO_2 concentrations (1530 to 1940-Ad) in air occluded in the GISP2 ice core from central Greenland, *Geophys. Res. Lett.*, *18*, 1457-1460, 1991.

Table 1. Solubilities of air components in water for Siple Dome.

	air	N_2	O_2	Ar	CO_2	Kr	Xe
X_{atm}	100%	78.08%	20.95%	0.93%	278 ppm	1.14 ppm	0.087 ppm
X_{H2O}	100%	62.38%	34.33%	1.68%	16230 ppm	4.21 ppm	0.679 ppm

X_{atm}, composition of atmospheric air; X_{H2O}, air dissolved in water at 0 °C and 937 mbar.

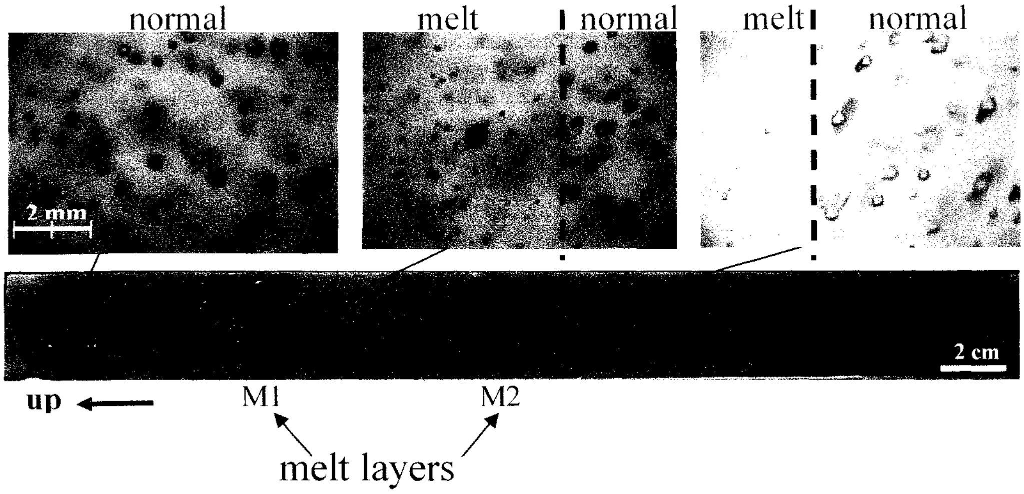


Figure 1. Photographs of air bubbles in the Siple Dome ice core. (a) Melt layers visually defined by small bubbles and relatively transparent layer. (b) Microphotographs of air bubbles around melt layers.

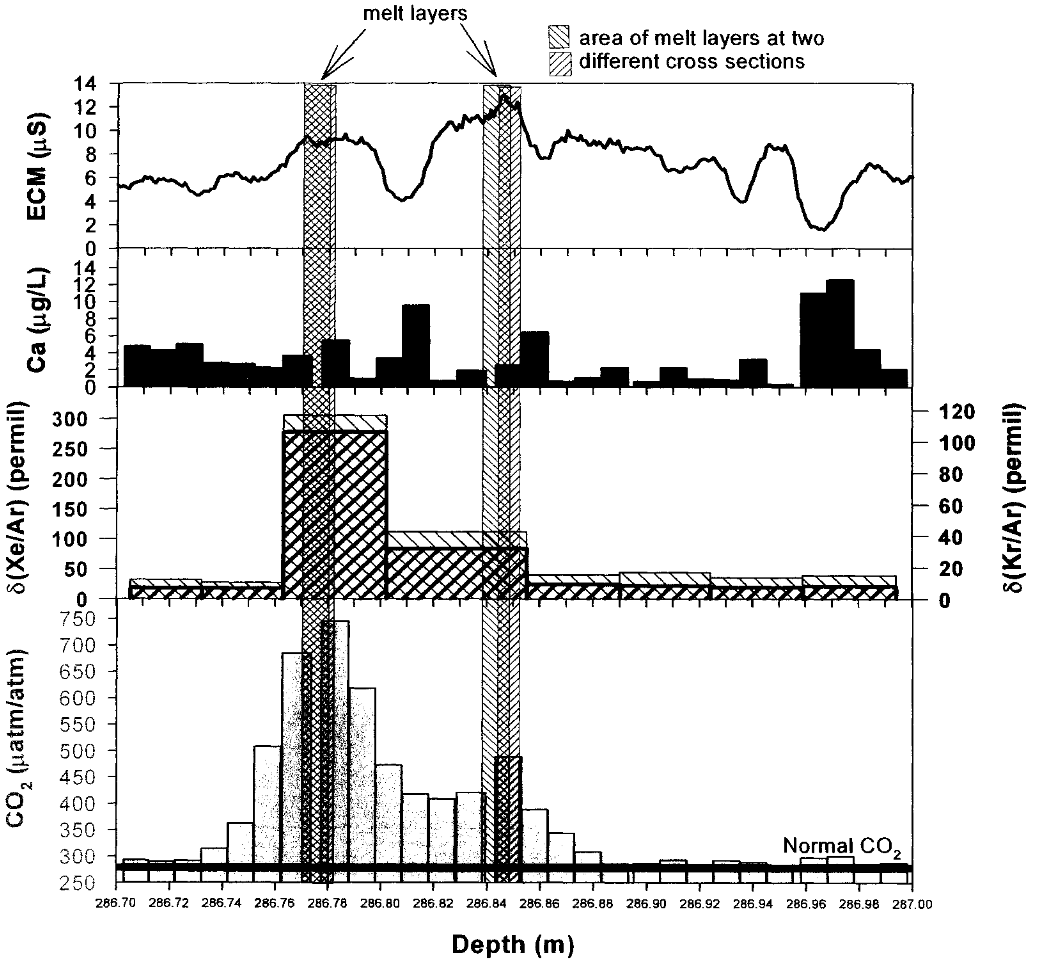


Figure 2. Variation of ECM (Electric Conductivity measurement, proxy for H^+) in units of μS (microsiemens), Ca^{2+} ion (upper limit of $CaCO_3$), Xe/Ar and Kr/Ar (melt layer indicators) and CO_2 around the melt layers shown in Figure 1. δ(Xe/Ar) and δ(Kr/Ar) are normalized to present atmospheric air. The minor and rather constant enrichment of Kr and Xe are due to gravitational settling in the firn and do not indicate substantial melting/refreezing.

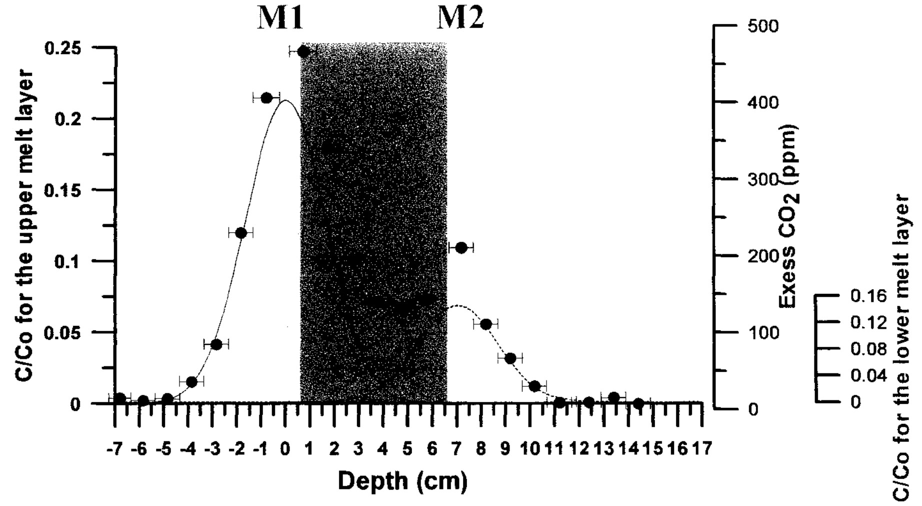


Figure 3. Comparison of excess CO_2 concentration from the observations (red dots) to the prediction by modeling (black line for M1 and blue broken line for M2). c_0, CO_2 volume concentration before diffusion; c, after diffusion. Two different (c/c_0)s are used for M1 and M2. The horizontal bars are depth intervals of samples. Purple and green areas denote melt layer (M1 and M2). Partial melt layers exist in between. The model curves are fitted to CO_2 observation in the normal layer. In this model, we assume constant gas content in the ice. Thus, the CO_2 concentrations from the melt layer or partial melt layer apparently show higher values than those in the fitting curve because of the small gas contents compared to normal layers.

CHAPTER IV

Excess CO_2 in an Antarctica ice core:

Observations from the Siple Dome

Abstract. The CO_2 records from Antarctic ice cores are considered to be more representative of paleoatmospheric concentrations than those from Greenland ice cores because the low dust content in Antarctic ice minimizes the in situ production of CO_2 by carbonate-acid reaction and/or oxidation of organic compounds as observed in Greenland ice cores. Despite general similarities in time series of CO_2 records with other Antarctic ice cores, the Siple Dome ice, at some age intervals, shows higher CO_2 concentrations of up to 20 ppm (μmol CO_2 / mol air) than those in other Antarctic ice cores [*Ahn et al.*, 2004]. In order to examine the possible mechanisms for the excess CO_2 in the Siple Dome ice core, we studied several sets of adjacent samples at high depth resolution. CO_2 concentrations are compared to melt layer distribution, major ions (Ca^{2+} and Na^{+}) contents, electric conductivity of ice, noble gas (Xe, Kr, and Ar) contents and $^{13}C/^{12}C$ of CO_2. The main process of the production of the excess CO_2 is possibly the snow melting/refreezing due to the high solubility of CO_2 relative to other atmospheric gas species. Our results show that Antarctic ice samples from relatively warm sites are not an accurate proxy for paleoatmospheric CO_2.

1. Introduction

The CO_2 records derived from Antarctic ice cores are widely believed to be representative of atmospheric concentrations over several glacial-interglacial cycles [*Fischer et al.*, 1999; *Petit et al.*, 1999; *Kawamura et al.*, 2003; *EPICA community members*, 2004]. This is not the case for CO_2 records from the Greenland ice cores where in situ production of CO_2 is due to high dust content including $CaCO_3$ and

$MgCO_3$ under acidic conditions [*Delmas*, 1993] and oxidation of organic compounds [*Tschumi and Stauffer*, 2000], which corrupt the atmospheric record of CO_2.

Ice cores from high-accumulation sites enable studies of abrupt climate change [*Severinghaus et al.*, 1998]. Samples from high accumulation sites allow studies with high temporal resolution and an accurate assessment of the relative timing between ice isotope variations (i.e., $\delta^{18}O_{ice}$ and $\delta^{18}D_{ice}$: surface temperature proxies) and variations in trapped gases such as atmospheric CO_2. However, the mean annual temperatures for the high accumulation sites are typically higher than those for low accumulation sites. This warm temperature may lead to the formation of excess CO_2 due to melting of the snow in summer as previously observed in Greenland ice cores [*Neftel et al.*, 1983; *Stauffer et al.*, 1985]. In the melt CO_2 is more soluble than other atmospheric gas species, leading to uptake of CO_2 from the atmosphere.

The Siple Dome ice core site is located near the Antarctic Ross Sea (Figure 1) where the snow accumulation rate is high (12.4 g cm^{-2} yr^{-1}) [*Hamilton*, 2003]. The annual mean temperature at Siple Dome (-25.4 °C) is warmer than at other Antarctic ice core sites (Table 1). While the summer air temperature is also well below the melting point, with mean summer temperature of -11.5 °C (standard deviation of 3.1 °C) [*Das and Alley*, in press], temperatures do reach the melting point during extreme and brief warming events at > 2 °C, and surface melting presently occurs on the order of two to four times per century [*Das*, 2003]. Observations and field experiments at Siple Dome by *Das and Alley* [in press] have shown that once the surface crust due to strong capillary forces. The refozen melt in the crust forms visually detectable melt layers in the ice core that are defined by reduced bubble sizes, and these melt layers have been logged throughout the Siple Dome ice core [*Das*, 2003].

Despite similarities in the general time series of the Siple Dome CO_2 record with other Antarctic ice cores, the Siple Dome ice, at some age intervals, shows higher CO_2 concentrations of up to 20 ppm (μmol CO_2 / mol air) than in other Antarctic ice cores (Ahn et al., 2004).

Here we discuss possible mechanisms for the production of excess CO_2 in the Siple Dome ice by studying the melt layer distribution, CO_2 concentration, major ion content (Ca^{2+}, Na^{+}), electric conductivity and $^{13}C/^{12}C$ of CO_2 in several sets of vertically adjacent samples.

2. Materials and Methods

Ten sets of vertically adjacent samples (1-2 cm depth interval for each) were measured over 10-30 cm intervals for CO_2, and major ions were measured for 3 of the 10 sets. All the 10 sets are compared to the electric conductivity measurements (ECM) at 1-mm depth resolution. Noble gas ratios (Xe/Ar, Kr/Ar) were measured in several samples to test for solubility effects independently of chemical and biological effects. In addition, $^{13}C/^{12}C$ of CO_2 was measured and is compared to the excess CO_2. All samples were carefully trimmed in order to minimize possible modern atmospheric contamination of ice near the outer surface of the core. Storing and cutting was done at –25 °C. The gas extraction and IR spectroscopic methods used are well established [*Wahlen et al.*, 1991; *Smith et al.*, 1997a; *Smith et al.*, 1997b; *Ahn et al.*, 2004]. Trapped air was dry extracted by a mechanical needle crusher of samples of ~ 4 to 6

cm^3 at ~ -50 °C. Then, the total liberated air was frozen into miniature cold traps at temperatures of ~ 32 K. The cooling was achieved with closed cycle He refrigerators. Three standard air samples encompassing the CO_2 concentrations (161.0, 240.3, and 329.5 ppm) were introduced over the crushed ice for every six samples after the ice had been pumped for 15 minutes, in order to most closely reproduce the conditions under which ice air from the samples was collected. Upon heating the trapped air, the samples were transferred with a metal bellow between two valves into an Infrared (IR) cell in order to obtain the same pressure and temperature for all samples. Measurements were performed several times with tunable diode laser spectroscopy by scanning the single mode laser IR output over a single vibrational-rotational CO_2 absorption line at low pressure (Doppler resolution). From calibrations with standard airs, we calculate the mixing ratio of CO_2 in the ice air (~500 μL STP of air). The internal precision of a CO_2 concentration measurement is ±2 ppm.

We used ~ 5 g of ice for major ion concentration measurements. The ice was prepared at the Scripps Institution of Oceanography, and measured at the Climate Change Institute at the University of Maine, using Dionex-500 Ion Chromatography. Major cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed on Dionex DX-500 ion chromatographs. The cations passed through a CS 12A Cation-exchange column with 25 mM methanesulfonic acid eluent, a self regenerating suppressor, and a conductivity detector. Sample size was 500 μL. An Ion Handler chromatograph was used with a Gilson Liquid autosampler.

3. Excess CO_2 and possible production mechanisms

In general the Siple Dome CO_2 record is similar to other Antarctic ice core records (Figure 2) [*Ahn et al.*, 2004]. However, as shown in figure 2b, in some time intervals, the Siple Dome CO_2 records show higher values than those from other Antarctic ice cores by up to 20 ppm. In order to decipher the major mechanisms of excess CO_2 production, we group data for five age intervals (A to E, Figure 2f) and use the CO_2 difference between Siple Dome and Taylor Dome or Dome C (Figure 2c). We call these CO_2 differences between cores "excess CO_2." Part of the CO_2 difference during rapid change (group D) can be explained by uncertainties in the age scales. However, during times of slow change in CO_2, (group A, B, C and E) differences cannot be explained by these uncertainties. During most of the cold period (E in Fig. 2f, 40 to 23 kyrBP) the CO_2 data from Siple Dome ice shows little difference when compared to other cores. Each data point in Figure 2b is an average of six neighboring samples and the scatter is indicated as an error bar (1σ, standard deviation of the mean). The average scatter of CO_2 for each age group is plotted in Figure 3 against excess CO_2 (A to E in Figure 2f) and shows a correlation ($R = 0.58$ and 0.42 for Siple Dome vs. Taylor Dome and Siple Dome vs. Dome C, respectively).

The above observations imply the possibility that there are some artifacts in the Siple Dome CO_2 record. Data scattering among neighboring samples can be attributed to variable conditions at the surface or during gas trapping in the firn layer (snowpack). Atmospheric CO_2 change cannot be the cause of the scattering of the record because it would be smoothed out by the gradual bubble close-off process. For example, for Siple Dome ice the smoothing due to the close-off process is about 20-120 years and corresponds to about 200-100 cm thickness of ice, which is much greater than the depth interval among six samples (usually 1-2 cm). Contamination by modern air through cracks in the ice cannot account for the excess CO_2 because there is high excess CO_2 in the late Holocene Siple Dome ice where fracturing is minimal, but low excess CO_2 in glacial ice where Siple Dome ice is highly fractured [*Ahn et al.*, 2004].

Possible mechanisms for the excess CO_2 include (1) snowmelting-refreezing [*Neftel et al.*, 1983; *Stauffer et al.*, 1985], (2) carbonate-acid reaction [*Delmas*, 1993; *Anklin et al.*, 1995; *Barnola et al.*, 1995; *Anklin et al.*, 1997; *Smith et al.*, 1997a; *Smith et al.*, 1997b], (3) oxidation of organic compounds abiologically [*Tschumi and Stauffer*, 2000], or biologically [*Campen et al.*, 2003]. Gravitational fractionation [*Craig et al.*, 1988] can only enrich the CO_2 concentration by about 1 ppm.

CO_2 is considerably enriched in melt layers due to the high solubility of CO_2 gas in the melt [*Neftel et al.*, 1983]. For example, at Dye 3, Greenland, the melt layers show a mean CO_2 concentration of 1500 ppm [*Stauffer et al.*, 1985]. The mean temperature of Siple Dome is –25.4 °C, and the mean summer temperature is -11.5 °C [Das and Alley, in press]. However, occasional melting events during austral summer were reported [*Das*, 2003]. At the present surface pressure condition at Siple Dome, we can expect 16,230 μmol CO_2 / mol air in melt water at 0 °C in equilibrium (Andrew Dickson, personal communication). Samples measured in Siple Dome shown in Figure 2 do not include any visible melt layers. However, the occurrence of excess CO_2 is weakly associated with that of melt layers (Figures 2c and 2d). If the melting on the surface is not enough to cause downward melt water percolation and concentration and refreezing in crusts or other high density layers, it may not form visible melt layers in the ice and cannot be detected solely by the size distribution of bubbles. Similarly, refrozen snow layers have been observed in the vicinity of melt layers during melt experiments at Siple Dome by Das and Alley (in press). However, the effect of this melting even without the formation of distinct melt layers could still be sufficient to increase the CO_2 concentration somewhat in the ice bubbles. For example, in order to produce 20 ppm of excess CO_2, only 0.5 % by volume of refrozen melt in the ice is required (Figure 4).

Acid-carbonate reactions were suggested to affect the Greenland ice-core CO_2 records [*Delmas,* 1993; *Barnola et al.*, 1995; *Anklin et al.*, 1995; *Smith et al*, 1997a and b]. *Neftel et al.* [1988] suggested that the most likely mechanism is the chemical reaction between $CaCO_3$ and H^+ ($CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$), which can occur only when the ice is sufficiently acidic to drive decarbonation, and some $CaCO_3$ remains in the ice after bubble formation [*Smith et al.*, 1997a]. The potential CO_2 production by the decarbonation reaction can be calculated as shown in figure 2e. During the Holocene period, the average potential CO_2 is 2.65 ppm, which is lower than the observed excess CO_2 values in the Siple Dome ice core (figure 2c). Moreover, it is unlikely that 100 % of the potential CO_2 is produced by decarbonation, because in the calculation we assume that (1) there is enough H^+, and (2) 100 % of Ca^{2+} originates from decarbonation.

Oxidation of organic compounds has been proposed to be at least as important as acid-carbonate reactions for CO_2 production (e.g., $2H_2O_2 + HCHO \rightarrow 3H_2O + CO_2$) [*Tschumi and Stauffer,* 2000] (Organic acid concentrations in the Siple Dome ice core have not yet been reported). Hydrogen peroxide (H_2O_2) is one of the important oxidants of organic compounds in ice. The top 100 m (except 0-2.5 m) of the Siple

Dome ice core shows concentrations near or below the detection limit of ~ 0.02 μM H_2O_2 [*McConnell*, 1997]. This H_2O_2 concentration is lower than in other Antarctic ice cores [*Tschumi and Stauffer*, 2000] and corresponds to a potential CO_2 production of less than 5 ppm, assuming an adequate supply of organic acids. This does not easily explain the 20 ppm excess CO_2. Beside H_2O_2, HCHO, CH_3COO^- and $HCOO^-$ are other oxidants [*Tschumi and Stauffer*, 2000].

Another possible CO_2 production mechanism is respiration by microorganisms (consuming organic matter and producing CO_2) within the ice [*Campen et al.*, 2003]. In the following section, results from the high depth-resolution study will be discussed to decipher the dominant mechanisms for production of excess CO_2 in the Siple Dome ice core.

4. High depth resolution study

In this section we will discuss results from ice samples of three categories: (1) ice with distinct melt layers, (2) ice near melt layers within 20 cm, and (3) ice more than one meter distant from melt layers.

4.1. 30-cm long ice core with strong melt layers

A 30-cm long ice core segment with strong melt layers was studied intensively. The age of this ice is ~3.04 kyrBP (thousand years before 1950). The depth is 286.7 to 287.0 m. Two melt layers (~1 cm thick) in this sample show smaller bubbles than those existing in a normal non-melt layer ice (Figure 5a). Around the melt layers, we observe increased levels of CO_2 (Figure 5b). The excess CO_2 reaches up to 470 ppm.

The Xe/Ar and Kr/Ar are used as indicators of extensive snow melting/refreezing, because Xe and Kr are about four and two times more soluble in liquid water, respectively, than Ar [*Severinghaus et al.*, 2003]. We observe significant increases of Xe/Ar and Kr/Ar from the samples that include melt layers or partial melt ice. However, increased levels of excess CO_2 around the melt layers are explained by CO_2 diffusion away from the melt layers toward the neighboring ice. The details of the diffusion are discussed in another paper [*Ahn et al.*, 2005]. The Ca ion content and electric conductivity measurements (ECM) do not correlate with excess CO_2, nor do they indicate that the excess CO_2 is caused by the decarbonation reaction. Oxidation of organic compounds cannot produce more than 30 ppm of excess CO_2 as shown by the difference between Antarctic and Greenland ice core records [*Anklin et al.*, 1995; *Barnola et al.*, 1995]. The above observations strongly suggest that snow melting/refreezing without formation of visible layers is the major mechanism for the production of excess CO_2 in the vicinity of melt layers.

4.2. Excess CO_2 near melt layers

Figure 6a is the enlarged portion of the right baseline part of Figure 5b. The excess CO_2 at the baseline value far outside the melt layers is 11.5 ± 6.0 ppm (1σ) (Figure 6a). Two more samples near melt layers were studied (Figures 6b and 6c). Figure 6b shows excess CO_2 up to about 30 ppm near a thin melt layer (2 mm thick). Near the sample adjacent to those shown in Figure 6c, another melt layer is located (6.5 cm from the upper end). The averages of excess CO_2 are 13.8 ± 10.2 ppm (1σ) and 15.8 ± 5.1 ppm for Figures 6b and 6c, respectively. If the excess CO_2 in the samples of Figure 6 (average 13.7 ± 7.5 ppm) originated from the refrozen melt, the volume ratio of refrozen melt to total ice is 0.0034 ± 0.0019. This small amount of melt may not be enough to create any observable size reduction of bubbles. This quantity of refrozen melt corresponds to δXe/Ar and δKr/Ar of 5.1 ± 2.8 ‰ and 2.8 ± 0.9 ‰, respectively. Unfortunately, these are within the experimental precision of 3.8 ‰ and 1.6 ‰ for δXe/Ar and δKr/Ar, respectively (pooled standard errors of triplicate measurements for the GISP2 ice core of the Holocene). Visible melt layers form at pre-existing horizontal strata when melt quantity is large. Therefore, any small-scale melting would not form visible melt layer. Moreover, the thickness of a micro-melt layer on the ice crystal surface increases rapidly as temperature approaches 0 °C with thicknesses of >15-40 nm depending on techniques used (e.g., *Döppenschmidt and Butt* [2000]; *Sadtchenko and Ewing* [2002]). Combined with a snow surface area of about 700 cm^2 g^{-1} ice [*Domine' et al.*, 2001], excess CO_2 due to micro-melt layers near 0 °C could approach 10 ppm.

The Na^+ concentration is considered to be an indicator of the flux of sea salt delivered to the ice sheet by snow. The Na^+ is well correlated with Ca^{2+} (R = 0.99, 0.68 and 0.79 for Figures 6a, 6b and 6c, respectively). Non-sea-salt Ca (nssCa) is calculated using the equation $nssCa = Ca_{ice}\ \{1 - Na_{ice}\ (Ca/Na)_{ocean}\}$. This is –80, +66, and +61% of the total Ca contents shown in Figures 6a, 6b and 6c. The above features indicate that a significant amount of Ca^{2+} originated from sea salt. We believe that most of the $CaCO_3$ originated from land near Antarctica [*Basile et al.*, 1997]. The correlation of CO_2 and Ca^{2+} is not significant (R=0.002, 0.252 and 0.145 for Figures 6a, 6b and 6c, respectively). Also, there is little correlation between CO_2 and ECM.

Thus, we conclude that the carbonate-acid reaction is not the main contributor to excess CO_2 in the Siple Dome ice core.

4.3. Excess CO_2 far from melt layers

We also studied ice samples at high depth-resolution where no melt layers are observed near samples (within 1 m) (Figure 7). The excess CO_2 and data scattering (1σ) is noted on the graphs in Figure 7 and averages 8.1 ppm. The average amounts of excess CO_2 are smaller than those near melt layers as shown in Figure 6. The glacial ice exhibits less scattering than Holocene ice (Figures 2b, 6, and 7). Even taking into account the smoothing of CO_2 records, the CO_2 scattering for the glacial ice is still significantly smaller than that for the Holocene ice. Each sample set does not show any significant correlation between CO_2 and ECM.

5. Stable isotopic study on $\delta^{13}C$ of CO_2

Natural organic acids and other organic materials have much lower values of $\delta^{13}CO_2$ $((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard(VPDB)} -1) \times 1000$ ‰), approximately -25 ‰, compared to atmospheric $\delta^{13}CO_2$ (preindustrial value of about -6.5 ‰) and $CaCO_3$ (0 ~ +4 ‰). Thus, precise $\delta^{13}CO_2$ values could be used to investigate the sources of excess CO_2. For example, if the early Holocene CO_2 record has excess CO_2 values of 20 ppm derived from organic materials, it would reduce the $\delta^{13}CO_2$ value by about 1 ‰. $^{13}CO_2$ analyses in the Siple Dome ice core are compared to those from the Taylor Dome ice core in Figure 8. Details of the methods and interpretations of the $\delta^{13}CO_2$

data are discussed in another paper. The $\delta^{13}CO_2$ values from the Siple Dome ice are more scattered than those of the Taylor Dome ice, and are depleted by 0.6 ‰ on average. The two minimal $\delta^{13}CO_2$ values around 12 kyrBP are related to excess CO_2 of ~ 20 ppm. However, the amount of the depletion (~2.3 ‰) is more than two times greater than that expected by the oxidation of the organic compounds (1 ‰). The scattering of the isotopic values are greater than experimental precision (~0.1 ‰) and can probably be attributed to a kinetic isotopic fractionation in the firn layer (snowpack), probably during snow melting/refreezing. For example, invasion of the light isotope is expected to be faster during uptake by melt water from the atmosphere. If correct, this interpretation implies an isotopic disequilibrium.

6. Conclusion

The Siple Dome ice shows higher CO_2 concentrations by up to ~20 ppm than those in other Antarctic ice cores at particular age intervals. This is attributed to non-atmospheric excess CO_2. Several possible mechanisms to produce excess CO_2 are discussed. The most probable process is melting/refreezing of snow. Elevated CO_2 around distinct melt layers supports this idea. This is the first evidence of excess CO_2 in an Antarctic ice core, and future coring at warm sites in Antarctica needs to be done cautiously.

Acknowledgments. We wish to greatly thank to Sharon Sneed and Jackson Wong for their assistance during experiments. We also give special thank to Bruce Deck for his technical advice. Alane Bollenbacher is appreciated for the preparation of the CO_2

standard air. Ice cores were kindly cut at the National Ice Core Laboratory. This early work was supported by the Office of Polar Program of the NSF (NSF OPP 99-80619). This chapter is reproduced fully, with permission from: Ahn, J., M. Wahlen, J. Severinghaus, M. Headly, P.A. Mayewski, E.J. Brook, S. Das and K. Taylor (2005) "Excess CO_2 in an Antarctic ice core: Observations from the Siple Dome". Quaternary Science Reviews (to be submitted).

References

Ahn, J., M. Wahlen, B.L. Deck, E.J. Brook, P.A. Mayewski, K.C. Taylor, and J.W.C. White, A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica ice core, *J. Geophys. Res.*, *109, doi:10.1029/2003JD004415,* 2004.

Ahn, J., J. Severinghaus, M. Headly, M. Wahlen, E.J. Brook, P.A. Mayewski, and K.C. Taylor, CO_2 diffusion in polar ice: Observations from the Siple Dome, Antarctic ice core, *Earth and Planett. Sci. Lett., submitted*, 2005.

Anklin, M., J.M. Barnola, J. Schwander, B. Stauffer, and D. Raynaud, Processes Affecting the CO_2 Concentrations Measured in Greenland Ice, *Tellus*, *47B*, 461-470, 1995.

Anklin, M., J. Schwander, B. Stauffer, J. Tschumi, A. Fuchs, J.M. Barnola, and D. Raynaud, CO_2 record between 40 and 8 kyr BP from the Greenland Ice Core Project ice core, *J. Geophys. Res.*, *102*, 26539-26545, 1997.

Barnola, J.M., M. Anklin, J. Porcheron, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 Evolution During the Last Millennium as Recorded by Antarctic and Greenland Ice, *Tellus*, *47B*, 264-272, 1995.

Campen, R.K., T. Sowers, and R.B. Alley, Evidence of microbial consortia metabolizing within a low-latitude mountain glacier, *Geol.*, *31*, 231-234, 2003.

Das, S., West Antarctic ice sheet surface melting and Holocene Variability, Ph.D. thesis, Pennsylvania State University, 2003.

Delmas, R.J., A Natural Artifact in Greenland Ice-Core CO_2 Measurements, *Tellus*, *45B*, 391-396, 1993.

Dome-F Deep Coring Group, Deep ice-core drilling at Dome Fuji and glaciological studies in east Dronning Maud Land, Antarctica. *Ann. Glaciol., 27,* 333-337, 1998.

Dominé, F., Cabanes, A., Taillandier, A., and Legagneux, L., Specific surface area of snow samples determined by CH4 adsorption at 77 K and estimated by optical microscopy and scanning electron microscopy, *Environ. Sci. Technol., 35*, 771-180, 2001.

Döppenschmidt, A., and H. Butt, Measuring the thickness of the liquild-like layer on ice surface with Atomic Force Microscopy, *Langmuir, 16*, 6709-6714, 2000.

EPICA Dome C 2001-02 Science and drilling teams, Extending the ice core record beyond half a million years, *Eos Trans. AGU, 83*(45), 509, 517, 2002.

EPICA community members, Eight glacial cycles from an Antarctic ice core, *Nature*, *429*, 623-628, 2004.

Etheridge, D. M. and C. W. Wookey, Ice core drilling at a high accumulation area of Law Dome, Antarctica, in Ice Core Drilling, edited by C. Rado and D. Beaudoing, pp. 86-96, *Proceedings of the Third International Workshop on Ice Core Drilling Technology,* Grenoble, France, October 10-14, 1988, CNRS, Grenoble, 1989.

Etheridge, D. M., L. P. Steele, R. L. Langenfelds, R. J. Francey, J.-M. Barnola and V. I. Morgan, 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, 1996.

Fischer, H., M. Wahlen, J. Smith, D. Mastroianni, and B. Deck, Ice core records of atmospheric CO_2 around the last three glacial terminations, *Science*, *283*, 1712-1714, 1999.

Hamilton, G.S. Mass balance and accumulation rate across Siple Dome, West Antarctica. *Annals of Glaciol., 35,* 102-106, 2002.

Kawamura, K., T. Nakazawa, S. Aoki, S. Sugawara, Y. Fujii, and O. Watanabe, Atmospheric CO_2 variations over the last three glacial-interglacial climatic cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique, *Tellus*, *55B*, 126-137, 2003.

McConnell, J.R., Investigation of the atmosphere-snow transfer process for hydrogen peroxide, Ph.D. thesis, University of Arizona, Tucson, 1997.

Neftel, A., H. Oeschger, J. Schwander, and B. Stauffer, Carbon Dioxide Concentration in Bubbles of Natural Cold Ice, *J. Phys. Chem.*, *87*, 4116-4120, 1983.

Petit, J.R., J. Jouzel, D. Raynaud, N.I. Barkov, J.M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429-436, 1999.

Raynaud, D., J. Jouzel, J. M. Barnola, J. Chappellaz, R. J. Delmas, and C. Lorius, The ice record of greenhouse gases, *Science, 259,* 926-934, 1993.

Sadtchenko, V., and G.E. Ewing, Interfacial melting of thin ice films: An infrared study, *J. Cehm. Phys.*, *116*, 4686-4697, 2002.

Severinghaus, J.P., T. Sowers, E.J. Brook, R.B. Alley, and M.L. Bender, Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice, *Nature, 391*, 141-146, 1998.

Severinghaus, J.P., A. Grachev, B. Luz, and N. Caillon, A method for precise measurement of argon 40/36 and krypton/argon ratios in trapped air in polar ice with applications to past firn thickness and abrupt climate change in Greenland and at Siple Dome, Antarctica, *Geochim. Cosmochim. Acta*, *67*, 325-343, 2003.

Schwander, J., J. Jouzel, C. U. Hammer, J.-R. Petit, R. Udisti, and E. Wolff, A tentative chronology for the EPICA Dome Concordia ice core, *Geophys. Res. Lett., 28,* 4243-4246, 2001.

Smith, H.J., M. Wahlen, D. Mastroianni, K. Taylor, and P. Mayewski, The CO_2 concentration of air trapped in Greenland Ice Sheet Project 2 ice formed during periods of rapid climate change, *J. Geophys. Res.*, *102*, 26577-26582, 1997a.

Smith, H.J., M. Wahlen, D. Mastroianni, and K.C. Taylor, The CO_2 concentration of air trapped in GISP2 ice from the last glacial maximum-holocene transition, *Geophys. Res. Lett.*, *24*, 1-4, 1997b.

Stauffer, B., A. Neftel, H. Oeschger, and J. Schwander, CO_2 concentration in air extracted from Greenland ice samples, in *Greenland Ice Core: Geophysics, Geochem. Environ.*, edited by C.C. Langway et. al., pp. 85-89, AGU, Washington, D.C., 1985.

Steig, E. J., D. L. Morse, E. D. Waddington and P. J. Polissar, Using the sunspot cycle to date ice cores, *Geophys. Res. Lett., 25,* 163-166, 1998.

Tabacco, I. E., A. Passerini, F. Corbelli, and M. Gorman, Determination of the surface and bed topography at Dome C, East Antarctica, *J. Glaciol., 44,* 185-191, 1988.

Taylor, K. C., J. W. C. White, J. P. Severinghaus, E. J. Brook, P. A. Mayewski, R. B. Alley, E. J. Steig, M. K. Spencer, E. Meyerson, D. A. Meese, G. W. Lamorey, A. Grachev, A. J. Gow and B. A. Barnett, Abrupt climate change around 22 ka on the Siple Coast of Antarctica, *Quat. Sci. Rev.*, 23, 7-15, 2004.

Tschumi, J., and B. Stauffer, Reconstructing past atmospheric CO_2 concentration based on ice-core analyses: open questions due to in situ production of CO_2 in the ice, *J. Glaciol.*, *46*, 45-53, 2000.

Waddington, E. D. and D. L. Morse, Spatial variations of local climate at Taylor Dome, Antarctica: Implications for paleoclimate from ice cores. *Ann. Glaciol., 20,* 219-225, 1994.

Wahlen, M., D. Allen, B. Deck, and A. Herchenroder, Initial measurement of CO_2 concentrations (1530 to 1940 AD) in air occluded in the GISP2 ice core form central Greenland, *Geophys. Res. Lett. 18*, 1457-1460, 1991.

Table 1. Glaciological characteristics of the Antarctic ice cores

Core sites	Mean annual temperature (°C)	Mean accumulation rate as water equivalent (g cm^{-2} yr^{-1})	Elevation (m)
Siple Dome	**-25.4**[a]	**12.4**[b]	**621**[c]
Law Dome	-22 ~ -19[d,e]	60 ~ 110[e]	1390[e]
Byrd[f]	-28	16	1530
Taylor Dome	-42[g]	7[h]	2374[h]
EPICA Dome C	-54[I]	3[j]	3233[k]
Vostok[f]	-55.5	2.3	3490
Dome Fuji[l]	-58	3.2	3810

[a][*Severinghaus et al.*, 2001]; [b][*Hamilton,* 2002]; [c][*Taylor et al.*, 2004b]; [d][*Etheridge and Wookey,* 1989]; [e][*Etheridge et al.*, 1996]; [f][*Raynaud et al.*, 1993]; [g][*Waddington and Morse,* 1994]; [h] as unit of cm ice equivalent per year [*Steig et al.*, 1998]; [i][*Schwander et al.*,2001];[j][*The EPICA Dome C 2001-02 science and drilling teams,* 2002]; [k][*Tabacco et al.*, 1998]; [l][*Dome-F Deep Coring Group,* 1998]

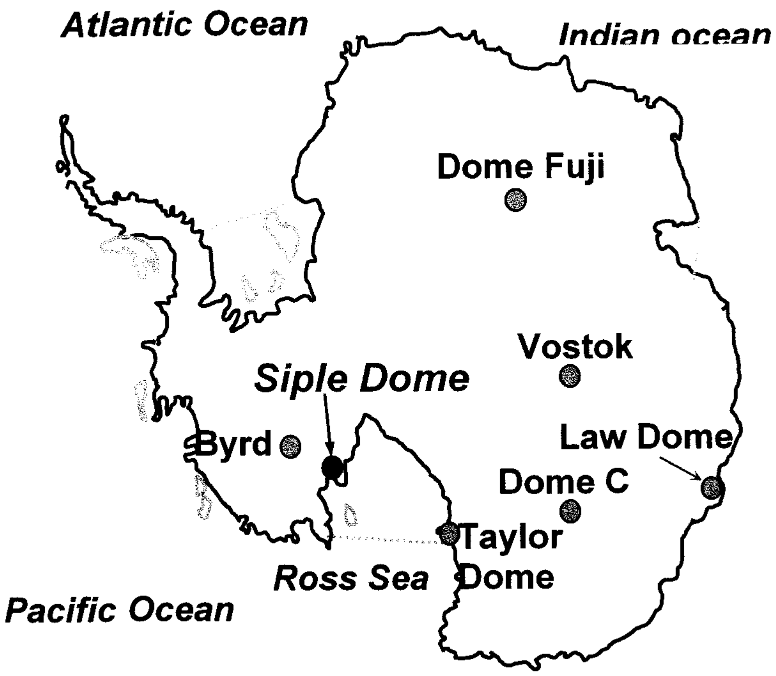


Figure 1. Location map of Antarctic ice cores.

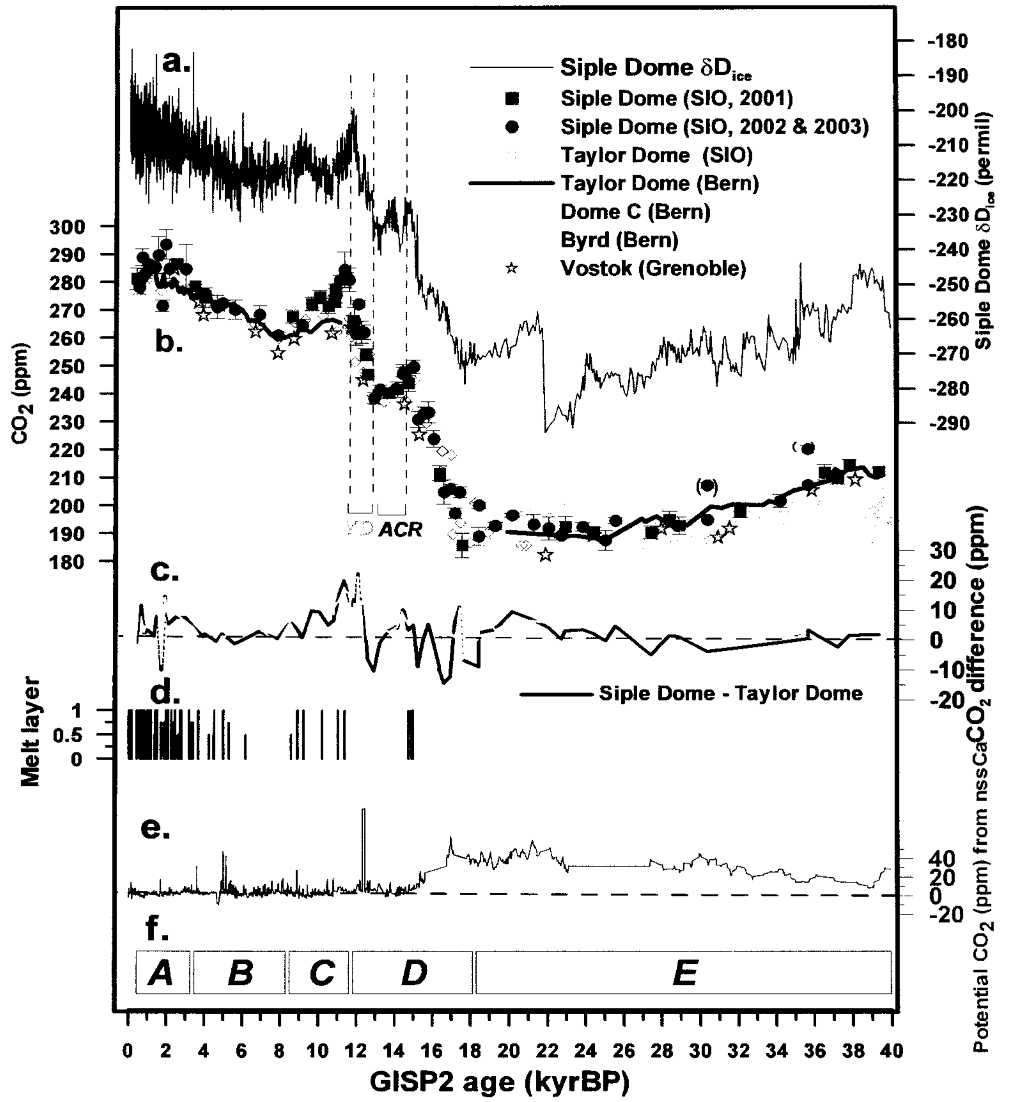


Figure 2. Comparison of Antactic ice core CO$_2$ records on GISP2 gas age scale (modified from *Ahn et al.* [2004]). (a) Siple Dome δD$_{ice}$. (b) Antarctic ice core CO$_2$ records. Error bars represent one standard deviation of replicate measurements at the same depth interval. The brackets indicate averages of two anomalously high values of the six samples from the same depth interval. (c) Difference in CO$_2$ records. (d) Melt layers [*Das*, 2003]. The lengths of bars indicate the confidence level. 1, sure; 0.75, probable; 0.5, possible. (e) Potential excess CO$_2$ from acid-carbonate reaction. The dashed horizontal line represents 0. Non-sea-salt Ca (nssCa) was assumed to have been in the form of CaCO$_3$ and totally reacted with excess H$^+$. (f) Data groups (A ~ E) for the analysis shown in Fig. 3. YD, Younger Dryas; ACR, Antarctic Cold Reversal.

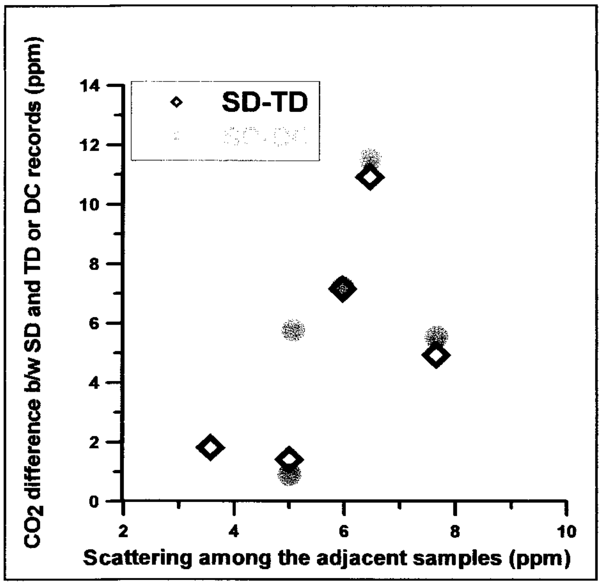


Figure 3. Correlation between data scattering among the adjacent samples (1σ) and excess CO_2 (CO_2 difference between Siple Dome (SD) and Taylor Dome (TD) or Dome C (DC)). Each symbol represents the average of data points from different age intervals as defined in Fig. 2F. There is a weak correlation between the CO_2 scattering among the adjacent samples and the excess CO_2 (R = 0.58 and 0.42 for SD vs. TD and SD vs. DC, respectively). This correlation would be expected if there were an artifact in Siple Dome samples.

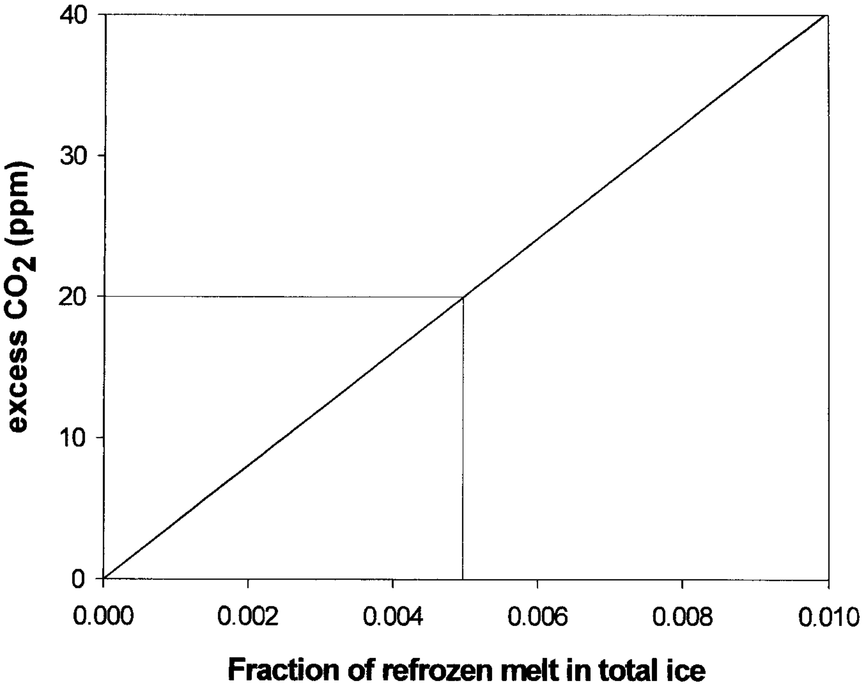


Figure 4. Excess CO_2 from the refrozen ice. 20 ppm of excess CO_2 corresponds to 0.5 % refrozen ice. This calculation assume an atmospheric CO_2 concentration of 278 ppm, barometric pressure of 937 mbar, and a gas contents of 0.111 cc STP air / g ice.

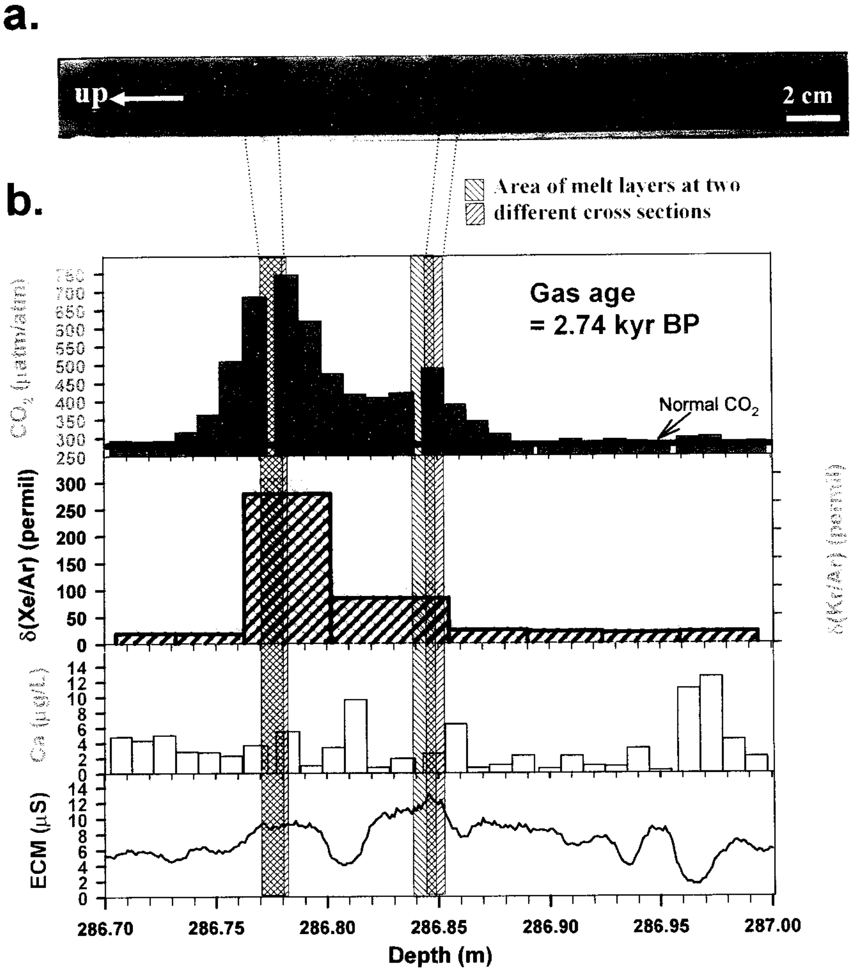
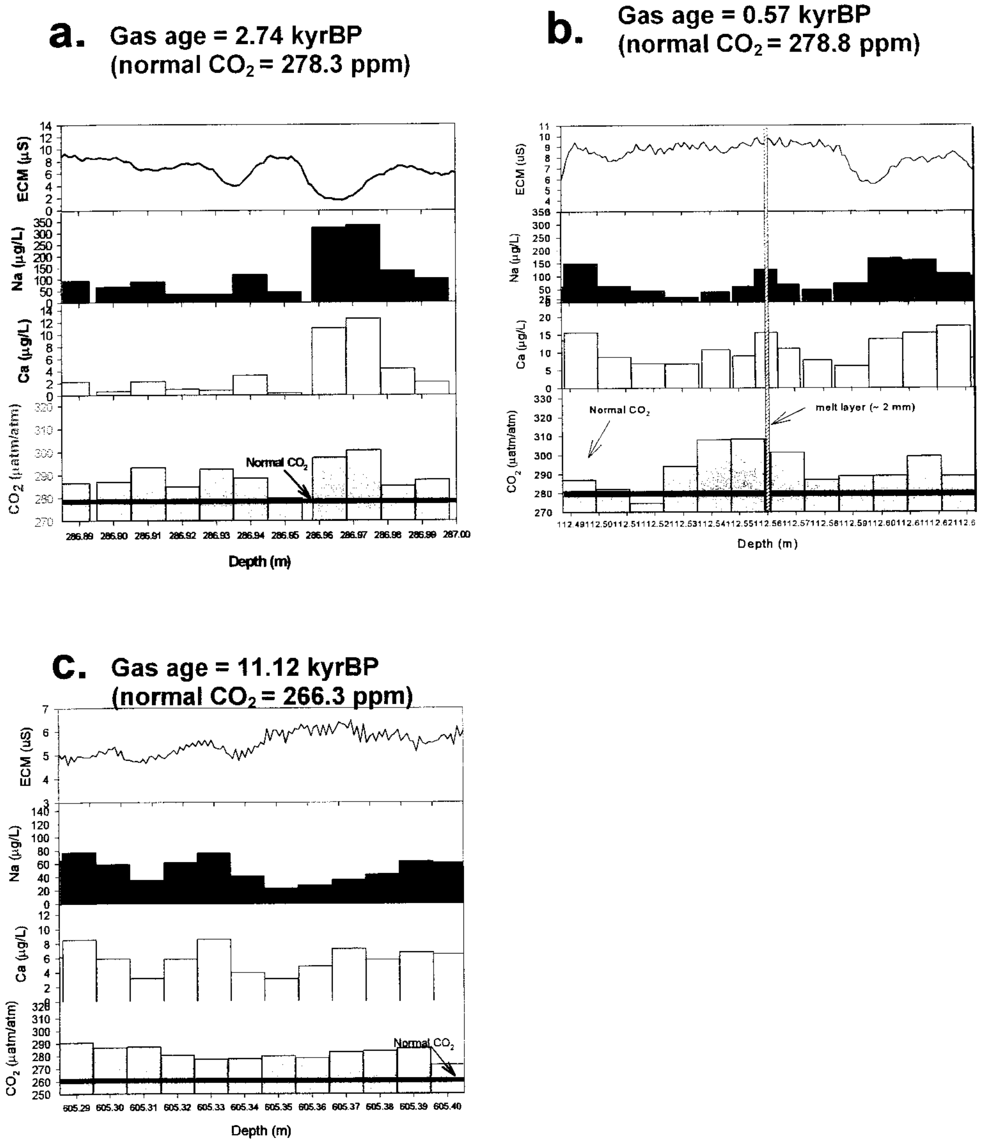


Figure 5. High resolution study around a 30-cm long sample including melt layers (1 cm thick) from the Siple Dome ice core. (a) Photograph of the ice sample (30 cm long). Two melt layers are visible due to reduced light scattering from bubbles. Some features between the two distinct melt layers seem to indicate partial melting. (b) Electric Conductivity Measurement (ECM) is a proxy for H^+. Ca^{2+} ion is used for the estimation of the maximum amount of $CaCO_3$ involved in the reaction between $CaCO_3$ and acid. δ(Xe/Ar) and δ(Kr/Ar) are melt indicators and normalized to modern atmospheric air.

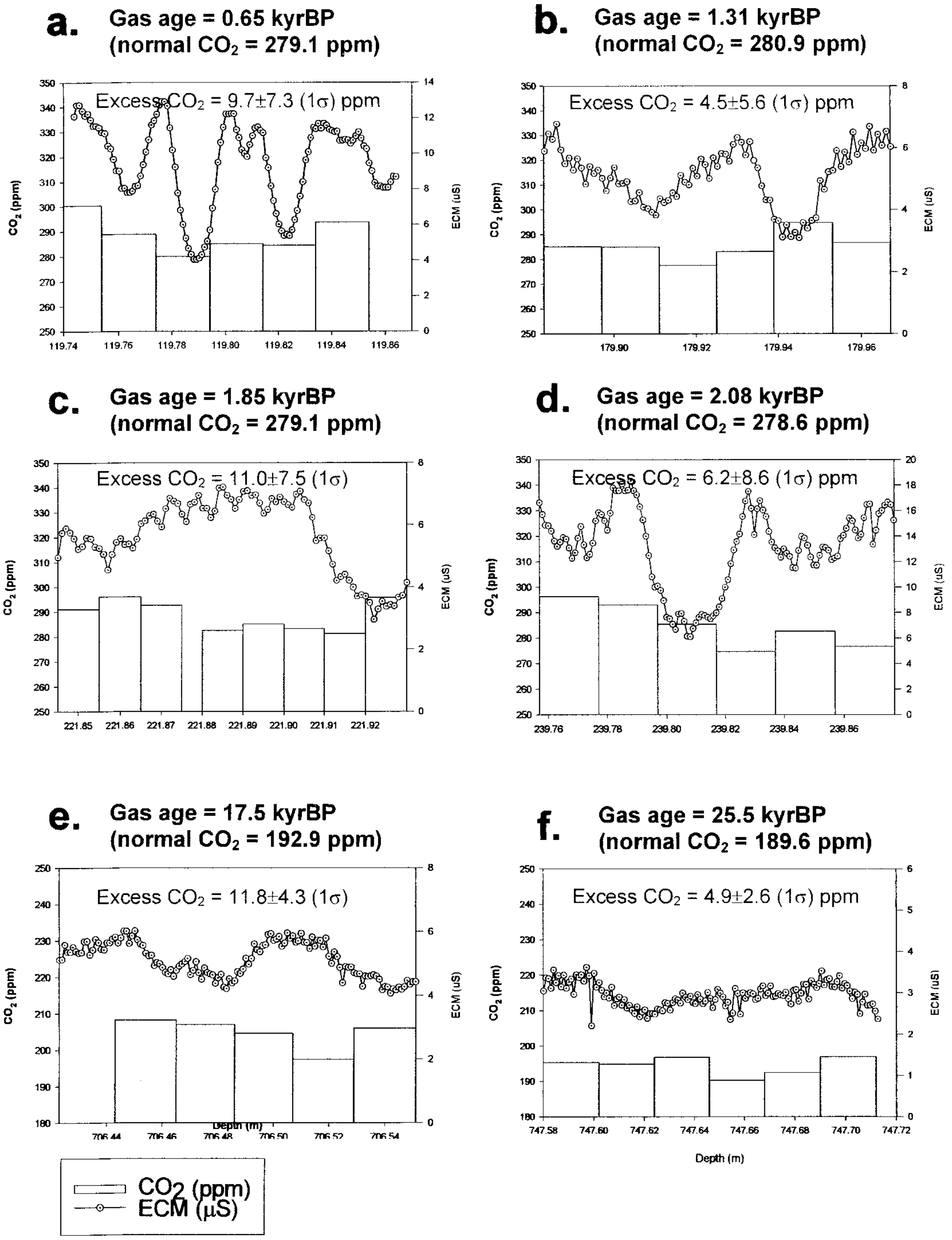


a. Gas age = 2.74 kyrBP (normal CO2 = 278.3 ppm)

b. Gas age = 0.57 kyrBP (normal CO2 = 278.8 ppm)

c. Gas age = 11.12 kyrBP (normal CO2 = 266.3 ppm)

Figure 6. High resolution study of samples near melt layers. Electric conductivity is expressed in µS, microsiemens. (a) is an enlarged portion of the right part of Figure 5b. Note a melt layer (~ 2mm thick) in (b). Another melt layer is located 6.5 cm above the top sample of Figure 6c. Normal CO_2 levels are average values of the records of Taylor Dome and Dome C.



a. Gas age = 0.65 kyrBP (normal CO_2 = 279.1 ppm)

b. Gas age = 1.31 kyrBP (normal CO_2 = 280.9 ppm)

c. Gas age = 1.85 kyrBP (normal CO_2 = 279.1 ppm)

d. Gas age = 2.08 kyrBP (normal CO_2 = 278.6 ppm)

e. Gas age = 17.5 kyrBP (normal CO_2 = 192.9 ppm)

f. Gas age = 25.5 kyrBP (normal CO_2 = 189.6 ppm)

Figure 7. Comparison between excess CO_2 and electric conductivity (ECM) at different depths where melt layers are not observed near the samples. Normal CO_2 levels are taken to be the average values of the records of Taylor Dome and Dome C.

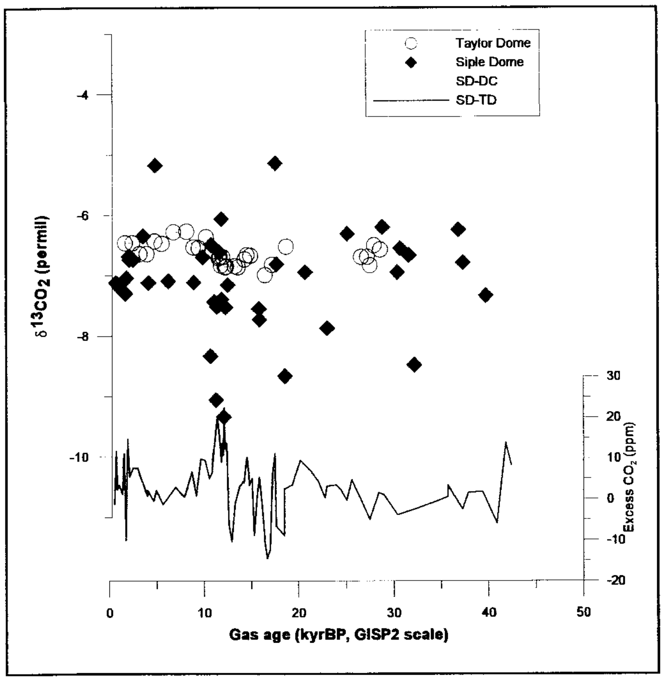


Figure 8. Comparison of $\delta^{13}C$ (VPDB) of CO_2 to excess CO_2 in Siple Dome records. Excess CO_2 is defined by the difference in CO_2 concentrations between Siple Dome and Dome C records (green line) or Siple Dome and Taylor Dome records (blue line).

CHAPTER V

Carbon isotope composition of CO_2 trapped in Antarctic ice cores covering the last two Terminations

Abstract. We present results of measurements on the carbon isotopic composition of CO_2 gas trapped in the Siple Dome and Vostok ice cores from Antarctica, covering the past 40 kyr BP (thousand years before 1950) and 160-110 kyrBP, respectively. The $\delta^{13}C$ values from the Siple Dome ice are slightly depleted on average by ~0.6 ‰ compared to those from the Taylor Dome ice records over the last 28 kyrBP. The scattering in the Siple Dome is much greater than the experimental precision (0.12 ‰). This may be due to variable conditions during gas trapping in the firn layer or laboratory artifacts. Data from the Vostok ice core implies that carbon cycle changes during Termination II occurred in a similar way to those found during Termination I, as observed in Taylor Dome ice. However, the absolute values of $\delta^{13}C$ for the Vostok ice samples are depleted by more than 1 ‰. This may be due to isotopic fractionation during incomplete gas extraction from the clathrate ice (bubble-free ice). Future studies should include sublimation in order to achieve an extraction efficiency of 100 %.

1. Introduction

Atmospheric CO_2 concentration measured at Mauna Loa, Hawaii, since 1958, shows a continuous increase of CO_2 concentration from 315 ppm (μatm/atm) to 377 ppm through 2004, with an average annual increase of 1.4 ppm [*Keeling and Whorf*, 2005]. This increase of the most important greenhouse gas, after water vapor, is caused by human activity, such as the combustion of fossil fuels, cement production and land use change including deforestation. To predict our future climate, an understanding of carbon cycling is a prerequisite. Therefore, understanding how the atmospheric concentration of CO_2 changed in the past in response to other changes in the climate system provides us with a better understanding of how current and future changes in the carbon cycle will influence our future climate. Ice cores extend the history of CO_2 concentration up to about 800 kyrs [*EPICA Community members*, 2004] and show that atmospheric CO_2 varied between 180-200 ppm (μatm/atm, Glacials) and 260-280 ppm (Interglacials) during the last four glacial cycles [*Petit et al., 1999*]. However, the causes of the atmospheric CO_2 change and its relationship with other climate factors are not well known.

Carbon isotopes of atmospheric CO_2 can be used to better characterize the global carbon cycle and carbon budgets [*Keeling et al.*, 1989; *IPCC*, 2001]. The sources and sinks of CO_2 including the major carbon reservoirs produce isotopically distinct CO_2. Therefore, comparison to the atmospheric inventory can yield constraints for the global budgets. Despite high demand for paleoatmospheric $\delta^{13}C$ $((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard(VPDB)} - 1) \times 1000$ ‰) to constrain carbon cycle models for the glacial-interglacial changes [*Broecker and Henderson*, 1998; *Sigman and Boyle*, 2000], only a few $\delta^{13}C$ ice core data may be confidently related to air prior to the Holocene period. *Leuenberger et al.* [1992] reported 0.3 ± 0.2‰ $\delta^{13}C$ differences between the glacial and Holocene periods from an ice core drilled at Byrd Station, Antarctica. Also, *Smith et al.* [1999] reported $\delta^{13}C$ changes during the last 27 kyrs (thousand years) using the Antarctic Taylor Dome ice core. For the average $\delta^{13}C$ difference between the Last Glacial Maximum (LGM) and the Holocene in the Taylor dome ice core, *Smith et al.* [1999] find 0.16 ‰. However, the difference during

Termination I (18 to 12 kyrBP) is 0.7 ‰ [*Smith et al.*, 1999]. Taylor Dome ice is considered as a better proxy for palaeoatmospheric CO_2 measurements than other Antarctic ice cores because of good core quality (no severe cracking) and the fact that it is entirely bubble ice. Bubble-free ice (clathrate ice) may induce isotopic fractionation during dry extraction (extraction efficiency < 100 %).

Possible causes of the atmospheric CO_2 change during glacial-interglacial periods are discussed in *Sigman and Boyle* [2000] and *Kohfeld et al.* [2005]. Table 1 summarizes the changes in atmospheric CO_2 and $\delta^{13}C$ due to known climatic changes during the glacial-interglacial transition. There are significant discrepancies between model predictions and observations by measurements. Many hypotheses are suggested to explain the gaps, like biological processes, such as a change in iron fertilization of marine biota due to variations in atmospheric dust deposition to the Southern ocean [*Martin*, 1990] or physical processes such as the changes in the sea ice coverage [*Stephens and Keeling*, 1999] or ocean stratification [*Toggweiler,* 1999].

In order to confirm the previous $\delta^{13}C$ data and reveal a longer history of the atmospheric glacial-interglacial carbon-isotope change, we studied the Siple Dome Antarctic ice covering the last 40 kyrs and the Vostok Antarctica core covering the Termination II (160-110 kyrBP).

2. Methods

2.1. Sample extraction and $\delta^{13}C$ measurements

This study used Siple Dome ice consisting of bubble ice and Vostok clathrate ice, which is bubble-free ice. The Siple Dome ice core, drilled in 1997–1999, was measured for $\delta^{13}C$ from 2001-2005. Also, six bubble-free Vostok ice samples from Termination II were measured in 2004 concurrently with the Siple Dome ice samples. The ice samples used for this study were physically adjacent to those used for CO_2 concentration measurements in *Ahn et al.* [2004] and *Fischer et al.* [1999]. The mean annual temperatures, accumulation rates and drilling fluids used for the Siple Dome, Taylor Dome and Vostok ice cores are listed in Table 1. The mean annual temperature and accumulation rate at Siple Dome (–25.4 °C; 12.4 g cm^{-2} yr^{-1}) are greater than those at Vostok (–55.5 °C; 2.3 g cm^{-2} yr^{-1}) and Taylor Dome (–42 °C; 7 g cm^{-2} yr^{-1}). All the samples were stored and crushed at –25 °C. 200 ~ 400 grams of ice were trimmed carefully using a band saw to minimize possible contamination by modern air and/or drilling fluid. However, in some Siple Dome samples the smell of drilling fluid was present even after the trimming of the ice surface by about 1 cm. The traces of drilling fluid may have isobarically interfered with CO_2 in the mass spectrometer. Different drilling fluids and their properties are shown in Table 1. For most of the Siple Dome samples, no significant drilling fluid fragments (produced in the ion source, possible isobaric interference) were detected by m/z scanning in the mass spectrometer. We used the same dry extraction technique as for the Taylor Dome ice [*Smith et al.*, 1999]. Sample disintegration was achieved by crushing in a stainless steel container that had inward-facing spikes (Figure 1). After about 1 hr crushing, CO_2 was then separated cryogenically [*Smith et al.*, 1999] in a glass vacuum extraction line (Figure 1).

After crushing, the sample gases were passed through three coil traps (T1~T3). The bleeding rate was controlled by a Gilmont® micrometer capillary valve (B) at a flow rate of < 3 cm^3 STP / min. Most water vapor was frozen on the glass coil T1 cooled with ethanol to ~ -80 °C. The other coils (T2 and T3) were immersed in liquid nitrogen (-196 °C) and as air passed through both H_2O and CO_2 were condensed. The path length of a coil was about 130 cm per glass coil. Non-condensable gases (e.g., O_2 and N_2) were pumped with mechanical and turbomolecular pumps through the main valves V11 and V12. The pressure within the extraction line was low enough not to trap O_2 in the liquid nitrogen traps by keeping the flow rate low. CO_2 was separated from H_2O through a series of transfers from T1 to T2 and T2 to T3, then T3 to a glass finger by warming up T3 to - 80°C while keeping the glass finger at –196°C. Fractionation during the gas extraction was determined using an air cylinder (tank #75859, see Table 3) which was compressed with dry air at high pressure. A series of aliquots, one-liter glass flasks, were filled with cylinder air to atmospheric pressure. Then, following the above protocol, flask air was introduced over the ice and bled and collected at the same flow rate.

The isotopic composition of the isolated CO_2 samples were measured on a triple-collector, VG-Prism II dual inlet mass spectrometer, following a strict analytical protocol. $\delta^{13}C$ of the CO_2 of standards relative to VPDB are listed in Table 3.

2.2. Data correction and precision

The protocol for determining isotopic ratios of CO_2 is outlined and summarized in Table 4. We followed the suggestions of *Francey and Allison* [1992], and measured our samples against pure CO_2 working standards (referenced against VPDB). We applied a 3 point NBS correction, applied a "daily correction" for gas fractionation during gas extraction and machine drift, and corrected for ^{17}O (Craig correction). We corrected for N_2O (which results in isobaric interference with CO_2), and corrected for gravitational fractionation using $\delta^{15}N$ to obtain a final value for the ratio of $^{13}C/^{12}C$ relative to VPDB. The composition of the working standard, MW1 is –42.405 ‰ for $\delta^{13}C$ and –27.767 ‰ for $\delta^{18}O$ (both relative to VPDB). A one-liter aliquot of this standard was used for mass spectrometric measurements [*Bollenbacher et al.*, 1998; *Guenther et al.*, 2001].

Correction for gas extraction fractionation and a "daily correction" for machine drift was inferred from standard air (Tank #75859) and secondary standards. The air was equilibrated over the ice sample and extracted on the same day as the sample. After following the same correction process as above, the difference between the assigned standard values and the extracted air was calculated and added to the ice sample value. Reproducibility from this extraction procedure was observed to be ± 0.11 ‰ for $\delta^{13}C$ of CO_2.

In addition, the $\delta^{13}CO_2$ values reported here were corrected for the gravitational fractionation of gases of different masses in the firn (snowpack), and for the presence of N_2O. Gravitational separation in the firn was determined by using the values of $\delta^{15}N$ of air trapped in Siple Dome ice from [*Brook et al.*, 2005] and in Vostok ice from [*Jeff Severinghaus*, unpublished data].

The total 1σ uncertainty for $\delta^{13}C$ of a single sample, including uncertainties in the gravitational and N_2O corrections, was 0.12 ‰. Most of the experimental uncertainty comes from the correction for the isotopic fractionation during the CO_2 separation.

3. Results

3.1. Siple Dome ice for the past 40 kyrs

In Figure 2, $\delta^{13}C$ of the Siple Dome ice samples is compared to that of Taylor Dome ice [*Smith et al.*, 1999]. On average, the $\delta^{13}C$ values of the Holocene (11.6-0 kyrBP) and Last Glacial Maximum (LGM, 28-17.5 kyrBP) are –7.04 (±0.79) ‰ and –7.32 (±0.94) ‰, respectively. The 0.28 ‰ difference between the average $\delta^{13}C$ values of the LGM and Holocene is greater than that of Taylor Dome (0.16‰) and comparable the results of 0.19 ± 0.18 ‰ by *Leuenberger et al.* [1992] for the Byrd ice core between the period 20-40 kyrBP and the early Holocene. However, the average $\delta^{13}C$ values of the Siple Dome are depleted compared to those from the Taylor Dome ice by 0.58 ‰ and 0.67 ‰ for the Holocene and LGM, respectively. The $\delta^{13}C$ of the Siple Dome data ranges from ~ -9.5 to –5 ‰ in contrast to the small range of the Taylor Dome record (–6.99 to –6.27 ‰). Considering the estimated analytical precision of about 0.12 ‰, the difference cannot be accounted for by analytical uncertainty during CO_2 separation or measurement in the mass spectrometer. The difference does not seem to be gas fractionation during the gas liberation from the crushed ice because we used the same tools and methods as for Taylor Dome ice [*Smith et al.*, 1999]. The only difference in methods between this study and *Smith et al.* [1999] is the duration of the crushing of ice (1 hour for the Siple Dome ice and 30 minutes for the Taylor Dome ice).

Figure 3 is a mixing diagram, where the $\delta^{13}C$ is plotted against inverse CO_2 concentration. Addition or removal of CO_2 with a given $\delta^{13}C$ would create a trend in the data with a nearly straight line with the *y*-intercept approximately equal to the isotopic composition of the net CO_2 added to, or subtracted from, the atmosphere. The *y*-intercepts are -13.7 (± 9.3) ‰, –12.5 (± 2.5) ‰, and 1.8 (± 7.5) ‰ for the Holocene (11.6-0 kyrBP), Termination I (17.5-11.6 kyrBP), and Glacial period (40-17.5 kyrBP), respectively. The net CO_2 source during Termination I seems to be lighter than that of the Glacial period. This is different from the previous results for the Taylor Dome ice core [Smith et al., 1999]. However, the interpretation of the Siple Dome $\delta^{13}C$ should be considered cautiously due to the mechanisms related to excess CO_2 production.

Despite similarities in general time series of the CO_2 records with other Antarctic ice cores, the Siple Dome ice, at certain age intervals, shows higher CO_2 concentrations of up to 20 ppm than those in other Antarctic ice cores [*Ahn et al.*, 2004]. This difference is attributed to the production of excess CO_2 in the ice. Possible mechanisms for the excess CO_2 include (1) snowmelting-refreezing [*Neftel et al.*, 1983; *Stauffer et al.*, 1985], (2) carbonate-acid reaction [*Delmas*, 1993; *Barnola et al.*, 1995; *Anklin et al.*, 1995; *Anklin et al.*, 1997; *Smith et al.*, 1997a; *Smith et al.*, 1997b], and (3) oxidation of organic compounds abiologically [*Tschumi and Stauffer*, 2000], or biologically [*Campen et al.*, 2003]. These processes would also alter $\delta^{13}C$. For example, 20 ppm of excess CO_2 by the carbonate-acid reaction would increase $\delta^{13}C$ by about 0.2 ‰ whereas oxidation of organic compounds would decrease $\delta^{13}C$ by about 1 ‰. In Figure 4, $\delta^{13}C$ is plotted against the CO_2 concentration difference between Siple Dome and Taylor Dome. Two distinct low $\delta^{13}C$ data points (~ -9 ‰) at around 11-12 kyrBP are observed. They were measured in a different year confirming their repeatability. They are lower than in the Taylor Dome ice by ~ 2.3 ‰. These data are observed for the maximum excess CO_2 (19.4 and 22.1 ppm). If these $\delta^{13}C$ depletions are caused by oxidation of organic compounds, 46 ppm of excess CO_2 are required. This is greater than our observation of excess CO_2 (~ 20 ppm). The most likely process for the excess CO_2 is the melting/refreezing process in the Siple Dome ice core as discussed in Chapter IV. CO_2 is highly soluble compared to other atmospheric gases. Isotopic fractionation in CO_2 could occur during both melting and refreezing. The isotopic fractionation of the air CO_2 in equilibrium with water at 0 °C is –10.83 ‰ [*Mook et al.*, 1974]. $\delta^{13}C$ of CO_2 of ice with melt layers have not been reported. However, these processes could significantly scatter the $\delta^{13}C$ of CO_2. In Figure 5, $\delta^{13}C$ is plotted against inverse excessCO_2 to decipher the major source for the excess CO_2 (Figure 5). The y-intercepts for the Holocene and the last glacial period are –6.78 ± 0.25 ‰ and –7.39 ± 0.18 ‰, respectively, and do not clearly identify any specific sources for the excess CO_2.

3.2. Vostok ice covering Termination II (160-110 KyrBP)

Six samples from Termination II are compared to the Taylor Dome record around Termination I (Figure 6). The samples from Vostok ice are clathrate ice (bubble-free ice), whereas the Taylor Dome samples are all bubble ice [*Smith et al.*, 1999]. We observe a $\delta^{13}C$ increase during the Termination II concurrent with the increase in CO_2 concentrations. Also, the trend is similar to that observed in Taylor Dome ice (open diamonds). This suggests that an isotopically heavy net source of CO_2 increased the atmospheric CO_2 inventory, although assignment of this CO_2 to a particular source is complex. However, the order of the change in $\delta^{13}C$ of the Vostok ice is much greater than in the Taylor Dome record by a factor of up to 4. Moreover, all the values of Vostok ice samples are more depleted by 1 to 3 ‰ than those of the Taylor Dome ice. One of the possibilities for the depletion in Vostok $\delta^{13}C$ is gas fractionation during the gas extraction caused by different gas diffusion in the clathrate ice. We expect different diffusion rates for atmospheric gas species when the air emerges from the clathrate ice [*Ikeda-Fukazawa et al.*, 2001; *Ikeda-Fukazawa et al.*, 2005]. The different gas diffusion rates may affect the isotopic fractionation for incomplete gas extraction from clathrate ice. The relative diffusion rates are not well established. To prevent this isotopic fractionation, we would have to increase the gas extraction yield to 100 %. Our crushing method gives an extraction yield of about 50%. Further study should include ice-sublimation in order to obtain 100% gas extraction from the clathrate ice and to avoid isotopic fractionation due to incomplete gas extraction (Figure 7). Our preliminary work for the sublimation took 5 to 7 hours for 200 g of ice and gave very depleted values for unknown reasons.

5. Conclusion

The measurements of the isotopic value of $\delta^{13}C$ of the CO_2 gas trapped in the Siple Dome and Vostok Antarctic ice cores show very scattered and somewhat depleted values compared to the $\delta^{13}C$ Taylor Dome ice core record. This may be related to surface conditions, possibly micro-scale melting on the snow surface, or laboratory artifacts. Vostok ice around Termination II shows a $\delta^{13}C$ increase during the atmospheric CO_2 concentration increase suggesting that the main net source for the atmospheric CO_2 change during the deglaciations is isotopically heavy. However, the magnitude of the $\delta^{13}C$ change is much greater than that in Taylor Dome ice and absolute values are also very depleted by 1-3 ‰. This depletion may be explained by isotopic fractionation during the gas extraction procedure with mechanical crushing of the ice. A sublimation technique may increase the extraction yield to 100 % and reduce the chance of isotopic fractionation during the gas extraction.

Acknowledgments. We wish to thank Alane Bollenbacher for the preparation of the CO_2 standard air. We also greatly thank Jackson Wong for assistance during experiments. Hubertus Fischer provided an apparatus for sublimation of ice. Ice cores were kindly cut at the National Ice Core Laboratory. This early work was supported by the Office of Polar Program of the NSF (NSF OPP 99-80619). This chapter is reproduced fully, with permission from: Ahn, J., M. Wahlen, and B. Deck (2005) "Carbon isotope composition of CO_2 trapped in Antarctic ice cores covering the last two Terminations" (to be submitted to a scientific journal).

References

Ahn, J., M. Wahlen, B.L. Deck, E.J. Brook, P.A. Mayewski, K.C. Taylor, and J.W.C. White, A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica ice core, *J. Geophys. Res.*, *109,* D13305, doi:10.1029/2003JD004415, 2004.

Anklin, M., J.M. Barnola, J. Schwander, B. Stauffer, and D. Raynaud, Processes Affecting the CO_2 Concentrations Measured in Greenland Ice, *Tellus, 47B*, 461-470, 1995.

Anklin, M., J. Schwander, B. Stauffer, J. Tschumi, A. Fuchs, J.M. Barnola, and D. Raynaud, CO_2 record between 40 and 8 kyr BP from the Greenland Ice Core Project ice core, *J. Geophys. Res.*, *102*, 26539-26545, 1997.

Barnola, J.M., M. Anklin, J. Porcheron, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 Evolution During the Last Millennium as Recorded by Antarctic and Greenland Ice, *Tellus*, *47B,* 264-272, 1995.

Bollenbacher, A.F., C.D. Keeling, E.F. Stewart, M. Wahlen, and T.P. Whorf, Calibration methodology for the Scripps $^{13}C/^{12}C$ and $^{18}O/^{16}O$ stable isotope program, 1998.

Broecker, W.S., and G.M. Henderson, The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes, *Paleoceanography*, *13*, 352-364, 1998.

Brook, E.J., J. White, A. Schilla, J. Severinghaus, K. Taylor, R. Alley, and E. Steig, Timing of millennial-scale climate change at Siple Dome, West Antarctica, during the last glacial period, *Quat. Sci. Rev., 24*, 1333-1343, 2005.

Campen, R.K., T. Sowers, and R.B. Alley, Evidence of microbial consortia metabolizing within a low-latitude mountain glacier, *Geol.*, *31*, 231-234, 2003.

Coplen, T.B., C. Kendall, and J. Hopple, Comparison of stable isotope reference material, *Nature*, 302, 236-238, 1983.

Craig, H., Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta, 12,* 133-149, 1957.

Delmas, R.J., A Natural Artifact in Greenland Ice-Core CO_2 Measurements, *Tellus*, *45B*, 391-396, 1993.

EPICA community members, Eight glacial cycles from an Antarctic ice core, *Nature*, *429*, 623-628, 2004.

Fischer, H., M. Wahlen, J. Smith, D. Mastroianni, and B. Deck, Ice core records of atmospheric CO_2 around the last three glacial terminations, *Science*, *283*, 1712-1714, 1999.

Fischer, H., M. Wahlen, and J. Smith, Reconstruction of glacial/interglacial changes in the global carbon cycle from CO_2 and $\delta^{13}CO_2$ in Antarctic ice cores, *Mem. Natl Inst. Polar Res., Spec. Issue, 57*, 121-138, 2003.

Francey, R.J., and C.E. Allison, Isotope variations of carbon dioxide and other tarce gases in the atmosphere, IAEA Technical Report Series, ed. By Rozanski, K., 1992.

Friedman, I., J.R. O-Neil, and G. Cebula, Two new carbonate stable isotope standards, *Geostandard Newslett., 6,* 11-12, 1982.

Guenther, P.R., A.F. Bollenbacher, C.D. Keeling, E.F. Stewart, and M. Wahlen, Calibration methodology for the Scripps $^{13}C/^{12}C$ and $^{18}O/^{16}O$ stable isotope program, 2001.

Hamilton, G.S. Mass balance and accumulation rate across Siple Dome, West Antarctica. *Ann. Glaciol., 35,* 102-106, 2002.

Ikeda-Fukazawa, T., T. Hondoh, T. Fukumura, H. Fukazawa, and S. Mae, Variation in N_2/O_2 ratio of occluded air in Dome Fuji antarctic ice, *J. Geophys. Res.*, *106*, 17799-17810, 2001.

Ikeda-Fukazawa, T., K. Fukumizu, K. Kawamura, S. Aoki, T. Nakazawa, and T. Hondoh, Effects of molecular diffusion on trapped gas composition in polar ice cores, *Earth Planet. Sci. Lett.*, *229* (3-4), 183-192, 2005.

IPCC (Intergovernmental Panel on Climate Change), Climate change 2001: The scientific basis, Cambridge university press, 2001.

Keeling, C.D., Bacastow, R.B., Carter, A.F., Piper, S.C., Whorf, T.P., Heimann, M., Mook, W.G., Roeloffzen, H., A three-dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis of observed data, in *AGU Monograph 55*, pp. 165-236, American Geophysical Union, Washington, 1989.

Keeling, C.D. and T.P. Whorf, Atmospheric CO_2 records from sites in the SIO air sampling network. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A., 2005.

Kohfeld, K.E., C.L. Quéré, S.P. Harrison, and R.F. Anderson, Role of marine biology in glacial-interglacial CO_2 cycles, *Science, 308*, 74-78, 2005.

Leuenberger, M., U. Siegenthaler, and C.C. Langway, Carbon isotope composition of atmospheric CO_2 during the last ice age from an Antarctic ice core, *Nature, 357,* 488-490, 1992.

Martin, J.H., R.M. Gordon, and S.E. Fitzwater, Iron in Antarctic waters, *Nature, 345*, 156-158, 1990.

Mook, W.G., J.C. Bommerso, and W.H. Staverma, Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide, Earth Planet. Sci. Lett., 22, 169-176, 1974.

Neftel, A., H. Oeschger, J. Schwander, and B. Stauffer, Carbon Dioxide Concentration in Bubbles of Natural Cold Ice, *J. Phys. Chem.*, *87*, 4116-4120, 1983.

Petit, J.R., J. Jouzel, D. Raynaud, N.I. Barkov, J.M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429-436, 1999.

Raynaud, D., J. Jouzel, J. M. Barnola, J. Chappellaz, R. J. Delmas, and C. Lorius, The ice record of greenhouse gases, *Science, 259,* 926-934, 1993.

Severinghaus, J.P., A. Grachev, and M. Battle, Thermal fractionation of air in polar firn by seasonal temperature gradients, *Geochem. Geophys. Geosys., 2*, 2000GC000146 JUL 31, 2001.

Sigman, D.M., and E.A. Boyle, Glacial/interglacial variations in atmospheric carbon dioxide, *Nature*, *407* (6806), 859-869, 2000.

Smith, H.J., M. Wahlen, D. Mastroianni, K. Taylor, and P. Mayewski, The CO_2 concentration of air trapped in Greenland Ice Sheet Project 2 ice formed during periods of rapid climate change, *J. Geophys. Res.*, *102*, 26577-26582, 1997a.

Smith, H.J., M. Wahlen, D. Mastroianni, and K.C. Taylor, The CO_2 concentration of air trapped in GISP2 ice from the last glacial maximum-holocene transition, *Geophys. Res. Lett.*, *24*, 1-4, 1997b.

Smith, H.J., H. Fischer, M. Wahlen, D. Mastroianni, and B. Deck, Dual modes of the carbon cycle since the Last Glacial Maximum, *Nature*, *400* (6741), 248-250, 1999.

Stauffer, B., A. Neftel, H. Oeschger, and J. Schwander, CO_2 concentration in air extracted from Greenland ice samples, in *Greenland Ice Core: Geophys. Geochem. Environ.*, edited by C.C.Langway et. al., pp. 85-89, AGU, Washington, D.C., 1985.

Steig, E. J., D. L. Morse, E. D. Waddington and P. J. Polissar, Using the sunspot cycle to date ice cores, *Geophys. Res. Lett., 25,* 163-166, 1998.

Stephens, B.B., and R.F. Keeling, The influence of Antarctic sea ice on glacial–interglacial CO_2 variations, *Nature, 404*, 171 ,2000.

Toggweiler, J.R., Variation of atmospheric CO2 by ventilation of the ocean's deepest water, *Paleoceanography, 14*, 572, 1999.

Tschumi, J., and B. Stauffer, Reconstructing past atmospheric CO_2 concentration based on ice-core analyses: open questions due to in situ production of CO_2 in the ice, *J. Glaciol.*, *46*, 45-53, 2000.

Waddington, E. D. and D. L. Morse, Spatial variations of local climate at Taylor Dome, Antarctica: Implications for paleoclimate from ice cores. *Ann. Glaciol., 20,* 219-225, 1994.

Table 1. The effect on atmospheric CO_2 and $\delta^{13}C$ of changes in various processes during the glacial-interglacial transition. Modified from *Fischer et al.* [2003].

Processes from LGM to Holocene	Change in atmospheric CO_2 (ppm)	Change in atmospheric $\delta^{13}C$ (‰)
Increase in terrestrial carbon (600 PgC)	-43 (-32 to –97)	0.36 (0.27 to 0.80)
Increase in sea surface temperature (5° low latitude, 2.5° high latitude)	30 (15 to 40)	0.43 (0.24 to 0.60)
Salinity decrease	-15	-
Sum	-28 (-97 to -7)	0.79 (0.51 to 1.40)
Measured	90	0.2 (0.7)

Table 2. Characteristics of the Antarctic ice cores from which $\delta^{13}C$ of CO_2 gas has been measured.

Core name	Mean annual temperature (°C)	Mean accumulation rate (water equivalent) ($g\ cm^{-2}\ yr^{-1}$)	Drilling fluid used Chemical formula (form. wt.)
Siple Dome	-25.4[a]	12.4[b]	n-butyl acetate $C_5H_{11}COOH$ (116.2)
Taylor Dome	-42[c]	7[d]	n-butyl acetate $C_5H_{11}COOH$ (116.2)
Vostok[e]	-55.5	2.3	Kerosene, ~n-dodecane $C_{12}H_{26}$ (170.3) Freon, CFC11 CCl_3F (137.4)

[a][*Severinghaus et al.*, 2001]; [b][*Hamilton*, 2002]; [c][*Waddington and Morse*, 1994]; [d] as unit of cm ice equivalent per year [*Steig et al.*, 1998]; [e][*Raynaud et al.*, 1993].

Table 3. Standards used to calibrate measurements

Standard	Description	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Ref.
Working standard				
MW1	pure CO_2	-42.405	-27.767	(1)
Reference materials				
NBS16	pure CO_2	-41.48	-36.09	(2)
NBS17	pure CO_2	-4.41	-18.71	(2)
NBS19*	limestone	1.95	-2.2	(3)
Secondary standards for daily correction				
Tk #39414	CO_2 (w/ N_2O)	-8.360	-5.244	
Tk #2407	CO_2 (w/ N_2O)	-7.740	-2.800	
Standard dry air used for the correction of the fractionation during CO_2 extraction				
Tk #75859	air (w/ N_2O)	-8.282	-0.266 ± 0.049 (9)	(1)

*A small fractionation exists in dissolution of limestone by phosphoric acid

Reference:
(1) *Bollenbacher et al.* [1998]; (2) *Coplen et al.* [1983]; (3) *Friedman et al.* [1982]

Table 4. Corrections applied to stable isotope measurements

	Corrections	
Sample-MW1	$\delta 45/44 = (\delta 45/44_{sample}/\delta^{13}C_{MW1\text{-}PDB}-1)*10^3$	(1)
	$\delta 46/44 = (\delta 46/44_{sample}/\delta^{18}C_{MW1\text{-}PDB}-1)*10^3$	
NBS	$\delta 45/44' = (0.995034*\delta 45/44) + 0.05901$	(1)
	$\delta 46/44' = (1.00758*\delta 46/44) + 0.21137$	
O-17	$\delta^{13}C_C = ((1.0676*\delta^{13}C_B)-(0.0338338*\delta^{18}O_B))/0.99992902$	(2)
(Craig corr.)	$\delta^{18}O_C = ((1.0010*\delta^{18}O_B)-(0.00224196*\delta^{13}C_B))/0.99992902$	
N_2O	$\delta^{13}C = ((2.24*I) + 221)*[N_2O]/[CO_2]$	(3)
	$\delta^{18}O = ((3.46*I) + 331)*[N_2O]/[CO_2]$	

I = current of mass 44 in nA.

Reference:
(1) *Bollenbacher et al.* [1998]; (2) *Craig* [1957]; (3) *Wahlen* [personal communication]

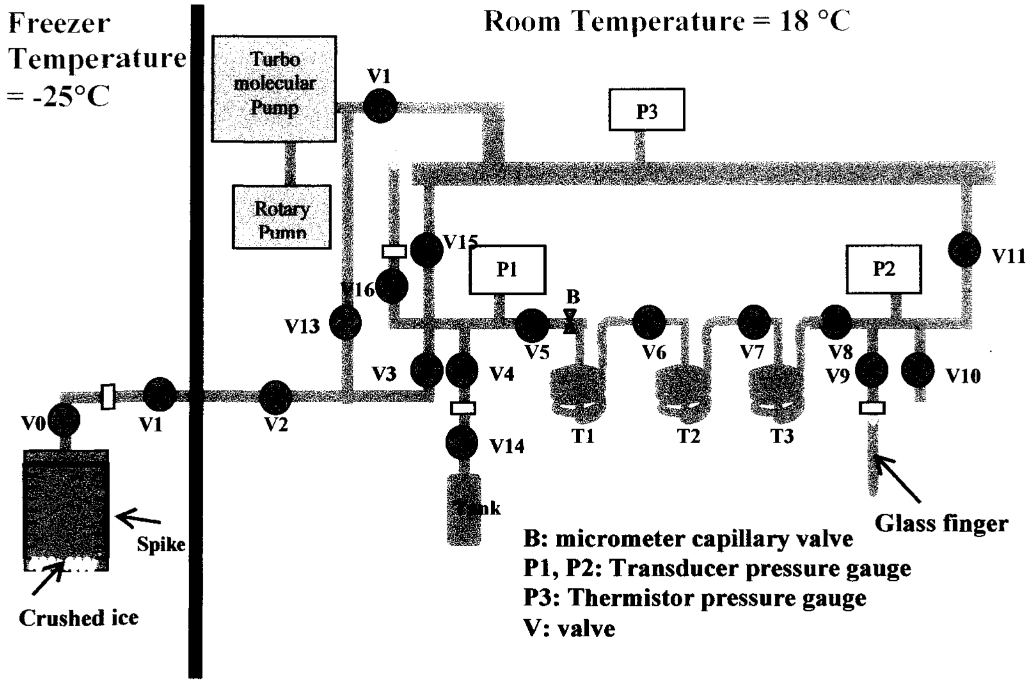


Figure 1. Schematic representation of the CO_2 extraction line for stable isotopic study. Details are in text.

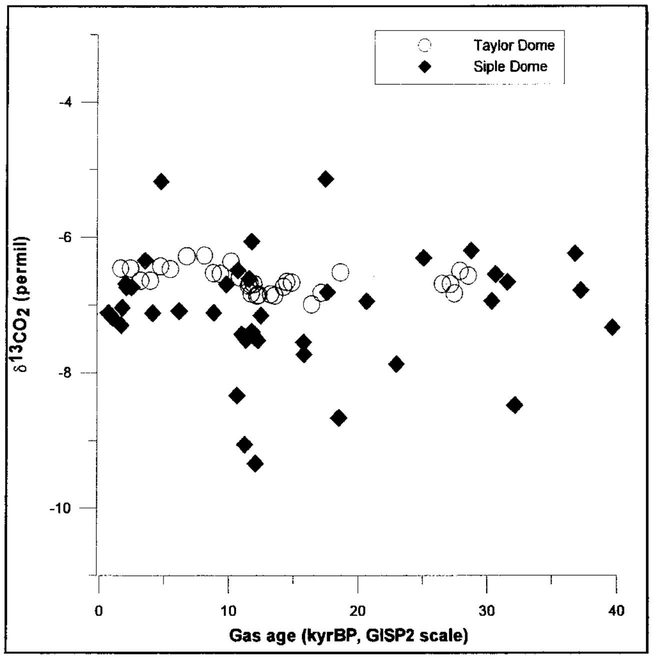


Figure 2. Siple Dome ice core $\delta^{13}C$ results. Internal precision is about 0.1 ‰. Corrected for gravitational fractionation using *Brook et al.* [2005].

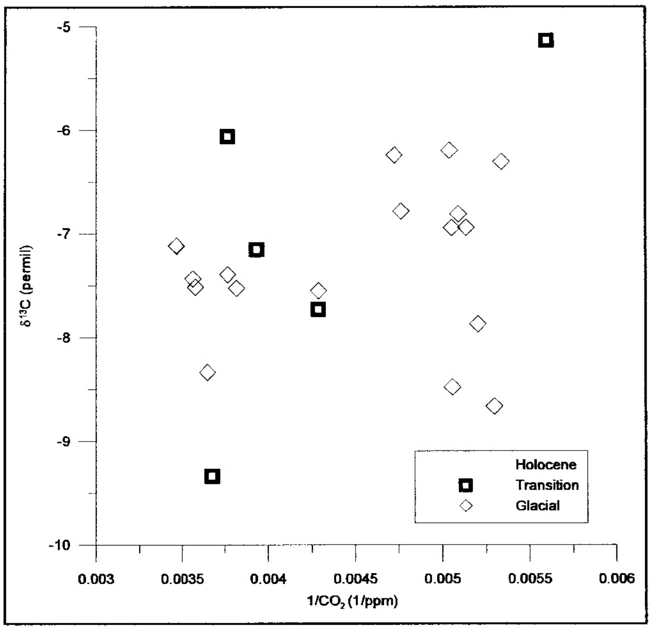


Figure 3. Siple Dome Ice core δ^{13}C of CO_2 versus 1/CO_2. Three different age groups are indicated by different colors.

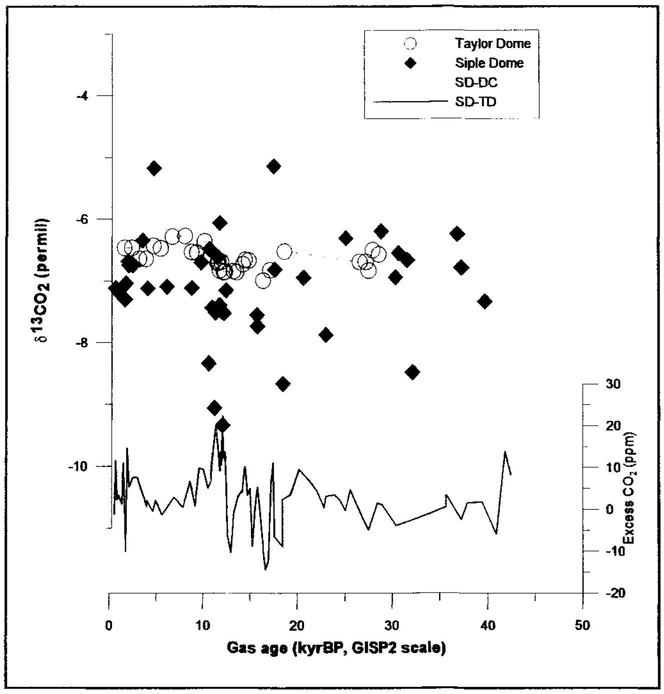


Figure 4. Comparison of Siple Dome Ice core $\delta^{13}C$ of CO_2 to excess CO_2 [*Ahn et al.*, 2004]. Excess CO_2 is defined by CO_2 difference between Siple Dome and Taylor Dome (blue line) or Dome C (green line).

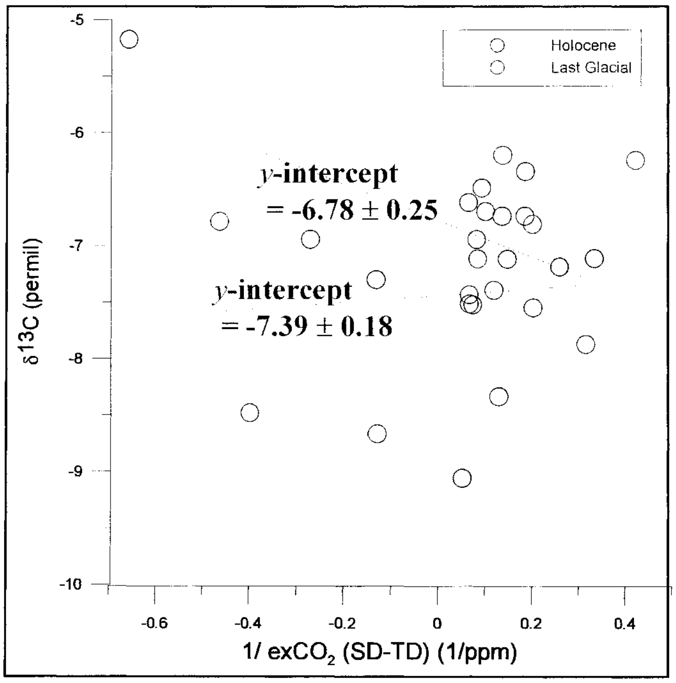


Figure 5. Comparison of Siple Dome Ice core $\delta^{13}C$ of CO_2 to 1/(excess CO_2). Excess CO_2 is defined by the difference between the Taylor Dome and Siple Dome.

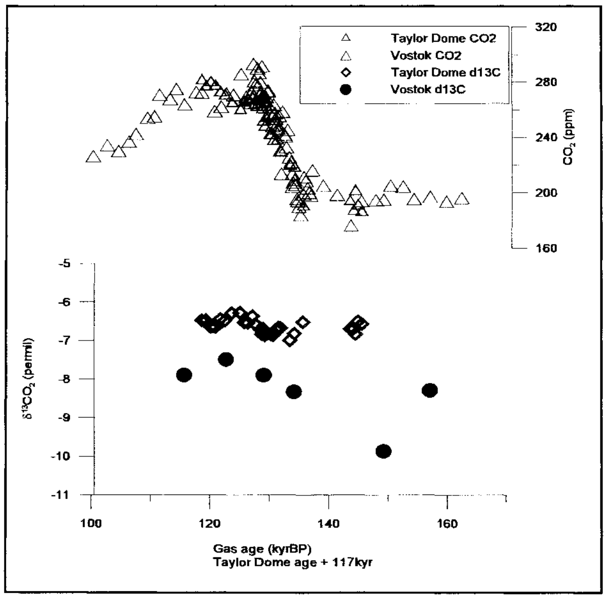


Figure 6. Comparison of $\delta^{13}C$ of CO_2 from Vostok Ice during Termination II and Taylor Dome during Termination I [*Smith et al.*, 1999]. In order to compare Termination I of Taylor Dome to Termination II of Vostok ice, ages for Taylor Dome are obtained using 117 kyr for the separation between Termination I and II. Correction for gravitational fractionation was done using [*Severinghaus*, unpublished data].

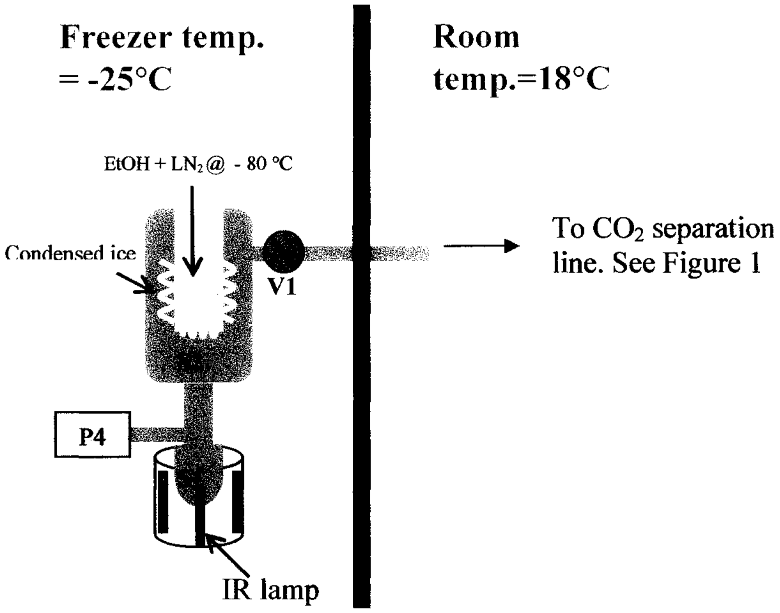


Figure 7. Schematic representation of the apparatus proposed for the sublimation of ice for $\delta^{13}CO_2$ measurement. Ice sample is put in glass tube (S1) and sublimated by IR lamps. Water vapor condenses on a cold trap (-80 °C) in S2. Air is further dried by subsequential cold traps cooled with liquid nitrogen (T1 at –80 °C , T2 and T3 at –196 °C in Figure 1).

CHAPTER VI

Conclusion

CO_2 is the most important greenhouse gas in the anthropogenic regime. Atmospheric CO_2 concentration has increased ~ 100 ppm (μatm/atm) from 280 ppm since the industrial revolution [*Etheridge et al.*, 1996; *Keeling and Whorf*, 2005]. One promising approach to reducing the uncertainties in present climate models for future prediction is to evaluate the carbon cycle in the past glacial-interglacial periods. Ice cores provide unique archives of past atmospheric air over the past 800 kyr [*EPICA Community members,* 2004]. The anthropogenic CO_2 increase of ~ 100 ppm is similar in magnitude to the natural CO_2 variation during the last four glacial-interglacial cycles (between 180-200 ppm for glacials and 260-280 ppm for interglacials) [*Petit et al.*, 1999]. However, the causes of the atmospheric CO_2 change and its relationship with other climate factors, such as temperature and ocean circulation, are not well known. This research project investigated paleoatmospheric CO_2 occluded in the Siple Dome ice core, Antarctica, as related to temperature change. In addition, the reliability of ice cores as a proxy of paleoatmospheric CO_2 was explored.

In order to assess the effect of atmospheric CO_2 on the past climate, this project necessitated a reconstruction of CO_2 occluded in the Siple Dome ice core, Antarctica. The Siple Dome ice core was chosen because its rather high snow accumulation rate gives a high temporal resolution.

In the reconstruction process, I persued the following four phases:

(1) Reconstruction of the paleoatmospheric CO_2 concentration and decipherment of the phase relationship between CO_2 concentration change and Siple Dome temperature change,

(2) Estimation of CO_2 diffusion in the solid ice phase of polar ice and evaluation of the smoothing of CO_2 records by gas diffusion in polar ice,

(3) Determination of the best explanation for the excess CO_2 observed in the Siple Dome ice core, and

(4) Measurement of the carbon isotope composition of CO_2 from the last two deglaciations.

Phase (1)

In Phase (1) paleoatmospheric CO_2 concentration for the past 40,000 years was retrieved from the Siple Dome ice core and compared to results from other ice cores. As found by previous studies on other ice cores [*Petit et al.*, 1999; *Monnin et al.*, 2001], the general trend of CO_2 concentration from Siple Dome ice follows the temperature inferred from the isotopic composition of the ice on a millennial time scale. The Siple Dome CO_2 record is mostly in agreement with previous Antarctic ice core CO_2 records. Initially, CO_2 rose at ~ 17.5 kyr, decreased slowly during the Antarctic Cold Reversal, rose during the Younger Dryas, fell to a local minimum at around 8 kyr, and rose continuously since then.

There are many hypotheses to explain the CO_2 increase during deglaciation [see *Sigman and Boyle*, 2000; *Kohfeld et al.*, 2005]. My results are only consistent with the hypotheses that explain the strong temporal correlation of CO_2 and Antarctic temperature during the last deglaciation. Two leading hypotheses involve physical processes in the Southern Ocean, the change in CO_2 gas exchange between the atmosphere and sea, due to varying sea ice coverage [*Stephens and Keeling*, 1999], and changes in the mixing between mid-depth water and deep water due to a change in ocean stratification [*Toggweiler*, 1999]. The Southern Ocean is the primary region for deep water ventilation and provides the CO_2 source from deep waters to the atmosphere. Hypotheses related to changes in nutrient utilization in the Southern Ocean have not been supported by the evidence in previous studies [*Kohfeld et al.*, 2005].

In addition to the linkage of temperature and CO_2 trends mentioned above, a small phase offset between the two was required by the data analysis. Gas chronologies on this core are relatively robust due to the high snow accumulation rate at Siple Dome, which produces relatively small uncertainties in the difference between the gas and ice ages. These small uncertainties permit a more accurate analysis of the phase relationship between CO_2 change and the ice-isotopic temperature than in other cores at low accumulation sites. During the last glacial termination, I found a lag of CO_2 after the Siple Dome isotopic temperature of ~ 300 years. The size of this lag is somewhat comparable to the time scale of ocean mixing that is necessary to provide a new CO_2 source from the deep ocean, consistent with the hypotheses related to the change in physical processes in the Southern Ocean. The CO_2 lag after Siple Dome temperature confirms that CO_2 is not the forcing that initially drives the climatic system during the last deglaciation as concluded by *Caillon et al.* [2003]. The time lag of CO_2 of ~ 300 years is short compared with ~ 7000 year total duration of the temperature and CO_2 increase during the last deglaciation. This finding therefore does not contradict the idea that CO_2 plays one of the key roles in deglaciation by amplifying the initial orbital forcing through its greenhouse effect.

While the predominant concept related to modern climate is that CO_2 increase drives global warming, this research shows that natural atmospheric CO_2 change is triggered by other climate factors. The recent anthropogenic CO_2 increase rate (1.4 ppm / yr) (due to human activities) [*Keeling and Whorf,* 2005] is two orders of magnitude greater than that of the natural change of CO_2 during the last deglaciation (~ 0.013 ppm / yr). This modern anthropogenic CO_2 enormously disturbs the natural carbon cycle, and plays a major role as an external radiative force (independent trigger) that causes global warming [*Kump*, 2002]. The natural carbon cycle during the last glacial-interglacial periods differs from that in our modern situation, and does not provide a useful analog.

Phase (2)

During Phase (2) the finding that diffusion of CO_2 in ice occurs significantly over millennial time scales was explored. As a result of diffusion in ice, an initially rapid change in CO_2 concentration in the ice may be smoothed out and can be altered during the clathrate (bubble-free) ice formation. If the smoothing were to happen extensively, we would underestimate the speed of real paleoatmospheric CO_2 variations from polar ice cores. The high resolution analyses performed in this work on the Siple Dome ice core show a gradual decrease of CO_2 mole fraction away from the refrozen melt layers. Combined with the noble gas study (Xe/Ar, Kr/Ar) and chemical and electric properties of the ice, I found that a melt-related CO_2 spike diffused measurably through the ice at a depth of 287 m. This is the first experimental evidence of CO_2 diffusion in polar ice. The reason laboratory studies have not been able to observe it is that it happens too slowly. The product of solubility and the diffusion coefficient of CO_2 was obtained as 4.3 (± 2.1) × 10^{-21} m^2s^{-1} $molCO_2$ $m^{-3}ice$ $(PaCO_2)^{-1}$ at –23 °C. Also, I found that the smoothing of the CO_2 record by diffusion is at least an order of magnitude smaller than that by the gas age distribution at the depth of 287 m (gas age = 2.74 kyr) in the Siple Dome ice. The extension of the modeling results from a shallow depth (287 m) to greater depths is limited and requires further study.

Phase (3)

Phase (3) investigated the difference in the CO_2 records between the Siple Dome and the other Antarctic ice cores. In certain time intervals (e.g., the last deglaciation and the Holocene period), Siple Dome CO_2 concentrations are greater than those in other Antarctic ice cores by up to 20 ppm (μmol CO_2 / mol air). This difference cannot be explained by local variations because atmospheric CO_2 is well mixed and homogenized within one hemisphere, so that gradients are much less than 1 ppm. In contrast, non-atmospheric excess CO_2 is likely to cause a ~ 20 ppm enhancement. It is plausible that melting/refreezing on a microscale in the snow is responsible for the excess CO_2. This is an exception to the belief that Antarctic ice cores are representative of paleoatmospheric concentrations, in contrast to those from Greenland or low-latitude ice cores. The low dust content in Antarctic ice minimizes the in situ production of CO_2 by the carbonate-acid reaction and/or oxidation of organic compounds, as observed in Greenland ice cores. This work shows the first experimental evidence of excess CO_2 measured in an Antarctic ice core, suggesting that future coring at warm sites in Antarctica requires a cautious approach.

Phase (4)

In Phase (4), the carbon isotope composition of CO_2 in polar ice was probed. Carbon isotopes of paleoatmospheric CO_2 combined with CO_2 concentration from ice cores may allow an additional constraint to aid in deciphering the carbon cycle over the past hundreds of thousand years. The $\delta^{13}C$ was measured for the gas trapped in the Siple Dome and Vostok ice cores from Antarctica, covering the past 40 kyr and 160-110 kyr, respectively. The $\delta^{13}C$ values from the Siple Dome ice are slightly depleted on average, and are more scattered compared to those from the Taylor Dome ice core, and are not considered as a reliable atmospheric record. This may be related to surface conditions, possibly micro-scale melting on the snow surface or laboratory artifacts. Vostok ice around Termination II shows a $\delta^{13}C$ increase during the atmospheric increase of CO_2 concentration. This trend is consistent with the previous results from the Taylor Dome ice core in that the main net source for the atmospheric CO_2 change during the deglaciations is isotopically heavy (but this isotopic study for the trend of some age intervals does not allow specific sources of CO_2 change to be constrained) [*Smith et al.*, 1999]. However, the magnitude of the $\delta^{13}C$ change is much greater than that in Taylor Dome ice. In addition, absolute values of $\delta^{13}C$ are very depleted by 1-3 ‰. This depletion may be explained by isotopic fractionation during the gas extraction procedure with mechanical crushing of the ice. A sublimation technique may improve the quality of the experiments, and could possibly reduce the chance of isotopic fractionation during the gas extraction. Deconvolution modeling with reconstructed high temporal resolution of the past $\delta^{13}C$ and CO_2 concentration may allow to reconstruct temporal carbon cycle change for the last deglaciations as shown in the previous works on the Holocene period [*Indermühle et al.*, 1999] and the last 1000 years [*Trudinger et al.*, 2005].

References

Caillon, N., J.P. Severinghaus, J. Jouzel, J.-M. Barnola, J. Kang, and V.Y. Lipenkov, Timing of Atmospheric CO_2 and Antarctic Temperature Changes Across Termination III, *Science, 299*, 1728-1731, 2003.

EPICA Community members, Eight glacial cycles from an Antarctic ice core, *Nature, 429*, 623-628, 2004.

Etheridge, D.M., L.P. Steele, R.L. Langenfelds, R.J. Francey, J.M. Barnola, and V.I. Morgan, 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, 1996.

Falkowski, P., R.J. Scholes, E. Boyle, J. Canadell, D. Canfield, J. Elser, N. Gruber, K. Hibbard, P. Högberg, S. Linder, F.T. Mackenzie, B. Moore III, T. Pederson, Y. Rosenthal, S. Seitzinger, V. Smetacek, and W. Steffen, The global carbon cycle: A test of our knowledge of earth as a system, *Nature, 290*, 291-296, 2000.

Indermühle A., T. F. Stocker, F. Joos, H. Fisher, H. J. Smith, M. Wahlen, B. L. Deck, D. Mastroianni, J. Tschumi, T. Blunier, R. Meyer and B. Stauffer, Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica, *Nature, 398*, 121-126, 1999.

Keeling, C.D. and T.P. Whorf, Atmospheric CO_2 records from sites in the SIO air sampling network. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A., 2005.

Kohfeld, K.E., C.L. Quéré, S.P. Harrison, and R.F. Anderson, Role of marine biology in glacial-interglacial CO_2 cycles, *Science, 308*, 74-78, 2005.

Kump, L.R., Reducing uncertainty about carbon dioxide as a climate driver, *Nature, 419*, 188-190, 2002.

Monnin, E., A. Indermühle, A. Daellenbach, J. Flückiger, B. Stauffer, T. F. Stocker, D. Raynaud, and J.-M. Barnola, Atmospheric CO_2 concentrations over the Last Glacial Termination, *Science, 291*, 112-114, 2001.

Petit, J. R., J. Jouzel, D. Raynaud, N. I. Barkov, J.-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature, 399*, 429-436, 1999.

Sigman, D.M., and E.A. Boyle, Glacial/interglacial variations in atmospheric carbon dioxide, *Nature, 407*, 859-869, 2000.

Smith H.J., H. Fischer, M. Wahlen, D. Mastroianni and B. Deck, Dual modes of the carbon cycle since the Last Glacial Maximum, Nature, 400, 248-250, 1999.

Stephens, B.B., and R.F. Keeling, The influence of Antarctic sea ice on glacial–interglacial CO_2 variations, *Nature, 404*, 171 ,2000.

Toggweiler, J.R., Variation of atmospheric CO_2 by ventilation of the ocean's deepest water, *Paleoceanography, 14*, 572, 1999.

Trudinger, C., I. Enting, D. Etheridge, R. Francey, and P. Rayner, The carbon cycle over the past 1000 years inferred from the inversion of ice core data, *in A history of atmospheric CO_2 and its effects on plants, animals, and ecosystems,* edited by J.R. Ehleringer et al., pp. 329-349, Ecological studies 177, Springer, 2005.