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US ITASE Glaciochemistry

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Principal Investigator: Mayewski, Paul A.
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Organization: University of Maine
Title:
US ITASE Glaciochemistry

Project Participants

Senior Personnel

Name: Mayewski, Paul
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Meeker, Loren
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Maasch, Kirk
Worked for more than 160 Hours: Yes
Contribution to Project:
Involved in statistics and interpretation.

Post-doc

Graduate Student

Name: Cruickshank, Tyler
Worked for more than 160 Hours: Yes
Contribution to Project:
Participated in 1999-2000 field season

Name: Souney, Jospeh
Worked for more than 160 Hours: Yes
Contribution to Project:
Field assistant 1999-2000 traverse

Name: Dixon, Daniel
Worked for more than 160 Hours: Yes
Contribution to Project:
Field Assistant and MSc project

Name: Kaspari, Susan
Worked for more than 160 Hours: Yes
Contribution to Project:
Field Assistant and MSc project

Undergraduate Student

Name: Cavallari, Benjamin
Worked for more than 160 Hours: Yes
Contribution to Project:
Participated in 2000-2001 traverse

Technician, Programmer

Name: Smith, Zachary
Worked for more than 160 Hours: Yes
Contribution to Project:
Participated in 2000-2001 traverse

Name: Sneed, Sharon
Worked for more than 160 Hours: Yes
Contribution to Project:
Laboarory analyses and sample processing

Name: Handley, Michael
Worked for more than 160 Hours: Yes
Contribution to Project:
Laboratory analyses and sample processing

Other Participant

Research Experience for Undergraduates

Organizational Partners

Boston Museum of Science
Shared outreach activity

CRREL

University of Arizona

Ohio State University

University of Washington

University of Colorado at Boulder

University of Pennslyvania

NASA Goddard

University of New Hampshire

Motorola Inc
Provided Iridium phones and related equipment for field work.

Other Collaborators or Contacts

Other members of the US ITASE project:
Investigators Institution Discipline

Mary Albert CRREL Snow and firn microstructure

Steve Arcone
Norbert Yankielun CRREL High resolution radar profiling

Roger Bales U Arizona Hydrogen peroxide, formaldehyde
Joe McConnell (DRI)

David Bromwich OSU Meteorology

Gordon Hamilton UMaine Satellite image analysis
Ian Whillans (OSU)

Gordon Hamilton UMaine Mass balance
Ian Whillans (OSU)

Bob Jacobel St. Olaf Deep radar

Paul Mayewski UMaine Glaciochemistry
Dave Meeker (UNH/UMaine)

Paul Mayewski UMaine Science management

Deb Meese
Tony Gow CRREL Stratigraphy

Eric Steig UWash Stable isotopes
Jim White (UColorado)
Chris Shuman (NASA/UMaryland)

Joe McConnell Desert Research Institute

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings: (See PDF version submitted by PI at the end of the report)

Training and Development:

1. Several students have participated in field and laboratory activities:
Tyler Cruickshank - 1999-2000 field season
Joe Souney (1999-2000 field season, MSc - University of New Hampshire)
Daniel Dixon (2001-2003 field seasons, MSc - University of Maine, PhD 2003-)
Benjamin Cavallari (2000-2001 field season, undergraduate - University of Maine)
Susan Kaspari (2001-2003 field seasons, MSc - University of Maine)

2. Data collected has been used in graduate course instruction in climate change and chemistry of the atmosphere.

3. Data and interpretation given at several scientific meetings (e.g., Holocene Workshop, Trins, Austria; Antarctic Autonomous Vehicle Workshop, Washington, D.C.), public lectures.

Outreach Activities:

Education and Outreach Activities for this project are in coordination with the US ITASE Science Management Office OPP-0096338 (PI - P.A. Mayewski). For details please see the Annual Report for OPP-0096338. Outreach activities conducted during the life of this project include:

presentations to schools and organizations around the country, enhancement of the US ITASE web sites (www.secretsoftheice.org, www.ume.maine.edu/USITASE), daily reporting of field activities to the public through the Boston Museum of Science, twice weekly live broadcasts to the Boston Museum of Science fromm the field, and the distribution of US ITASE posters and standards-based educational materials through scheduled teacher workshops.

Journal Publications

Arcone, S. A., Spikes, V.B., Hamilton, G., and Mayewski, P.A., "Continuity, vertical resolution and origin of stratigraphy in 400-Mhz short-pulse radar
profiles of firn in West Antarctica", Annals of Glaciology, p. , vol. 39, (2004). In press

Arcone, S.A., Spikes, V.B. Hamilton, G.S., "Phase structure of radar stratigraphic horizons within Antarctic firn", Annals of Glaciology, p. , vol. 41, (2004). In press

Bertler, N.A.N., and 54 others, "Antarctic Snow Chemistry", Annals of Glaciology, p. , vol. , ( ). Submitted

Bertler, N.A.N., P.J. Barrett, P.A. Mayewski, R.L. Fogt, K.J. Kreutz, and J. Shulmeister,, "El Niño suppresses Antarctic warming", Geophysical Research Letters, p. L15207, vol. 31, (2004). Published

Bertler, N.A.N., P.J. Barrett, P.A. Mayewski, R.L. Fogt, K.J. Kreutz, and J. Shulmeister, "Reply to comment by Doran et al. on "El Niño suppresses Antarctic warming"", Geophysical Research Letters, p. L07707, vol. 32, (2005). Published

Bertler, N.A.N., P.A. Mayewski, P.J. Barrett, S.B. Sneed, M.J. Handley, and K.J. Kreutz,, "Monsoonal circulation of the McMurdo Dry Valleys -Signal from the snow chemistry", Annals of Glaciology, p. , vol. 39, (2004). In press

Bertler, N.A.N., T.R. Naish, P.A. Mayewski, and P.J. Barrett, "Opposing oceanic and atmospheric ENSO influences on the Ross Sea Region, Antarctica", Advances in Geoscience, p. , vol. , ( ). Submitted

Bertler, A.N., Barrett, P.J., Mayewski, P.A., Sneed, S.B., Naish, T.R., and Morgenstern, U, "Solar forcing recorded by aerosol concentrations in coastal Antarctic glacier ice, McMurdo Dry
Valleys", Annals of Glaciology, p. , vol. 41, (2004). In press

Conway, H., Neumann, T.A., Price, S., Waddington, E.D., Morse, D., Taylor, K., Mayewski, P.A., Dixon, D., Pettit, E., and Steig, E.J, "Candidate drill site near the Ross-Amundsen ice divide, West Antarctica", Report to Office of Polar Programs, p. 1, vol. , (2005). Published

Curran, M.J., Palmer, A.S., van Ommen, T.D., Morgan, V., Phillips, K.L., McMorrow, A.J., and Mayewski, P.A.,, "Post-depositional methanesulphonic acid movement in Law Dome and the effect of
accumulation rate", Annals of Glaciology, p. 333, vol. 35, (2002). Published

Dixon, D., Mayewski, P.A., Kaspari, S., Sneed, S. and Handley, M.,, "A 200 year West Antarctic paleoclimate record from U.S. ITASE ice cores", Annals of Glaciology, p. , vol. 39, (2004). In press

Gao, C., Robock, A., Self, S., Witter, J., Steffenson, J.P., Clausen, H.B., Siggaard-Anderson, M.-L., Johnsen, S., and Mayewski, P.A.,, "The 1452 AD Kuwae eruption signal derived from multiple ice core records: Greatest eruption
of the past 700 years", Journal of Geophysical Research, p. , vol. , ( ). Submitted

Genthon, C., Kaspari,S. and Mayewski, P.A.,, "Inter-annual variability of surface mass balance in West Antarctica from ITASE cores and ERA40 reanalyses", Climate Dynamics, p. 382, vol. 21, (2005). Published

Goodwin, I.D., Mayewski, P.A., and Curran, M, "Antarctic ice core evidence of Holocene circumpolar circulation variability", Proceedings of the PAGES PEP II Meeting, Singapore, p. 10, vol. , (2001). Published

Goodwin, I.D., van Ommen, T.D., Curran, M.A.J., and Mayewski, P.A.,, "Mid-latitude climate variability in the south Indian Ocean and

southwest Pacific regions since
AD1300", Climate Dynamics, p. , vol. , ( ). Accepted

Gow, A.J., Meese, D. Bialas, R, "Density profiles and crystal-growth trends observed in U.S. ITASE firn and ice cores from
West Antarctica", Annals of Glaciology, p. , vol. 39, (2004). in press

Hamilton, G, "Topographic forcing of local accumulation rate variability and implications for ice-core
interpretation", Annals of Glaciology, p. , vol. 39, (2004). In press

Han, J., Xie, Z., Zhang, Xinping, Z., Dai, D. and Mayewski, P.A.,, "Methanesulfonate in the firn of King George Island, Antarctica", Journal of Glaciology, p. 589, vol. 47, (2001). Published

Isaksson, E., Karlén, W., Mayewski, P., Twickler, M., and Whitlow, S, "A high-altitude snow chemistry record from Amundsenisen, Dronning Maud Land, Antarctica", Journal of Glaciology, p. 489, vol. 47, (2001). Published

Kaspari, S., Mayewski, P.A., Dixon, D., Sneed, S.B., and Handley, M.J, "Sources and transport pathways for marine aerosol species into West Antarctica", Annals of Glaciology, p. , vol. 41, (2004). in press

Kaspari, S.D., Mayewski, P.A., Sneed, S.B., Handley, M.J, "West Antarctic climate reconstruction based on the 2001?2002 U.S. ITASE ice cores", Annals of Glaciology, p. , vol. 39, (2004). In press

Kreutz, K.J., Mayewski, P.A., Whitlow, S.I. and Twickler, M.S.,, "The effect of spatial variability and temporal accumulation rate variability in West Antarctica
on soluble ion deposition", Geophysical Research Letters, p. 2517, vol. 27, (2000). Published

Kreutz, K.J., Mayewski, P.A., Pittalwala, I.I., Meeker, L.D., Twickler, M.S., and Whitlow, S.I.,, "Sea-level pressure variability in the Amundsen Sea region inferred from a West Antarctic
glaciochemical record", Journal of Geophysical Research, p. 4047, vol. 105, (2000). Published

Kurbatov, A.V., Zielinski, G.A., Dunbar, N.W., Mayewski, P.A., Meyerson, E.A., and Sneed, S.B, "Holocene explosive volcanism recorded in the Siple Dome A ice core, Antarctica", Journal of Geophysical Research, p. , vol. , ( ). Near Submission

Maasch, K., Mayewski, P.A., Rohling, E., Stager, C., Karlén, K., Meeker, L.D., and Meyerson, E, "Climate of the past 2000 years", Geografiska Annaler, p. , vol. , ( ). Accepted

Mayewski, P.A., Maasch, K.A., Yan, Y., Kang, S., Meyerson, E.A., Sneed, S.B. Kaspari, S.D., Dixon, D.A., Osterberg, E.C., Morgan, V.I., van Ommen, T., Curran, M.A.J, "Solar Forcing of the Polar Atmosphere Data, Mechanism, and Implications", Annals of Glaciology, p. , vol. 41, ( ). Accepted

Mayewski, P.A., Rohling, E.E., Stager, J.C. Karlén, W., Maasch, K.A., Meeker, L.D., Meyerson, E.A., Gasse, F., van Kreveld, S., Holmgren, K., et al, "Holocene climate variability", Quaternary Research, p. 243, vol. 62, (2004). Published

Mayewski, P.A, "Antarctic oversnow traverse-based Southern Hemisphere climate reconstruction", EOS Newsletter, p. 205, vol. 84, (2003). Published

Mayewski, P.A., Maasch, K., Morgan, V., van Ommen, T., Goodwin, I, "A 700 year record of the Aantarctic Oscillation and implications for understanding the global
climate system", Annals of Glaciology, p. , vol. 39, (2004). Accepted

Mayewski, P.A., Maasch, K., Yan, Y., Kang, S., Meyerson, E., Sneed, S., Kaspari, S., and Dixon, D, "Solar forcing of the polar atmosphere", Nature, p. , vol. , ( ).

Mayewski, P.A. and Maasch, K, "Recent warming inconsistent with natural climate variability", Nature, p. , vol. , ( ). Submitted

Mayewski, P.A., Frezzotti, M., Bertler, N., van Ommen, T., Hamilton, G.H., Jacka, J., Welch, B. and Frey, M, "The International Trans-Antarctic Scientific Expedition (ITASE), An Overview", Annals of Glaciology, p. , vol. , ( ). Accepted

Meyerson, E.A., Mayewski, P.A., Whitlow, S.I., Meeker, L.D.and Kreutz, K.J. and Twickler, M.S, "The extratropical expression of ENSO recorded in a South Pole glaciochemical time series", Annals of Glaciology, p. 430, vol. 35, (2002). Published

Palmer, A.S.,Van Ommen, T., Curran, M.A., Morgan, V., Souney, J., and Mayewski, P.A, "High-precision dating of volcanic events (AD 1301-1995) using ice cores from Law Dome,
Antarctica", Journal of Geophysical Research, p. 28080, vol. 106, (2001). Published

Palmer, A.S., Morgan, V., Curran, M.J., van Ommen, T.D., and Mayewski, P.A, "Antarctic flux ratios from Law Dome", Annals of Glaciology, p. 329, vol. 35, (2002). Published

Pruett, L.E., Kreutz, K.J., Mayewski, P.A., Kurbatov, A., and Wadleigh, M, "Sulfur isotopic measurements from a West Antarctic ice core: implications for sulfate source
and transport", Annals of Glaciology, p. , vol. 39, ( ). Accepted

Reusch, D.B., P.A. Mayewski, S.I. Whitlow, and M.S. Twickler, "Spatial variability and past atmospheric circulation patterns from central West Antarctic
glaciochemistry", Journal of Geophysical Research, p. 5985, vol. 104, (1999). Published

Schneider, D.P., Steig, E.J., Bitz, C.M., Dixon, D., Mayewski, P.A., van Ommen, T.D. and Jones, J.M, "Antarctic temperatures over the past two centuries from ice cores.", Science, p. , vol. , ( ). Submitted

Shulmeister,J., I. Goodwin, J. Renwick, K. Harle, L. Armand, M. S. McGlone, E. Cook, J. Dodson, Hesse, P.P, Mayewski, P., and M. Curran, "The Southern Hemisphere Westerlies in the Australasian sector: A synthesis", Quaternary International, p. , vol. , ( ). Accepted

Souney, J., Mayewski, P.A., Goodwin, I.D., Morgan, V., and van Ommen, T, "A late Holocene climate record from Law Dome, East Antarctica", Journal of Geophysical Research, p. 4608, vol. 107, (2002). Published

Steig, E.J., P.A. Mayewski, D. Dixon, S. Kaspari, M. Frey, D.P. Schneider, S.A. Arcone, G. Hamilton, B. Spikes, M.R. Albert, D.A. Meese, A. Gow, C.A. Shuman, J. White, S. Sneed, J. Flaherty, M. Wumkes and US ITASE Project Members, "High-resolution ice cores from US ITASE (West Antarctica): development and validation of
chronologies and determination of precision and accuracy", Annals of Glaciology, p. , vol. 41, (2004). Accepted

Xiao, C., Kreutz, K.J., Mayewski, P.A., and Qin, D, "Ice core based estimates of the Trans Polar Index for the last 700 years", Geophys. Res. Lett, p. , vol. , ( ). Submitted

Xiao, C., Mayewski, P.A., Qin, D., Li, Z., Zhang, M., and Yan, Y, "Sea level pressure variability in the Southern Indian Ocean inferred from a glaciochemical
record in the Princess Elizabeth L and East Antarctica", Jour. Geophys. Research, p. D16101, vol. 109, (2004). Published

Yan, Y., Mayewski, P.A., Kang, S., and Meyerson, E, "An ice core proxy for Antarctic circumpolar wind intensity", Annals of Glaciology, p. , vol. 41, (2004). Accepted

Books or Other One-time Publications

Paul A. Mayewski and Frank White, "The Ice Chronicles", (2001). Book, Published
Bibliography: University Press of New England

Web/Internet Site

URL(s):

1) www.secretsoftheice.org 2) http://www.ume.maine.edu/USITASE 3) http://climatechange.umaine.edu 4) http://gcmd.nasa.gov/getdif.htm?US_ITASE_GLACIOCHEMICAL_DATA

Description:

1) The site, "Secrets of the Ice" is maintained by the Boson Museum of Science, with the assistance of the Science Management Office, University of Maine, and contributions from US ITASE PIs. Resources for teachers, and general information about Antarctica and activities designed for school children.
2) The US ITASE web site is maintained by the University of Maine as the official science web site. Science and Implementation Plans, links to researchers, abstracts of projects and draft proposals are all available here. Daily logs from the team while they were in the field along with photos are archived here. An extensive teacher's resource section including activities and lesson plans are here as well.
3) The Climate Change Institute, University of Maine web site. Research project descriptions, laboratory and equipment descriptions.
4) GCMD web site for data collected.

Other Specific Products

Product Type:

Data or databases

Product Description:

Glaciochemical time series from snowpits and ice cores.

Sharing Information:

Data will be submitted to the WDC-Paleoclimatology within 12 months of completion to assure QA/QC.

Product Type:

Physical collection (samples, etc.)

Product Description:

Snow and ice samples from snowpits and ice cores.

Sharing Information:

Samples are shared with the Universities of Arizona, Washington and Colorado.

Product Type:

Audio or video products

Product Description:

Draft video was shot on the 1999-2000 and the 2000-2001 field seasons. The Boston Museum of Science has utilized sections of the video for their display on US ITASE.

Sharing Information:

Shared through Boston Museum of Science and on a per request (eg., National Geographic Documentary on Wallace Broecker).

Product Type:

Teaching aids

Product Description:

Laboratory exercises for grade schoolers.

Sharing Information:

Laboratory exercises have been developed by Zach Smith for grade schoolers. These exercises are distributed at Teacher Workshops sponsored by Tufts University Wright Center and the Climate Change Institute at University of Maine.

Contributions

Contributions within Discipline:

This research is intended to contribute to two other broad scientific activities:
(1) The West Antarctic Ice Sheet (WAIS)
Our project (US ITASE Glaciochemistry) provides data which is essential to the selection of deep ice core drilling activities conducted by WAIS and also provides spatially distributed data necessary to the interpretation of WAIS ice core data.
(2) The International; Trans Antarctic Scientific Expedition (ITASE)
US ITASE is a contributor to the twenty nation internationally sponsored (SCAR (Scientific Committee on Antarctic Research) and IGBP International Geophysical Biosphere Project)) ITASE program. US ITASE Glaciochemistry provides 200 year plus chemical time series from selected sites in West Antarctica that are added to similar data provided by other countries in other parts of Antarctica for purposes of continent wide interpretations of change in climate and chemistry of the atmosphere.

Contributions to Other Disciplines:

US ITASE is a contributor to the twenty nation internationally sponsored (SCAR (Scientific Committee on Antarctic Research) and IGBP International Geophysical Biosphere Project)) ITASE program. US ITASE Glaciochemistry provides 200 year plus chemical time series from selected sites in West Antarctica that are added to similar data provided by other countries in other parts of Antarctica for purposes of continent wide interpretations of change in climate and chemistry of the atmosphere. The resultant chemical data can be used by a variety of disciplines e.g., (meteorology, climatology, atmospheric chemistry, glaciology).

Contributions to Human Resource Development:

US ITASE is coordinated by a Scientific Management Office (US ITASE SMO - OPP-0096338) that has developed educational materials for schools based upon the science activities generated by US ITASE Glaciochemistry and the other US ITASE disciplines.

Contributions to Resources for Research and Education:

Laboratory supplies and replacement equipment plus partial year support for laboratory staff are provided by this grant.

Contributions Beyond Science and Engineering:

Results from this project have direct implications for understanding change in climate and chemistry of the atmosphere. Antarctica provides the largest storehouse on Earth for the recovery of such information. Scientific results from this project are presented to the public several times per year. Focus for talks deals with Antarctica's unique resources (eg., fresh water, marine biology), the continent's influence on the rest of the Earth (eg., through controls on oceanic and atmospheric circulation) and, the continent's vulnerability to human activities (eg., CFC influence on the Antarctic ozone hole and human source acidity and toxics in the Antarctic atmosphere).

Categories for which nothing is reported:

UMaine Continuous Ice Core Melter (UMCoM) System with Discrete Sampling

Introduction

The UMaine Continuous ice core Melter (UMCoM) system is a modified Wagenbach-style continuous melter system (Rothlisberger et al., 2000) with three important differences. First, we have constructed the melthead as two separate pieces, a base and a melter plate, so that it can be easily dismantled and cleaned between melting sessions. Second, the melter plate in contact with the ice is composed of pure nickel (>99.9% Ni) so that trace element measurements can be made from the meltwater stream. Third, in contrast to ice core melter systems in which the meltwater is directly channeled to online instruments for continuous flow analyses (e.g. Sigg et al., 1991; Rothlisberger et al., 2000; Huber et al., 2001; McConnell et al., 2002; Knusel et al., 2003), the UMCoM system collects discrete, high-resolution (<1-2 cm/sample), co-registered samples for each chemical analysis under ultraclean conditions using three or more (if needed) Gilson® fraction collectors (a fraction collector is a device that automatically apportions a liquid flow into discrete samples based on volume). This third modification provides exceptional flexibility in tailoring specific chemical analyses to each project. Currently, the UMCoM system is producing samples from the 2001 Mt. Logan summit ice core for analysis of 30 trace elements (Ca, Al, Fe, S, Sr, Cs, Bi, U, Tl, As, Ti, V, Cr, Mn, Co, Cu, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) by inductively coupled plasma mass spectrometry (ICP-MS), 8 major ions (Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, MSA) by ion chromatography (IC), stable water isotopes ($\delta^{18}O$, δD, *d*) by isotope ratio mass spectrometry (IRMS), and volcanic tephra. The list of analytes can be adjusted to address the specific needs of each project.

The UMCoM system combines the speed, cleanliness and high-resolution sampling of continuous melting with the flexibility and precision of discrete sampling. Continuous melting with discrete sampling is advantageous over melter systems with online analyses for several reasons. With discrete sampling, an archive of each sample remains after initial analyses, allowing for additional chemical measurements (including trace element isotope ratios) should they become desirable, or should they become necessary because of an instrument malfunction during the initial analysis. Discrete samples can be scanned for longer intervals and in replicate, which lowers detection limits and increases measurement precision. Discrete samples can also be frozen and analyzed off-site, enhancing the potential range of analyses that can be performed. The physical separation of the analytical instruments (IC, ICP-MS and IRMS) from the ice core melter system reduces the complexity of the system, decreasing the potential for costly difficulties during ice melting. Should an instrument require maintenance or repair, the other instruments and the ice melting system can continue operating, reducing the total "down time".

Methods

Modified Wagenbach-Style Firn and Ice Melthead

We have constructed a modified Wagenbach-style (Rothlisberger et al., 2000) firn and ice melthead with a pure Ni (>99.9% Ni) melter plate (in contact with the ice/firn core) mounted on a heated aluminum base. The melter plate and base can be separated for easy cleaning between melting sessions, and different melter plates can be constructed to accommodate cores of varying dimensions. The Ni melter plate splits the meltwater into two channels: meltwater from the potentially-contaminated outer portion of the ice core is directed to the "outer channel" for stable isotope, particle and tephra analyses, and meltwater from the uncontaminated, innermost portion of the ice core is directed to the "inner channel" for major and trace chemical analyses.

Meltwater from the inner channel passes through the Ni melter plate and into a polypropylene conduit nested within the aluminum base so that the meltwater is never in contact with the aluminum. The 0.2 mm-wide slits in the Wagenbach-style melter plate produce a downward capillary force that prevents wicking of the meltwater into unmelted core, thereby allowing both firn and ice to be melted (Rothlisberger et al., 2000).

The melter plate is machined from pure nickel because of its favorable thermal properties, availability in pure form, relatively low cost, and because Ni sample and skimmer cones are used in the UMaine ICP-MS (see Table 1), already precluding meaningful measurements of Ni. Our extensive testing indicates that a melter plate coated with metal, ceramic or polymers is problematic because the coating degrades over time, exposing the base metal underneath and potentially contaminating the sample. A solid, pure Ni melter plate can degrade without ever contaminating the sample. In addition, applying any coating within the narrow slits of the Wagenbach-style melthead (Rothlisberger et al., 2000) is technologically difficult and expensive.

Ice Core Melting with Discrete Sampling

The entire UMCoM system is housed in a dedicated clean room with HEPA filtered air. Non-particulating suits and booties, facemasks and wrist-length polypropylene gloves are worn during melting. Deionized water (>18.2 megaohm) is constantly pumped through the entire melter system (including the melthead) between melting sessions to keep the system clean. The aluminum base of the melthead is heated with two 250-W cartridge heaters to a temperature of 15-30^{o}C (depending on ice/firn density), resulting in a 2-3 cm/min ice melt rate. The ice core or slab is mounted in a 1 m-long, pre-cleaned Plexiglas box open only towards the bottom where the ice is in contact with the melter plate. The melthead and core holder are housed within a dedicated freezer maintained at –20^{o}C, while the pumps and fraction collectors described below are all located outside of the freezer within the clean room.

Meltwater from the uncontaminated inner channel is pumped from the melthead through ultra-clean STA-PURE® (Gore and Assoc., Elkton, MD USA) and Teflon tubing using two peristaltic pumps. The incorporation of custom-made, STA-PURE® peristaltic pump tubes eliminated trace element contamination commonly found in peristaltic pump tubing. A third peristaltic pump controls meltwater from the outer channel. Pump rates are determined by ice melt rate and ice core/slab dimensions, and are adjusted so that there is always net flow from the inner towards the outer part of the core to prevent contamination of the inner sample.

Meltwater from the inner channel is then split between two Gilson (Middleton, WI USA) fraction collectors; one that accumulates ICP-MS samples in acid pre-cleaned, 4 ml polypropylene vials under a class-100 HEPA clean bench, and a second fraction collector that collects IC samples in 6 ml vials pre-cleaned with deionized water. A third Gilson fraction collector accumulates isotope and tephra samples from the potentially contaminated outer channel. The “master” IC fraction collector measures the sample volume and triggers the ICP-MS and isotope/tephra fraction collectors to advance to the next sample when the pre-determined volume is collected. Additional fraction collectors could be added to either channel for additional analyses if desired. Constant and correct sample volumes in the two “slave” fraction collectors (ICP-MS and isotope) provide a simple visual confirmation that the melting system is operating properly. IC and ICP-MS samples are collected in the vials in which they are analyzed, reducing sample manipulation (i.e. no aliquoting) and therefore reducing potential contamination. The fraction collectors can be programmed to collect samples in vials of varying dimensions, providing additional analytical freedom. Pump rates and tubing lengths are adjusted for each core so that IC, ICP-MS and isotope samples are exactly co-registered, meaning that the

meltwater collected by each fraction collector originates from the same interval (<1-2 cm) of the core. Sample co-registration is confirmed by comparing the concentrations of elements measured on both the IC and the ICP-MS (sulfur/sulfate and calcium; see "sample co-registration" below).

Ice and Sample Preparation

As with other continuous melter systems, the separation of meltwater from the inner (uncontaminated) and outer (potentially contaminated) parts of the ice core precludes the need to physically decontaminate the sides of the core, greatly reducing ice preparation time. However, the ends of each piece of firn or ice must be decontaminated. The outermost 6 mm of ice or firn are removed from each end with a ceramic (ZrO) scalpel under a class-100 HEPA clean bench in the dedicated UMaine ice core freezer. Non-particulating suits, facemasks and wrist-length polypropylene gloves are worn during the decontamination procedure. The decontaminated ice is then loaded into a pre-cleaned Plexiglas box for melting, taking care not to touch the decontaminated ends of the core even with gloved hands.

Immediately after melting, all ICP-MS samples are acidified with double-distilled $HNO3^-$ under a class-100 HEPA clean bench, and allowed to react with the acid for approximately 2 hours before being frozen. Samples are defrosted at room temperature approximately 6-12 hours prior to analysis. Repeat measurements on samples that were left unfrozen and acidified for varying lengths of time over a 48 hour period showed no change in trace element concentrations. Isotope and IC samples are frozen immediately after melting without acidification.

Sample Vial Cleaning Method

All 4 ml polypropylene ICP-MS vials are soaked in 15% HNO_3^- for 1 week, triple-rinsed in DI water, soaked in DI water for 3 additional days, dried under a class-100 HEPA clean bench, capped and stored dry until use. ICP-MS vials are never uncapped outside of a class-100 HEPA clean bench during the cleaning, drying or melting processes. 6 ml polyethylene IC sample vials are triple-rinsed in DI water, soaked in DI water for 3 days, triple rinsed in DI water again and dried under a class-100 HEPA clean bench. Extensive testing of both IC and ICP-MS vials confirms their cleanliness.

Results

ICP-MS Analysis and Detection Limits

All trace element analyses were performed using the UMaine ThermoFinnigan Element2 ICP-MS according to the method described in Table 1. The use of an ESI Apex high sensitivity inlet system increases instrument sensitivity and reduces oxide formation in the plasma, lowering detection limits and allowing less abundant isotopes to be measured. The ICP-MS autosampler is located within a class-100 HEPA clean bench to further reduce contamination. The instrument is calibrated daily with 5 standards that bracket the expected concentration range. Correlation coefficients of the calibration curves are always >0.999. Although no standard reference material currently exists for trace elements in polar ice, analysis of the precipitation reference material TMRAIN-95 (Environment Canada) produces concentrations within the certified range (Table 2). Instrument detection limits, equivalent to three times the standard deviation (3σ) of 10 acidified (1% optima $HNO3^-$) deionized water samples, are listed in Table 2. These detection limits are similar to or better than published detection limits on similar instruments (e.g. Barbante et al., 1999; Knusel et al., 2003). Method detection limits, calculated from DI water blanks passed through the entire UMCoM system and subsequently acidified, are listed in Table 3 along with estimated maximum, minimum and average concentrations from Greenland ice

(Boutron et al., 1993; Candelone et al., 1995, 1996; Hong et al., 1996a, b; unpublished UMaine data). The UMCoM method detection limits are almost always lower than minimum Greenland ice values and an order of magnitude below average Greenland ice values. The method detection limit for Fe, Mn and Cu will decrease further by January, 2005 when construction of a new melter plate composed of a purer grade of Ni (>99.99% Ni) will be completed.

Reproducibility of UMCoM Trace Element Analyses

Two meters of ice from the GISP2 B core (meters 100-102; ~1675 A.D.; Meese et al., 1997) were cut into parallel 4.5x4.2 cm slabs and melted to demonstrate the reproducibility of trace measurements made with the UMCoM system. GISP2 B core was chosen because of its low chemical concentrations, its availability in large enough dimensions to facilitate producing parallel ice slabs, and because of the abundance of trace element data from Greenland. Figure 1 displays major ion data from the IC, and Figures 2-5 show trace element data from the ICP-MS. Outliers due to noise spikes in the mass spectra caused by small particles (Knusel et al., 2003) have been removed, but the data have not been smoothed. Sample resolution is ~1.7 cm ice/sample for this experiment, although higher resolution sampling is possible. Concentrations span 8 order of magnitude from several hundred parts per billion (ppb) for some major ions to <10 parts per quadrillion (ppq) for some rare earth elements.

All chemical series closely match, with minor differences between the parallel slabs due to natural chemical variability within the ice itself, and the non-uniform distribution of small particles (Knusel et al., 2003). Even when chemical concentrations do not exactly match for a particular sample, the patterns of high and low intervals are nearly identical in the parallel slabs. Note that different elements with the same likely source (i.e. dust, sea-salt, etc.) strongly co-vary. For example, sea-salt proxies Na and Cl are highly correlated (Figure 1), as are dust proxies such as Al and Fe. Rare earth elements (Figures 3, 4), which are valuable dust source tracers, all show a similar pattern as would be expected because of their small mass range and uniform transport properties (Kreutz and Sholkovitz, 2000). The UMCoM system is the first ice melter system to measure rare earth element concentrations. Copper has a distinctly different timeseries, which may be related to anthropogenic smelting activities as has been previously found (Hong et al., 1996b). Bismuth has been identified as a potential volcanic proxy (Candelone et al., 1995), and shows a distinct timeseries marked by a high-concentration event that is present in both slabs. There is no relationship between concentration levels and core breaks for any of the elements.

Efficiency of Ice Decontamination

Figure 6 displays examples of concentration cross-sections from the 2001 Mt. Logan summit ice core generated by melting small pieces of the slab sideways through the UMCoM system at extremely high resolution. Each data point in the cross-sections represents 3 mm of firn. Mt. Logan firn was chosen because contamination will penetrate further into firn than ice, and thus the firn represents a worse-case scenario for dry-drilled cores (Boutron and Batifol, 1985). The cross-sections reveal the extent to which contamination has penetrated into the core, and are analogous to cross-sections generated by physically removing successive veneers of ice and analyzing each veneer (Boutron and Batifol, 1985; Knusel et al., 2003). In all cases, contamination is limited to the outermost 3-6 mm of the slab, and good low concentration plateaus are observed. Consequently, a 6 mm buffer between the slab edge and the inner sample is always maintained when melting.

Different elements show different degrees of outer contamination, as has been previously documented by Boutron and Batifol (1985) and Knusel et al. (2003). For example, heavy metals with low concentrations in the ice but high concentrations in ice coring equipment, such as Cr, V

and Cu, consistently show outer contamination 2-5 times higher than the true ice concentration. Major dust constituents such as Ca, Fe and Al show a 1-3 fold outer contamination, and elements such as Tl, As and Cs show only minor outer contamination because they are not present at high concentrations in either coring equipment or ambient dust. All rare earth element cross-sections strongly resemble the La and Lu cross-sections in Figure 6.

Sample Co-registration

The co-registration of samples collected by different fraction collectors is essential because major ion samples from the IC must correspond to the same ice depth as the equivalent trace element and isotope samples for timeseries analysis purposes. Pump speeds and tubing lengths are adjusted for each project to ensure sample co-registration. We currently measure Ca^{2+} and SO_4^{2-} on the IC and Ca and S on the ICP-MS, providing two timeseries with which to confirm sample co-registration. Figure 5 (bottom 2 panels) shows that Ca and S ($SO_4^{2-}/3$) concentrations measured on the two instruments are very highly correlated (Figure 5, bottom 2 panels; $R>0.88$, $P>0.99$) confirming sample co-registration. This comparison also provides a validation of the concentration values produced by the two different instruments.

References

Barbante, C., G. Cozzi, G. Capodaglio, K. Van de Velde, C. Ferrari, C.F. Boutron, and P. Cescon, 1999. Trace element determination in alpine snow and ice by double focusing inductively coupled plasma mass spectrometry with microconcentric nebulization, *Journal of Analytical Atomic Spectrometry* 14, 1433-1438.

Boutron, C.F., and F.M. Batifol, 1985. Assessing laboratory procedures for the decontamination of polar snow or ice sample for the analysis of toxic metals and metalloids, *Annals of Glaciology* 7, 7-12.

Candelone, J.P., Candelone, J.P., M.A. Bolshov, S.N. Rudinev, S. Hong, and C.F. Boutron, 1995. Bismuth in recent snow from central Greenland: preliminary results, *Atmospheric Environment* 29, 1843-1848.

Candelone, J.P., J.L. Jaffrezo, S. Hong, C.I. Davidson, and C.F. Boutron, 1996. Seasonal variations in heavy metals concentrations in present day Greenland snow, *Science of the Total Environment* 193, 101-110.

Hong, S,. J.P. Candelone, C. Turetta, and C.F. Boutron, 1996a. Changes in natural lead, copper, zinc and cadmium concentrations in central Greenland ice from 8250 to 149,100 years ago; their association with climatic changes and resultant variations of dominant source contributions, *Earth and Planetary Science Letters* 143, 233-244.

Hong, S., J.P. Candelone, C.C. Patterson and C.F. Boutron, 1996b. History of ancient copper smelting pollution during the Roman and medieval times recorded in Greenland ice, *Science* 272, 246-249.

Huber, T.M., M. Schwikowski, H.W. Gaggeler, 2001. Continuous melting and ion chromatographic analyses of ice cores, *Journal of Chromatography A* 920, 193-200.

Knusel, S., D. Puget, M. Schwikowski, H.W. Gaggeler, 2003. Accuracy of continuous ice-core trace-element analyses by inductively coupled plasma sector field mass spectrometry, *Environmental Science and Technology* 37, 2267-2273.

Kreutz, K.J., and E.R. Sholkovitz, 2000. Major element, rare earth element, and sulfur isotopic composition of a high-elevation firn core: Sources and transport of mineral dust in Central Asia, *Geochemistry, Geophysics, Geosystems (G3)* 1, paper 20000GC000082.

McConnell, J.R., G.W. Lamorey, S.W. Lambert, and K.C. Taylor, 2002. Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry, *Environmental Science and Technology* 36, 7-11.

Meese, D.A., A.J. Gow, R.B. Alley, G.A. Zielinski, P.M. Grootes, M. Ram, K. Taylor, P.A. Mayewski, and J.F. Bolzan, 1997. The GISP2 depth-age scale: methods and results, *Journal of Geophysical Research* 102, 26411-26423.

Rothlisberger, R., M. Bigler, M. Hutterli, S. Sommer, B. Stauffer, H.G. Junghans and D. Wagenbach, 2000. Technique for continuous high-resolution analysis of trace substances in firn and ice cores, *Environmental Science and Technology* 34, 338-342.

Sigg, A., K. Fuhrer, M. Anklin, T. Steffelbach, D. Zurmuhle, 1994. A continuous analysis technique for trace species in ice cores, *Environmental Science and Technology* 28, 204-209.

Table 1. Details of the UMaine ICP-MS instrument, components and settings used in the analyses discussed here.

Instrument	ThermoFinnigan Element2
RF Power	1280 W
Sample gas	~1.0 l min^{-1}
Sample cone	Ni, 1.1mm
Skimmer cone	Ni, 0.8mm
Sample inlet	ESI Apex high sensitivity inlet system
Nebulizer	ESI PFA-ST 100µL/min
Sensitivity	800 000 cps for 100ng l^{-1} ^{115}In
Runs and passes	3x3
Isotopes Measured	Low Resolution (300) ^{75}As, ^{88}Sr, ^{133}Cs, ^{39}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{205}Tl, ^{209}Bi, ^{238}U Medium Resolution (4000) ^{27}Al ^{32}S ^{44}Ca ^{47}Ti ^{51}V ^{52}Cr ^{55}Mn ^{56}Fe ^{59}Co ^{63}Cu

Table 2. Comparison of precipitation standard reference material TMRAIN-95 certified values (Environment Canada) with values determined from the UMaine ICP-MS

Element	UMaine Analyzed µg/L	Certified µg/L
Al	1.887 ±0.059	1.7 ±0.91
Cr	0.842 ±0.02	0.79 ±0.17
Co	0.225 ±0.004	0.22 ±0.037
Cu	6.853 ±0.046	6.2 ±0.93
Fe	25.61 ±0.44	24.2 ±3.64
Mn	6.268 ±0.219	6.1 ±0.78
Sr	1.705 ±0.013	1.7 ±0.26
U	0.281 ±0.0015	0.25 ±0.06
V	0.697 ±0.006	0.64 ±0.12
Ca	0.684 ±0.019	0.66
Ti	0.462 ±0.02	0.47

Table 3. Instrument detection limits (3σ) of the UMaine ICP-MS determined from 10 acidified (1% Optima HNO_3^-) dionized (DI) water blanks (ng/L; μg/L*)

	Blank 1	Blank 2	Blank 3	Blank 4	Blank 5	Blank 6	Blank 7	Blank 8	Blank 9	Blank 10	Average DI Blank	**Instrument Detection Limits**
Sr	0.1581	0.1432	0.2948	0.1587	0.2083	0.1607	0.1784	0.1998	0.3104	0.1954	0.2008	**0.1731**
Cs	0.0111	0.0101	0.0108	0.0122	0.0122	0.0183	0.0115	0.0108	0.0122	0.0104	0.0120	**0.0071**
La	0.0009	0.0022	0.0070	0.0026	0.0074	0.0009	0.0052	0.0061	0.0044	0.0026	0.0039	**0.0073**
Ce	0.0022	0.0018	0.0062	0.0040	0.0040	0.0035	0.0009	0.0044	0.0035	0.0035	0.0034	**0.0045**
Pr	0.0020	0.0007	0.0000	0.0000	0.0003	0.0000	0.0000	0.0007	0.0010	0.0007	0.0005	**0.0019**
Nd	0.0079	0.0000	0.0079	0.0060	0.0139	0.0079	0.0040	0.0040	0.0000	0.0060	0.0058	**0.0124**
Sm	0.0000	0.0000	0.0000	0.0000	0.0046	0.0000	0.0000	0.0000	0.0046	0.0000	0.0009	**0.0058**
Eu	0.0000	0.0000	0.0000	0.0015	0.0015	0.0022	0.0015	0.0007	0.0015	0.0022	0.0011	**0.0026**
Gd	0.0010	0.0000	0.0019	0.0000	0.0000	0.0000	0.0000	0.0029	0.0000	0.0000	0.0006	**0.0031**
Tb	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	**0.0004**
Dy	0.0037	0.0000	0.0018	0.0055	0.0074	0.0018	0.0018	0.0055	0.0110	0.0000	0.0039	**0.0105**
Ho	0.0000	0.0000	0.0000	0.0000	0.0005	0.0005	0.0000	0.0000	0.0009	0.0000	0.0002	**0.0010**
Er	0.0000	0.0040	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0027	0.0027	0.0009	**0.0046**
Tm	0.0000	0.0000	0.0000	0.0000	0.0024	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	**0.0023**
Yb	0.0023	0.0000	0.0046	0.0000	0.0069	0.0023	0.0000	0.0000	0.0000	0.0092	0.0025	**0.0099**
Lu	0.0014	0.0020	0.0039	0.0048	0.0011	0.0017	0.0000	0.0014	0.0051	0.0022	0.0024	**0.0050**
Bi	0.0111	0.0068	0.0111	0.0094	0.0094	0.0213	0.0111	0.0111	0.0077	0.0111	0.0110	**0.0118**
U	0.0048	0.0067	0.0041	0.0041	0.0054	0.0102	0.0086	0.0064	0.0048	0.0054	0.0060	**0.0059**
As	0.6657	0.2684	0.4174	0.2503	0.5889	0.4760	0.2999	0.1058	0.4625	0.3091	0.3844	**0.5083**
Tl	0.0940	0.0769	0.0722	0.0896	0.0880	0.0987	0.0942	0.0976	0.1038	0.0834	0.0898	**0.0299**
Ti	0.7870	0.7287	0.2623	0.5247	0.4664	0.9036	0.3498	0.9036	0.4081	0.4664	0.5800	**0.6976**
V	0.0738	0.0246	0.0492	0.0307	0.0615	0.0615	0.0553	0.0799	0.0615	0.0123	0.0510	**0.0656**
Cr	0.2038	0.2242	0.2038	0.1223	0.1291	0.1563	0.1223	0.2514	0.1971	0.1631	0.1773	**0.1360**
Co	0.0578	0.0263	0.1262	0.2471	0.0631	0.0263	0.4732	0.1209	0.0789	0.0789	0.1299	**0.4099**
Al*	0.0527	0.0503	0.0643	0.0651	0.0903	0.0704	0.0832	0.0812	0.0652	0.0597	0.0682	**0.0394**
S*	0.3298	0.0179	0.1465	0.1072	0.1717	0.1747	0.0577	0.0263	0.1216	0.2624	0.1416	**0.2988**
Ca*	0.0322	0.0313	0.0747	0.0312	0.0885	0.0444	0.0441	0.0774	0.1449	0.0730	0.0642	**0.1070**
Mn*	0.0000	0.0002	0.0004	0.0002	0.0010	0.0002	0.0001	0.0002	0.0002	0.0003	0.0003	**0.0008**
Fe*	0.0011	0.0010	0.0041	0.0010	0.0020	0.0100	0.0014	0.0020	0.0017	0.0014	0.0026	**0.0083**
Cu*	0.0015	0.0013	0.0018	0.0010	0.0028	0.0013	0.0021	0.0032	0.0045	0.0015	0.0021	**0.0032**

Table 4. Method detection limits (3σ) for the UMaine Continuous Melter System determined from 10 deionized (DI) water blanks passed though the entire melter system and compared to estimated Greenland concentration ranges from published and unpublished data (ng/L; μg/L*)

	Blank 1	Blank 2	Blank 3	Blank 4	Blank 5	Blank 6	Blank 7	Blank 8	Blank 9	Blank 10	Avg. DI Blank	**Method D.L.**	Estimated Greenland Conc.[#] Min	Max	Avg
Sr	0.4673	0.9014	0.6171	0.7061	0.8993	0.9908	1.1926	0.6834	1.1699	0.8158	0.8444	**0.7033**	44.821	890.51	275.62
Cs	0.0216	0.0208	0.0216	0.0238	0.0261	0.0280	0.0200	0.0117	0.0257	0.0632	0.0263	**0.0412**	0.072	0.72	0.23
La	0.0304	0.0509	0.0391	0.0309	0.0391	0.0795	0.0700	0.0286	0.0559	0.0427	0.0467	**0.0519**	0.568	19.30	6.42
Ce	0.0627	0.0912	0.0622	0.0552	0.0669	0.0865	0.0982	0.0655	0.0720	0.0781	0.0738	**0.0425**	1.585	39.61	12.00
Pr	0.0127	0.0107	0.0076	0.0072	0.0090	0.0141	0.0193	0.0076	0.0114	0.0086	0.0549	**0.0113**	0.104	4.34	1.38
Nd	0.0293	0.0503	0.0377	0.0314	0.0440	0.0503	0.0649	0.0461	0.0670	0.0314	0.0452	**0.0401**	0.378	15.80	5.22
Sm	0.0090	0.0067	0.0067	0.0090	0.0090	0.0022	0.0201	0.0090	0.0045	0.0157	0.0092	**0.0157**	0.068	2.43	0.83
Eu	0.0007	0.0045	0.0037	0.0022	0.0022	0.0015	0.0022	0.0007	0.0022	0.0000	0.0020	**0.0041**	0.011	0.45	0.14
Gd	0.0000	0.0021	0.0010	0.0031	0.0041	0.0041	0.0103	0.0031	0.0031	0.0031	0.0034	**0.0083**	0.026	1.05	0.38
Tb	0.0004	0.0008	0.0012	0.0000	0.0000	0.0033	0.0004	0.0008	0.0008	0.0004	0.0008	**0.0029**	0.008	0.34	0.12
Dy	0.0000	0.0034	0.0068	0.0119	0.0068	0.0102	0.0102	0.0051	0.0102	0.0085	0.0073	**0.0111**	0.004	0.14	0.05
Ho	0.0009	0.0005	0.0009	0.0014	0.0005	0.0014	0.0060	0.0005	0.0000	0.0018	0.0014	**0.0051**	0.011	0.37	0.13
Er	0.0000	0.0044	0.0029	0.0029	0.0000	0.0015	0.0059	0.0044	0.0059	0.0000	0.0028	**0.0070**	0.027	1.04	0.39
Tm	0.0016	0.0000	0.0005	0.0000	0.0005	0.0000	0.0005	0.0005	0.0011	0.0000	0.0005	**0.0016**	0.003	0.13	0.05
Yb	0.0025	0.0050	0.0000	0.0000	0.0050	0.0025	0.0000	0.0076	0.0000	0.0000	0.0023	**0.0083**	0.039	0.76	0.26
Lu	0.0058	0.0009	0.0012	0.0003	0.0009	0.0017	0.0009	0.0026	0.0003	0.0012	0.0016	**0.0049**	0.004	0.10	0.04
Bi	0.0808	0.1221	0.1635	0.1304	0.1129	0.1653	0.1341	0.1203	0.1451	0.1478	0.1322	**0.0758**	0.005	0.93	0.03
U	0.0286	0.0330	0.0286	0.0219	0.0259	0.0381	0.0344	0.0263	0.0253	0.0424	0.0305	**0.0192**	0.283	15.40	1.29
As	1.2526	1.4322	1.3263	1.2941	1.1743	1.5980	1.6396	1.4554	1.1375	1.2158	1.3526	**0.5199**	0.626	6.45	1.48
Tl	0.1561	0.1791	0.1828	0.1678	0.1710	0.1833	0.1786	0.1862	0.1637	0.3575	0.1926	**0.1762**	0.015	0.41	0.17
Ti	1.4157	1.8163	1.7629	0.8280	1.8965	1.8697	2.5909	1.8697	2.2170	1.8697	1.8136	**1.3840**	9.500	206.01	34.27
V	0.1991	0.2101	0.1216	0.1604	0.1327	0.2101	0.2156	0.1216	0.2212	0.1880	0.1780	**0.1208**	0.544	9.37	2.09
Cr	1.1541	2.0573	1.7761	1.8059	1.7461	1.8179	1.8059	1.5846	1.8059	1.4112	1.6965	**0.7601**	0.678	9.00	3.44
Co	2.9672	3.8363	3.2749	3.2401	3.7418	3.3942	3.4340	3.0659	3.1460	3.2601	3.3360	**0.8317**	0.207	30.44	8.82
Al*	0.2772	0.6314	0.4802	0.4285	0.8545	0.5895	0.5986	0.6421	0.7116	0.6051	0.5819	**0.4741**	0.354	650.00	3.41
S*	1.4394	1.9644	1.7861	1.4766	1.7058	2.5665	2.3509	2.0761	1.6999	1.1658	1.8231	**1.2825**	9.670	129.02	52.90
Ca*	0.1781	0.3512	0.2286	0.2639	0.3918	0.3881	1.5862	0.2671	0.4070	0.3492	0.4411	**1.2289**	6.087	155.43	43.96
Mn*	0.0472	0.0667	0.0572	0.0573	0.0651	0.0735	0.0641	0.0578	0.0616	0.0621	0.0613	**0.0211**	0.031	4.80	0.27
Fe*	0.0259	0.0477	0.0492	0.0460	0.0394	0.0406	0.0381	0.0397	0.0458	0.0397	0.0412	**0.0200**	0.114	259.00	0.48
Cu*	0.0552	0.0778	0.0647	0.0663	0.0718	0.0737	0.0719	0.0645	0.0730	0.0667	0.0686	**0.0193**	0.025	0.39	0.11

[#] Boutron et al., 1993; Candelone et al., 1995, 1996; Hong et al., 1996a, b; and unpublished UMaine data

Fig. 1 GISP2 Parallel Sticks Tests
Unpublished data by Erich Osterberg, Paul Mayewski, Karl Kreutz, Mike Handley & Sharon Sneed

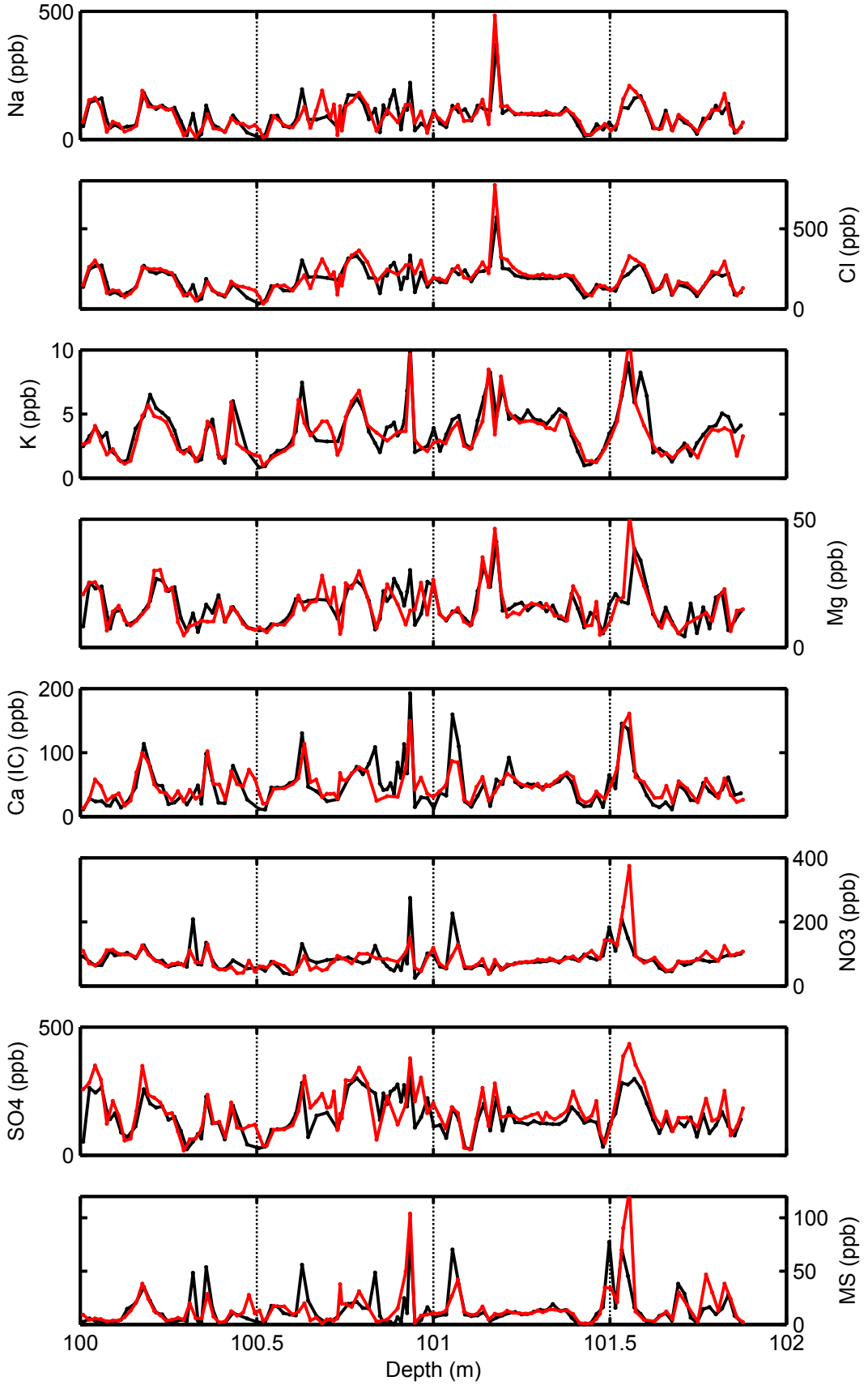


Fig. 2 GISP2 Parallel Sticks Tests
Unpublished data by Erich Osterberg, Paul Mayewski, Karl Kreutz, Mike Handley & Sharon Sneed

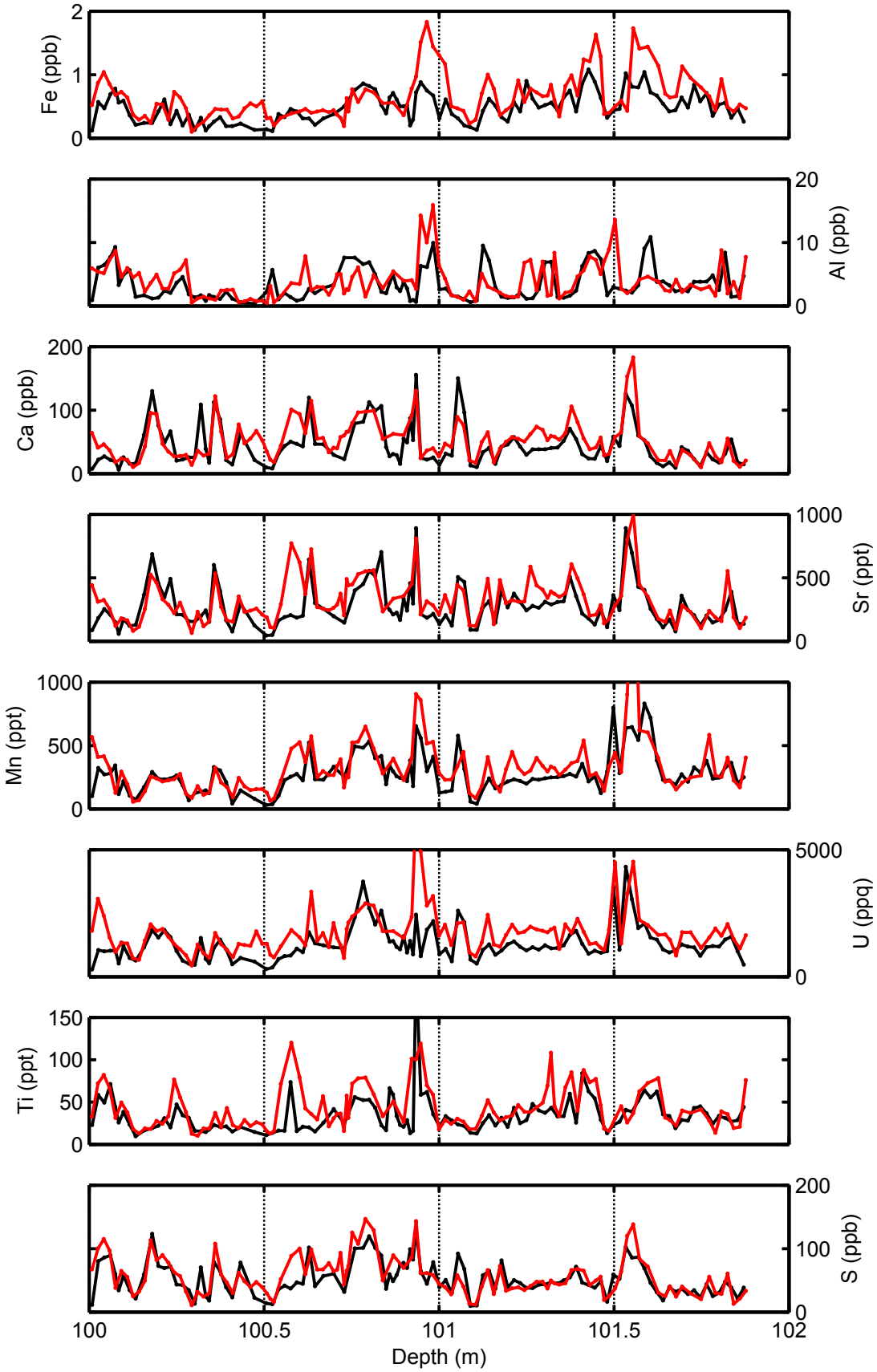


Fig. 3 GISP2 Parallel Sticks Tests
Unpublished data by Erich Osterberg, Paul Mayewski, Karl Kreutz, Mike Handley & Sharon Sneed

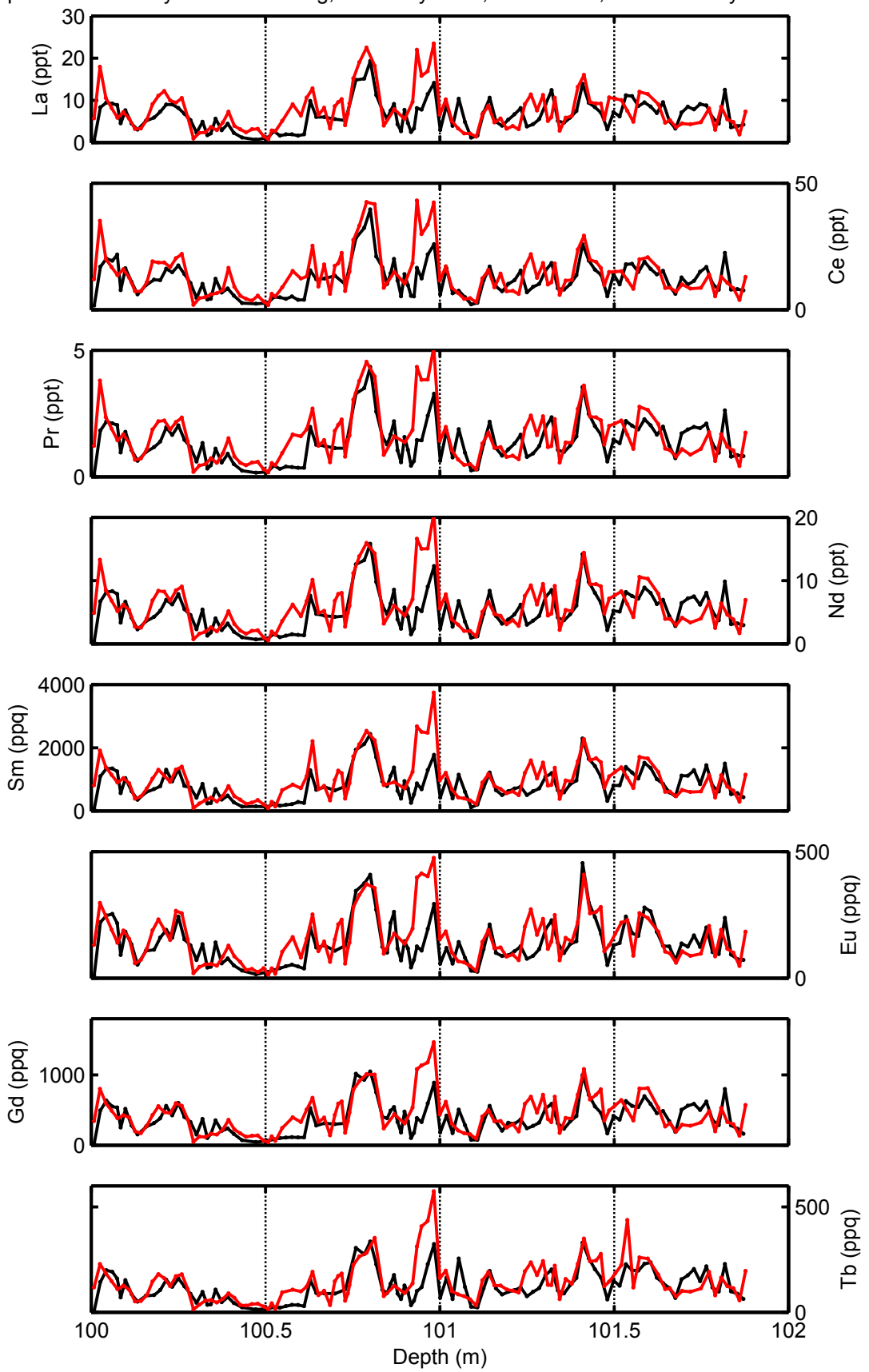


Fig. 4 GISP2 Parallel Sticks Tests
Unpublished data by Erich Osterberg, Paul Mayewski, Karl Kreutz, Mike Handley & Sharon Sneed

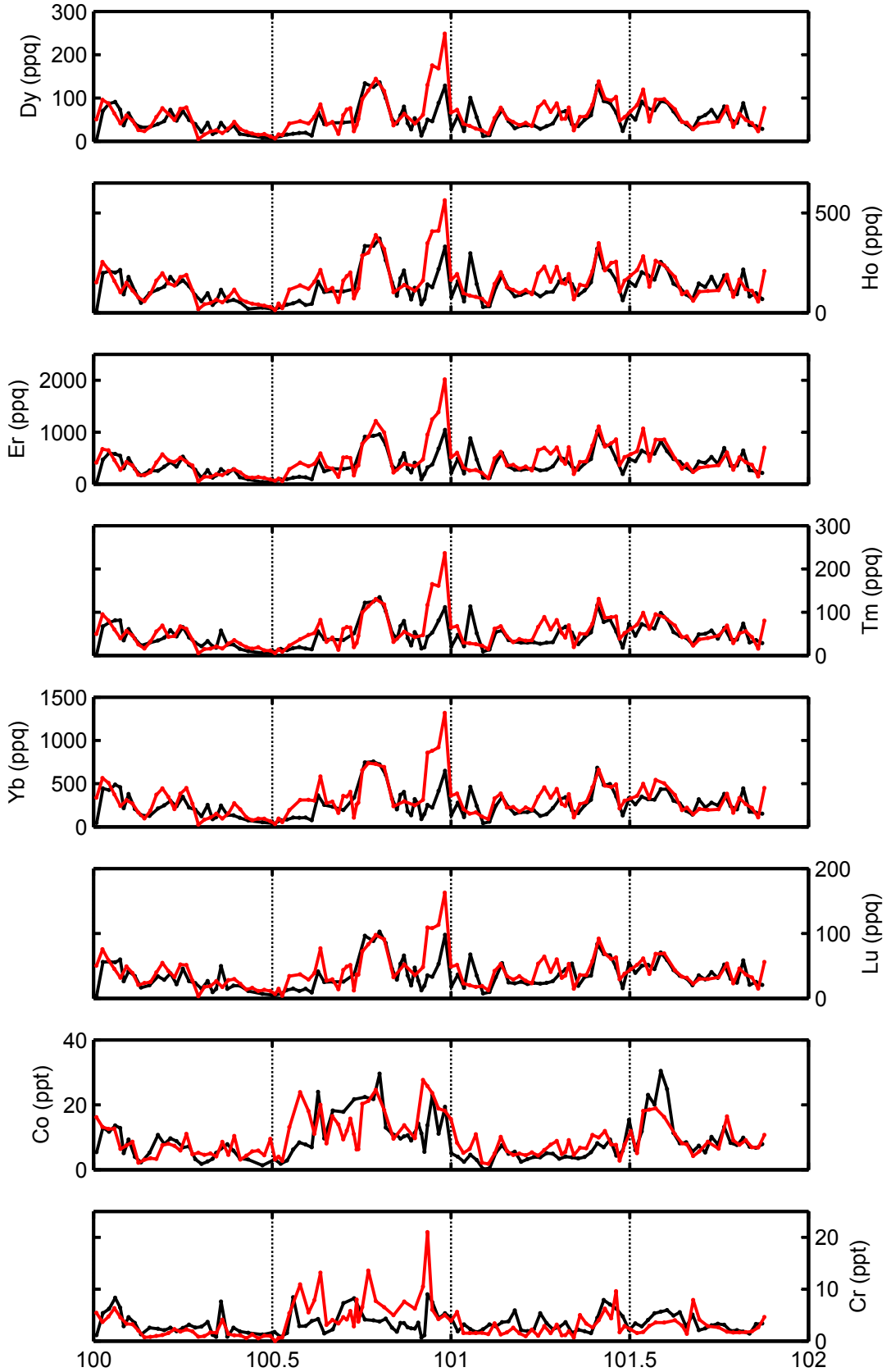


Fig. 5 GISP2 Parallel Sticks Tests
Unpublished data by Erich Osterberg, Paul Mayewski, Karl Kreutz, Mike Handley & Sharon Sneed

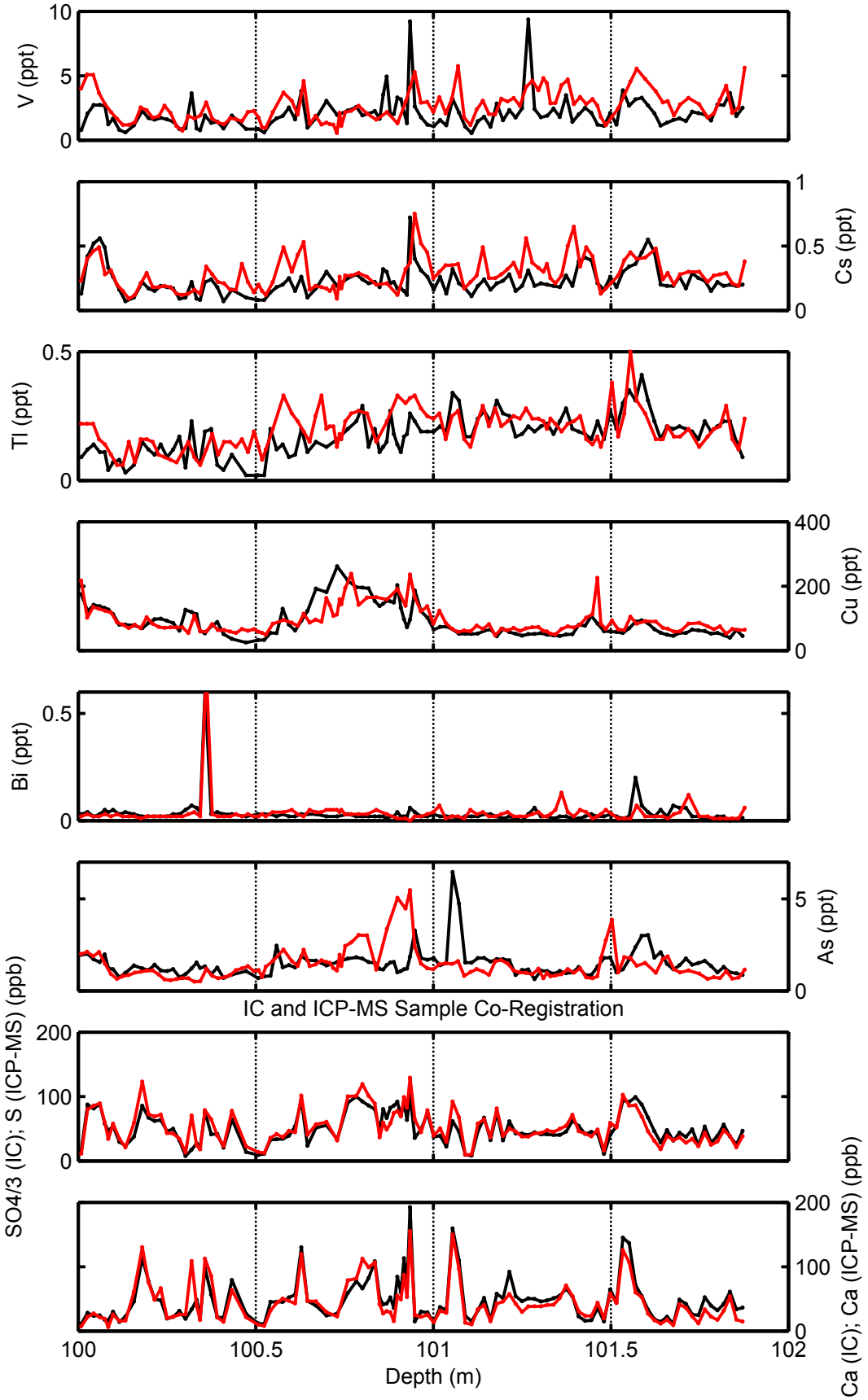


Figure 6a. Concentration cross-sections from the Mt. Logan summit core. Only the outer 3-6 mm of firn is contaminated.

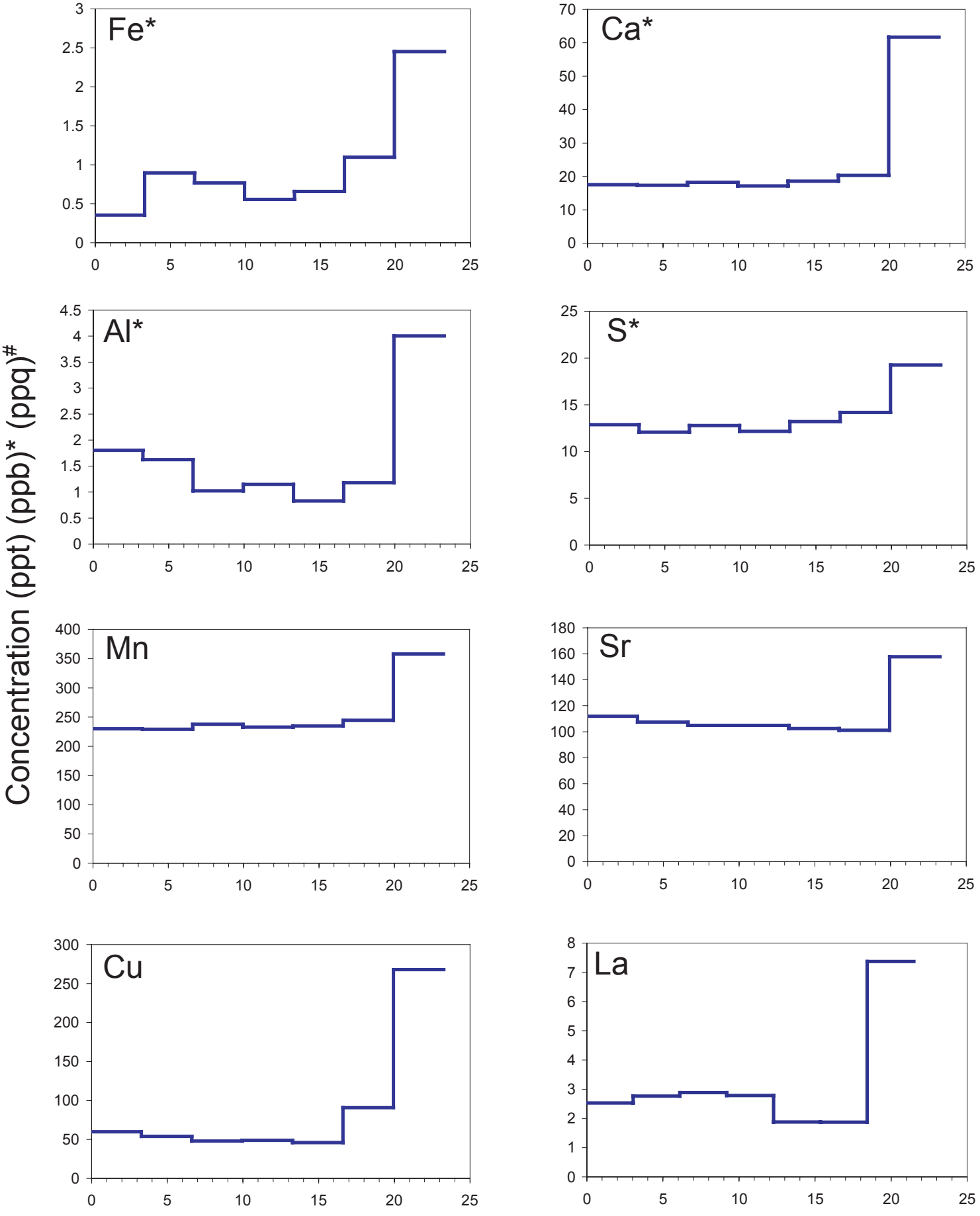
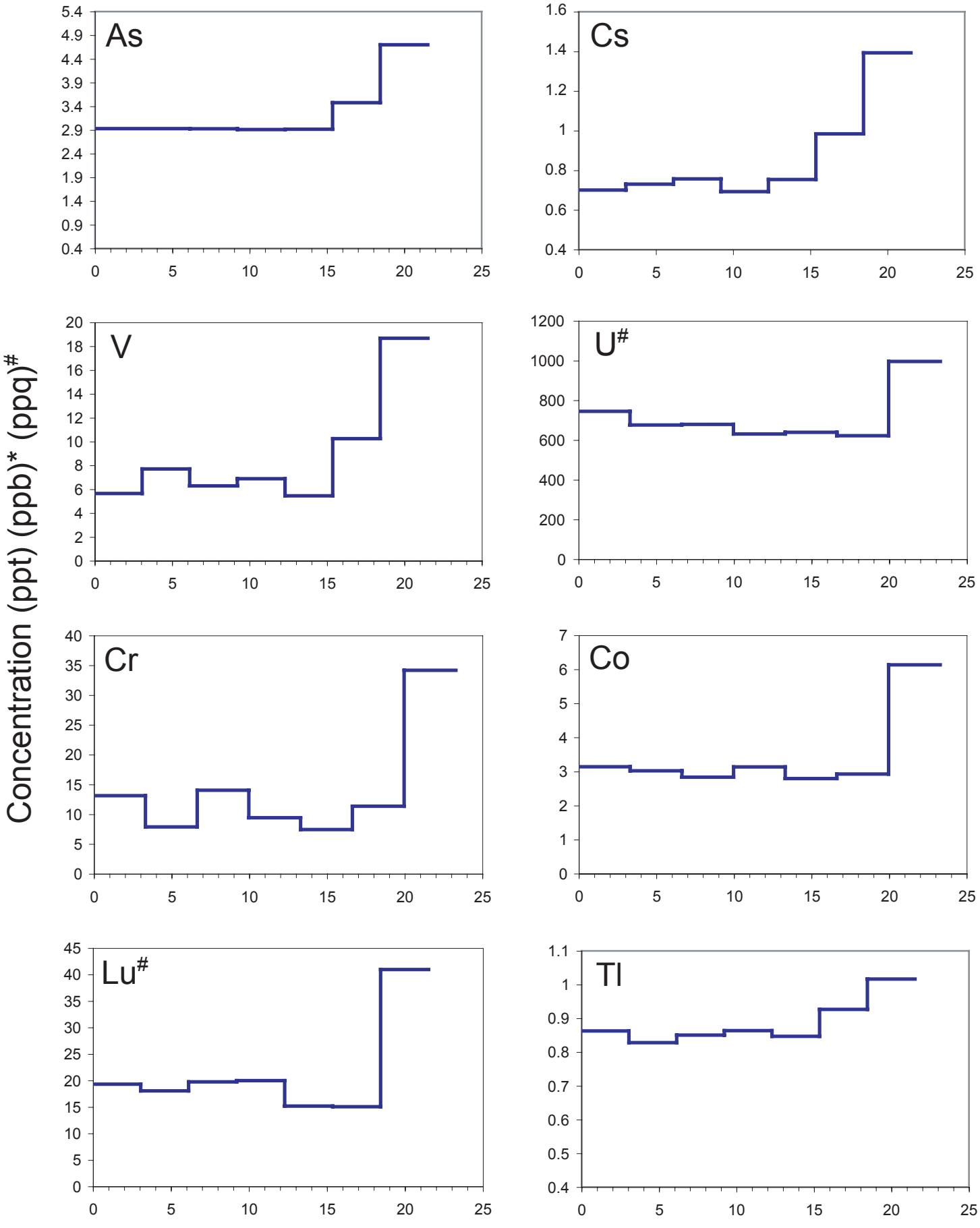


Figure 6b. Concentration cross-sections from the Mt. Logan summit core. Only the outer 3-6 mm of firn is contaminated.



Our approach to the research described in this proposal and the challenge of assessing Antarctica's role in global change depends on the analysis and interpretation of glaciochemical series (concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and methanesulfonate ($CH_3SO_3^-$). The ionic composition of polar ice cores provides not only a stratigraphic tool for relative dating (that appears to be extremely effective in the WAIS region) but also documents changes in chemical species source emissions and allows characterization of the major atmospheric circulation systems affecting WAIS. These qualities of the glaciochemical record combined with sampling at ultra-high resolution (8-10 samples/year), over periods of 200+ years, along community determined traverse routes, at a spacing of approximately every 100-200 km, resulting in several, typically, 6-10 cores per season over four field seasons (1999-2003) are used to address the following scientific questions.

(1) What is the current rate of change in mass balance over West Antarctica?
(2) What is the influence of major atmospheric circulation systems (e.g., ENSO, ACW) and oceanic circulation on the moisture flux over West Antarctica?
(3) How does climate (e.g., accumulation rate, atmospheric circulation) vary over West Antarctica on seasonal, inter-annual, decadal and centennial scales, and what are the controls on this variability?
(4) What is the frequency, magnitude and effect of any extreme climate events recorded in West Antarctica?
(5) What is the impact of anthropogenic activity (e.g., ozone depletion, pollutants) on the climate and atmospheric chemistry of West Antarctica?
(6) How much has biogeochemical cycling of S and N, as recorded in West Antarctica, varied over the last 200+ years?

1999-2000 Field Season:
The first field season for this project was conducted from Oct-Dec 1999. The following was accomplished during the field season:

Three snow pits located from Byrd Surface camp west to the Swithinbank AWS, and two ice cores were retrieved:

One core located mid-way between Byrd Surface camp and the Swithinbank AWS and one core co-located with the Swithinbank AWS.
Elevation of snow pit and ice core retrieval locations decreases westward by approximately ~500 m .

Byrd Surface (80.01 S 119.40 W):
180 cm UNH chemistry snow pit at 2 cm sample resolution.
Sampled for C. Shuman - snow pit density (2 cm resolution)

Mid-Swith (80.37 S 122.37 W):

58 meter ice core
192 cm UNH chemistry snow pit at 2 cm sample resolution.

Sampled for C. Shuman - snow pit density (2 cm resolution) and stratigraphy data
Sampled for E. Steig - snow pit oxygen isotope at 2 cm sample resolution
Sampled for R. Bales - snow pit peroxide at 2 cm sample resolution
Sampled for M. Albert - snow pit permeability measurements
Sampled for M. Albert - snow pit thick section samples

Swithinbank (81.20 S 126.17 W)

49 meter ice core
200 cm UNH chemistry snow pit at 2 cm sample resolution
Sampled for C. Shuman - snow pit density (2 cm resolution) and stratigraphy data
Sampled for E. Steig - snow pit oxygen isotope at 2 cm sample resolution
Sampled for R. Bales - snow pit peroxide at 2 cm sample resolution
Sampled for M. Albert - snow pit permeability measurements
Sampled for M. Albert - snow pit thick section samples

2000-2001 Field season:
During the 2000-2001 US ITASE we sampled snowpits and retrieved (with the support of Mark Wumkes) and prepared ice cores for the following projects: University of Maine (major anions, cations and MS), University of Arizona (reversible ionic species), CRREL (permeability and firn structure), CRREL (ice core stratigraphy), University of Washington and University of Colorado (stable isotopes), University of Maryland and NASA (snowpit stratigraphy).
Ice cores (total 660 m, 9000lbs) and snowpits (2m per site) were recovered and packaged at seven sites for the common use of the research teams noted above. The ice cores ranged from 105m in depth at the proposed WAIS core site to on average 60m at other sites plus several 15-30m ice cores dedicated to other projects.

Accomplishments of the US ITASE ice core and snowpit glaciochemistry sampling program include:
(1) Snowpit and ice core sample coverage over the regions bounded by 77-82 degrees South and 105-130 degrees West.
(2) Integration with surface glaciology activities conducted by Gordon Hamilton and Leigh Stearns to allow deconvolution of local topographic effects from the accumulation rate record.
(3) Integration with shallow radar activities conducted by Steve Arcone to assess the source of radar reflectors and to enhance interpretation of ice core records through 3D views of core sites.
Our major research goals are to establish:
(1) Calibrated proxies for atmospheric circulation features such as the Amundsen Sea Low, ENSO, the Antarctic Circumpolar Wave and katabatic flow.
(2) Calibrated records that document variability in, for example, sea ice extent, volcanism, marine biogenic activity and trends in major ion chemistry deposited over Antarctica.
(3) Detailed understanding of the spatial and temporal (sub-annual to multi-decadal) complexities in climate within and related to Antarctica.

US ITASE 2000-2001 End of Year Stats

Core recovered (Chemistry

Location	Lat.	Long.	Elevation	Depth
	(°S)	(°W)	(m)	(m)
ITASE 00-1 'A'(WAI S)	79.3831	111.2390	1791	105
ITASE 00-2 'C'	78.7330	111.4966	1675	61
ITASE 00-3 'D'	78.4330	115.9172	1741	60
ITASE 00-4 'E'	78.0829	120.0764	1697	58
ITASE 00-5 'F'	77.6830	123.9950	1828	60
ITASE 00-6 'H'	78.3325	124.4840	1639	60
ITASE 00-7 'I'	79.1330	122.2670	1495	63

Snow Pits

Site	lat/	long	date	sample	depth
	(°S)	(°W)			
ITASE 00-1 'A'(WAI S)	79° 22.985	111° 13.720	12/1/00	1-200	200cm
ITASE 00-2 'C'	78° 25.004	115°55.034	12/13/00	1-200	200cm
ITASE 00-3 'D'	78° 4.973	120°4.587	12/15/00	1-200	200cm
ITASE 00-4 'E'	77° 40.931	123°59.485	12/19/00	1-200	200cm
ITASE 00-5 'F'	78° 19.95	124° 28.70	12/24/00	1-200	200cm
ITASE 00-6 'H'	79° 8.042	122° 16.341	12/27/00	25-199	150cm

Sample Processing and Chemical Analyses:
Sample processing for this project includes contamination free-techniques such as:
(1) field collection of snow pit samples in 125 ml cups
(2) hand-scraping of the upper few meters of cores collected in the field, followed by cutting and placing samples into 125 ml cups
(3) development of continuous melting techniques for use in the laboratory
(4) utilization of ion chromatography and ICP techniques.

In 2000 the PI and several others transferred from the University of New Hampshire to the University of Maine. This transition led to reducedout put for several months because: new, larger, and cleaner freezer facilities were constructed by UMaine, and the ion chromatograph softwareand plumbing were found to have defects that appeared immediately upon the transfer to UMaine, perhaps from transit or during final weeks at UNH. In addition since arriving at UMaine new continuous melting techniques have been developed and new interfaces with analyticalequipment not previously available at UNH

were implemented.
To date all of the major ion analyses on 99-00 and 00-01 snow pits and surface samples have been completed. Most of the major ion analyses on the 99-00 cores are complete and analyses of 00-01 core samples is well underway.

Field Season 2001-2002

During the 2001-2002 field season a total of 771m of core was collected. This included six primary core sites noted below (utilizing the 3' diameter Eclipse drill) plus numerous shallow (3-20m)2.2' diameter cores (utilizing the University of Maine Rongbuk drill) and two snow pits. The Rongbuk drill was used to replace snow pits because it is faster than snow pit sampling (allowing more sites to be sampled) and because it reduces potential contamination versus exposed pit walls. Numerous fresh snow samples were collected to examine chemical species variability through snowstorm events plus spatial variability.

Location	Lat.	Long.	Elevation	Depth
	(°S)	(°W)	(m)	(m)
ITASE 01-1	79.1597	104.9672	1843	73
ITASE 01-2	77.8436	102.9103	1353	71
ITASE 01-3	78.1202	95.6463	1633	71 & 70
ITASE 01-4	77.6116	92.2483	1484	68
ITASE 01-5	77.0593	89.1375	1246	115
ITASE 01-6	76.0968	89.0147	1232	18

Core sites were selected through a combination of initial observations using RADARSAT imagery and then refined in the field through near real-time observation of continuous time-stratigraphic radar reflectors.

Field Season 2002-2003

During the fourth US ITASE season (2002-2003) the field team traversed 1250 km from Byrd to South Pole. The traverse was comprised of 13 members, two Challenger 55s, and various heavy and light sleds. The bulk of the fuel used by the Challengers was air dropped to four sites along the route. Route selection was based upon the science objectives of the US ITASE researchers and safe route selection was aided by examination of RADARSAT images and an onboard crevasse detection system. Eleven, integrated science programs were supported by US ITASE in 2002-2003. Science was conducted both during travel and at eight sites. Continuous shallow (~120 m) and deep (>3000m) radar, high precision kinematic GPS, and surface snow sampling comprised the travel component of the science. Near real-time shallow radar information was used to finely tune the location of study sites and to tie these sites together via identification of long distance subsurface marker horizons. At each site 3” and 2” diameter ice cores were collected that will provide samples for stable isotopes, major soluble ions, water soluble trace gases, trace elements, organic acids, b activity, stratigraphy, porosity, permeability, and density. A total of 920 m of ice core was collected. Atmospheric sampling of surface

air and air to a height of 23 km was conducted as well as high precision GPS surveys to determine mass balance, ice flow direction and speeds, and ice surface topography.

Major Scientific and Logistical Accomplishments of the 2002-2003 Field Season Related to the US ITASE Glaciochemistry Project:
Between 23 November 2002 when the US ITASE team arrived at Byrd and 7 January 2003 when the team departed South Pole the glaciochemical team collected the following ice cores:

Location	Lat. (°S)	Long. (°W)	Elevation (m)	Depth (m - approx.)
ITASE 02-BYRD	80.0093	119.4249	1530	40.8
ITASE 02-1	82.0010	110.0082	1746	62.5
ITASE 02-2	83.5008	104.9868	1957	62.1
ITASE 02-3	85.0005	104.9953	2396	46.5
ITASE 02-4	86.5025	107.9903	2586	72
ITASE 02-5	88.0022	107.9833	2747	54.5
ITASE 02-SPRESO	89.9333	144.3938	2890	295*
ITASE 02-100K	88.9989	59.9744	3000	15.2

*295 m collected by ICDS SPRESO team for US ITASE

A total of 920 m of ice cores were recovered utilizing both the 3” diameter Eclipse drill purchased by NSF for use by US ITASE and a 2.2” diameter lightweight drill built by Glacier Data for the University of Maine. Analyses to be conducted on these cores include: stable isotopes (UWash), major ion chemistry (UMaine), trace and reversible species chemistry (UArizona), beta activity (UMaine), stratigraphy, porosity, and permeability (CRREL).

Activities covering the period March 2003 - to present
To date more than every second ice core collected plus all surface snow and snow pit samples have been processed and analyzed for major anions and cations and for many cores compared to complementary stable isotope (University of Washington) and hydrogen peroxide (University of Arizona) measurements.

Since March 2003 the ITASE glaciochemistry team has been involved in the analysis and interpretation of glaciochemical records and has
presented numerous papers at the following meetings:
(1) US ITASE Workshop (Castine, Maine - June)
(2) SCAR/IGS Symposium (Milan, Italy - August)
(3) Fall AGU (San Francisco December).
(4) SCAR/IGS Symposium (Bremen, Germany August 04)
(5) SCAR/AGCS (Cambridge, UK June 05)
(6) Modes of Climate Variability mtg (Cambridge, UK June 05)

Paper topics are outlined under the major findings section of this report. In addition we have continued to work with our other US ITASE colleagues (10 institutions), international ITASE colleagues (20 countries), and a new collaboration with Alan Robock (Rutgers) investigating the impact of volcanism on climate utilizing ITASE and other ice core sulfate series.

In addition ICPMS measurements for trace elements have been conducted on selected surface and core samples. This analysis required considerable attention to the calibration of our NSF MRI supported ICPMS and to the development of new techniques for ice core processing. (see attached file with a complete description).

Findings:
Topics being considered for publication over the period of US ITASE field activities:

1. Modern day persistence of LIA atmospheric variability in West Antarctica.

2. West Antarctic accumulation histories.

3. Role of topographic divides on atmospheric dynamics and accumulation in West Antarctica.

4. Detailed proxy of strength and position of the Amundsen Sea Low and associated long wave patterns in West Antarctica with implications for investigations of the Antarctic Circumpolar Wave.

5. Variability in the frequency and strength of atmospheric short waves in West Antarctica.

6. ENSO, as manifested in West Antarctica.

7. Comparison of near surface glaciochemistry from inland West Antarctica to the Siple Dome deep drilling program.

8. Development of new techniques for identifying core sites. US ITASE is unique because it has the capability to identify potential core sites using a host of satellite imagery plus near real-time observations of radar reflectors provided by the CRREL shallow radar component of US ITASE (CRREL - Arcone). Without this capability core sites could easily be selected that are biased by local topography and ice flow.

9. US ITASE ice cores are unique because they have the capability of including and do include up ice flow adjustments for local effects on accumulation rate through collaboration with US ITASE surface glaciology activities (Hamilton - UMaine).

Major findings (with citations) developed from US ITASE glaciochemical research as of March 2004:

(1) Established seasonal timing, source contributions, controls on spatial distribution, and covariance association with moisture flux for all major ions (Han et al., 2001; Isaakson et al., 2001; Curran et al., 2002; Kaspari et al., in press; Kaspari et al., in review; Dixon et al., in press; Pruett et al., in press).

(2) Provided precise annual layer counting for all ice cores resulting in estimates of past mass balance, identification of moisture source regions, concentration-flux deconvolutions, and environmental interpretations (Palmer et al., 2002; Kaspari et al., in press; Dixon et al., in press; Spikes et al., in press (a); Bertler et al., in review (a)).

(3) Derived glaciochemically differentiated annual layers to demonstrate that shallow and deep radar reflectors are truly isochrones (Arcone et al., in press; Spikes et al., in press (9b)).

(4) Developed the most highly resolved, temporally and spatially, 200+ year long volcanic event record for WAIS (Palmer et al., 2001; Dixon et al., in press; Kurbatov et al., in review).

(5) Identified stratospheric versus tropospheric source volcanic emission input pathways to WAIS and utilized stratospheric source events as evidence of emission plume history over the ice sheet (Dixon et al., in press).

(6) Differentiated the relative influence of sea salt spray and salt flowers on Na+ loading over WAIS (Kaspari et al., in review).

(7) Confirmed and significantly expanded our earlier single ice core calibrations between major ions and several major atmospheric phenomena (eg., Amundsen Sea Low, ENSO, westerlies, circumpolar circulation) resulting in more robust ice core proxies for atmospheric circulation (Souney et al., 2002; Yan et al., in review; Mayewski et al., in review; Goodwin et al., in press; Xiao et al., in review).

(8) Developed new instrumentally calibrated proxies for strength of the zonal westerlies, circumpolar circulation, ice surface wind drainage, impact of radiative forcing on atmospheric circulation, and sea ice extent (Bertler et al., in press; Bertler et al., in review (b); Goodwin et al., 2004; Mayewski et al., in review; Yan et al., in review).

(9) Integrated US ITASE spatial records and existing shallow to deep ice core records to significantly refine paleoclimate reconstructions leading to the identification of the AD 1700-1850 abrupt climate change event that affected Antarctica, demonstration of the past 700 years of behavior of the Antarctic Oscillation (Mayewski et al., in press), and global scale correlations (Shulmeister et al., in press; Mayewski et al., in press; Maasch et al., in review).

(10) Developed the "Solar Polar" hypothesis for the initiation of annual to decadal scale variability over Antarctica and the Southern Ocean and potentially global scale abrupt climate change events (Mayewski et al., in review). Demonstration invokes a combination of NCEP/NCAR re-analysis data, several US ITASE ice cores, and cores from South Pole, Siple Dome, and Law Dome. The Solar Polar hypothesis opens a major opportunity as a predictive tool and offers suggestions for the cause of Australian drought cycles, the major Southern Hemisphere event of 2001-2002 ("Summer from Hell"), and partial deconvolution of the interaction between ENSO and the ACW.