

**A Glaciochemical Record of Natural and Anthropogenic Environmental
Change in the Northwestern North American Arctic
NSF Award No.: OPP-0136146 (UNH); OPP-0136005 (UMaine)**

UNH-UMaine - Report of Activities - May 2003 to April 2004

MAJOR ION AND STABLE ISOTOPE ANALYSIS

Both the 130 m (Core 3) and 345 m (Core 2) firn and ice cores recovered from Eclipse Icefield during the 2002 field season have been sampled continuously at high resolution for major ions and stable isotopes (except for the top 60 m of the 345 core that was drilled with the titanium barrel). There is 60 years of overlap (1970- 1910) between the two cores. A sampling resolution of 10- 15 cm was used for the portion of core 2 from 0- 200 m water equivalent (w.e.) depth and all of core 3, yielding around eight samples per year. All of these samples have been analyzed for major ions and stable isotopes (see details below). Annual layer thinning required resampling of the lower portion of core 2 at higher resolutions (beginning at 6 cm per sample, increasing to 2 cm per sample near the bottom) to obtain an annually dated record. The higher resolution samples have been analyzed for stable isotopes and for major ions around select high sulfate horizons (i.e. volcanic horizons).

All ice core processing using the original 10-15 cm sample resolution was performed in a clean bench in a freezer at the UNH Climate Change Research Center (CCRC) using established techniques for ultra-clean sample preparation. Above the firn/ice transition, the core was scraped on an acrylic lathe system under a laminar flow bench using a titanium scraper so that all surface and sub-surface contamination from the drilling process was removed. Below the firn/ice transition, samples were cut into 3 x 3 cm pieces 10 cm long and the middle of the samples melted out using a custom made melter used to sample the GISP2, Penny, Devon, and Eclipse 1996 ice cores. Blanks (artificial core made by freezing 18m³ Milli-Q water) were processed frequently in the same manner as the core to ensure samples are uncontaminated by core processing. All samples were placed in LDPE bottles cleaned by successive soaking and rinsing in 18m³ Milli-Q water. Sample aliquots (5 ml) were taken for major ion and stable isotope analysis. The remaining sample volume was archived and frozen for trace element analysis.

Samples were analyzed for major ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻) via ion chromatography using a 0.5 ml sample loop in a dedicated laboratory at the CCRC. The cation system used a CS12A column with CSRS-ultra suppressor in auto suppression recycle mode with 20 mM MSA eluent. The anion system used an AS11 column with a CSRS-ultra suppressor in auto suppression recycle mode with 6 mM NaOH eluent. Stable isotopes (¹⁸O and ²D) were analyzed at the University of Maine Stable Isotope Laboratory with an Autoprep CO₂ equilibration system coupled to a VG

SIRA instrument. Kaplan Yalcin, a Ph.D. student at UNH funded on this, has been centrally involved in core processing, sample analysis and interpretation.

ICE CORE DATING

We have developed a detailed chronology for Core 3 and the upper 240 m of Core 2 using multi-parameter annual layer counting of seasonal oscillations in the $\delta^{18}\text{O}$ and major ion records (Figure 1). The annual cycle of $\delta^{18}\text{O}$ maxima in summer precipitation and $\delta^{18}\text{O}$ minima in winter precipitation observed at Eclipse and other ice core sites is related at least in part to the temperature at which evaporation and condensation occurs. The annual cycle of sodium concentration maxima in winter and minima in summer is related to pronounced seasonal changes in the influx of marine aerosols due to increased storminess in the Gulf of Alaska during winter resulting in higher wind speeds, enhanced entrainment of sea salt aerosols, and more frequent advection of marine air masses into the Saint Elias Mountains in winter, producing the observed peaks in sodium concentrations. The spring/summer peak in ammonium concentrations is presumably due to increased biological activity.

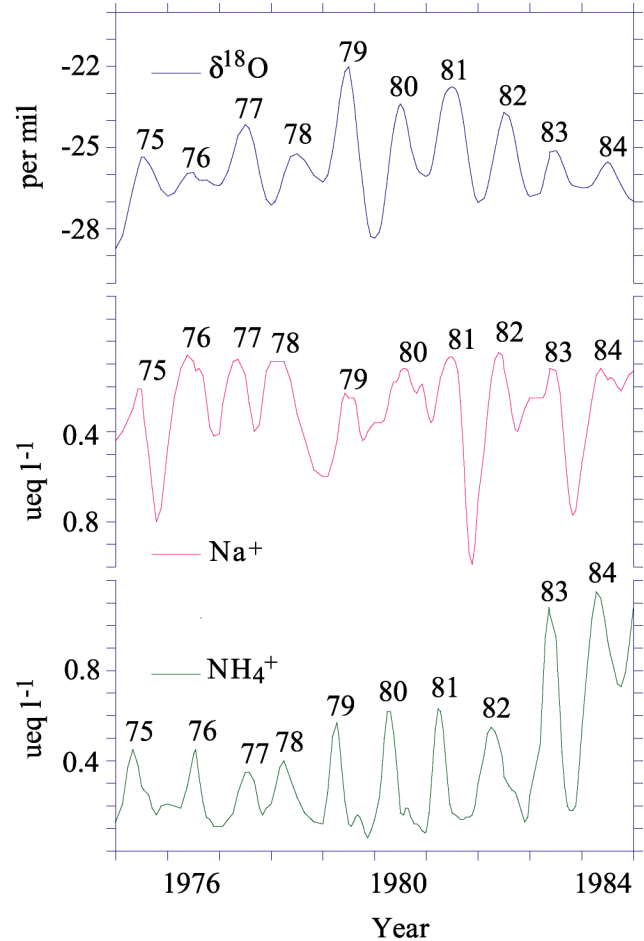


Figure 1. Seasonal oscillations in the smoothed Eclipse $\delta^{18}\text{O}$, Na^+ , and NH_4^+ records from Core 2 used to date the cores via annual layer counting. Sodium is plotted on an inverse scale since concentrations peak in winter.

Age control on the chronology established via annual layer counting is provided by identification of ^{137}Cs peaks from atmospheric thermonuclear weapons testing. Dr. Jack Dibb (UNH) oversaw ^{137}Cs analysis via gamma spectroscopy and assisted in data reduction and interpretation. Snow and ice samples for radionuclide analysis were collected from the outside of the core, and then melted, acidified, and gravity filtered twice through ion exchange filters. Radionuclide concentrations (including ^{137}Cs) were determined by non-destructive gamma spectrometry using a Canberra gamma spectrometer with a germanium well detector and computer based, multi-channel analyzer at UNH (Dibb, 1990). The radionuclide concentration profiles were dated by comparison to real-time aerosol samples from Whitehorse, Yukon Territory (Holdsworth et al., 1984). The 130 and 345 m ice cores show nearly identical ^{137}Cs profiles, with clear identification of the 1963, 1961, and 1959 radionuclide peaks from atmospheric nuclear weapons testing (Figure 2).

Average annual accumulation from 2002 to 1963 was 1.30 m water equivalent, which compares favorably to the value of 1.38 m water equivalent determined for the Eclipse 1996 core.

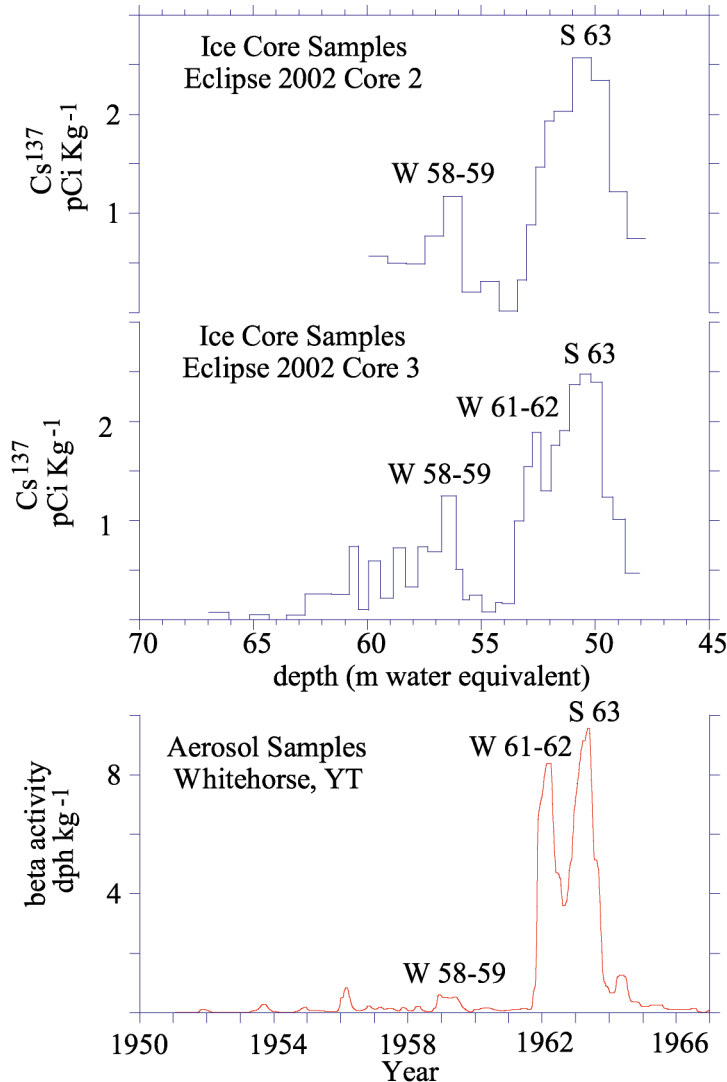


Figure 2. Comparison of Eclipse ice core ^{137}Cs profiles with real-time aerosol samples from Whitehorse, Yukon Territory, shows clear identification of the 1963 and 1961 radionuclide peaks from atmospheric nuclear weapons testing.

The resulting depth-age relationships indicate that Core 3 (130 m) covers the period 2002-1910, while annual layer counting of Core 2 (345 m) presently extends to the year 1622 at 278 m depth. We estimate dating error at this depth to be +/- two years. We are continuing high-resolution isotope analysis of the remaining 67 m of Core 2 in order to extend the counting of annual layers as close to the bottom of the core as possible, and expect to complete analysis of these samples in the next two months. Given the observed annual layer thickness (20 cm) at 278 m depth, we estimate the bottom 67 m of core 2 to cover at least an additional 350 years.

VOLCANIC HORIZONS AND TEPHROCHRONOLOGY

Volcanic horizons were identified using statistical analysis of the high-resolution sulfate record (Zielinski *et al.*, 1994; Yalcin *et al.*, 2003). First, we estimated the sulfate contribution from sea salt using the ratios of sulfate to other ions in seawater, resulting in an excess or non-sea-salt (nss) fraction. Sea-salt SO_4^{2-} is a small fraction of the total sulfate in the Eclipse ice core (<5%) with sodium the limiting sea salt species in 83% of the samples. We then used a low-tension robust spline (tension parameter set to 0.1 resulting in a 98% smooth) to remove long term trends in nss sulfate deposition

associated with anthropogenic sulfur emissions and considered the resulting residuals above the spline.

We also used an empirical orthogonal function (EOF) decomposition to describe the variance in the Eclipse glaciochemical data set. The EOF technique splits the temporal variance of a data set into spatial patterns termed empirical eigenvectors that are orthogonal in nature. The first eigenvector explains the greatest percentage of variance in the dataset, with each successive eigenvector describing the maximum remaining variance. Since the modes are orthogonal, any two modes are neither spatially nor temporally correlated. This allows differentiation of sources and transport characteristics by relationships between individual species as described by each EOF. Therefore, each EOF often provides information on a different environmental parameter.

Applying EOF analysis to the suite of ions measured in the Eclipse ice cores [excluding NH_4^+ ; Zielinski *et al.*, 1996] reveals that, for both cores, EOF 5 is loaded solely with sulfate and describes 3.9 - 5.2 % of the variance in the full dataset, but 13.6-15.7% of the variance in the sulfate time series (Table 1). Volcanic eruptions have been identified as the source of this sulfate (Yalcin *et al.*, 2003). As in our previous work, comparison of the results from these two analyses shows that nss sulfate residuals are two to three times the EOF 5 sulfate values, since the EOF analysis more robustly accounts for sulfate from non-volcanic sources, such as continental dust or anthropogenic sulfur emissions [Yalcin and Wake, 2001]. We focused on those events with an EOF 5 sulfate value greater than one standard deviation above the mean positive EOF 5 sulfate value as most likely to represent an identifiable volcanic eruption.

We used these two techniques to identify 95 volcanic horizons in Core 2 and 35 volcanic horizons in Core 3, including hemispheric and globally important eruptions such as Katmai (1912), Krakatau (1883), Cosiguina (1835), Tambora (1815), Laki (1783), and Kuwae (1452), as well as many regionally significant eruptions such as Redoubt (1989), Katla (1918), Ksudach (1907), and many more Alaskan and Kamchatkan eruptions (Figure 3). An abstract has been accepted for a presentation on these results at the May 2004 AGU General Assembly in Montreal, and a manuscript is currently being prepared for submission to *Journal of Geophysical Research*.

Table 1. EOF analysis of the variance in the data set of seven of the eight species measured in the Core 2 from Eclipse Icefield (NH_4^+ was excluded). Note that EOF 5 is loaded solely on sulfate and explains a large proportion of the variance in the sulfate time series.

Species	Eigenvector Components							Percent Variance Explained						
	E1	E2	E3	E4	E5	E6	E7	E1	E2	E3	E4	E5	E6	E7
Na^+	0.47	0.82	-0.15	0.07	0.06	0.23	-0.16	21.8	67.6	2.2	0.4	0.4	5.1	2.5
K^+	0.37	0.32	0.82	-0.28	-0.12	-0.02	0.00	13.9	10.1	66.4	8.1	1.5	0.0	0.0
Mg^{2+}	0.79	-0.16	-0.34	-0.42	-0.08	-0.18	-0.14	62.4	2.7	11.4	17.6	0.6	3.3	2.0
Ca^{2+}	0.87	-0.30	-0.15	-0.22	0.00	0.21	0.20	75.2	9.2	2.2	5.0	0.0	4.4	4.1
Cl^-	0.51	0.78	-0.12	0.17	0.11	-0.21	0.16	26.3	61.1	1.5	2.9	1.2	4.4	2.6
NO_3^-	0.68	-0.48	0.27	0.22	0.44	-0.03	-0.07	45.8	22.5	7.2	4.8	19.2	0.1	0.5
SO_4^{2-}	0.74	-0.26	0.06	0.50	-0.37	-0.01	-0.03	54.2	6.7	0.3	24.7	14.0	0.0	0.1
Percent Total Variance								42.8	25.7	13	9.1	5.3	2.5	1.7

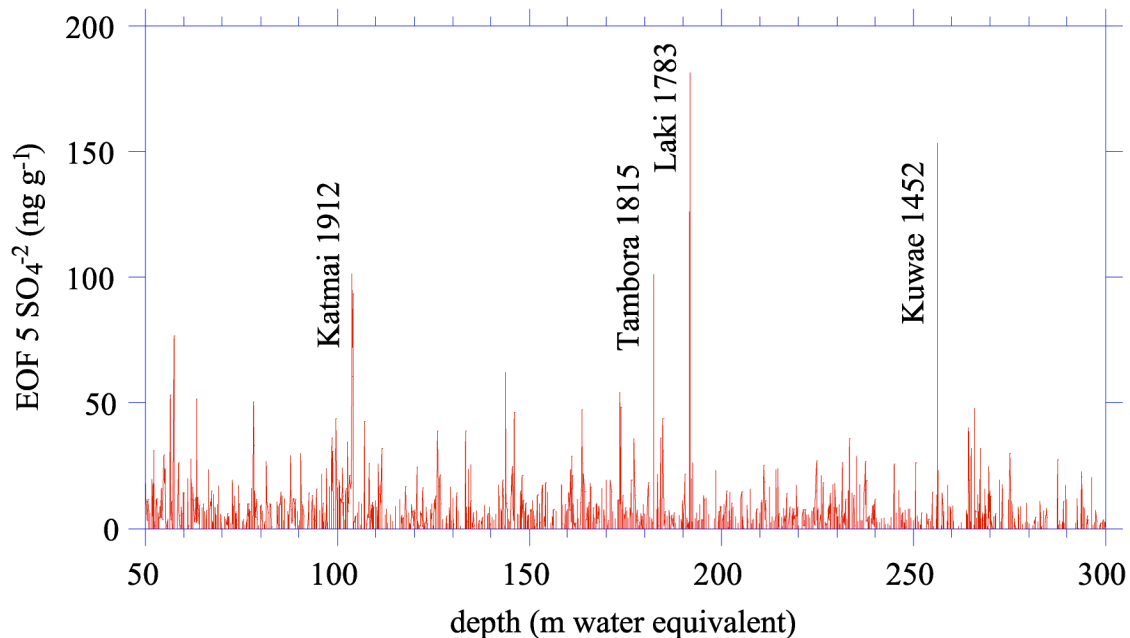


Figure 3. The EOF 5 sulfate record of volcanism for the portion of Core 2 from 50 to 300 m water equivalent depth. Select major volcanic eruptions are labeled.

In some cases, these identifications have been independently verified by means of tephrochronology. Tephra associated with select volcanic sulfate horizons (four in core 3 and seven in Core 2) was collected by filtering of melt water through a 0.2-micron polycarbonate membrane filter and individual particles analyzed for major oxide composition using an automated scanning electron microscope (SEM; Hitachi S-570) at

Micromaterials Research (Germani and Buseck, 1991). Individual particles greater than 4 micrometers that have glass shard morphology were selected for x-ray microanalysis of major oxide composition. Particles greater than 4 micrometers were selected because analyzing larger particles minimizes the effect of particle size and shape on quantitative x-ray microanalysis.

Tephra from the plinian 1912 Katmai, Alaska, eruption, and the caldera-forming 1552 Kuwae, equatorial Pacific, eruption were positively identified by comparing the chemical composition of tephra found in the Eclipse ice core with reference tephtras from the source volcano. Ternary plots of CaO vs. Fe₂O₃ vs. K₂O (Figure 4) show a close composition match between tephra from the Eclipse ice core and reference tephtras from the source volcano. Furthermore, tephra in the Eclipse ice core from the 1912 Katmai eruption shows the progression from rhyolitic to dacitic composition during the eruption (Fierstein and Hildreth, 1992). Identification of tephra from these eruptions provides additional confidence on the ice core chronology established via annual layer counting.

We have also collected tephra from the Eclipse ice core associated with the unknown 1809 volcanic horizon seen in ice cores worldwide. In a manuscript being prepared for submission to the journal *Science* we compare analyses of this tephra to tephra found in Antarctic ice cores to suggest a possible source for this eruption.

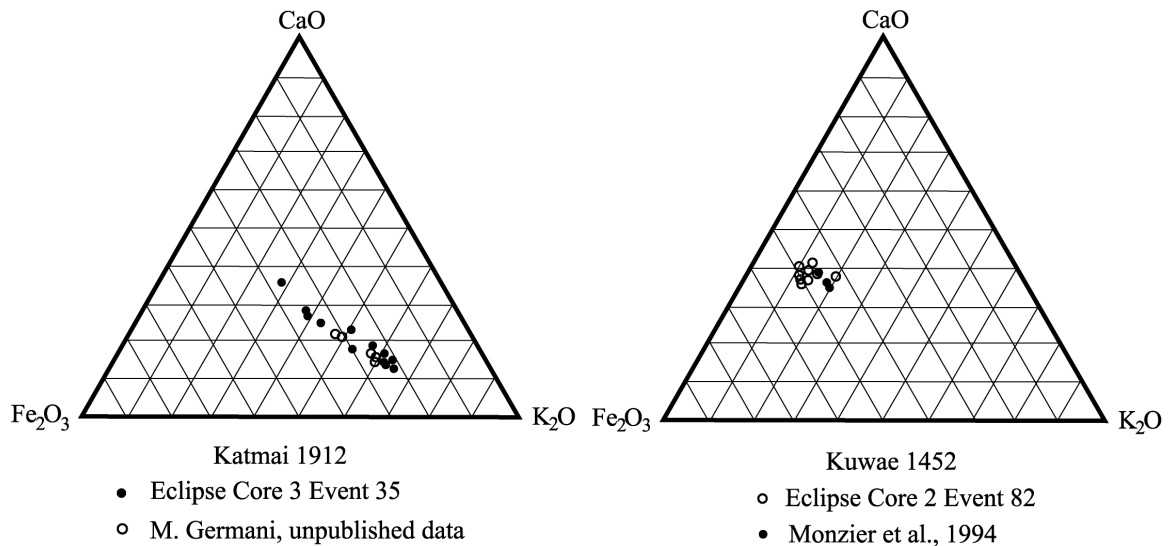


Figure 4. Ternary plots of CaO vs. Fe₂O₃ vs. K₂O of individual glass shards from the 1912 eruption of Katmai, Alaska (left) and the 1452 eruption of Kuwae, equatorial Pacific Ocean; as observed in the Eclipse ice core (solid circles) and in reference tephtras analyzed by other investigators (open circles).

SNOWPIT AND FRESH SNOW STUDIES

Snow samples collected from four 4 m snowpits at Eclipse Icefield, Yukon Territory, Canada during the 2002 field season were analyzed for stable isotopes and major ions to assess spatial variability in snow chemistry. Each pit is about 100 m in a different direction from the 2002 ice core-drilling site and represents approximately one year's accumulation. Stratigraphic properties, seasonal variations in $\delta^{18}\text{O}$, and two high Ca^{2+} and Mg^{2+} events were used place each pit on a common depth- age scale. Accumulation since the end of the 2001 summer season over the 0.1 km² area sampled ranges from 0.78 to 1.24 m water equivalent. An empirical orthogonal function (EOF) analysis was used to assess the signal common to the four snowpits for each glaciochemical species measured. The first EOF describes the variance (signal) common to all four snowpits, and ranges from 49% of the total variance for Na^+ and Cl^- to as high as 80% of the total variance for SO_4^{2-} . Particle- associated species derived from sea- salt and dust display more spatial variability in their glaciochemical concentrations than do aerosol species with gas- phase precursors, as evidenced by lower EOF 1 loadings for particle associated species (Na^+ , Cl^- , Ca^{2+} , Mg^{2+}) than for aerosol species with gas- phase precursors (SO_4^{2-} , NH_4^+ , NO_3^-). A manuscript is currently being prepared for submission to the journal *Geophysical Research Letters*.

TRACE ELEMENT ANALYSES

We have recently begun analysis of trace elements in snowpit and ice core samples. The core will be sampled for trace elements at subannual resolution (2 samples/yr) to 1950, annual resolution to 1900, and biannual resolution to the bottom of the core (~ 1800). Before analyzing ice core samples, we will process several sets of blanks and sections of the test core and have them analyzed via inductively coupled plasma mass-spectrometry (ICP- MS) to ensure our sampling procedures are sufficiently clean at the ppt level. We will also analyze 72 large- volume snowpit samples collected during the 2002 field season for trace elements to investigate seasonal signals. Sample archive prepared during core processing using a titanium scraper for major ions and stable isotopes will be used for trace element analysis. Samples will be melted under a laminar flow bench in a Class 100 clean room and filtered. The soluble fraction will be acidified with 1N HNO_3 , evaporated to dryness by sub-boiling evaporation (~55° C) inside a HEPA- filtered laminar flow box, and resuspended with 1N HNO_3 for analysis. The insoluble fraction will be covered with 1:3 HF: HNO_3 for pressurized acid digestion of sample particulates and resuspended in 1N HNO_3 for analysis. Thus our concentration data will represent total sample concentration (both soluble and insoluble fractions). Samples prepared at UNH will be analyzed using a Finnigan Element ICP-MS at the University of Maine for major elements (S, Fe, Al), trace elements (As, Cd, Cu, Mn, Ni, Pb, Se, V, Zn), and rare earth elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). We expect to complete trace element analyses by early summer 2004.

Collaborative arrangements have been made to analyze core sections not used for stable isotope, major ion, and trace element analyses for Hg with Dr. Daniel Cossa (IFREMER Centre de Nantes, France) using sampling techniques developed jointly through the analysis of container blanks, processing blanks, and test core sections. Analysis of test core sections indicates concentrations of mercury in ice at Eclipse are very low, less than 1.0 ng g^{-1} , while blank concentrations are near 0.4 ng g^{-1} . With blank concentrations close to sample concentrations, obtaining reliable mercury concentration data will require developing cleaner sample processing and analytical procedures.

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