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A 100-year record of North Pacific volcanism in an ice core from Eclipse Icefield, Yukon Territory, Canada

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[1] A record of regionally significant volcanic eruptions in the North Pacific over the last century has been developed using a glaciochemical record from Eclipse Icefield, Yukon Territory, Canada. Tephrochronology of the Eclipse ice core provides positive identification of the 1907 Ksudach, Kamchatka, the 1912 Katmai, Alaska, the 1947 Hekla, Iceland, and the 1989 Redoubt, Alaska, eruptions. Non-sea-salt SO_4^{2-} residuals above a robust spline and empirical orthogonal function (EOF) analysis were used to identify volcanic SO_4^{2-} signatures. Volcanic sulfate values are more conservatively identified by the EOF analysis as sulfate deposition from other sources is more robustly accounted for. Some eruptions are also recorded as peaks in non-sea-salt chloride. The volcanic signals in the Eclipse ice core are mostly attributable to Alaskan, Aleutian, or Kamchatkan eruptions. Conversely, the Eclipse ice core provides a poor record of globally significant tropical eruptions. These results are promising for the development of longer ice core based records of paleovolcanism in the North Pacific rim. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 8409 Volcanology: Atmospheric effects (0370); *KEYWORDS:* Yukon Territory, ice cores, volcanism, atmospheric effects, Kamchatka, Alaska

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1. Introduction

[2] Volcanoes are widely recognized as an important component of the climate system. Volcanic SO_2 injected into the stratosphere is slowly converted to sulfuric acid aerosol and can remain aloft for as much as 3 years after an eruption. Stratospheric sulfuric acid aerosols affect climate by backscattering incoming solar radiation, thereby increasing stratospheric optical depth and reducing the amount of solar radiation reaching the surface. These aerosols also cause absorption of terrestrially radiated infrared radiation. The net effect of stratospheric sulfate aerosols is to cool the troposphere and warm the stratosphere [*Toon and Pollack*, 1980]. Volcanic eruptions that produce large amounts of sulfate aerosols can cool tropospheric temperatures on regional to hemispheric scales for as much as 2–3 years after an eruption [*Lamb*, 1970; *Hansen et al.*, 1978; *Self et al.*, 1981; *Rampino and Self*, 1984; *Angell and Korshover*, 1985; *Bradley*, 1988; *Sigurdsson*, 1990]. Some volcanoes also emit large quantities of chloride aerosols to the atmosphere. Although chloride aerosols do not have radiative forcing properties, volcanic chloride emissions play an important role in the stratospheric chloride budget and may influence stratospheric ozone concentrations [*Johnson*, 1980; *Symonds et al.*, 1988]. Volcanic eruptions can also perturb tropospheric chemistry on regional scales by injecting large quantities of sulfur and chlorine rich aerosols into the free troposphere, although the residence time for tropospheric aerosols is not as long as for those in the stratosphere.

[3] Understanding the role of volcanic eruptions in regulating past climates is hampered by a poor understanding of the amount of sulfur produced by specific eruptions and an incomplete record of volcanism in some regions [e.g., *Bradley and Jones*, 1992]. Direct measurements of volcanic aerosol loading and dispersion are only available since 1979 for comparison with instrumental temperature records [*Bluth et al.*, 1993; *McCormick et al.*, 1993]. Furthermore, the historical record of volcanism is incomplete; especially in remote areas such as Alaska and Kamchatka where major eruptions may have gone unnoticed as late as 1960 [*Newhall and Self*, 1982].

[4] Since the pioneering work of *Hammer* [1977], valuable records of past volcanism have been developed from ice cores. Detection of volcanic acids as elevated levels of electrical conductivity in ice cores first underscored the usefulness of ice cores as an index of past volcanism [*Hammer et al.*, 1980; *Clausen and Hammer*, 1988]. Later,

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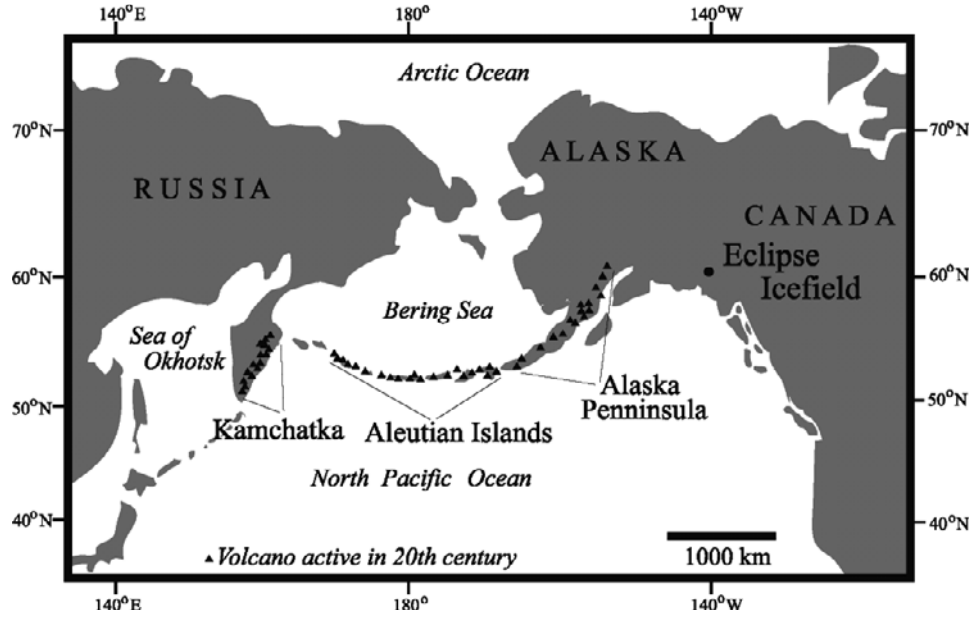

Figure 1. Eclipse Icefield is located at 60.51°N, 139.47°W, 3017 m elevation in the St. Elias Mountains, Yukon Territory, Canada. The Eclipse site is directly downwind of vigorous volcanic arcs in the Alaska Peninsula, Aleutian Islands, and Kamchatka, making the Eclipse site ideally located to record volcanic eruptions in these regions.

the advent of glaciochemistry (multiparameter measurement of soluble impurities in glacial ice) enabled the development of robust statistical analyses for the identification of volcanic signals in ice cores [*Zielinski et al.*, 1994, 1996]. A close match between glaciochemical signals identified as volcanic with the known record of volcanism [*Simkin and Siebert*, 1994] validates the use of ice cores in reconstructing past volcanism. Indeed, valuable records of volcanic aerosol deposition spanning hundreds to tens of thousands of years have been developed from ice cores collected from both Greenland [*Lyons et al.*, 1990; *Zielinski et al.*, 1996; *Clausen et al.*, 1997] and Antarctica [*Delmas et al.*, 1992] and have enhanced our understanding of past volcanism.

[5] As no single ice core can provide a complete record of even the largest volcanic eruptions [*Delmas et al.*, 1985; *Clausen and Hammer*, 1988; *Zielinski et al.*, 1997], volcanic records should be developed using ice cores from a diversity of regions. Here we report on a high resolution, one hundred year record of North Pacific volcanism developed from an ice core obtained from Eclipse Icefield (60.51°N, 139.47°W, 3017 m elevation), Yukon Territory, Canada (Figure 1). The Eclipse site is located in the Saint Elias Mountains adjacent to the Gulf of Alaska, an area of intense cyclogenesis. Air masses reaching the Eclipse site frequently originate in the Gulf of Alaska and are advected into the Saint Elias Mountains by the passage of frontal systems moving onshore [*Taylor-Barge*, 1969]. Due to the west-east movement of frontal systems in this region, the Eclipse site is directly downwind of vigorous volcanic arcs in the Alaska Peninsula, the Aleutian Islands, and Kamchatka. Ice cores from this region should therefore provide a Northern Hemisphere volcanic record complementary to the record from Greenland, where the effects of Icelandic eruptions predominate [*Hammer*, 1984]. The Eclipse site is located 45 km northeast of and 2.3 km lower than the ice core site at 5340 m on Mount Logan [*Holdsworth et al.*, 1984; *Holdsworth and Peake*, 1985]. The higher accumulation rate at Eclipse (1.38 m water equivalent (w.e.) per year) compared to Mount Logan (0.30 m w.e. per year) provides a higher resolution record with more complete preservation of glaciochemical signals.

2. Development of the Record

[6] A 160-m firn and ice core was recovered from Eclipse Icefield in the summer of 1996. Visible stratigraphy (location and thickness of ice layers) and density measurements were made in the field, and then the core was shipped frozen to the University of New Hampshire. The core was continuously sampled in 10-cm segments, corresponding to a minimum of 12 samples per year. Stringent core processing techniques [*Mayewski et al.*, 1993] were used to ensure samples were contamination free at the ng g^{-1} level. Blanks prepared on a frequent basis showed no contamination of samples during processing of the core. Samples were analyzed for major ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) using a Dionex™ model 2010 ion chromatograph [*Buck et al.*, 1992] in a dedicated laboratory at the University of New Hampshire and for oxygen isotopes at the Stable Isotope Laboratory in Copenhagen, Denmark. A section of the core from 50 to 76 m depth was analyzed for beta activity.

[7] Analysis of the beta activity profile and comparison with real-time precipitation measurements from Whitehorse, Yukon Territory [*Holdsworth et al.*, 1984] shows clear identification of the 1961 and 1963 beta activity peaks from atmospheric thermonuclear weapons testing (Figure 2). Average annual accumulation from 1963 to 1996 was 1.38 m water equivalent. The presence of discrete ice layers in the Eclipse ice core accounting for 5% of the net accumulation by weight demonstrates that a limited amount of surface

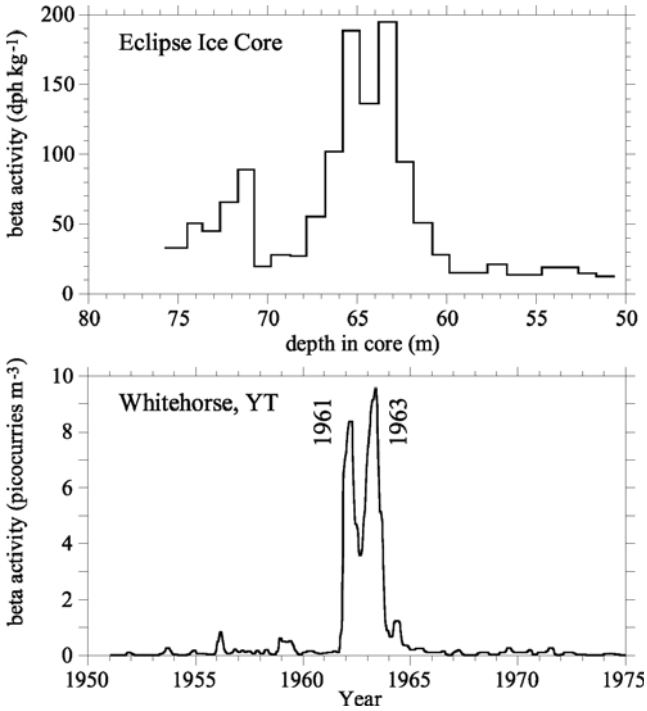

Figure 2. Comparison of the Eclipse beta activity profile with real-time precipitation measurements from Whitehorse, Yukon Territory [*Holdsworth et al.*, 1984] shows clear identification of the 1961 and 1963 beta activity maximums from atmospheric thermonuclear weapons testing.

melting occurs at the Eclipse site during summer. Meltwater percolation does not significantly alter the glaciochemical records available from the Eclipse ice core as evidenced by the preservation of clear seasonal signals in the major ion and oxygen isotope records, allowing dating of the core via annual layer counting [*Yalcin and Wake*, 2001].

[8] Annual layers were identified by seasonal oscillations in both the oxygen isotope ratio and sodium concentrations measured in the Eclipse ice core (Figure 3). The annual cycle of $\delta^{18}O$ maxima in summer precipitation and $\delta^{18}O$ 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 [*Dansgaard*, 1961]. 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 [*Whitlow et al.*, 1992]. Increased storminess in the Gulf of Alaska during winter results 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.

[9] Age control on the chronology established via annual layer counting is provided by the 1963 and 1961 beta activity reference horizons and four volcanic reference horizons identified by tephrochronology. Core sections containing volcanic fallout were identified by analysis of the high-resolution sulfate record. Meltwater from select volcanic horizons was filtered through a 0.2-micrometer pore-diameter polycarbonate membrane filter. We used a 2.0-micrometer pore-diameter filter for the 1912 horizon as it contained visible tephra. An automated scanning electron microscope (SEM; Hitachi S-570) at MicroMaterials Research was used to locate volcanic glass particles utilizing established procedures [*Germani and Buseck*, 1991]. Individual particles greater than 4 micrometers that have a glass shard morphology were selected for x-ray microanalysis of major oxide composition. Particles greater then 4 micrometers were selected because analyzing larger particles minimizes the effect of particle size and shape on quantitative x-ray microanalysis.

[10] We also prepared particle dispersions on polycarbonate membrane filters of tephra samples from the 1912 Katmai eruption for direct comparison with glass shards found in the Eclipse ice core. The samples were prepared by grinding the tephra under ethanol using a mortar and pestle. An aliquot of particle suspension was filtered through a 0.2-μm pore diameter polycarbonate membrane filter. Glass particles >4 μm in diameter were selected for quantitative x-ray analysis.

[11] Comparison of the mean composition of individual glass shards in the Eclipse ice core with volcanic tephra samples shows a close match between the chemistry of glass shards in the Eclipse ice core and tephra from the 1907 Ksudach, Kamchatka; 1912 Katmai, Alaska; 1947 Hekla, Iceland, and 1989 Redoubt, Alaska eruptions (Table 1). Variation between our results and those of other investigators could be due to differences in analytical techniques. Ternary plots of CaO versus Fe_2O_3 versus K_2O demonstrate that tephras from these four volcanoes generally plot in distinct chemical fields, with some overlap between the Hekla and Ksudach fields and between the Redoubt and Katmai fields (Figure 4). However, separation of each of these horizons by a minimum of 5 years of accumulation places a time limit on which eruption could be responsible for the glass found in a particular horizon. Furthermore, our tephra from the 1912 Katmai eruption shows the characteristic bimodal (rhylotic and dacitic) composition also recognized in nearby pumice beds [*Palais and Sigurdsson*, 1989; *Fierstein and Hildreth*, 1992] as well as distal tephra deposits collected from lake [*Beget et al.*, 1994] and marine [*Federman and Scheideregger*, 1984] sediment cores.

[12] In summary, chronology of the Eclipse ice core is based on the counting of annual layers delineated by summer maxima in $\delta^{18}O$ and winter maxima in sodium concentrations. Age control on the chronology is based on the 1963 and 1961 beta activity time markers and the 1989, 1947, 1912, and 1907 volcanic time markers. We estimate

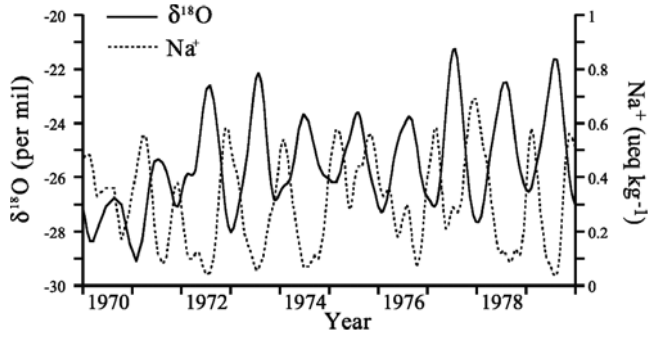

Figure 3. Seasonal signals in the smoothed oxygen isotope and sodium records from the Eclipse ice core used to date the core via annual layer counting.

Table 1. Major Oxide Composition of Tephra Found in Select Volcanic Horizons in the Eclipse Ice Core Compared to Published Reference Tephras[a]

Sample	n	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Reference
Eclipse event 5	12	74.6 (1.6)	0.4 (0.2)	13.1 (0.5)	1.9 (0.7)	0.7 (0.6)	1.2 (0.5)	5.3 (0.6)	3.2 (0.3)	this work
Redoubt 1989–90		78.2 (0.1)	0.2 (0.1)	12.2 (0.2)	1.1 (0.1)	2.8 (1.3)	0.9 (0.1)	3.7 (0.1)	3.5 (0.1)	*Beget et al.* [1994]
Eclipse event 31	15	61.7 (6.2)	1.4 (0.9)	14.9 (1.7)	8.2 (3.5)	1.8 (1.1)	4.2 (1.9)	5.8 (1.3)	1.5 (0.5)	this work
Hekla 1947		58.7 (2.6)	1.0 (0.3)	16.7 (1.2)	8.5 (1.2)	2.6 (0.9)	5.8 (0.6)	3.7 (1.5)	2.0 (1.0)	*Thorarinsson* [1954]
Eclipse event 41	10	75.8 (0.8)	0.3 (0.1)	12.5 (0.4)	1.7 (0.4)	-	0.9 (0.3)	5.6 (0.6)	3.3 (0.2)	this work
Katmai 1912		76.8 (2.3)	0.5 (0.1)	12.7 (1.3)	1.9 (0.2)	0.3 (0.1)	1.6 (0.2)	2.8 (1.2)	3.4 (0.2)	M. Germani, unpublished data, 1994
Eclipse event 44	9	54.3 (2.4)	2 (0.6)	14.1 (1.5)	11.4 (1.6)	3.2 (0.8)	8.3 (2.3)	5.3 (0.7)	1.4 (0.3)	this work
Ksudach 1907		60.8 (5.4)	0.7 (0.2)	16.3 (1.2)	6.8 (1.7)	2.8 (1.3)	6.6 (2.3)	4.4 (0.8)	0.8 (0.3)	*Macias and Sheridan* [1995]

[a]Composition is given as weight %, recalculated to a sum of 100%, where n is the number of samples analyzed in ice core samples. Values are means for the specified number of samples, with the standard deviation in parentheses. Double dash denotes element below detection limits. Total iron is given as Fe_2O_3.

dating error in the core to be no more than ±1 year, given the clear delineation of annual layers in the ice core supported by six independent time markers.

3. Identification of Volcanic Signals

[13] Volcanic eruptions are recorded in ice cores as large SO_4^{2-} spikes above background levels independent of continental dust (Ca^{2+}) or sea salt (Na^+) deposition, sometimes accompanied by other volcanic acids (such as HCl and HF) and/or tephra [*Herron*, 1982; *Zielinski et al.*, 1994]. However, the identification of volcanic eruptions from sulfate in ice cores is not straightforward due to the presence of other sulfate sources including sea salt, continental dust, biogenic reduced gases, and anthropogenic activity [*Zielinski et al.*, 1996]. Furthermore, the relative magnitude of the sulfate

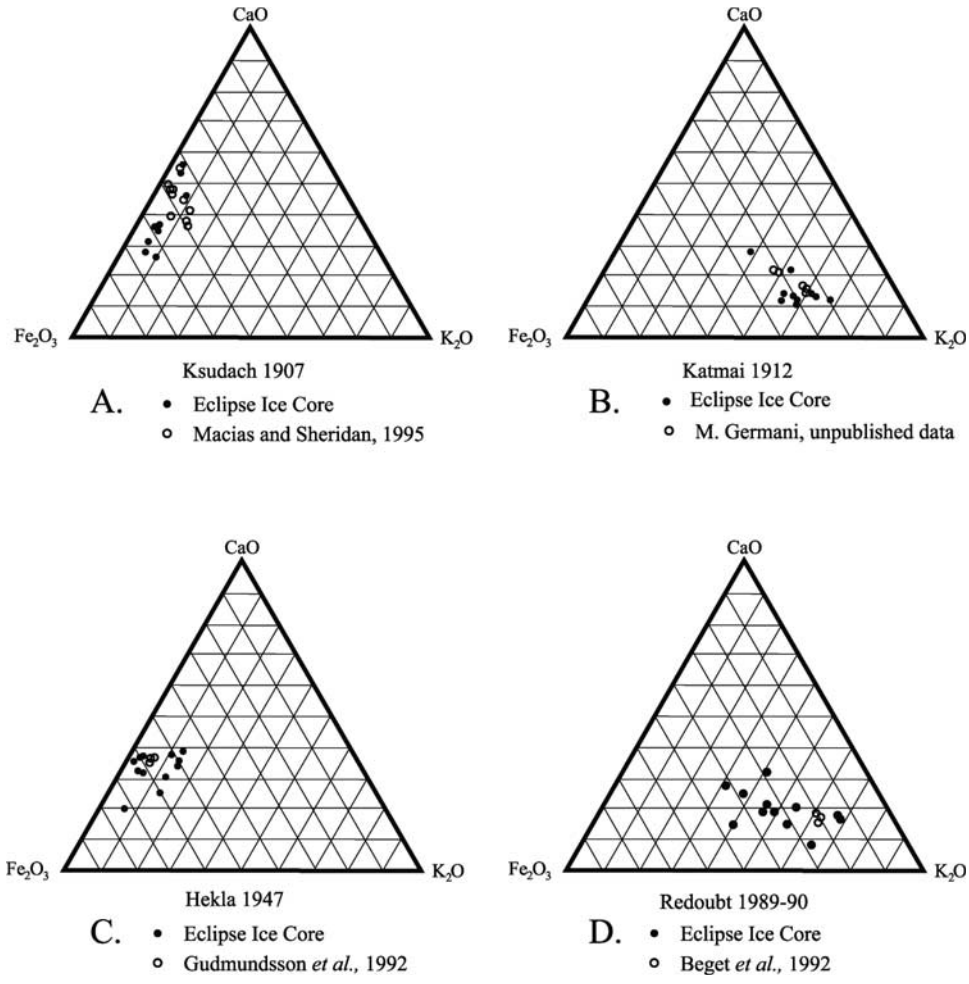

Figure 4. Ternary plots of CaO versus Fe_2O_3 versus K_2O of individual glass shards from the (a) 1907 eruption of Ksudach, Kamchatka; (b) 1912 eruption of Katmai, Alaska; (c) 1947 eruption of Hekla, Iceland; and (d) 1989–1990 eruption of Redoubt, Alaska; as observed in the Eclipse ice core (solid circles) and in reference tephras analyzed by other investigators (open circles).

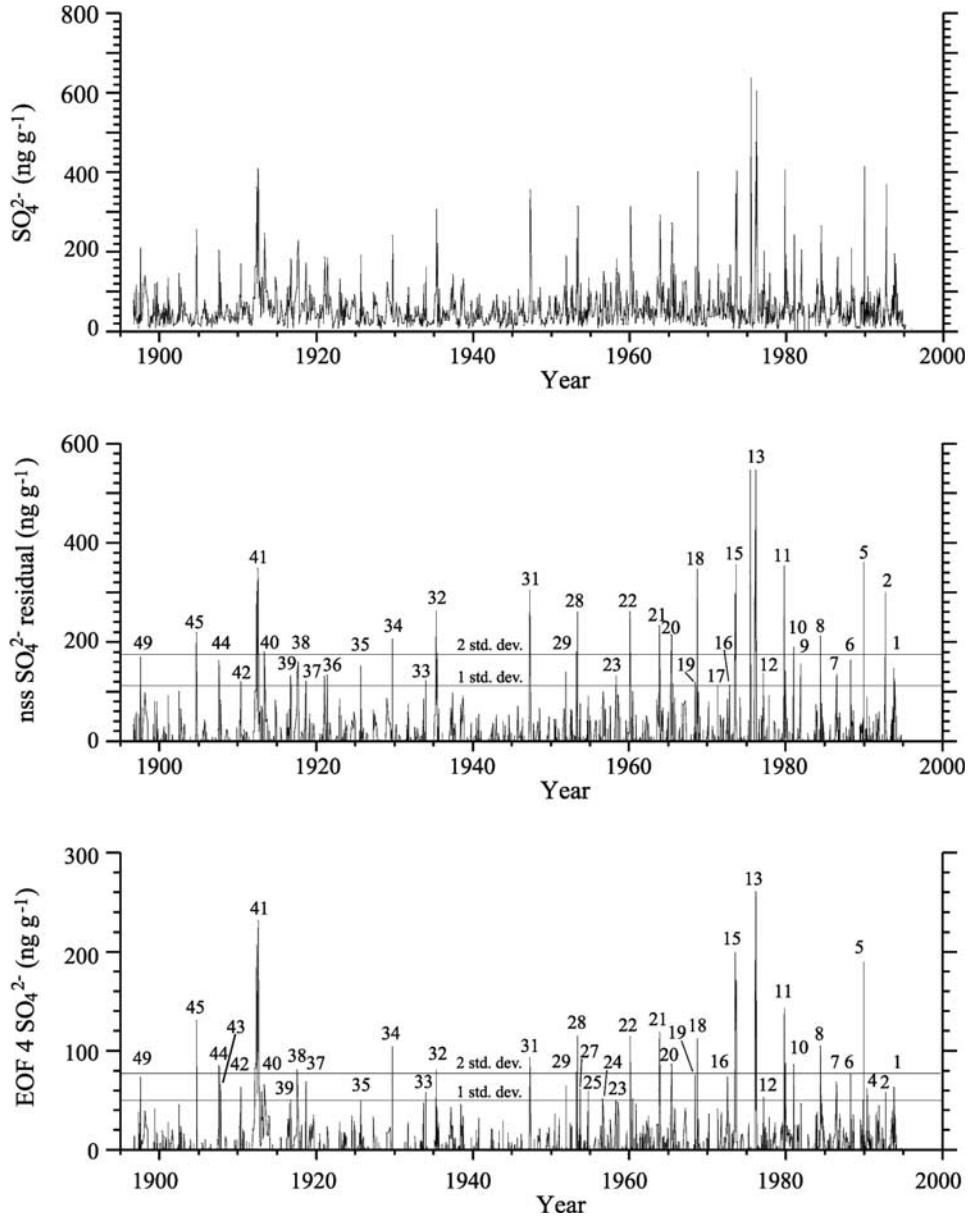

Figure 5. Volcanic SO_4^{2-} signals in the Eclipse ice core: (top) raw SO_4^{2-} time series; (middle) nss SO_4^{2-} residuals; (bottom) EOF 4 SO_4^{2-} values (ng g^{-1}), 1 and 2 standard deviations above the mean as indicated. Numbering corresponds to event numbers in Table 3 (volcanic sulfate signals).

signal in an ice core will depend on the size of the eruption, the location of the source volcano, atmospheric circulation and depositional processes, and post depositional alteration due to wind scour and melting. In addition, the lag between the time of an eruption and deposition of the resulting aerosols in a snowpack can be as much as two years, depending on latitude of the eruption and time of year [*Zielinski et al.*, 1994]. Assigning a signal in the Eclipse ice core to a specific eruption is further complicated by the high frequency of eruptions in the North Pacific, resulting in closely spaced signals in our record that can be difficult to attribute to an individual event.

[14] We used two methods to identify volcanic sulfate signals in our record (Figure 5). First, we estimated the sulfate contribution from sea salt using the ratios of sulfate to other ions in seawater [*Keene et al.*, 1986], 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 (<7%) with sodium the limiting sea salt species in 92% 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 [*Zielinski et al.*, 1994]. We identified 37 events with nss sulfate residuals greater than 110 ng g^{-1} (2.5 times the mean positive residual) as possibly reflecting the deposition of volcanic aerosols. Of these 37 events, 18 were greater than 176 ng g^{-1} (4 times the mean positive residual).

[15] The second method used an empirical orthogonal function (EOF) decomposition to describe the variance in

Table 2. EOF Analysis of the Variance in the Data Set of Six of the Eight Species Measured in the Eclipse Ice Core[a]

	Eigenvector Components						Percent Variance Explained					
Species	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6	EOF 1	EOF 2	EOF 3	EOF 4	EOF 5	EOF 6
Na^+	23.5	26.0	−4.2	−10.1	16.0	1.7	34.3	42.2	1.1	6.3	15.8	0.2
K^+	25.6	17.8	−19.6	−1.5	−15.8	−0.9	40.8	19.6	23.8	0.1	15.6	0.6
Mg^{2+}	29.8	−19.8	5.5	−15.1	−0.3	−8.4	55.1	24.4	1.9	14.3	0.0	4.4
Ca^{2+}	32.5	−20.8	0.5	−1.5	−1.1	10.8	65.7	26.8	0.0	0.6	0.1	7.3
Cl^-	17.0	18.8	30.0	2.7	−7.4	0.7	18.0	22.1	56.0	0.4	3.4	0.0
SO_4^{2-}	31.3	−4.0	−2.9	**23.3**	6.5	−4.2	61.1	1.0	0.5	**33.8**	2.6	1.1
						Percent Total Variance						
							45.8	22.7	13.9	9.2	6.2	2.2

[a]NO_3^- and NH_4^+ were excluded. Note that EOF 4 is loaded solely on sulfate and explains a large proportion of the variance in the sulfate time series (as indicated by bold entries).

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 [*Peixoto and Oort*, 1992]. The first eigenvector explains the greatest percentage of variance in the data set, 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 [*Mayewski et al.*, 1994]. Therefore, each EOF often provides information on a different environmental parameter controlling the glaciochemistry of an ice core.

[16] Applying EOF analysis to the suite of ions measured in the Eclipse ice core (excluding NO_3^- and NH_4^+ [*Zielinski et al.*, 1996]) reveals that EOF 4 is loaded solely with sulfate and describes 9.3% of the variance in the full data set, but 34% of the variance in the sulfate time series (Table 2). Since EOF 4 is not loaded in either sea salt species (Na^+) or continental dust species (Ca^{2+}), the sulfate contributed by EOF 4 is not associated with sea salt or continental dust deposition. The lack of any trends in the EOF 4 sulfate record that could be ascribed to trends in fossil fuel combustion [*Yalcin and Wake*, 2001] makes an anthropogenic source unlikely. The lack of any association with other species indicative of a marine air mass is an encouraging sign that the sulfate is not from a marine biogenic source. However, different production and transport mechanisms make it possible that marine biogenic sulfate could be deposited at Eclipse without any concurrent sea salt input [*Bates et al.*, 1992]. Concentrations of methanosulfonate acid measured on short sections of the Eclipse ice core both near the surface and at depth yield MSA fractions (5–9%) lower than those observed in marine aerosols at high latitude sites [18–25%; *Galloway et al.*, 1993, *Savoie et al.*, 1993] and comparable to recent values in the GISP2 ice core (6–12% [*Saltzman et al.*, 1997]). These values suggest that sulfate of marine biogenic origin is not a major contributor to the overall sulfate budget at Eclipse, making it unlikely that a large portion of the EOF 4 sulfate is of marine biogenic origin. The only other major source of sulfate in ice cores is volcanic emissions [*Zielinski et al.*, 1996]; therefore we believe that EOF 4 primarily represents the deposition of sulfate from volcanic aerosols. Again, we focused on those events with an EOF 4 sulfate value greater than 1 standard deviation above the mean positive EOF 4 sulfate value as most likely to represent an identifiable volcanic eruption. This technique identified 39 volcanic events in our ice core greater than 48 ng g^{-1} (1 standard deviation above the mean), with 18 of these events greater than 77 ng g^{-1} (2 standard deviations above the mean).

[17] Comparison of the results from these two analyses (Figure 5) shows that nss sulfate residuals can be as much as twice the EOF 4 sulfate values. We feel this is a result of the nss sulfate residuals including contributions from other sources such as continental dust or anthropogenic sulfur emissions [*Yalcin and Wake*, 2001]. We therefore believe EOF 4 provides a more robust record of sulfate deposition from volcanic sources, as sulfate deposition identified by EOF 4 is not associated with continental dust deposition or attributable to anthropogenic sulfur emissions.

[18] Nonetheless, it is still possible that the eigenvector simply represents high frequency noise rather than a volcanic signal. However, several aspects of the data argue against this. First, the eigenvector represents a high proportion of the variance in the sulfate time series, and is loaded solely on sulfate. If the eigenvector is capturing noise rather than a volcanic signal, we would not expect it to be loaded solely on sulfate nor would we expect it to capture such a large proportion of the variance in the sulfate time series. Second, we have confirmed that four of the larger signals in the eigenvector are indeed volcanic by collecting tephra from these horizons in the core. This confirms that the sulfate signal captured by the eigenvector, at least for these four events, is indeed representing volcanic fallout since it is associated with volcanic glass.

[19] Furthermore, the relative magnitude of the eigenvector sulfate signals is consistent with the location and magnitude of the source eruptions as identified by tephrochronology. For example, the 1912 Katmai signal (VEI 6) is the largest eruption in the high northern latitudes over the last century. It is also the largest sulfate signal, in terms of total sulfate deposition, identified by the eigenvector. The peak concentration of 231 ng g^{-1} associated with the Katmai event is exceeded only by the 1976 eruption of Augustine, Alaska. However, total sulfate fallout of the Katmai eruption (115 kg km^{-2}) as measured by summing EOF 4 sulfate deposition for adjacent samples influenced by the eruption exceeds sulfate deposition following the Augustine eruption (75 kg km^{-2}). Finally, the frequency of volcanic sulfate signals identified by the eigenvector agrees well with the historical record of North Pacific eruptions. Although large eruptions are rather frequent in this region, there are periods of time over the last century where eruptions are more (the late 1950s and early 1960s, the late 1970s and early 1980s) or less frequent (the middle

and late 1910s, most of the 1920s and 1930s). These changes in the frequency of eruptions are also reflected in the number of volcanic sulfate signals identified by the eigenvector. Taken collectively, these observations provide evidence that the eigenvector is indeed representing a volcanic signal in the sulfate time series and not high-frequency noise.

4. Correlation With Known Eruptions

[20] To validate our record, we used the chronology of *Simkin and Siebert* [1994] to match events we identified as volcanic using both the robust spline and EOF techniques with known eruptions. In assigning individual signals to specific eruptions, we considered high- and mid-latitude Northern Hemisphere eruptions of volcanic explosivity index (VEI) 4 or greater, as one of the criteria for a VEI of 4 is stratospheric injection [*Newhall and Self*, 1982]. These Plinian or ultra- Plinian type eruptions produced at least 10^8 m^3 of ejecta with eruptive columns reaching heights of 10–25 km. Such injection and subsequent transport in the stratosphere would favor long-range transport of eruptive products and their deposition in glacial ice [*Zielinski et al.*, 1994]. We also considered Alaskan, Aleutian, and Kamchatkan eruptions of VEI 3; as such magnitude eruptions are capable of ''substantial'' tropospheric injection [*Newhall and Self*, 1982]. Due to the proximity of Eclipse to these regions, transport of volcanic sulfate aerosols entirely within the troposphere is capable of delivering these products to Eclipse. Furthermore, at least some VEI 3 eruptions are likely to have a stratospheric component, increasing the likelihood of detecting a signal from such an eruption [*Newhall and Self*, 1982].

[21] We also considered low northern latitude eruptions of VEI 5 or greater, as ''significant'' stratospheric injection from eruptions of such magnitude could enable fallout to be detectable at Eclipse. Furthermore, time lags of up to two years could exist between the eruption and aerosol deposition [*Zielinski et al.*, 1994]; however we do not think this is a common occurrence at Eclipse due to the close proximity of many of the source volcanoes we have identified. Using the above outlined criteria, we matched 40 of the 49 volcanic signals in our core to a documented eruption (Table 3) within the time constraints we have established on each signal via annual layer counting, validating the statistical techniques we used to identify the deposition of volcanic aerosols at Eclipse Icefield.

[22] Thirty of the forty volcanic signals we were able to attribute to specific eruptions were from Alaskan, Aleutian, or Kamchatkan volcanoes. We also identified eight eruptions from the western Pacific Rim, and two Icelandic eruptions. In some cases, eruptions closely spaced in time make assignment of a signal to a single eruption ambiguous; in these cases we list multiple potential source volcanoes. Such is the case with the fall 1984 signal that could be attributable to both the October 1984 eruption of Bezymianny and the November 1984 eruption of Kliuchevoskoi. In other cases, high-resolution sampling (10–20 samples per year) has allowed us to resolve signals closely spaced in time and attribute them to individual eruptions. Signals separated by at least 0.40 m of water equivalent accumulation (representing 3–6 months) were our criteria for separately resolvable signals and assignment of an individual source. For example, two signals in the 1953 annual layer, the first deposited in winter and the second during summer, are separated by 0.70 m of water equivalent accumulation. We therefore attribute these peaks separately, the first to the February 1953 eruption of Trident and the second to the July 1953 eruption of Spurr, underscoring the utility of developing subseasonal glaciochemical records from high accumulation areas.

[23] Nine of the 49 volcanic events in our record cannot be matched to an eruption that met our criteria outlined above. Of these nine, seven could be attributed to multiple VEI 2 eruptions in Alaska, the Aleutians, and Kamchatka. Since VEI 2 eruptions are capable of ''moderate'' tropospheric injection, the cumulative tropospheric sulfur loading of multiple, contemporaneous VEI 2 eruptions could result in a detectable signal at a relatively low elevation site such as Eclipse. An alternative explanation that becomes increasingly likely in the earlier part of our record is that an undocumented North Pacific eruption is responsible for these signals. Perhaps this is the case with the summer 1916 signal (event 39), for which the only eruption that could have produced this signal within the time constraints we have established on the core through annual layer counting is a single Kamchatkan eruption of VEI 2. Furthermore, we point out that this signal is the second smallest in our record that meets our selection criteria for an identifiable volcanic eruption. Nonetheless, we feel the good agreement between the historical record of explosive volcanism and the glaciochemical signals we identified as volcanic validates our use of the Eclipse glaciochemical record as a proxy for regionally significant volcanic activity.

[24] However, several significant North Pacific eruptions are missing from our record, such as Tolbachik, Kamchatka, 1975 (VEI 4); Avachinsky, Kamchatka, 1945 (VEI 4); and Kliuchevoskoi, Kamchatka, 1931 (VEI 4). Several mechanisms may be responsible for missing volcanic sulfate signals in our record. First, circulation patterns at the time of the eruption may not have been favorable for transport of the aerosols to the Eclipse site. Second, there may not have been sufficient snowfall at Eclipse while the aerosol cloud was over the site to produce a distinguishable glaciochemical signal. Last, post- depositional modification of the signal, i.e. by wind scouring and/or surface melting in summer, may have removed the signal. The lack of signal preservation from regionally significant eruptions is not unique to the Eclipse ice core. For example, *Robock and Free* [1995] found that when eight ice core based volcanic records from the circum- Arctic covering the period 1850 to the present were compared, only the 1912 Katmai eruption was recorded at all sites. In fact, all of the sites included in their study were missing signals from at least some major eruptions in the high northern latitudes.

[25] The Eclipse site does not provide a good record of major tropical eruptions, such as Pinatubo, Philippines, 1991 (VEI 6); El Chichon, Mexico, 1982 (VEI 5); and Santa Maria, Guatemala, 1902 (VEI 6). This is probably a result of the remoteness of the Eclipse site, at 60°N latitude, relative to the location of these volcanoes. Stratospheric transport would be needed for aerosols from tropical eruptions to reach the Eclipse site. Variability in sulfate deposition from nonvolcanic sources is probably too large at Eclipse to confidently distinguish stratospheric volcanic

Table 3. Volcanic Signals in the Eclipse Ice Core[a]

Event	Depth, m. w. e.	Year	Season	SO_4^{2-}, ng g^{-1}		Cl^- nss res, ng g^{-1}	Possible Source(s) with Date	VEI
				EOF 4	nss res.			
1	3.79	1993	fall	64	147	-	Bezymianny (Kamchatka) 10/1993	3
2	5.78	1992	summer	57	299	23	Spurr (Alaska) 6/1992	4
3	8.35	1991	winter	-	-	22	Avachinsky (Kamchatka) 1/1991	3
4	9.41	1990	summer	62	-	-	Sheveluch (Kamchatka) 8/1990	3
5	10.32	1989	winter	189	361	87	Redoubt (Alaska) 12/1989	3
6	12.48	1988	spring	76	163	21	???[b]	
7	15.59	1986	summer	68	135	-	Sheveluch (Kamchatka) 8/1986	3
8	17.04	1984	fall	104	212	-	Bezymianny (Kamchatka) 10/1984	3
							Kliuchevoskoi (Kamchatka) 11/1984	3
9	19.30	1982	winter	-	154	-	Gareloi (Aleutians) 1/1982	3
10	21.32	1981	winter	86	190	-	Pavlof (Alaska) 11/1980	3
11	22.69	1980	winter	143	353	33	Kliuchevoskoi (Kamchatka) 1/1980	3
12	26.14	1977	winter	53	137	-	Unkreik Maars (Alaska) 3/1977	3
13	27.77	1976	winter	261	547	-	St. Augustine (Alaska) 1/1976	4
14	30.48	1974	winter	-	-	20	Kliuchevoskoi (Kamchatka) 4/1974	3
15	31.41	1973	summer	199	356	67	Tiatia (Kurile Is.) 7/73	4
16	33.32	1972	spring	74	113	-	Bezymianny (Kamchatka) 3/72	3
17	34.99	1971	spring	-	112	-	???[c]	
18	37.05	1970	spring	112	346	-	Karymsky (Kamchatka) 5/70	3
19	38.11	1968	fall	75	118	-	Trident (Alaska) 11/68	3
							Kliuchevoskoi (Kamchatka) 7/68	3
20	42.81	1965	summer	86	215	-	Bezymianny (Kamchatka) 3/65	3
							Karymsky (Kamchatka) 5/65	3
21	45.15	1963	fall	119	234	-	Trident (Alaska) 10/63	3
22	50.04	1960	summer	115	260	-	Sarychev (Kurile Is.) 8/60	3
23	52.96	1958	summer	49	131	19	Okmok (Aleutians) 8/58	3
24	54.89	1956	summer	52	-	23	Bezymianny (Kamchatka) 3/56	5
25	57.29	1955	spring	59	-	-	???[d]	
26	59.03	1954	winter	-	-	46	???[e]	
27	60.18	1953	summer	61	-	30	Spurr (Alaska) 7/53	4
28	60.99	1952	fall	115	261	-	Tao-Rusyr (Kurile Is.) 11/52	3
29	63.75	1950	fall	64	139	-	???[f]	
30	67.39	1948	winter	-	-	34	???[g]	
31	68.95	1947	spring	93	304	-	Hekla (Iceland) 3/47	4
32	83.41	1935	summer	80	262	-	St. Augustine (Alaska) 6/35	3
33	84.77	1934	winter	58	123	-	Kuchinoerabu (Ryukyu Is.) 12/33	4?
34	90.34	1930	summer	104	205	-	Gorely (Kamchatka) 9/30	3
35	95.66	1925	summer	49	151	-	Iriomate- Jima (Ryukyu Is.) 10/24	4
36	101.06	1921	summer	-	134	-	???[h]	
37	104.60	1918	fall	68	120	-	Katla (Iceland) 10/18	4
38	105.33	1917	summer	81	160	-	Mutnovsky (Kamchatka) 7/17	3?
							Agrigan (Mariana Is.) 4/17	4
39	106.15	1916	summer	50	132	98	???[i]	
40	109.61	1913	summer	65	180	35	Katmai/Novarupta (Alaska) 6/12	6
41	111.38	1912	summer	231	349	1663	Katmai/Novarupta (Alaska) 6/12	6
42	113.64	1910	summer	63	120	-	???[j]	
43	115.68	1907	fall	65	-	-	Bogoslof (Aleutians) 9/7	3
44	117.22	1907	summer	85	162	-	Ksudach (Kamchatka) 4/7	5
45	120.37	1904	summer	131	220	63	Shin- Iwo -Jima (Japan) 11/04	3
46	122.42	1902	winter	-	-	23	Redoubt (Alaska) 1/1902	3
47	123.15	1901	spring	-	-	67	Ilyinsky (Kamchatka) ?1901	3
48	128.03	1899	winter	-	-	27	Okmok (Aleutian Is.) ?1899	2
49	130.28	1897	spring	74	169	65	Mayon (Philippines) 5/97	4

[a]Event number corresponds to the numbering in Figures 5 and 7. Table includes depth in core, year of signal, season (as defined using the oxygen isotope curve), EOF 4 SO_4^{2-}value, nss SO_4^{2-} residual, nss Cl^- residual, and suspected source(s). Volcanic eruptions are from the chronology of *Simkin and Siebert* [1994].

[b]VEI 2 eruptions of Akutan, Aleutian Islands; Kliuchevoskoi, Kamchatka; Okmok, Aleutian Islands; and Pavlof, Alaska in spring and summer 1988 may be responsible for this signal.

[c]VEI 2 eruptions of Bezymianny, Tolbachik, and Karymsky, Kamchatka during 1971 may be responsible for this signal.

[d]VEI 2 eruptions of Karymsky and Tolbachik, Kamchatka during 1955 may be responsible for this signal.

[e]VEI 2 eruptions of Shishaldin, Aleutian Islands; Tolbachik, Kamchatka; and Trident, Alaska during late 1953 and early 1954 may be responsible for this signal.

[f]VEI 2 eruptions of Trident and Pavlof, Alaska during summer 1950 may be responsible for this signal.

[g]VEI 2 eruptions of Gorely and Sheveluch, Kamchatka; as well as Shishaldin, Aleutian Islands during late 1947 and 1948 may be responsible for this signal (VEI 2).

[h]The only documented eruption that could contribute to this signal within the dating constraints we have established is Karymsky, Kamchatka (VEI 2), summer 1921.

[i]The only documented eruption that could contribute to this signal within the dating constraints we have established is Mutnovsky, Kamchatka (VEI 2), summer 1916.

[j]VEI 2 eruptions of Pavlof, Alaska, Kliuchevoskoi, Kamchatka, and Bogoslof, Aleutian Islands, during the summer of 1910 may be responsible for this signal.

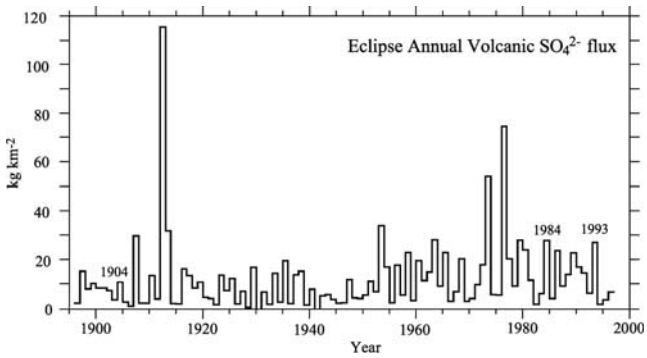

Figure 6. Annual volcanic sulfate flux at Eclipse calculated as the product of the EOF 4 sulfate value and the water equivalent length of each sample, summed by year. Elevated volcanic sulfate deposition possibly due to equatorial eruptions in 1902, 1982, and 1991 is seen in 1904, 1984, and 1993. This 2-year lag is consistent with the time lag observed for deposition of El Chichon aerosols in Greenland snow [*Zielinski et al.*, 1997].

signatures. We therefore believe that the eruptions we have identified at Eclipse involved tropospheric aerosol transport.

[26] Likewise, a distinct sulfate signal attributable to the El Chichon eruption was not found in the GISP2, Summit, Greenland ice core, at a high northern latitude comparable to Eclipse [*Zielinski et al.*, 1994], nor have there been distinct sulfate peaks attributable to the 1991 Pinatubo eruption reported in Greenland snow [*Zielinski et al.*, 1997]. The GISP2 ice core does record a distinct sulfate peak attributed to the 1902 Santa Maria eruption [*Zielinski et al.*, 1994]. To further investigate the preservation of signals from tropical eruptions, *Zielinski et al.* [1997] investigated variability in sulfate deposition during the 1980s using 12 snowpits from across the Greenland ice sheet. Distinct peaks in sulfate concentrations related to the 1982 El Chichon eruption were found in only half the snowpits sampled. However, when the snowpit records were smoothed and examined on an annual sulfate flux basis, 75% of the snowpits were found to record sulfate deposition attributable to El Chichon as anomalously high sulfate fluxes in 1984. Zielinski et al. concluded that evidence for volcanic aerosol deposition from tropical eruptions at high northern latitude ice core sites may be detected as periods of enhanced sulfate deposition relative to the prevailing background, even when distinct sulfate spikes from such an eruptions are missing.

[27] To see if similar smoothing might reveal a signal from tropical eruptions at Eclipse, an annual volcanic sulfate flux was calculated using our record of volcanism provided by EOF 4. This was done by calculating the volcanic sulfate deposition represented in each sample as the product of the EOF 4 sulfate concentration and the water equivalent length of the sample. The volcanic sulfate deposition recorded by individual samples was then summed by year to give an annual volcanic sulfate flux (Figure 6). Anomalously high volcanic sulfate fluxes in 1902, 1984, and 1993 could partially reflect aerosol deposition from the 1902 Santa Maria, the 1982 El Chichon, and the 1991 Pinatubo eruptions. However, no conclusive evidence (i.e., tephra) exists to confirm the deposition of aerosols from these eruptions at Eclipse. In fact, the only published identifications of tropical eruptions from Arctic ice core sites that we are aware of are the eruptions of El Chichon (1982) in Summit, Greenland snowpits [*Zielinski et al.*, 1997], Agung (1963) in the GISP 2 [*Zielinski et al.*, 1994], Crete [*Hammer*, 1977] and 20D [*Lyons et al.*, 1990], Greenland ice cores, and Santa Maria (1902) in the GISP2, and 20D ice cores. Tephrochronological evidence supporting these identifications exists only in the case of El Chichon fallout observed in Greenland snowpits [*Zielinski et al.*, 1997].

5. Volcanic Chloride Signals at Eclipse

[28] We also evaluated the chloride record contained in the Eclipse ice core. Some volcanic eruptions are known to produce detectable spikes in chloride in polar snow [*Herron*, 1982], providing an additional line of evidence for detecting volcanic aerosol deposition in glacial ice. To identify volcanic chloride spikes in our record, we first calculated a non-sea-salt chloride fraction [*Keene et al.*, 1986], and then considered the residuals above a robust spline (Figure 7). We identified 20 nss Cl^- residuals greater than one standard deviation above the mean, 13 of which are associated with a previously identified volcanic sulfate spike (Table 3). Of the remaining seven, four can be confidently linked to a known eruption, and the rest could be related to multiple VEI 2 eruptions in Alaska, the Aleutian Islands, and Kamchatka. We caution that some of these identifications must be considered tenuous, especially events 47 and 48 that are linked only to eruptions thought to have occurred in the same year. Of special note is the 1912 signal we have identified as the June 1912 eruption of Katmai, Alaska, which is the largest nss Cl^- residual in our record by an order of magnitude.

6. Comparison With the Mount Logan Record

[29] We also applied both the nss residual and EOF techniques for identifying volcanic signals to the glaciochemical record available from Mount Logan [*Holdsworth and Peake*, 1985]. The drill site on Mount Logan is 45 km southwest of the Eclipse site and over 2 km higher in elevation. In the case of Mount Logan, we found that EOF 3 is loaded solely with sulfate and describes 14% of the variance in the full data set and 65% of the variance in the sulfate time series. As is the case with Eclipse, most of the events recorded at Mount Logan are eruptions of Alaskan, Aleutian, or Kamchatkan volcanoes (Table 4) [*Holdsworth and Peake*, 1985]. The range of sulfate concentrations due to volcanic eruptions is similar at the two sites. The flux of volcanic aerosols preserved in snow at Eclipse is 4–5 times that at Mount Logan primarily due to greater amounts of wet deposition at Eclipse.

[30] There are 33 eruptions recorded at Eclipse over the 80+ years of overlap between the two cores, while only eight eruptions are recorded at Mount Logan. There could be a variety of reasons for this discrepancy. First, higher accumulation rates and limited windscour at Eclipse result in more complete preservation of glaciochemical signals relative to Mount Logan, as demonstrated in snowpit studies at the two sites [*Holdsworth and Peake*, 1985]. Second, aero-

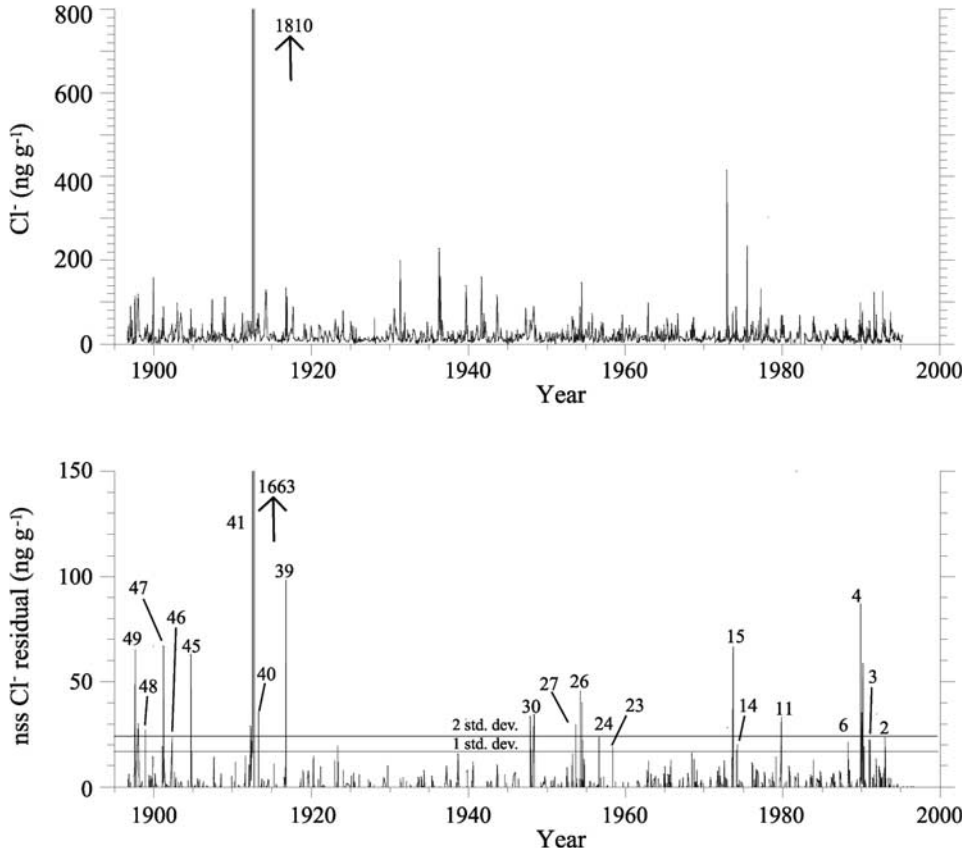

Figure 7. Volcanic Cl^- signals in the Eclipse ice core: (top) raw Cl^- time series; (bottom) nss Cl^- residuals (ng g^{-1}), 1 and 2 standard deviations above the mean as indicated. Numbering corresponds to event numbering in Table 3.

sols from local eruptions, especially those smaller than VEI 4, may be transported primarily in the lower troposphere and not leave detectable signals in glaciochemical records from the summit plateau of Mount Logan, as was the case with the 1986 Augustine eruption that was detected in a snowpit at Eclipse but not at Mount Logan [*Holdsworth and Peake*, 1985]. Furthermore, the non-sea-salt sulfate in the Mount Logan core has been shown to originate primarily from the middle and upper troposphere [*Monaghan and Holdsworth*, 1990]; therefore volcanic sulfate aerosols transported in the

Table 4. Volcanic SO_4^{2-} Signals (ng g^{-1}) in the Mount Logan Ice Core Greater Than 1 Standard Deviation Above the Mean Compared to the Corresponding Signal in the Eclipse Ice Core Over the Period of Overlap Between the Two Cores (1896–1980)[a]

	Mount Logan SO_4^{2-}		Eclipse SO_4^{2-}			
Year	EOF 3	nss Res.	EOF 4	nss Res.	Possible Source(s) with Date	VEI
1976	160	162	261	547	St. Augustine (Alaska) 1/1976[b]	4
1968	-	127	112	346	Trident (Alaska) 11/1968	3
					Kliuchevoskoi (Kamchatka)	3
					Redoubt (Alaska) 2/1968	3
1965	-	107	86	215	Bezymianny (Kamchatka) 3/1965	3
					Karymsky (Kamchatka) 5/65	3
1935	151	327	80	262	St. Augustine (Alaska) 6/1935[b]	3
1927[c]	128	152	-	-	??	
1925[d]	-	105	49	151	Iriomate- Jima (Ryukyu Is.) 10/1924	4
					Raikoke (Kurile Is.) 2/1924[b]	4
1912	518	120	231	349	Katmai (Alaska) 6/1912[b]	6
1907[e]	-	125	85	162	Ksudach (Kamchatka) 3/1907	5

[a]Dates of eruptions are from the chronology of *Simkin and Siebert* [1994].
[b]Previously identified by *Holdsworth and Peake* [1985] in their analysis of the Mount Logan ice core.
[c]This signal is not seen in the Eclipse ice core.
[d]This signal was dated to 1924 in the Mount Logan ice core [*Holdsworth and Peake*, 1985], hence their identification of the signal as Raikoke. We have dated it to 1925 in the Eclipse core and therefore attribute it to Iriomate- Jima. The common shape and seasonality of the signal between the two cores suggests it represents the same event.
[e]*Holdsworth and Peake* [1985] dated this signal to 1908 in the Mount Logan ice core. A volcanic identification was not offered.

lower troposphere would not be sampled at the Mount Logan site. The presence of a detectable anthropogenic sulfate input at Eclipse [*Yalcin and Wake*, 2001] but not at Mount Logan [*Mayewski et al.*, 1993] further illustrates that the two sites are sampling air masses with distinct source inputs and transport histories, therefore it is not surprising that the volcanic records at the two sites are different.

7. Conclusions

[31] We have developed a high-resolution, 100-year record of regionally significant volcanic eruptions using an ice core from the Saint Elias Mountains, Yukon Territory, Canada. Volcanic horizons were identified by statistical analysis of the high-resolution sulfate and chloride records available from the Eclipse ice core. Tephrochronology provides positive identification of four of the volcanic horizons identified in the Eclipse ice core and improves confidence in the ice core chronology established from the counting of annual layers. Our ice core records a large number of eruptions in Alaska and Kamchatka, therefore providing a Northern Hemisphere volcanic aerosol record complementary to the records already available from Greenland where Icelandic eruptions predominate. The large number of Alaskan and Kamchatkan eruptions identified in the Eclipse ice core is encouraging for the development of longer paleovolcanic records of these poorly known and active volcanic regions using ice cores from the Saint Elias Mountains.

[32] However, there are some notable eruptions in the North Pacific missing from our record. Likewise, few tropical eruptions are recorded in the Eclipse ice core due to its remoteness from eruptive centers in the low latitudes. Nonetheless, the lower elevation Eclipse site records many more eruptions than at nearby Mount Logan, suggesting that aerosols from many of these eruptions may have been transported mostly in the lower troposphere. The acquisition of additional, longer ice cores during the 2002 field season from sites in and around the Saint Elias Mountains, including Eclipse Icefield, the Mount Logan summit plateau, King Col, and Bona-Churchill Col in conjunction with the already developed glaciochemical records from Eclipse and Mount Logan should provide a more complete picture of regionally significant volcanic eruptions.

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