Statistical extraction of volcanic sulphate from nonpolar ice cores

J. C. Moore,[1,2,3] E. Beaudon,[2] Shichang Kang,[4,5] D. Divine,[6] E. Isaksson,[7] V. A. Pohjola,[3] and R. S. W. van de Wal[8]

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[1] Ice cores from outside the Greenland and Antarctic ice sheets are difficult to date because of seasonal melting and multiple sources (terrestrial, marine, biogenic and anthropogenic) of sulfates deposited onto the ice. Here we present a method of volcanic sulfate extraction that relies on fitting sulfate profiles to other ion species measured along the cores in moving windows in log space. We verify the method with a well dated section of the Belukha ice core from central Eurasia. There are excellent matches to volcanoes in the preindustrial, and clear extraction of volcanic peaks in the post-1940 period when a simple method based on calcium as a proxy for terrestrial sulfate fails due to anthropogenic sulfate deposition. We then attempt to use the same statistical scheme to locate volcanic sulfate horizons within three ice cores from Svalbard and a core from Mount Everest. Volcanic sulfate is <5% of the sulfate budget in every core, and differences in eruption signals extracted reflect the large differences in environment between western, northern and central regions of Svalbard. The Lomonosovfonna and Vestfonna cores span about the last 1000 years, with good extraction of volcanic signals, while Holtedahlfonna which extends to about AD1700 appears to lack a clear record. The Mount Everest core allows clean volcanic signal extraction and the core extends back to about AD700, slightly older than a previous flow model has suggested. The method may thus be used to extract historical volcanic records from a more diverse geographical range than hitherto.

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1. Introduction

[2] Ice cores are wonderful archives of past environment and climate variations. However, to be useful a reliable dating for the ice in the core must be obtained. This has long been a major difficulty for ice cores located in low-lying ice caps or mountain glaciers where seasonal melting, and typically high concentrations of multiorigin impurities are the norm. Ice cores are often dated by reference horizons such as radioactivity from well dated bomb test fallout or acidic deposits from historically known volcanic eruptions [e.g., *Kekonen et al.*, 2005a, 2005b; *Palais et al.*, 1992], and some may also be dated by annual cycle counting [*Pohjola et al.*, 2002b; *Kaspari et al.*, 2008; *Kang et al.*, 2002; *Karlöf et al.*, 2005], or flow models [e.g., *Nye*, 1963; *Kaspari et al.*, 2008]. Reference horizons, particularly volcanic signatures are often assumed to be recorded as acidic sulfate [*Kekonen et al.*, 2005a], and more recently and rarely in the bismuth concentration record along a core [e.g., *Kaspari et al.*, 2007; *Xu et al.*, 2009]. The individual sulfate spikes are often accepted to be specific eruptions on the basis of other evidence leading to an approximate dating, but they are seldom proven to be specific eruption signatures since the evidence relies on finding volcanic tephra with a chemical signature that matches the known composition of the eruption in question. This is a time consuming task as often tephra particles are very rare in ice cores drilled at remote locations [*Palais et al.*, 1992], or the tephra may be outnumbered tens of thousands of times by local country rock swept into the atmosphere by the eruption [*Kekonen et al.*, 2005b].

[3] Major ionic impurities in ice cores may be categorized by their typical sources [e.g., *Legrand and Mayewski*, 1997; *Moore et al.*, 2006; *Moore et al.*, 2005; *Kekonen et al.*, 2005a; *Eichler et al.*, 2011; *Kaspari et al.*, 2007; *Kang et al.*, 2000; *Matoba et al.*, 2002]. Marine ions originating from oceanic sea spray are dominated by soluble salt derived ions, typically Na^+ and Cl^- with significant amounts of SO_4^{2-} and Mg^{2+}. Terrestrial ions come from

[1]College of Global Change and Earth System Science, Beijing Normal University, Beijing, China.
[2]Arctic Centre, University of Lapland, Rovaniemi, Finland.
[3]Department of Earth Sciences, Uppsala University, Uppsala, Sweden.
[4]Key Laboratory of Tibetan Environmental Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, China.
[5]State Key Laboratory of Cryospheric Sciences, Chinese Academy of Sciences, Lanzhou, China.
[6]Department of Mathematics and Statistics, University of Tromsø, Tromsø, Norway.
[7]Norwegian Polar Institute, Tromsø, Norway.
[8]Institute for Marine and Atmospheric Research, Utrecht University, Utrecht, Netherlands.

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wind blown dust and are dominated by Ca^{2+}, but also include Na^+, Mg^{2+}, SO_4^{2-} and K^+. Anthropogenic sources of ions have grown in importance since the industrial revolution and mainly affect concentrations of SO_4^{2-}, NO_3^-, and NH_4^+. Biogenic sources provide ions such as methane sulfonate ($CH_3SO_3^-$ or MSA), SO_4^{2-}, NH_4^+, and formate ($HCOO^-$). Volcanic emissions, while certainly complex, affect only concentrations of SO_4^{2-} in the set of ions routinely measured in ice cores. Though HF may be emitted, we do not measure F^- ions. HCl in ice cores is sometimes associated with reaction of NaCl with H_2SO_4 in the atmosphere during long-distance transport, hence is likely not significant except in fallout over the polar ice sheets. As large volcanic eruptions do not occur in most years, and since the volcanic SO_4^{2-} is removed from the atmosphere in the year or two after the eruption, a volcanic SO_4^{2-} signal appears as a narrow spike in concentrations. Hence volcanic eruptions are typically simply assumed to be the cause of peaks in sulfate. While this assumption may be true in central Antarctica [*Legrand and Mayewski*, 1997], in Svalbard and mountain glacier areas this is a very poor assumption since volcanic acids account for only 5–10% of sulfate in Svalbard [*Moore et al.*, 2006], and even less when terrestrial input is large, such as in Tibet [*Kang et al.*, 2000; *Cong et al.*, 2009]. In considering the sources of ions, sulfate from volcanic sources has two features that point to a less ambiguous way identifying volcanic markers: (1) the sulfate is not associated with any other ions, and (2) the signal appears as a sharp spike in concentrations.

[4] Sulfate measurements are typically done by ion chromatography which has heteroscedastic (that is systematically varying) errors, in this case proportional to the measured value, and simultaneously the sulfate concentrations tend to be Lognormally distributed, as is the case for the cores studied here. This means that elementary procedures such as determining a significant peak by testing if it stands 2 standard deviations above the mean sulfate level are statistically invalid.

[5] In this paper we present a more rigorous approach based on extracting spikes in the sulfate residual after fitting the sulfate to empirical regression, in log space, on all other measured ions. This process accounts for terrestrial, marine, biogenic and anthropogenic sulfate deposition fractions as well as postdepositional relocation of ions, leaving only stochastic sources, effectively volcanic fallout. We verify the procedure on ice cores from Svalbard and central Asia. These cores present similar problems in interpreting the sulfate profile, despite coming from very different environments: that is the sulfate signal has many additional sources rather than volcanoes. Additionally both regions experience large melt either prolonged through a polar day when temperatures may be at the melting point for 2 months, or daily freeze-thaw cycles. Although we anticipate that the method is most useful on ice cores from alpine or maritime sites, there are regions of the large ice sheets where ice cores are difficult to interpret such as coastal sites with large marine and biogenic sulfate inputs, or blue ice areas where local terrestrial sources are important.

2. Ice Cores

[6] In this paper we use ice collected from Svalbard, Altai mountains, and from Mount Everest (Figure 1). The core details are summarized in Table 1. The Svalbard cores come from: (1) Lomonosovfonna, central Spitsbergen, influenced by westerly and arctic airflow [*Kekonen et al.*, 2005a]; (2) Holtedahlfonna a western plateau site close to the Spitsbergen coast and subject to more westerly influences and with Arctic haze events [*Virkkunen et al.*, 2007; *Ruggirello et al.*, 2010]; and (3) Vestfonna ice cap in Nordaustlandet, a more high arctic site with dominant Arctic Ocean influence [*Matoba et al.*, 2002; *Beaudon and Moore*, 2009]. The three sites have distinct environmental chemistry, despite being located within a relatively small area, however they are conspicuous in their abundance of marine derived species [*Kekonen et al.*, 2005a, *Matoba et al.*, 2002, *Moore et al.*, 2006]. In contrast, the Mount Everest and Belukha (Altai mountains) cores come from central Asia far from marine sources of ions. At Everest impurities are deposited from mixed westerly and monsoon circulation regimes, and are dominated by terrestrially derived ion chemistry [*Kang et al.*, 2007; *Zhang et al.*, 2009]. The climatology of the Altai is dominated by the regular development of the Siberian High in winter, leading to extreme cold and dry conditions in this season. Humid air masses from the Atlantic Ocean as well as recycled moisture are the main sources of precipitation in summer [*Aizen et al.*, 2006]. This core has been exceptionally well dated using the sulfate and calcium ion concentrations from AD1250 to 1940 [*Eichler et al.*, 2009a], and we use it here to verify the volcanic sulfate extraction method, and then to extract volcanic signals in the post-1940 ice.

[7] The Lomonosovfonna core has been the subject of intense research on the influence of postdepositional processes on ion chemistry [*Moore et al.*, 2005] and structure [*Pohjola et al.*, 2002a], and dating [*Divine et al.*, 2011]. The Holtedahlfonna core was drilled 8 years after and has been much less reported. Dating of the Holtedahlfonna core is uncertain due to difficulties in determining bed depth and flow geometry in the saddle location [*Divine et al.*, 2011]. The Vestfonna core dating was reliant on 2 fixed horizons and no layer thinning model. The Everest core has been partially analyzed for bismuth, and several peaks in concentration have been tentatively assigned to eruptions over the last 200 years [*Xu et al.*, 2009], however for earlier periods the Mount Everest core dating has been largely reliant on a flow model and cycle counting [*Kaspari et al.*, 2007, 2008].

3. Methods

[8] All chemistry data discussed here were measured using ion chromatography. Postdepositional processes, basically seasonal melting, play a large role in Svalbard and low-latitude ice cores [*Koerner*, 1997; *Moore et al.*, 2005]. Postdepositional processes also affect high-altitude polar ice cores which never experience melting conditions [*Karlöf et al.*, 2005]. Postdepositional processes are chemical species dependent with some ions more conservative than others [*Karlöf et al.*, 2005; *Moore et al.*, 2005; *Goto Azuma et al.*, 2002]. These effects produce both small-scale disturbance due to local topography, and longer-range noise due to meteorology. For the Lomonosvfonna core, measurement and short range depositional noise errors are only about 8%. Longer-range noise may be estimated by the

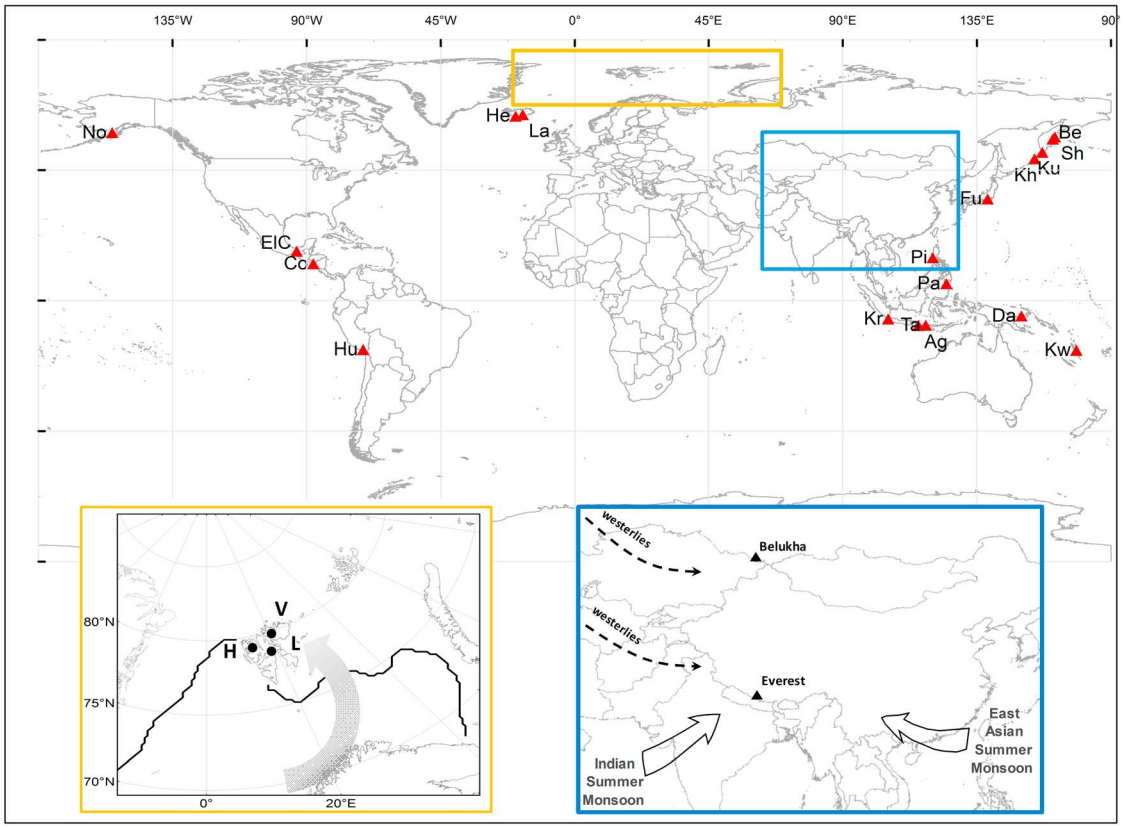

Figure 1. Map of ice core locations. Boxed insets show the Belukha, the Everest and 3 Svalbard core sites Lomonosovfonna (L), Holtedahlfonna (H) and Vestfonna (V), 1979–2000 monthly median sea ice position (black line) and principal wind directions. Also shown are the volcanoes detected in the ice cores in this paper (see Table 2 for details).

correlations of the climate related signals in cores over meters to kilometer scales, and observations from both the Canadian Arctic [*Goto Azuma et al.*, 2002], and Svalbard ice cores suggest noise may be as large as the climate signal. Hence we expect that the sulfate records will be a complex superposition of different environmental inputs and postdepositional processes. Figure 2 shows an illustrative set of ion concentrations of all 9 species measured along a 20 m long section of the Lomonosovfonna core from the early to mid 20th century. It is obvious that the sulfate profile is correlated with ions of various origins: marine, e.g., Na^+; terrestrial, e.g., Ca^{2+}; anthropogenic, e.g., NO_3^-; and biogenic, e.g., MSA ($CH_3SO_3^-$).

[9] *Moore et al.* [2006] showed that the different contributions to the sulfate budget along the core can be estimated based on multiple linear regression analysis, (MLR) between sulfate and the other ions in the core. The Lognormally distributed ion errors demand log transformation of concentrations before regression analysis. Because of the log transformation the regression coefficients are not simple multipliers of concentrations, but exponents (M_i) and the model residuals at any depth in the ice core are, R:

$$R = \log\left[SO_4^{2-}\right] - K - \sum_i^L M_i \log[s_i], \quad (1)$$

Table 1. Ice Core Characteristics[a]

Name	Latitude (°N)	Longitude (°E)	Altitude (m asl)	Drill Date	Ice Depth (m)	Drill Depth (m)	1963 Depth (m)	Mean Concentration (μEq/L)				
								SO_4^{2-}	NO_3-	Cl^-	NH_4^+	Ca^{2+}
Belukha	49.81	86.58	4062	2001	139	139	18.8	6.7	3.3	0.8	9.3	8.4
Lomonosovfonna	78.86	17.43	1250	1997	123	121	18.5	4.0	0.9	8.1	1.2	1.7
Mount Everest	28.03	86.98	6518	2002	108	108	31.5	1.3	1.9	0.5	N.A	8.9
Holtedahlfonna	79.14	13.27	1150	2005	180?	125	28.4	2.8	0.7	12.6	0.1.1	1.2
Vestfonna	79.97	21.02	600	1995	320	210	15.3	2.7	1.1	39.4	N.A	1.4

[a]NO_3^-, Cl^-, NH_4^+, and Ca^{2+} concentrations since 1800 are indicative of anthropogenic, marine, biogenic, and terrestrial SO_4^{2-} sources, respectively. An independent reference horizon comes from the radioactivity associated with the 1963 bomb fallout.

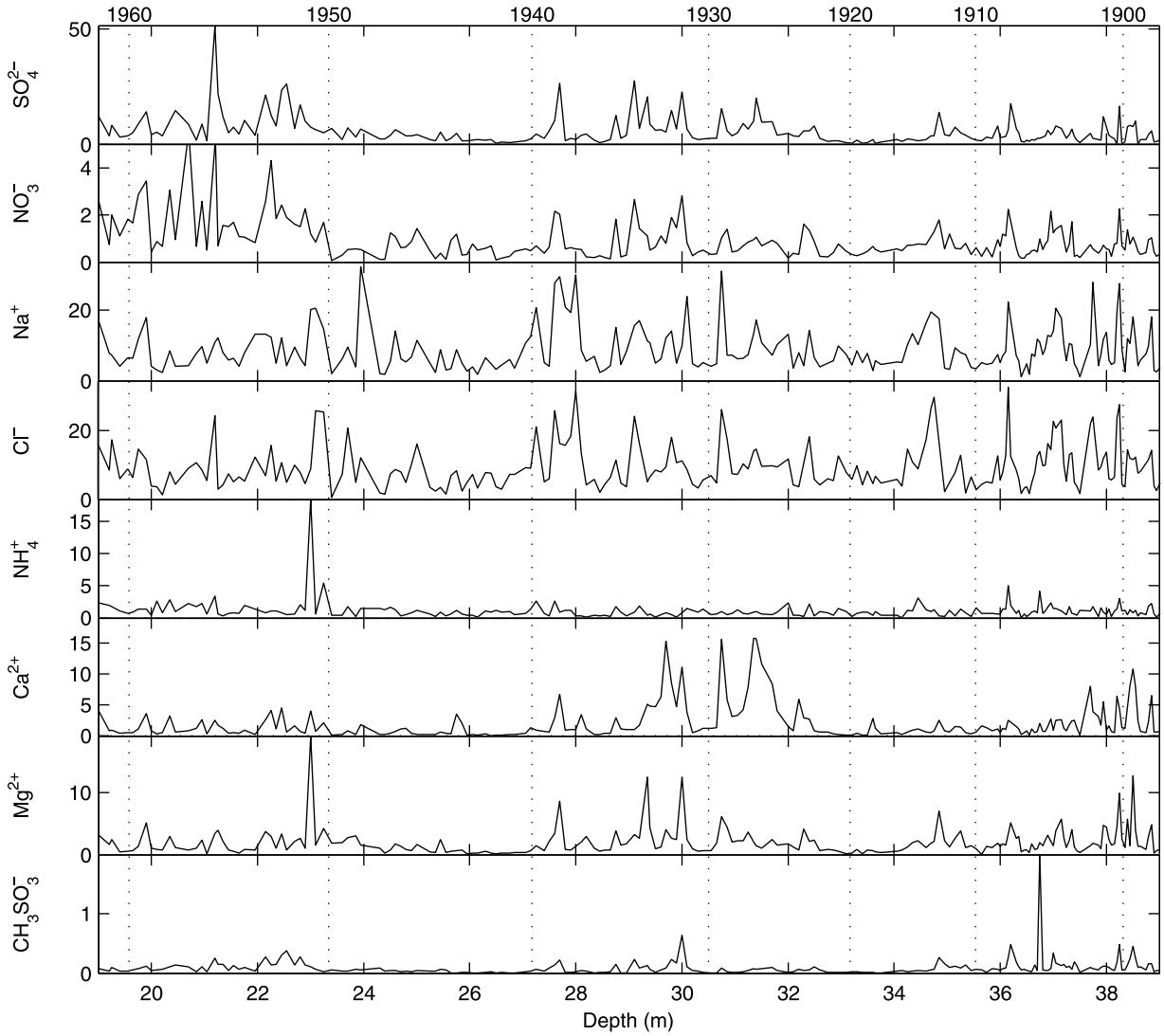

Figure 2. Ion concentration (in μEq/L) for all species measured profiles for 19–39 m depths of the Lomonosovfonna ice core with dates from *Divine et al.* [2011].

where K is the MLR intercept, $[s_i]$ denote the L other ionic species concentrations, L = 8 for Lomonosovfonna and Holtedahlfonna, and 6 for Everest and Vestfonna cores where NH_4^+ and MSA were not analyzed. In contrast to the approach used by *Moore et al.* [2006] where the best models were determined by the F statistic to avoid over fitting, here we are simply concerned with the residual, that is the part of the sulfate that cannot be related to any of the other ions—and which we expect to be stochastic or volcanic in origin. Hence we use all available ion species in the model fit, equation (1), even though most of the time several ions will make insignificant contributions to the model fit. We also allow both M and K to change over time (e.g., in response to climatic change) by running the MLR model in a moving window of data (e.g., 100 points long—we will show an example of how window length choice affects results in section 4.1). Thus a typical sulfate concentration at a given depth point of the ice core would have 100 models fit to it as the window moves past it. We smooth the ion data with 3-point running means to reduce short wavelength, species-dependent elution rate variations. By analyzing the time series in the original sampling intervals, we ensure that the MLR analysis window contains the same number of independent data points, and therefore allow the significance level of the fits to be comparable along the entire core.

[10] Estimating the significance level of a residual spike is possible in several ways. We can determine the 95% significance level in log space of each residual. This procedure effectively calculates the ratio of the measured SO_4^{2-} concentration relative to the model fit (e^R), hence a perfect model with no residual has an $e^R = 1$ and if $e^R > 2.72$ then there is more unexplained variance in sulfate concentration than modeled variance at that depth. Alternatively the absolute confidence interval of the residual in concentration space can be estimated. While the significance estimate from log space is more natural, it can be very sensitive to experimental errors, so that a small absolute sulfate concentration may be poorly fitted by the model and hence have a large

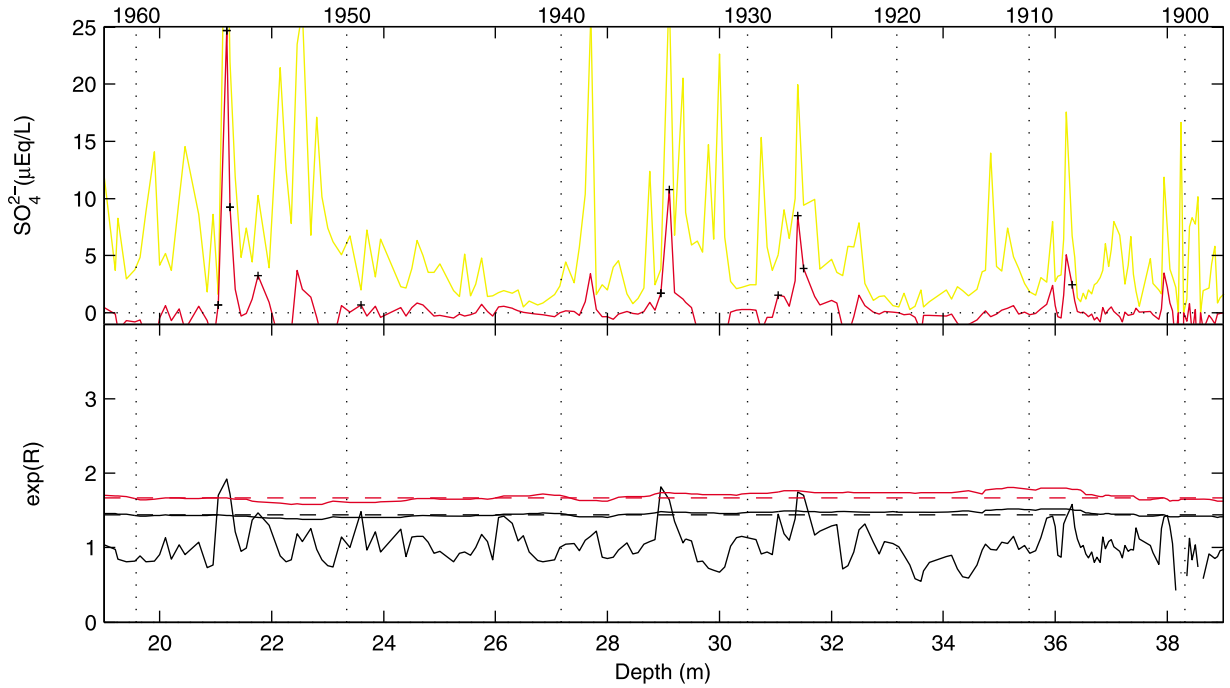

Figure 3. Sulfate (yellow) and residual (red) in uEq/L as a function of core depth. Bottom e^R (equation (2)) for the Lomonosovfonna ice core over the same depth range as in Figure 2. 99% and 95% significance levels are shown as red and black lines, with dashed lines based on the variance of the whole core, while solid lines are the based on variance within the 100 point window used for MLR fits in log space. Crosses indicate significant peaks at 95% level of residual of whole core or at 99% significance in the windowed test. Dates are from *Divine et al.* [2011]. Significant residuals correspond with Bezymianny 1956, Kharimokotan 1934, Kuril islands 1924–1929, and Novarupta 1912.

residual in log space, but amount to a only a few ppb in concentration space. The value of the residual $V[SO_4^{2-}]$ in concentration units is given at each measurement point along the core by:

$$V\left[SO_4^{2-}\right] = \left[SO_4^{2-}\right]\left(1 - 1/\left(e^R\right)\right). \quad (2)$$

[11] The size of the window used to determine the fit of SO_4^{2-} determines the size of the residual produced. A long window, say 400 points results in a less responsive fit, and hence stochastic peaks are less able to influence the fit, and so produce larger residuals than short windows, such as 50 points. While the longer windows produce more uniform background SO_4^{2-} levels for the core which is a positive feature, they are also less able to respond to changing environment or climate that can drive changes in the deterministic relationship between the ions in the core. Probably a better estimate of the significance of any peak comes from assessing the variance of the residuals within the sliding window used for the MLR, than using the variance of the residuals along the whole core. This compensates for large concentration peaks that bias the variance in quieter sections of core. Figure 3 shows results of the MLR analysis which can be compared with the ion concentration profiles in Figure 2. It should be obvious that $V[SO_4^{2-}]$ is a small fraction of the sulfate ion concentrations. Both the MLR models and the variance calculation are limited at the data boundary as the window starts to overlap, so that for the start and end points only one single MLR model is possible compared with typically 100 models per point if the window is 100 points long. At the data boundaries only half the usual number of residuals are available to compute the significance levels, since the window only exists within the data.

4. Results and Interpretation

4.1. Belukha Ice Core: Verification of the Method

[12] We make use of the well-dated Belukha ice core [*Eichler et al.*, 2009a] from the Altai Mountains (Figure 1) to verify our volcanic sulfate method. The ice core site is at high altitude and extremely continental, far from marine sources, but influenced by biogenic productivity over Southern Siberia and local dust sources [*Eichler et al.*, 2009b, Table 1]. Ion chemistry was performed at 3–4 cm (subseasonal to AD1800) resolution, for Na^+, Cl^- SO_4^{2-}, $HCOO^-$, Mg^{2+} Ca^{2+}, K^+, NO_3^-, and NH_4^+, [*Eichler et al.*, 2009a, 2009b, 2011] and all were used in the MLR analysis. The ratio of calcium to sulfate in the 1817–1899 interval is 0.21, and so an excess sulfate fraction $X[SO_4^{2-}]$, attributable to anthropogenic and volcanic sources was estimated to be $X[SO_4^{2-}] = [SO_4^{2-}] - 0.21[Ca^{2+}]$. This ice core shows a nice and simple series of spikes in $X[SO_4^{2-}]$ that can be easily identified with volcanic eruptions, from AD1250 to 1940 [*Eichler et al.*, 2009a]. After 1940 the rise in anthropogenic sulfate emissions means that volcanic sulfate is

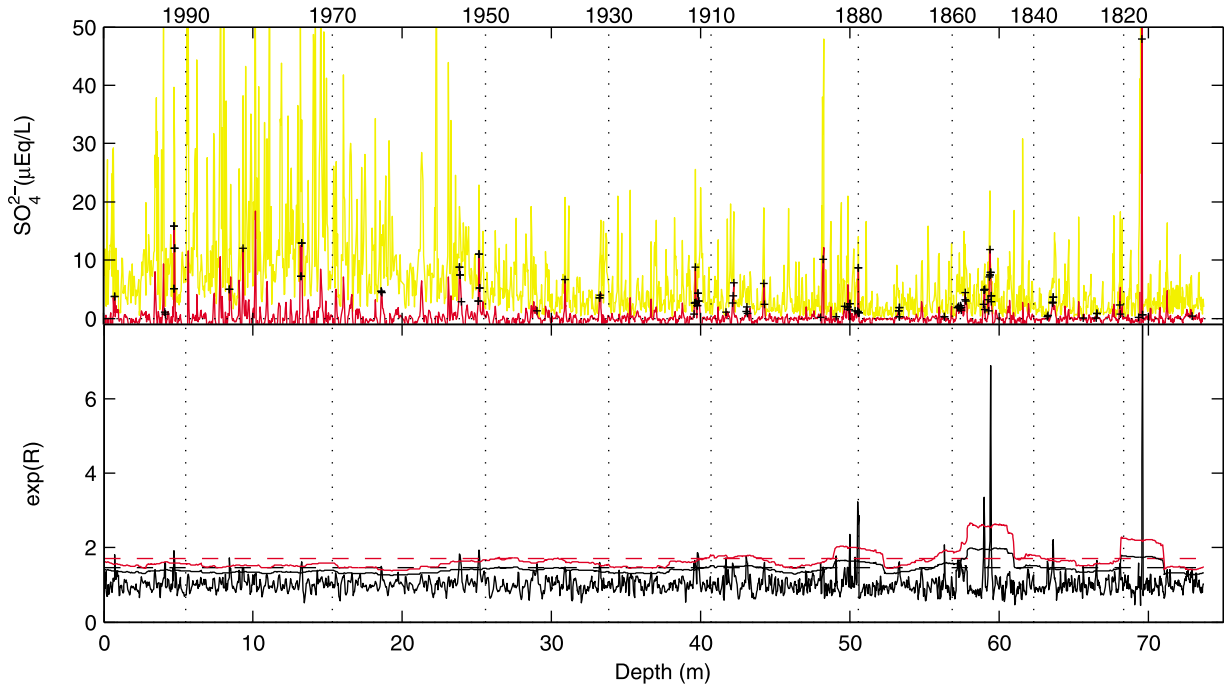

Figure 4. Same as for Figure 3 but for Belukha 2001 core sulfate from 1800 to 2001. Dates are from *Eichler et al.* [2009a, 2009b, 2011].

hidden. Therefore we can both test our data on a well dated and simple part of the ice core, such as that between 1800 and 1940, and examine how good the method is at extracting information when anthropogenic sulfate becomes increasingly important over the 20th century.

[13] Figure 4 shows the results of extracting volcanic sulfate spikes in the Belukha core from 1800 to 2001. *Eichler et al.* [2009a] identify volcanic signals from Tambora (1815), Shiveluch (1854), Novarupta (1912) and Kharimkotan (1932) between 1800 and 1940. All those peaks are clearly shown in Figure 4. In addition the third largest residual and significant e^R peak is at 50.5 m dated at 1880. This peak is assigned to Krakatau. It is noticeable that there is a larger peak in sulfate at 48.3 m depth, 1887 that may be misinterpreted as Krakatau (and may be Tarawera 1886), but there is only a single data point significant at the 95% level in e^R whereas we observe 4 data points above 99% significance level for the 1880 peak.

[14] In Figure 5 we compare the magnitude of $V[SO_4^{2-}]$ from equation (2) with $X[SO_4^{2-}]$ from *Eichler et al.* [2009a] for the period before significant anthropogenic sulfate deposition. The simple correlation coefficient is 0.91 between the 2 estimates of volcanic sulfate. Naturally the data should be regressed on a log plot so that the large magnitude and large uncertainty points from Tambora do not unduly affect the regression, but we want to show how the method compares in a simple way with an excess sulfate method. The result is essentially identical if those points are removed or a log plot is made. However, the slope of the linear regression line is only 0.42 implying that the $X[SO_4^{2-}]$ estimate based only on Ca^{2+} concentrations is twice the estimate from equation (2) found using all ion relationships to nonvolcanic sulfate sources. The contribution of other sulfate sources is also reflected in the higher correlation coefficient between $[SO_4^{2-}]$ and $X[SO_4^{2-}]$ of 0.95 compared with 0.87 between $[SO_4^{2-}]$ and $V[SO_4^{2-}]$.

[15] Since we find good correlation between our new method of extracting volcanic sulfate and the simpler method used by *Eichler et al.* [2009a], for the 1800–1940 period, we examine the peaks detected in the anthropogenic period post-1940 that *Eichler et al.* [2009a] could not find based simply on using Ca^{2+} as a SO_4^{2-} dust source proxy.

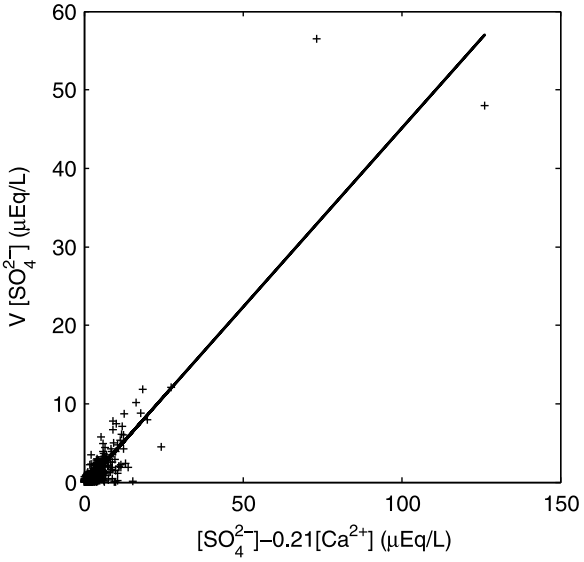

Figure 5. Relationship in Belukha ice core between volcanic sulfate estimated from equation (2) and that estimated by removing terrestrial sulfate from total sulfate. The regression line is $V[SO_4^{2-}] = 0.42\ X[SO_4^{2-}] - 0.46$. All data points where $V[SO_4^{2-}]$ and $X\ [SO_4^{2-}] > 0$ between 1800 and 1940, n = 561.

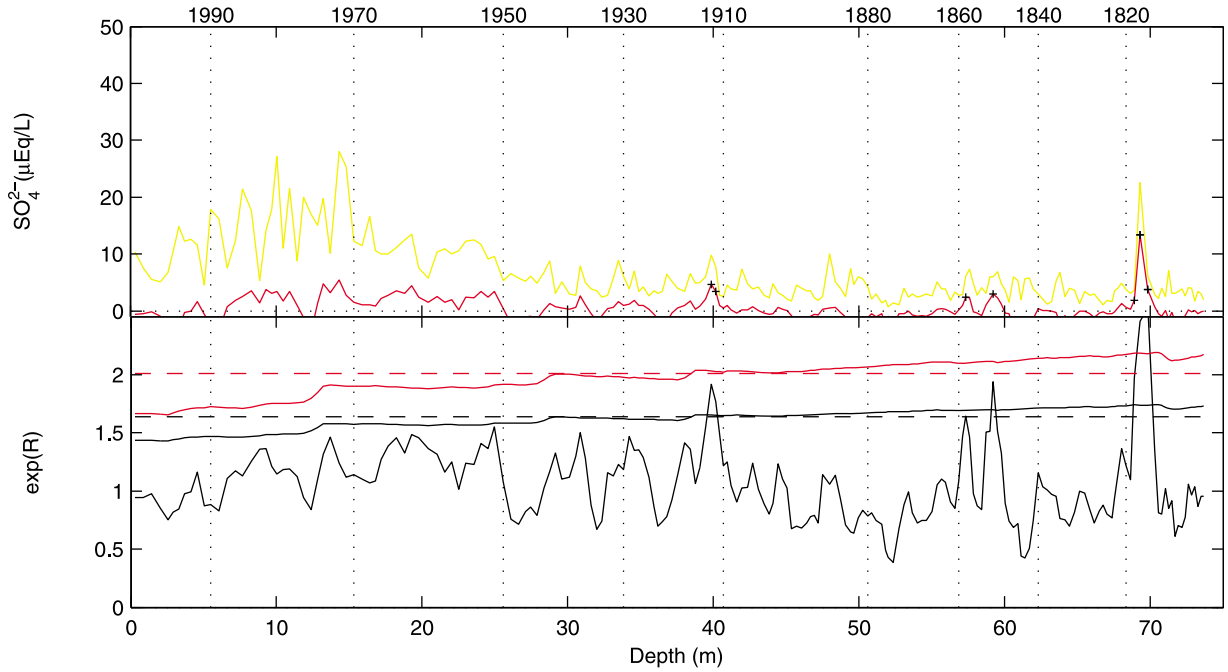

Figure 6. Same as Figure 4 but with a window length of 200 points, and with the original data down sampled to annual resolution.

There are 2 significant peaks at 23.7 and 25.1 m (1953 and 1951), and another at 18.5 m (1963). The 1963 horizon was confirmed with ^{3}H measurements indicating atmospheric nuclear fallout. Other peaks significant at the 95% level are at 13.3 m (1973), 9.4 and 8.4 m (1983.5 and 1984.5), and finally 4.6 m (1992). It is very tempting to assign three of these peaks to large well-known eruptions: Pinatubo (1991), El Chichón (1982) with fallout in 1983, and a second year of fallout in 1984, and Agung (1963). The Agung plume stayed almost exclusively in the Southern Hemisphere [*Robock*, 2000] and yet seems present and well dated. All these volcanic peaks appear within 3 years of the dates from *Eichler et al.* [2009a]. The peaks at 1951, 1953 and 1973 do not correspond to well known large eruptions, though several smaller candidates appear in the Global Volcanism Program (http://www.volcano.si.edu/world/largeeruptions.cfm).

[16] Finally we can illustrate the impact of low-resolution measurements, and changing the window width of the method by using the same post-1800 section of Belukha core but resampled to annual averages (Figure 6). The 200 point window in a sample size of only 202 points produces a very stiff response, which is essentially a linear significance level tilted by the Tambora high-magnitude points. There are far fewer significant eruptions, not due to the long window (a shorter window would produce even fewer significant points), but because the smoothing of the original sub-seasonal data to annual averages. This not only reduces the magnitude of volcanic peaks above background, but also modifies the correlation structure between SO_4^{2-} and all other ions. We return to this in section 5.

4.2. Volcanic Records From Nonpolar Cores

[17] The largest events recorded in ice cores from Antarctica and Greenland over the last millennium are the unknown eruption of 1259, Kuwae in 1453 and the 1815 Tambora eruption, and the event of unknown origin in 1809 [e.g., *Gao et al.*, 2008; *Gao et al.*, 2006]. It must however be emphasized that even in the dry snow regions far from large other sources of SO_4^{2-}, most ice cores typically lack 30% of volcanic signals that may be expected simply because of the stochastic nature of snow deposition and redistribution [*Legrand and Mayewski*, 1997; *Gao et al.*, 2008; *Moore et al.*, 2006, *Pälli et al.*, 2003; *Karlöf et al.*, 2005] this may also be seen in Figure 4 where the 1809 event is undetected both by *Eichler et al.* [2009a] and from the volcanic peak extraction method used here. Indeed *Robock* [2000] notes that for the northern hemisphere "the individual ice core records are, in general, not well correlated with each other or with any of the [volcanic] indices." Hence both the appearance of the volcanic spike and its relative magnitude may vary between ice cores. Since ice cores containing easily interpretable sulfate records have generally been confined to small geographical regions such as central Antarctica and Greenland ice sheets, estimates of fallout from ice cores in other regions may be valuable for atmospheric research.

[18] Preliminary timescales for all cores discussed below were made using the 1963 radioactive horizon (Table 1), and usually some seasonal layer counting based on variations in ions or stable isotopes of water. Inferred accumulation rates can be found using the simplest layer thinning model [*Nye*, 1963] based only on the core density profile, depth of the 1963 horizon at time of drilling, and estimates of total ice thickness (Table 1). We may expect variations in accumulation rates on decadal and century scales of 30% [e.g., *Pohjola et al.*, 2002b; *Kaspari et al.*, 2008].

4.3. Lomonosovfonna

[19] The 1997 Lomonosovfonna core is the best dated of the Svalbard cores [*Divine et al.*, 2011]. Ion chemical

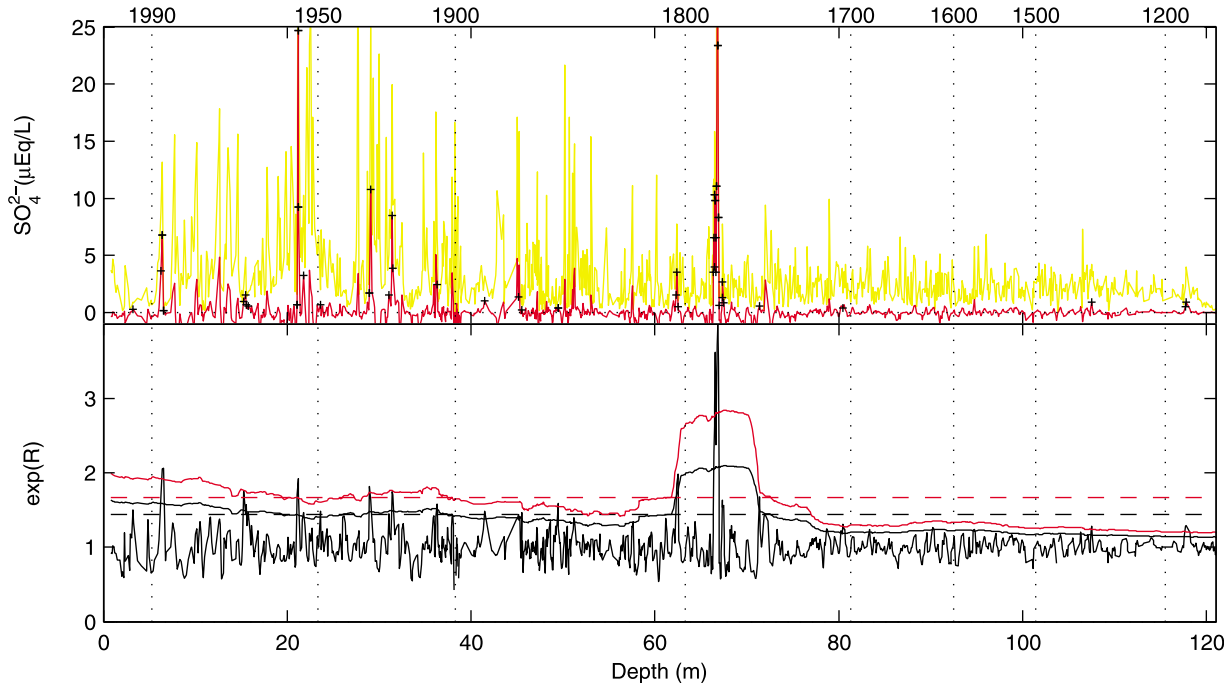

Figure 7. As for Figure 3 but for Lomonosovfonna 1997 core sulfate. Dates are from *Divine et al.* [2011] constrained by 1963 and 1783 horizons. Assignment to eruptions is discussed in the text.

analysis was done at 5–10 cm resolution along the core [*Kekonen et al.*, 2005a], corresponding to subseasonal resolution in the upper core, to approximately annual at 100 m depth. Below that depth some isolated core sections were not measured for chemistry due to bad core quality, [*Divine et al.*, 2011]. The ions measured were Na^+, Cl^- SO_4^{2-} MSA, Mg^{2+} Ca^{2+}, K^+, NO_3^-, and NH_4^+, and all were used in the MLR analysis. *Virkkunen et al.* [2007] show that 21st century summers are warmer than any in the ice core record since the 13th century. However, despite melt rates of 30–50%, isotopic variations [*Pohjola et al.*, 2002a] and chemical records [*Moore et al.*, 2005] of climate are well preserved on annual or multiyear scales. *Moore et al.* [2006] used a simplified version of the present scheme to find volcanic eruptions in the 1997 Lomonosovfonna core. Recently the timescale has been revised as updated ice thickness measurements and extended layer counting to 1613 [*Divine et al.*, 2011] became available. Unfortunately, the change in timescale leads to us to the conclusion that the 1259 eruption signal around 118 m depth may have been misidentified in the work of *Moore et al.* [2006], as it is quite likely the horizon was located in a badly damaged core section and was not found in the chemical analysis, instead this peak was suggested to be Hekla- 1104 or 1158. It is this revised timescale we use here. The 1783 Laki peak at 66.8 m is by far the largest in the core (Figure 7). Other signals clearly significant were discussed by *Moore et al.* [2006], however some small differences are noticeable in the new method of calculating the residual, with significant peaks deeper than Laki at 80.5 m (1705), which we have assigned previously to Fuji 1707. A peak at 107.5 m was assigned to Badarbunga 1477 in Iceland by *Moore et al.* [2006], however with the dating used here we feel it is more likely the 1453 eruption of Kuwae that is seen in many polar ice cores [*Gao et al.*, 2006]. The 117.7 m, peak dated at AD1100 in the *Divine et al.* [2011] dating was already discussed. A good candidate for Krakatau is at 45.5 m (Figure 7). Tambora, on the *Divine et al.* [2011] timescale at 1805, is a highly significant peak at 62.3 m.

[20] Figure 3 shows the period spanning the large Bezymianny 1956 signal at 21.1 m; and two significant peaks in 1934 and about 6 years previously that we consider to be the Kuril island eruption of Kharimokotan and one of several candidates in Japan and the Kuril islands that occurred between 1924 and 1929. The 1912 signature of Novarupta appears at 36.2 m (1909 on the *Divine et al.* [2011] timescale). It is worthwhile noting that tephra from the small Grimsvötn eruption of 1903 was found in the core at 37.3 m depth [*Wastegård and Davies*, 2009] but this corresponds with no significant sulfate residual and only a broad and modest sulfate concentration rise (Figure 3).

4.4. Mount Everest

[21] Mount Everest is a much different ice core location than Svalbard (Figure 1 and Table 1), and is another good test of our methodology since the ice has been subject to some independent dating and volcanic signal extraction. In addition the core presents some difficulties in volcanic sulfate extraction because of the domination of terrestrial sources in the sulfate budget (Table 1). Ion chemical analysis was done at 3–4 cm resolution along the core, corresponding to subseasonal resolution in the upper core, to approximately semiannual at 100 m depth. The ions measured [*Kaspari et al.*, 2007] were Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, and NO_3^- so no species traditionally representative of biogenic SO_4^{2-} (Table 1) was analyzed, but all available ions were used in the MLR analysis. Owing to the relatively high-accumulation rate (0.52 m w.e a^{-1}), seasonal variations in

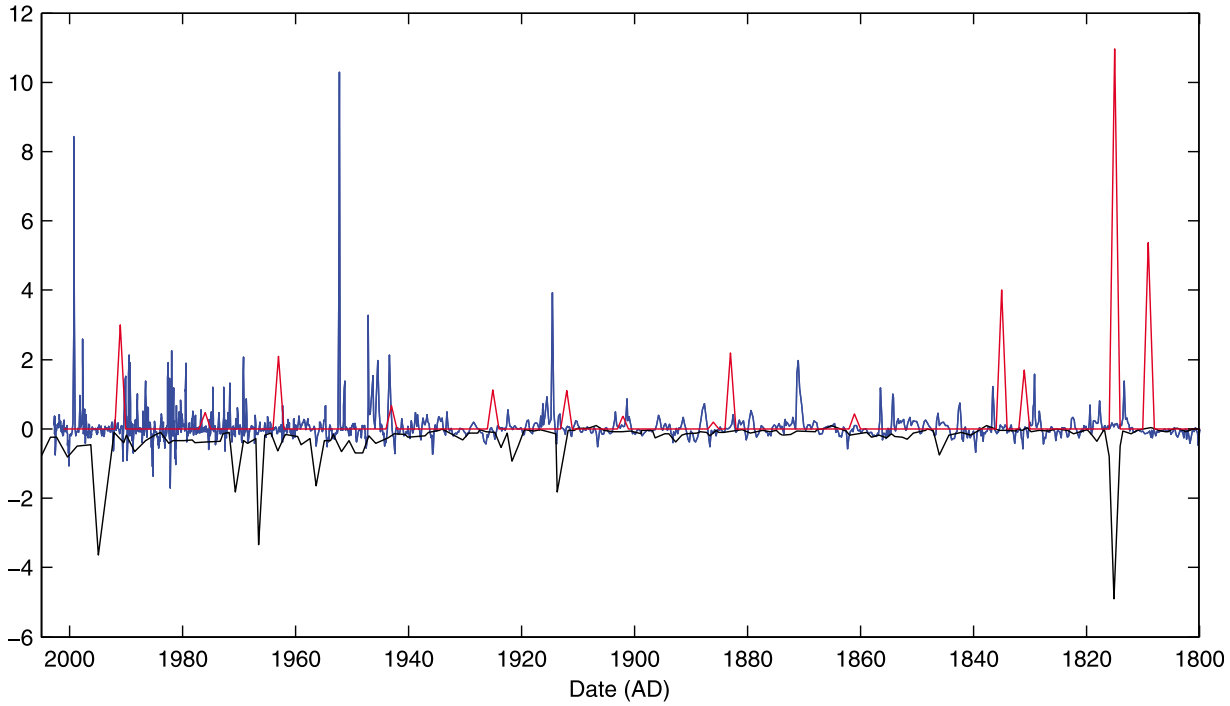

Figure 8. Comparison of the global ice core volcanic index [*Gao et al.*, 2008], red curve, $V[SO_4^{2-}]$ from the Mount Everest core (blue) and inverted Bi concentrations [*Xu et al.*, 2009], black curve. Data are arbitrarily scaled for clarity, time scale is from *Kaspari et al.* [2008].

water isotopes, soluble ions and trace elements are well preserved in the core, and were used to date ice in the core by counting annual layers [*Kaspari et al.*, 2008] to a depth of 86 m. The timescale was verified using high-resolution measurements of bismuth (Bi) to identify major volcanic horizons, including Pinatubo, Agung and Tambora [*Kaspari et al.*, 2007]. Other eruptions may be more tentatively assigned [*Xu et al.*, 2009], however Krakatau, 1883 is not present in the Bi profile. Dating uncertainties are estimated to be about 5 years at 1534, at 86.8 m depth. The method presented here based on ion concentrations has advantages because those data cover the whole length of the core, which was until now dated by cycle counting since 1534 and flow modeling with no fixed horizons beyond Tambora 1815 [*Kaspari et al.*, 2008].

[22] Figure 8 shows a comparison between the Bi profile [*Xu et al.*, 2009] and sulfate residual found from equation (2), and the averaged volcanic signature from polar ice cores [*Gao et al.*, 2008]. When comparing the ice core data with the volcanic index we use the published *Kaspari et al.*

Table 2. Volcanic Signatures Identified in Four Cores by Volcanic Sulfate Residual

			Lomonosovfonna			Everest			Holtedahlfonna			Vestfonna		
Eruption	Figure 1 Name	Year	Depth (m)	Model Date	Diff[a] (year)	Depth (m)	Model Date	Diff[a] (year)	Depth (m)	Model Date	Diff[a] (year)	Depth (m)	Model Date	Diff[a] (year)
Pinatubo	Pi	1991	6.5	1987.9	3.1	10	1990.1	0.9						
El Chichón	ElC	1982				13	1986.7	−4.7						
Agung	Ag	1963							28	1963.9	−0.9			
Bezymianny	Be	1956	21.1	1955.7	0.3	37.8	1952	4				18	1958.2	−2.2
Kharimkotan	Kh	1934	29	1935.4	−1.4									
Kuril	Ku	1928	31.5	1926.9	1.1									
Novarupta	No	1912	36.2	1907.4	4.6				55.5	1910.7	1.3	41.2	1907.7	4.3
Krakatau	Kr	1883	45.5	1871.3	11.7	56.2	1870.7	12.3	68.5	1873.4	9.6	55.5	1872.1	10.9
Coseguina	Co	1835				62.5	1836.2	−1.2						
Tambora	Ta	1815	62.3	1803.9	11.1				95.5	1805.8	9.2			
Laki	La	1783	67	1781.3	1.7				103.6	1781.9	1.1	86.8	1780.6	2.4
Fuji	Fu	1707	80.5	1706.8	0.2									
Parker	Pa	1641				90.8	1621.7	19.3						
Huaynaputina	Hu	1600										136.5	1617	−17
Kuwae	Kw	1453	107.5	1403.8	49.2	101.2	1490.9	−37.9						
Unknown	-	1259				105.1	1317.1	−58.1						
Hekla	He	1105?	117.7	1095.5	9.5									
Dakataua?	Da	738				107.8	861.3	−123.3						

[a]Diff is eruption date minus model dating.

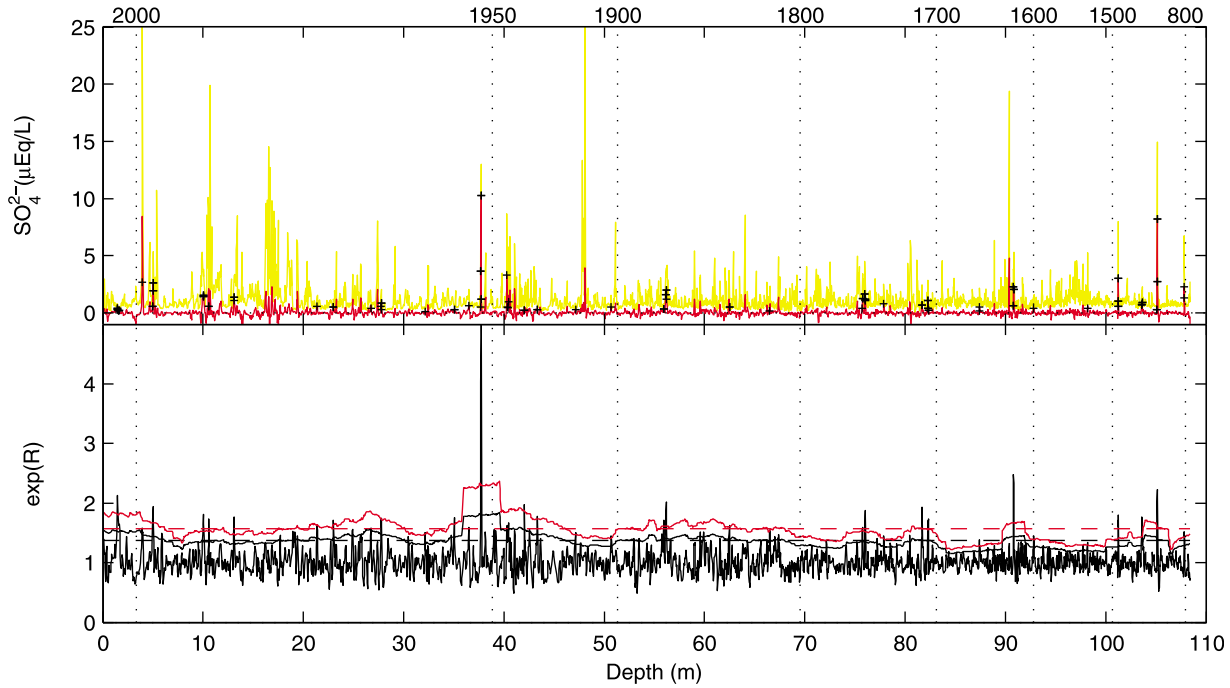

Figure 9. As for Figure 3 but for Everest 2002 core sulfate. Dates are from the *Kaspari et al.* [2008] model.

[2007] timescale, which was tied to the 1815 Tambora signal. For example it is tempting to align the peak dated at 1873 in the Everest core with the Krakatau eruption of 1883. Similarly peaks sulfate residual in the 1830 s may be linked to large eruptions recorded in polar ice cores (Table 2). It is clear that there are significant differences between the Bi and sulfate peaks, with only a few common signals, and in those cases the exact timing of the peak may differ by a year or two. This may be explained by different transport paths for Bi particles and aerosols. In several cases peaks in one method are completely absent or much smaller in the other.

[23] The whole record of volcanic sulfate is plotted in Figure 9. The recent large eruption of Pinatubo 1991 may be the signal at 10 m (1990), and El Chichón 1982 could be detected at 13 m (1986). Agung is not clearly seen in sulfate, though a peak at 1966 in Bi is associated with it by *Xu et al.* [2009]. A sulfate anomaly on the Kaspari *et al.* time scale at 1953 is dominant at 37.8 m and may be associated with a Bi peak at 1956 that *Xu et al.* [2009] assign to Kelut 1951 (Figure 8). We may tentatively reassign this peak to the Bezymianny (1956) eruption which as a high latitude, but very large eruption, and well recorded in several Arctic ice cores (e.g., Lomonosovfonna shown in Figure 3 [*Fritzsche et al.*, 2005]). This assignment of the peak to a large Kamchatka eruption is also consistent with the 1912 peak seen in SO_4^{2-} residual and Bi that *Xu et al.* [2009] assigns to Novarupta, Alaska 1912, a similarly large eruption from a similar location. However, the peaks at 1953 and 1951 in the well dated Belukha core (Figure 4) may have the same origin as those here, which tends to argue against the cause being Bezymianny (1956). The Krakatau eruption in 1883 is presumably the large residual peak at 56.2 m, 1872 in the Kaspari timescale, which was absent from the Bi analysis. The Tambora 1815 peak is significant at 99% level in e^R, at 66.5 m but has only a fairly modest residual of about 2 μEq/L. A clearer residual peak at 62.5 m (1836), is presumably the 1835 eruption of Coseguina. There are significant 18th century peaks at both 76 m (1758) and 82 m (1710), however the polar ice core volcanic records discussed by *Gao et al.* [2008] exhibit no large eruptions between Laki (1783) and Parker (1641), so assigning them to a specific volcano is problematic. Another large anomaly is seen around at 90.8 m (AD1620). This may be attributed to Huaynaputina (1600), however, possible a better candidate here is Parker (1641) in The Philippines which is much closer to Everest.

[24] One of the most obvious signals, even from the raw SO_4^{2-} profile is seen at 105.1 m, corresponding to about AD1310 in the Kaspari time scale. However, that is almost certainly the largest eruption signal of the last millennium: the unknown eruption seen in polar ice cores around 1259 [*Gao et al.*, 2008]. This signal must be from the tropics as it is seen in both polar ice sheets, hence it is also likely visible in Tibet. The 1453 eruption of Kuwae, again a very significant event globally [*Gao et al.*, 2006; *Gao et al.*, 2008], is likely the residual spike at 101.2 m dated just before 1500 on the Kaspari scale with a residual of 3 μEq/L, the dating difference is consistent with the offset for the large 1259 peak. There is one final signal at 107.8 m (0.6 m from the bottom of the core) that is highly significant around 450 years earlier than the 1259 peak, or about AD800. This may be the large eruption Dakataua in New Britain dated at 800 + −50 radiocarbon years, or 720 ± 80 calendar years. The largest signal in the polar ice cores between 540 and 1170 [*Gao et al.*, 2008] is dominant in Antarctic records at about AD738, and so consistent with the Dakataua eruption in an Everest core.

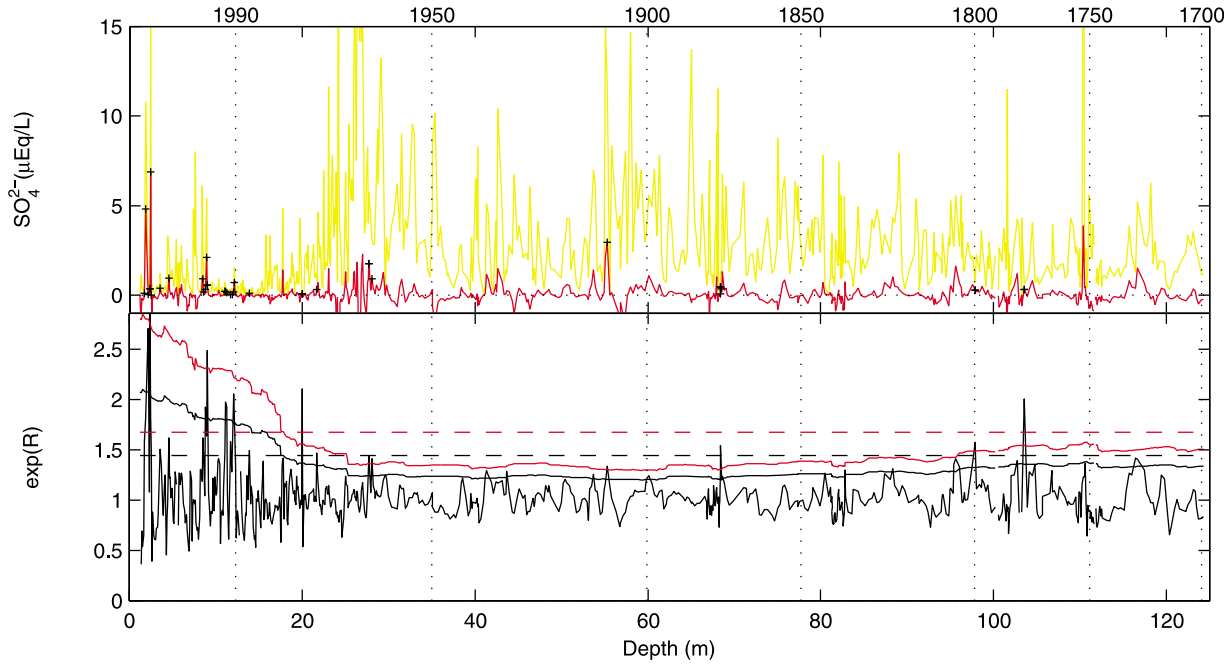

Figure 10. As for Figure 3 but for Holtedahlfonna 2005 core sulfate. Dates are from annual layer counting *Divine et al.* [2011] constrained by 1963 horizon.

4.5. Holtedahlfonna

[25] Having shown that the method appears to detect volcanic signals in settings as different as Altai, Everest and Svalbard, we now apply it to ice cores that have not been extensively studied to date, and which pose similar problems in dating as those found for Everest and Lomonosovfonna.

[26] In April 2005 an ice core was drilled at Holtedahlfonna on the west coast of Spitsbergen (Table 1). Ion chemical analysis was done at typically 10–25 cm resolution along the core, corresponding to seasonal resolution in the upper core, to approximately semiannual at 100 m depth. As with Lomonosovfonna, seasonal melt and percolation will act to reduce the useable resolution. The ions measured were Na^+, Cl^-, SO_4^{2-} MSA, Mg^{2+}, Ca^{2+}, K^+, NO_3^-, and NH_4^+, and all were used in the MLR analysis. Radar measurements showed that the ice depth in the area is highly variable and that it is approximately 150–250 m at the drill site. However, due to water-saturated ice layers and steep topography in the area, the exact depth from radar surveys is uncertain. Preliminary dating of the core can be based on a combination of counting summer peaks in the oxygen isotope stratigraphy [*Pohjola et al.*, 2002b], the tritium date at 1963, and a Nye model with the prescribed ice depth at the core site. Comparing layer counting with the Nye thinning model using 300 m bed depth gives ages of 1699 and 1740 at the core bottom, whereas a depth of 200 m gives model dates about 8 years different from counting dates. Although the 200 m depth model gives a closer match with counting dates, we prefer the 300 m depth model since it matches better the observed thinning rates of the annual layers, and gives a better statistical fit between the chemical series of the well dated Lomonosovfonna core and the Holtedahlfonna core. A depth of 300 m is also more consistent with the temperature profile along the borehole. The reason why the counting ages agree better with the 200 m depth model rather than 300 m depth model may be that some annual layers are miscounted. However, the dating issue cannot be resolved with the data and methods we have used, hence there is a need to explore the volcanic sulfate record in more detail.

[27] It is immediately clear from Figure 10 that, in contrast to Lomonosovfonna (Figure 7), there is no large peak which can be assigned to Laki 1783. The peak at 110 m depth (AD1755 in the preliminary dating) is not significant in the log ratio test despite it being the largest residual in the lower part of the core. The ionic chemical signature shows high levels of all species, which is very different from a typical eruption record in ice cores. Searching for a Laki eruption in the SO_4^{2-} residual is problematic, however, there is a large and highly significant peak in e^R with small absolute residuals values at 103.6 m, AD1780 in the tentative dating. There are 2 small peaks in absolute residual that are also significant at 95% on each side of the central highly significant peak in e^R. This feature at 103.6 m is our best candidate for Laki 1783. There is another significant peak at 116.5 m (AD1730), and there is a peak at 28 m close to the measured depth of the radioactive fallout layer in 1963 (Table 1), which is plausibly Agung, 1963. Similarly a peak in residual significant at 99% windowed test is observed at 55.5 m or 1910 that is plausibly Novarupta (1912). Another small peak at 95.5 m is dated at 1805 and is perhaps Tambora, and a similar peak at 68.5 m (1885), possibly Krakatau (1883).

4.6. Vestfonna

[28] Vestfonna is the second largest ice cap on Nordaustlandet, the adjacent Austfonna being the largest one. Vestfonna contains a record of chemistry that despite being altered by melting has provided reliable climatic and environmental information [*Watanabe et al.*, 2001; *Matoba*

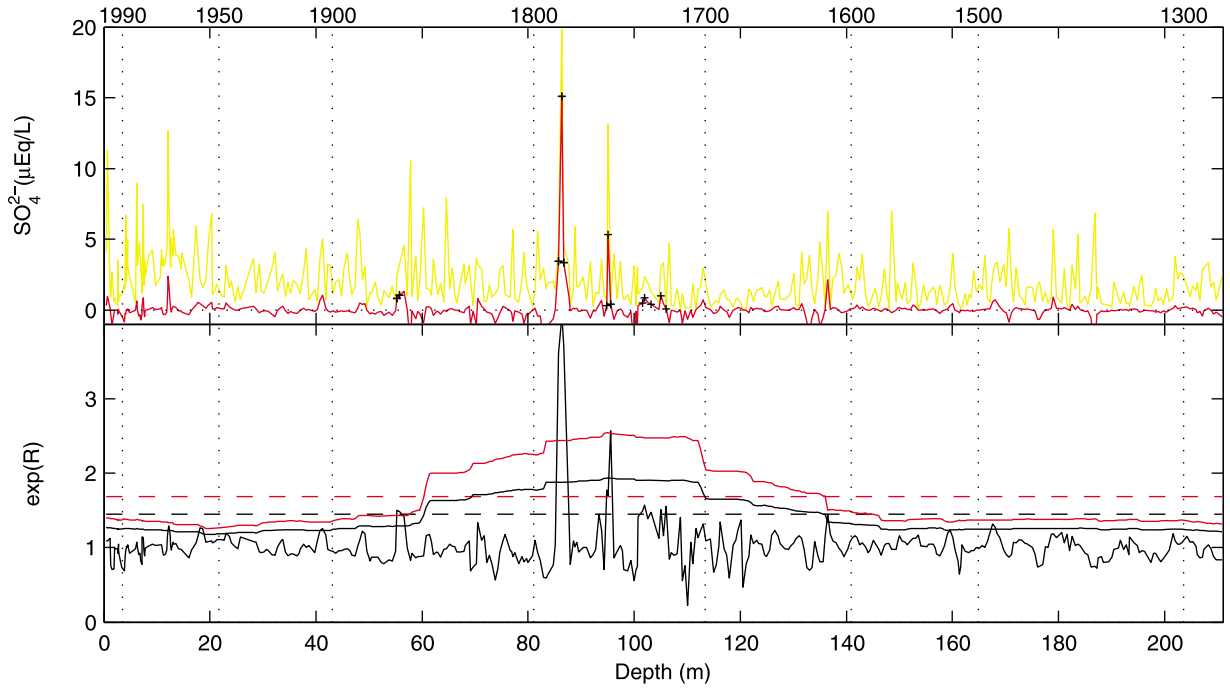

Figure 11. As for Figure 3 but for Vestfonna 1995 core sulfate. Dates are from the 1963 and 1783 horizons and a Nye thinning model with bedrock at 320 m.

et al., 2002]. Ion chemical analysis was done at typically 10–50 cm resolution along the core, corresponding to annual resolution in the upper core, to approximately biannual at 100 m depth. The ions measured were Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, and NO_3^- so no species traditionally representative of biogenic SO_4^{2-} (Table 1) was analyzed, but all available ions were used in the MLR analysis. The ice core was dated by *Matoba et al.* using the 1963 horizon, a prominent peak in SO_4^{2-} identified as 1783 Laki at 86.8 m (Figure 11) with interpolation between the dates and extrapolation to the bottom of the core. No flow model was made hence the dating was rather uncertain since the bedrock depth was not known in 2002 [*Watanabe et al.*, 2001]. In fact the depth at the drill site is about 320 m (Table 1) according to recent radar surveys [*Pettersson et al.*, 2011]. Using this bedrock depth, and the depths of the 1963 and obvious Laki peak we made a preliminary dating scale.

[29] Other significant peaks include one dated at 1873, presumably Krakatau 1883 at 55.5 m depth. Several peaks in the mid 18th century date around 1758 with smaller residuals in the 1720 s and 1730 s (insignificant in the windowed significance tests). It is possible that one of these may be the same 1730 peak seen in the Holtedahlfonna core. There is another peak significant at the 95% level dated at 1617 (136.5 m depth), which is plausibly the 1600 Huaynaputina signal seen in polar ice cores [*Gao et al.*, 2008]. The deepest signal of any note is at 167.5 m (AD1488), which we may tentatively suggest is Kuwae 1453 since below that depth very little is significant even in the windowed tests. The lack of peaks may be due to the low-resolution chemistry sampling available. Several residual peaks in the 20th century are significant in the windowed test: one dated at 1908 at 41.2 m depth, which may be Novarupta, 1912, and a very small residual at 1958 (18 m) that may be Bezymianny (1956), a very large signal at 1957 in the Lomonosovfonna core, and finally a peak in 1972, that we do not assign to any eruption.

5. Discussion and Conclusions

5.1. Dating Complex Ice Cores

[30] Many of the volcanic composite indicators [e.g., *Gao et al.*, 2008; *Robock*, 2000] dating to before 1880 are based on ice core records from the polar ice sheets. This is a relatively small region, 10%, of the Earth's surface. Here, we present some of the first time series of volcanic signatures in ice cores from outside the large ice sheets. The method, in common with all others, is however only useful used in combination with extra information such as annual layer counting since age—depth relations for ice cores can vary enormously between high accumulation rate and thin coastal glaciers, to thick dry interiors of ice sheets. Hence identification of a particular volcano is ambiguous. A comparison of the dating found from the 4 "complex" cores from the volcanic signals identified with the model dates extracted from earlier results or layer counting is shown in Figure 12. It is notable that despite the differences in the ice cores several eruptions signals are common to all the Svalbard cores: Krakatau, Tambora, Novarupta (Table 2 and Figure 1), despite the very low-level residuals in SO_4^{2-}. The 1956 Bezymianny eruption, which is seen as a small signal in Greenland ice cores [*Gao et al.*, 2008] is rather prominent in the Svalbard cores; in Lomonosovfonna it appears as the second largest signal. Atmospheric transport patterns will lead to quite different deposits from Icelandic eruptions in Greenland and Svalbard and the same appears true for a Kamchatka eruption since the 1956 signal is the largest in the Franz Josef Land Akadamii Nauk ice core [*Fritzsche*

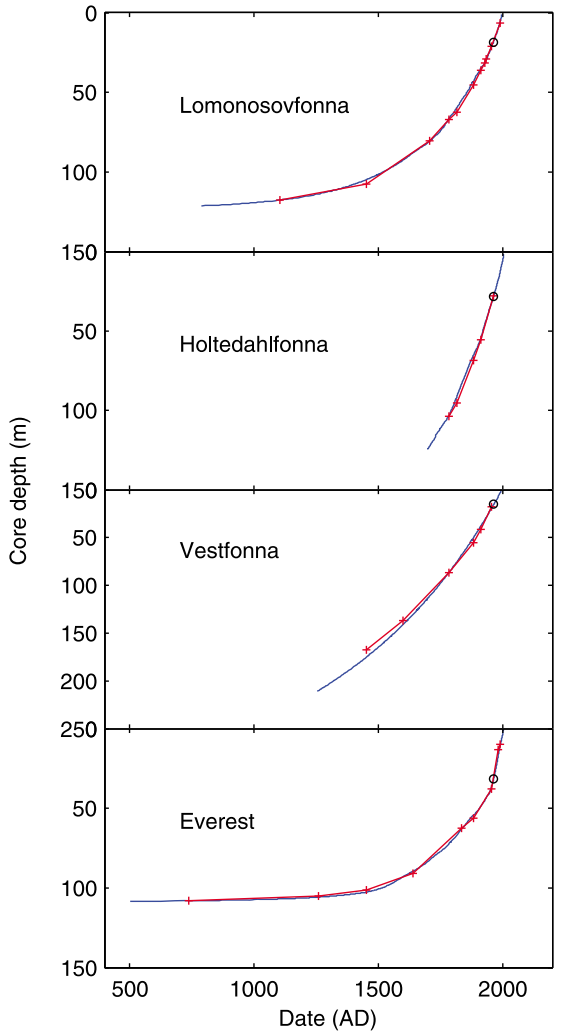

Figure 12. Dating models for the 4 ice cores studied here. Dating based on flow models constrained by layer counting and reference horizons are blue curves. The 1963 radioactivity layer depth is shown as a circle. "Plus" symbols are volcanic eruptions identified as significant in Figures 7, 9, 10, 11 and matched to plausible dated eruptions as discussed in the text; the eruptions are simply joined by red lines.

et al., 2005]. It is also common that cores contain a signal around 1730 that may be the 1732 Jan Mayen eruption. Both the Krakatau and the Tambora signals appear about 10 years prior to the dating model estimates while Laki is at its fixed date, which suggests that there may have been a period of relatively lower accumulation rates in 1783–1815 than the simple flow models use [*Pohjola et al.*, 2002b], and which may have been low enough to cause errors in layer counting. This would be consistent with extended disruption of North Atlantic oceanic circulation as noted by *Bjerknes* [1964] from British Admiralty data that northerly parts of the ocean were 2–3°C cooler and southerly parts 3°C warmer than normal from 1780 to 1820.

[31] The total fraction of the SO_4^{2-} extracted as residual from the MLR and defined to be volcanic is 4.5%, 1.4%, 1.7%, and 3.6% for Lomonosovfonna, Holtedahlfonna, Vestfonna, and Mount Everest, respectively. Comparing Figures 7, 10, and 11 and Table 2 it is very clear that the signals deposited in the cores are quite different. We may expect considerable variation, as has been noted previously; typically 30% of eruption signals may be missing from cores due to differences in local precipitation and postdepositional effects. However, the degree of dissimilarity (Table 2) is rather larger than that, especially between Lomonosovfonna and Holtedahlfonna, which are most similar in environment (Table 1 and Figure 1). This may be because of the vagaries of the local deposition regime in the two ice core locales: Lomonosovfonna is an ice cap frozen to bed with fairly gentle slopes at higher elevation than the local nunatak dust sources. The accumulation gradients in the region show a rising trend with elevation between 1000 and 1200 m, but then decreasing to lower accumulation above about 1200 m [*Pälli et al.*, 2003], which may suggest that wind scouring occurred at the drill site. However, *van der Wel et al.* [2011] show that the 1963 tritium peak from Holtedahlfonna and Lomonosovfonna has the same amplitude in both ice cores and is consistent with other radioactive measurements from Svalbard ice cores [*Pinglot et al.*, 1999]. Moreover ^{137}Cs on Lomonosovfonna has the same mean value at the summit drill site region and lower on the glacier ruling out significant removal of snow by wind scouring [*Isaksson et al.*, 2001]. On the other hand Holtedahlfonna drill site lies on a saddle and has a temperate rather than frozen bed. Holtedahlfonna is closer to the western fjords and seems to be within the air masses affected by Arctic haze [*Virkkunen et al.*, 2007], while Lomonosovfonna appears to sample more regional environmental signals, with much sulfate coming from Europe [*Moore et al.*, 2006]. Holtedahlfonna has only about 25% as much volcanic SO_4^{2-} as Lomonosovfonna, partly due to its higher sea salt loading, hence its poorer volcanic record.

[32] Vestfonna is significantly lower in elevation than either the other two Svalbard sites, but is well within the Arctic Ocean sphere of influence, hence it seems to suffer relatively little seasonal melt. The ice cap is frozen to the bed at the core site [*Watanabe et al.*, 2001], as is much of the central region of the ice cap [*Pettersson et al.*, 2011], so the site should be less influenced by melt processes and have a simpler flow pattern than the warm based Holtedahlfonna. Vestfonna and Holtedahlfonna are the warmest of the 4 sites studied, hence percolation and postdepositional impacts may be greater and make volcanic sulfate harder to identify. On the other hand the Vestfonna record studied here is relatively low resolution which may explain the low fraction of volcanic SO_4^{2-} since a smoothed volcanic spike will be harder to detect as an anomaly in the MLR. The detection of reasonable numbers of volcanic signals, however argues for a potentially good volcanic record if a higher-resolution record could be recovered.

[33] The Svalbard sites may well have volcanic records less reproducibly preserved than other ice core records with less seasonal melt. However, we also emphasize that even in Greenland, relative volcano magnitudes can vary, or be absent completely from the record due to stochastic processes [e.g., *Friedmann et al.*, 1995]. Of the 4 cores studies here, Everest has the cleanest volcanic record, and in many ways resembles the well preserved and high-altitude Belukha core. This may be because its location samples more of the better known tropical eruptions than the high-

latitude polar regions where historical eruption magnitudes are relatively less well reported than in the populated regions (Figure 1). The record is also high resolution in contrast to Vestfonna, easing the detection of anomalies in MLR. The site is much less dusty than central Tibet ice cores, but even there the volcanic SO_4^{2-} fraction was apparently less than at Lomonosovfonna, though greater than at the other Svalbard cores. It is interesting to note that there are some agreements with the Bi record of volcanism for the core (as far as the record extends), but several large signals are detected by the Bi method (such as Agung, 1963) that are absent in the sulfate analysis. Similarly we detected Krakatau clearly while it is absent in the Bi profile. Hence it is not immediately clear which locations will offer the best records of volcanic deposition since it is a combination of relative sulfate sources, volcanic plume chemistry and postdepositional effects that determine the final ice core record.

5.2. Remarks on the Methodology

[34] A key problem in interpreting sulfate records as a proxy for volcanic peaks in most ice cores is that there is significant deposition of sulfate from other sources: anthropogenic, marine, terrestrial or biogenic. This leads to the need for a more sophisticated approach in determining the origin of sulfate concentration spikes, a difficulty even in remote places as anthropogenic pollution grows, making small and moderate eruption signals hard to detect. This issue has restricted volcanic time series to mainly the central ice sheets, or to high-altitude ice caps. Our analysis of the Belukha ice core shows that the method we describe detects volcanic signatures well where sulfate sources from terrestrial dust have been easily corrected for by a simple regression on calcium. However, that simple method breaks down in the 20th century due to increased anthropogenic sulfate deposition. Our new method continues to function well and extracts the significant eruptions of the recent decades even when the volcanic fallout is much smaller than the background sulfate concentrations. Furthermore, comparison of the excess sulfate calculated by correcting for dust using calcium concentration leads to a high correlation with the $V[SO_4^{2-}]$ concentration from equation (2), but which is more than twice as large. The coefficient changes as a function of MLR variables, the fewer the ions used in the model, the closer the coefficient becomes to the simple $X[SO_4^{2-}]$ model. This is because more of the sulfate will be covarying with some particular ion or other, hence the more ions used the less stochastic sulfate residual will be left assigned to volcanoes.

[35] Limitations of the method are also highlighted in Belukha analysis. Transportation of impurities as well as sources and postdepositional effects change the association between ions. In running our analysis on individual samples we impose a varying sample rate along the core. This preserves as much information as possible, and the impact of lower resolution can be seen by comparing Figures 4 and 6. In particular, common seasonal transport of all the ions is important. In winter pollutants are trapped in a low-altitude boundary layer in the Arctic, but in summer there is much more mixing with the free troposphere. While in Alpine settings during summer stronger vertical transport of pollutants from the boundary layer produces higher concentrations than in the winter season that are more representative of the free troposphere. If measurement resolution is subseasonal near the surface but multiannual deeper then the transport factors become blurred. This can be seen in the correlation coefficient between SO_4^{2-} and $HCOO^-$ of 0.26 in the full resolution Belukha data compared with -0.003 in the annual down-sampled data. Postdepositional effects especially seasonal melt may produce similar smoothing of the original ionic covariation. Down sampling the data to annual or lower resolution would help to remove the effects of changing resolution along a core, however we think that the advantage of being able to use all the data points in the analysis is beneficial. In practice we suggest that the method is used with various input variables, window lengths and down sampling to common resolution to gain confidence in the robustness of peaks and hence volcanic signal identification. The method will also fail if there is an overwhelming dilution of volcanic sulfate, for example if there is simply too much dust so that any volcanic sulfate would be well within the experimental measurement of the sulfate concentration.

[36] In comparing our record of $V[SO_4^{2-}]$ with the volcanic proxy Bi in the Everest core we noticed quite low correlation: some eruption signals are present in $V[SO_4^{2-}]$ and not Bi, and vice versa. Given the success of $V[SO_4^{2-}]$ in matching the Belukha core signals, we argue that it is a good record of volcanic SO_4^{2-}, but it may not be the complete record of volcanic fallout at the core site. Bi is transported in the solid phase on dust particles, these may be rather heterogeneously dispersed following an eruption. Sulfate in contrast comes from gaseous aerosol precursors which would tend to be much better mixed. However, even these do depend on the initial plume trajectory in the first days of the eruption [*Robock*, 2000], and in the transfer of the sulfate from the stratosphere to troposphere which maybe by removal via steady sedimentation or by capture of material by "tropospheric folds" [*Sassen et al.*, 1995]. A further illustration of the differences between the dust and sulfate records can be seen in the Laki fallout at Lomonosovfonna [*Kekonen et al.*, 2005b] where the microparticle rich layer is separated from the sulfate deposit by 20 cm. Another example is the absence of any sulfate from the Grimsvötn eruption of 1903 despite tephra being found [*Wastegård and Davies*, 2009]. We should again note that individual ice core records—and it seems even volcanic proxies within the same ice core—are, in general, not well correlated with each other or with any of the composite volcanic indices. This is the result of stochastic variability associated with the transport and preservation of volcanic fallout to an ice core.

[37] Finally we point out that the method does not rely on measurement technique, so an ionic record from a continuous flow measurement system would be processed in exactly the same way as an ion chromatograph record since the errors are also proportional to magnitude. If errors differ between species then the species should be weighted accordingly in the MLR. Ice cores from regions such as Iceland where melting is severe may be problematic since the method relies on the correlation between ions being maintained to some degree. The method would fail if postdepositional processes move all ions to the same sample. However, where relationships between ions are not well understood the method can produce useful results since it requires no prespecified relations between ions, nor attempts

to find volcanic sulfate directly, rather the method simply tries to find the best explanation for sulfate in terms of other ions, and whatever is left is quite likely to be volcanic sulfate. Our method is reproducible and consistently applied, does not rely on dubious statistics, and does not arbitrarily correct only for, e.g., calcium ions. If it was applied to many cores it may give an indication of volcanic sulfate fallout which would in turn provide data for radiative forcing calculations which is a key element in climate change attribution studies [*Jansen et al.*, 2007; *Jevrejeva et al.*, 2009], and also give more geographic control for atmospheric transport models [e.g., *Gao et al.*, 2008].

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E. Beaudon, Arctic Centre, University of Lapland, PO Box 122, FI-96101 Rovaniemi, Finland.

D. Divine, Department of Mathematics and Statistics, University of Tromsø, N-9018 Tromsø, Norway.

E. Isaksson, Norwegian Polar Institute, N-9296 Tromsø, Norway.

S. Kang, Key Laboratory of Tibetan Environmental Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100085, China.

J. C. Moore, College of Global Change and Earth System Science, Beijing Normal University, 19 Xinjiekou Wai St., Beijing 100875, China. (john.moore.bnu@gmail.com)

V. A. Pohjola, Department of Earth Sciences, Uppsala University, Villavägen 16, SE-75236 Uppsala, Sweden.

R. S. W. van de Wal, Institute for Marine and Atmospheric Research, Utrecht University, PO Box 80005, NL-3508 TA Utrecht, Netherlands.