

CHAPTER 14

Ice Cores as a Unique Means of Retrieving Records of Chemical Compounds in the Atmosphere: Evidence of an Undocumented Tropical Volcanic Eruption in the Early 19th Century

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I. INTRODUCTION

The history of the composition of the Earth's atmosphere is critical to understanding the present and forecasting the future role of the dynamic atmosphere in the global climate system. Polar ice sheets of Greenland and Antarctica and certain nonpolar glaciers, through continuous preservation of precipitation, contain proxy records of atmospheric chemistry covering hundreds of thousands of years.¹ Ice cores from carefully selected sites provides a unique means of retrieving these records.² For example, air trapped in ice bubbles provides a sample of the history of the atmosphere. Atmospheric components incorporated in the snow/ice lattice contain clues of chemical changes in the atmosphere. Analysis of insoluble particles in the ice and snow can provide information about atmospheric turbidity. However, the extrapolation of ice core results to atmospheric composition records requires caution and development of valid transfer functions.

On a global scale atmospheric chemical composition is affected by volcanism, changes in climate, anthropogenic emissions, as well as other factors. For example, explosive volcanic eruptions emit large amounts of ash and gaseous aerosols to the atmosphere. Most of the gaseous aerosols are sulfur compounds, mainly SO₂, that can have atmospheric residence times from weeks to several years. The effects of these atmospheric changes can be reconstructed from the analyses of ice cores retrieved from sites in strategic locations. This work illustrates the use of ice cores for recovering the record of a large tropical volcanic eruption around 1809 A.D. which significantly altered the global atmospheric sulfur burden for 2 years. This apparently explosive eruption has not been previously recorded in historic chronologies of volcanic eruptions.

In 1985, an ice core 302 m long was recovered from Siple Station in West Antarctica (75°S, 84°W) as part of an extensive glaciologic investigation. In 1989, a core 84 m long was recovered from central Greenland (72°N, 38°W) near the summit of the Greenland Ice Sheet.

II. ICE CORE RETRIEVAL

Recovery of uncontaminated ice cores is the first step in ice core research. The precipitation over the polar areas is the cleanest in the world. Major atmospheric chemical species are present in polar snow and ice in low parts per billion (nanogram per gram of ice) levels.^{3,4} The ice core retrieval process consists of the

following steps: (1) surveying and selecting an appropriate site; (2) core drilling, recovery, and logging; (3) preliminary analyses if feasible; and (4) packaging for shipment to the laboratory.

The ice cores, cylinders of 8–13 cm in diameter and usually 100 cm in length, are in constant contact with drill, analytical equipment, or packing materials. Efforts are made at each of these steps to prevent serious contamination. In the recovery of the 1985 Siple core, the drill site was selected 2 km upwind from Siple Station so that the chance for contamination from station activities would be minimized. The drilling of the 302-m core was conducted in a 3-m snow trench to avoid contamination by drifting snow and for ease of drill operation.⁵

Similar practices that minimize contamination should be applied to all ice core recovering operations. These include: (1) selecting a drilling site away from stations and camps, (2) pretesting equipment that will come into contact with the snow and ice, (3) using clean laboratory clothing when working and sampling, and (4) precleaning containers and tools.

III. SAMPLE PREPARATION AND ANALYSIS

After the frozen ice cores have been transported to the laboratory, they are prepared and decontaminated for chemical analysis. Stringent contamination control procedures must be applied in the sample preparation process. In this work, a low temperature (-15°C) clean-air room was used to prepare ice samples for ion chromatographic analysis. When handling cores, the analyst wore clean surgical gloves. The cores were sectioned into individual samples (3–5 cm in length) with a precleaned band saw. A minimum amount of snow or ice that came into contact with field gear and containers (even precleaned) used in transportation was removed during sample preparation. Contamination removal consisted of rinsing the ice sample with ultraclean deionized water to melt away exposed ice surfaces. The upper part of a core is firm, or condensed porous snow, that cannot be rinsed without introducing a substantial amount of deionized water. In this case, the exposed outer layers were carefully cut off with the band saw. The decontaminated ice or snow samples were then allowed to melt in precleaned containers. The sample preparation procedures are different for various analyses. For analysis of major chemical species of ice impurities, the decontamination step (removal of exposed ice) is necessary, whereas for oxygen isotope analysis, this rigorous decontamination is not necessary.

Analytical techniques for ice core chemistry include ion chromatography for major ions,^{6,7} atomic absorption for metal elements,⁸ and acid titrimetry for acidity⁹ determinations. For this work all analyses except for oxygen isotope ratio determination were conducted in a Class 100 clean room laboratory. When determining species that may be present in ambient lab air (e.g., trace gases), it is important to melt the samples in capped containers and to determine the analytical background. Three common inorganic anions (chloride, sulfate, and nitrate) were

measured with a Dionex 2010i ion chromatograph with an AS4A anion separator column. The eluent was a solution of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ (0.0022/0.007 M). The detection limits for Cl^- , NO_3^- , and SO_4^{2-} were ≈ 1 ng/g, with an analytical uncertainty of $\leq 5\%$ at the 50 ng/g level. Working standards were prepared daily from stock solutions and procedural blanks were included in each analytical session for every step in sample preparation beginning with band saw cutting.

IV. DATING OF ICE CORES

Determination of the depth-age relationship for an ice core is essential for meaningful interpretation of proxy data obtained through the analyses. Seasonal (annual) signals in the strata, similar to growth rings in trees, are used to count years from the surface downward.

In polar areas, winter snow is generally isotopically lighter than summer snow. Oxygen isotopic ratios ($\delta^{18}\text{O}$) usually provide a reliable method of dating ice cores from areas where annual accumulation of snow exceeds 0.25 m of water equivalent.^{10,11} $\delta^{18}\text{O}$ for the Siple core is illustrated in Figure 1. The $\delta^{18}\text{O}$ oscillations correspond to changes in season and to a large extent reflect seasonal temperature cycles, with less negative (peak) values indicating warmer, summer precipitation.¹¹ Also shown in Figure 1 are SO_4^{2-} and NO_3^- concentrations. The seasonal variation of SO_4^{2-} is apparent and confirmed when compared to the $\delta^{18}\text{O}$ profile. Concentrations of other chemical species have also been found to vary seasonally in polar snow, and the dating technique based on seasonal concentration variations has been referred to as glaciochemical dating.¹² Parameters such as $\delta^{18}\text{O}$ and SO_4^{2-} concentration are important tools for dating ice cores. However, the seasonality of a parameter may be different from location to location. For instance, NO_3^- concentrations exhibit a strong seasonal signal in Greenland cores (Figure 2) where they are often used for dating. In contrast, NO_3^- concentrations are much less seasonal in Antarctic cores (Figure 1) and cannot be used as a consistently reliable dating tool. Microparticle concentrations have also been shown to exhibit an excellent seasonal signal in Greenland cores¹³ (Figure 2).

The seasonal concentration cycles of some chemical species in snow correspond directly to concentration cycles in atmospheric aerosols.¹⁴ The processes controlling the seasonal variations of the atmospheric species are not very well understood in most cases. It has been proposed that the strong SO_4^{2-} seasonality in Antarctic snow and aerosol results from the available solar radiation controlling the rate of oxidation of reduced atmospheric sulfur species to SO_4^{2-} .¹⁵ Conversely, seasonal characteristics of chemical species concentrations can be used to study the geochemical and atmospheric processes that affect the presence of the airborne chemicals and their relative abundance in the atmosphere.

Using the combination of $\delta^{18}\text{O}$ and SO_4^{2-} concentration, the 302-m Siple core was dated to 1417 A.D. with an uncertainty of ± 1 year for the most recent 200 years. The Greenland summit core was dated with the seasonal NO_3^- and insoluble

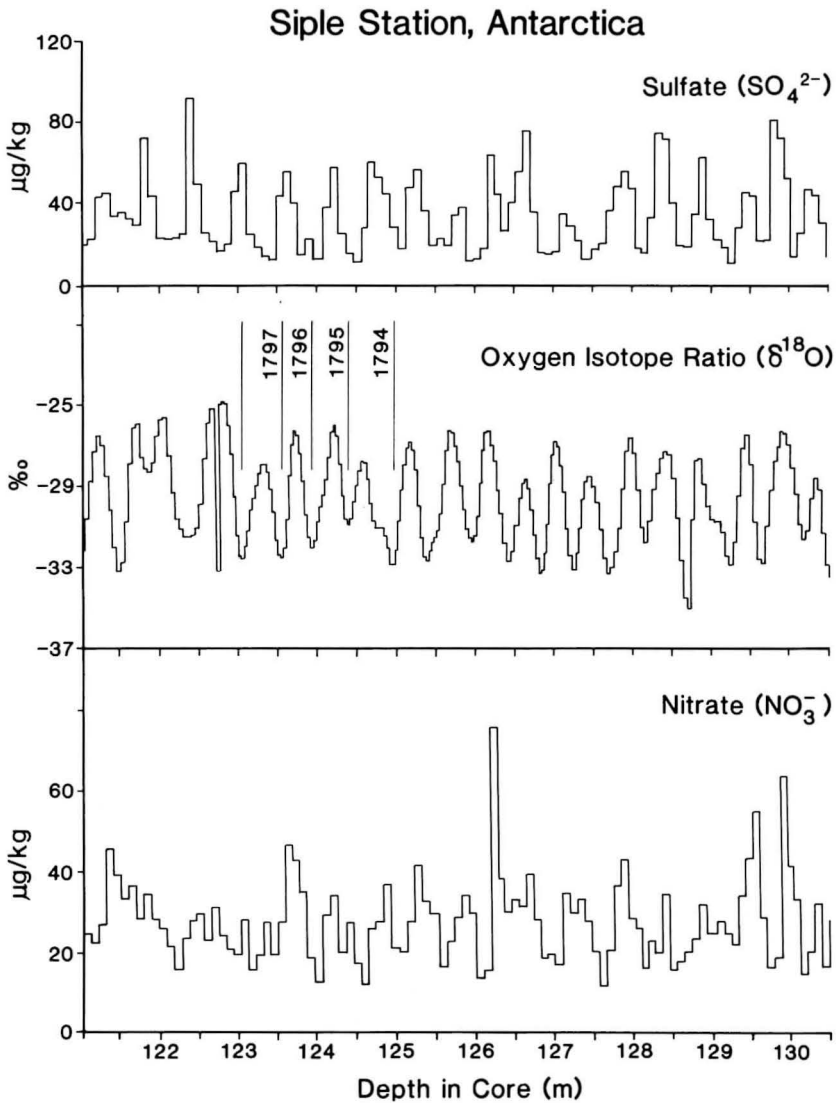


FIGURE 1. Seasonal variations of $\delta^{18}\text{O}$ and concentrations of SO_4^{2-} and NO_3^- in the Siple, Antarctica core provide a means for dating the cores. The definition of a "year" in ice cores is different from a calendar year, but covers approximately the same length of time (12 months). Notice the irregular cycles in NO_3^- concentrations relative to SO_4^{2-} and $\delta^{18}\text{O}$.

Summit, Central Greenland

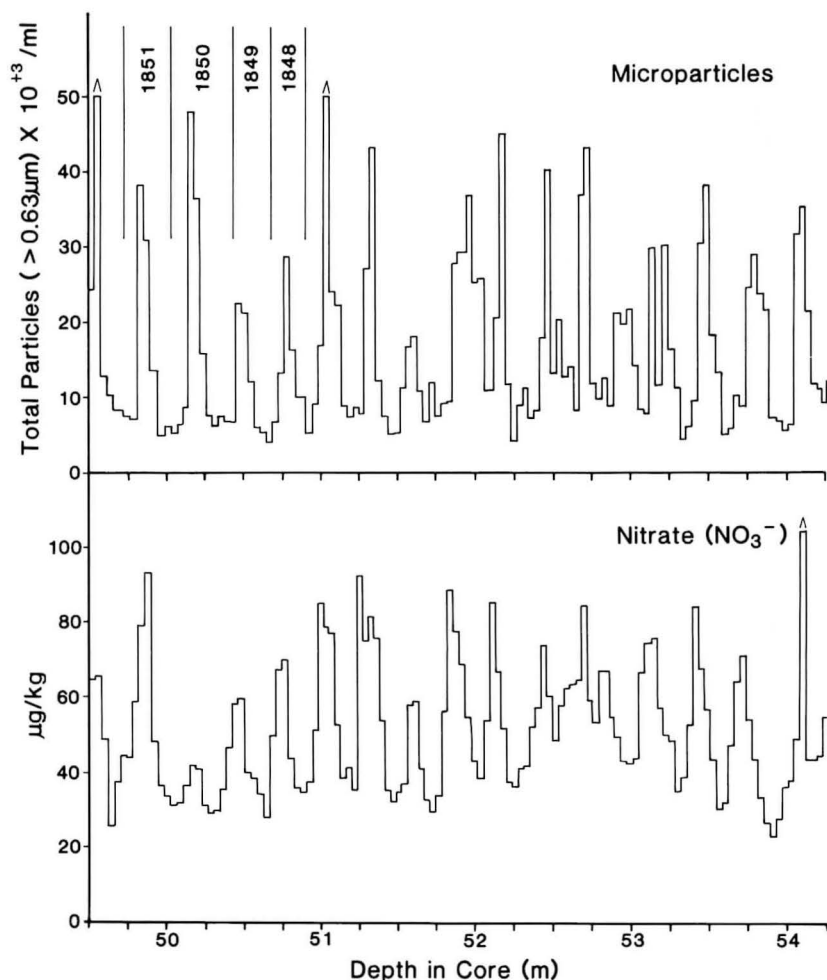


FIGURE 2. Seasonal variations of microparticle concentrations and NO_3^- in the Greenland summit core provide a means for dating the cores. The seasonality of $\delta^{18}\text{O}$ (not shown here) is not as well preserved at this site due to isotopic diffusion. Note that SO_4^{2-} concentration variations are not reliable for dating.

microparticle concentrations (Figure 2). The accuracy of the time scales can be verified with the so-called time stratigraphic "horizons" in cores. The 1783 eruption of the Icelandic volcano, Laki, distributed large amounts of ash and gaseous aerosols to the high northern latitudes. Extremely high SO_4^{2-} or acidity levels associated with

Laki Eruption in Greenland Ice Summit, Central Greenland

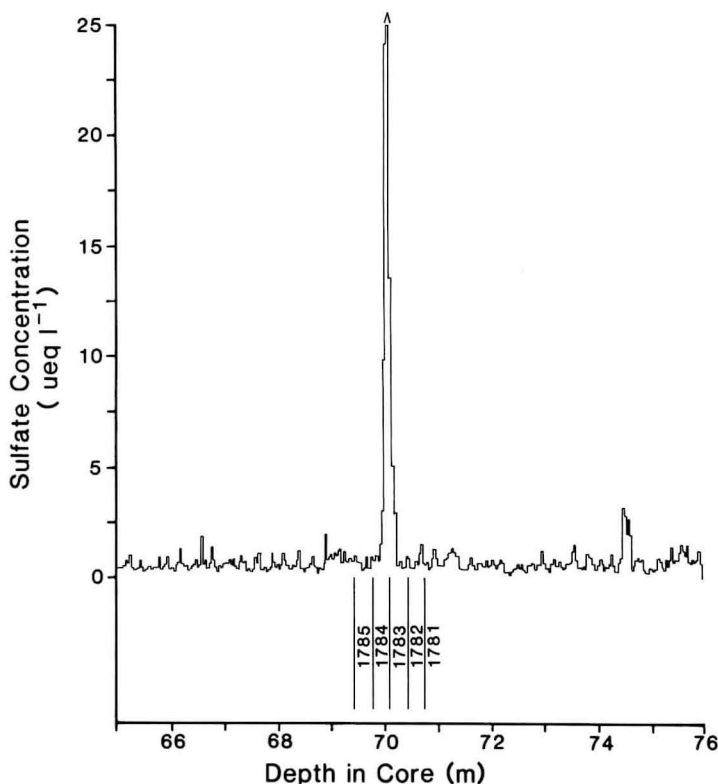


FIGURE 3. The time stratigraphic "horizon" of the 1783 Laki eruption is evident in the Greenland summit core. The extremely high SO_4^{2-} concentrations occur in 1783 according to the time scale established using dust and NO_3^- concentrations from the top of the core. In the Siple, Antarctica core (not shown here) SO_4^{2-} concentrations were not elevated above background at the depth corresponding to 1783. See text for discussion.

Laki have been found in all Greenland ice cores.^{12,16} It has been demonstrated¹⁷ that the Laki acidity or SO_4^{2-} levels in Greenland snow are the highest in the last 1000 years. In the Greenland summit core, extremely high concentrations of SO_4^{2-} from the Laki eruption were found at the depth of 70.2–70.4 m (Figure 3). The time scale was produced independently using seasonal variations in microparticle and NO_3^- concentrations and the occurrence of Laki in the 1783 horizon confirmed the time scale. The SO_4^{2-} concentrations measured in this summit core are in agreement with previously reported Laki SO_4^{2-} concentrations.¹⁶

V. VOLCANIC ERUPTIONS AND SULFATE IN ICE CORES

Volcanoes are an important source of sulfur compounds in the atmosphere. Worldwide they contribute up to 15% of the total global sulfur emissions to the atmosphere.¹⁸ Compounds such as SO_2 and H_2S are major components of gases emitted from eruptions, and they are oxidized to SO_4^{2-} in the atmosphere.¹⁸ Small and moderate eruptions affect atmospheric chemistry on a regional scale. Large explosive eruptions inject gases directly into the stratosphere, where the chemical species along with fine dust particles are spread globally.¹⁹ The residence time of stratospheric volcanic sulfur can be as long as several years. Stratospheric aerosols consisting largely of sulfuric acid particles²⁰ can interact with solar radiation and thermal emission from the earth's surface and therefore affect the global radiation balance and initiate changes in the global climate system.^{21,22} Recently, the impact of explosive volcanic eruptions on climate has been a subject of intense research.^{23,24}

Proxy records of global volcanism are preserved in ice cores as impurity SO_4^{2-} or sulfuric acid concentrations which are elevated above natural background levels, such as in the case of Laki in Greenland cores. Within the depth range 113.3–113.6 m of the Siple core, SO_4^{2-} concentrations of up to 270 ng/g were found vs a background of 10–90 ng/g (Figure 4). This layer of ice was dated as 1816 ± 1 A.D. using $\delta^{18}\text{O}$ and SO_4^{2-} seasonal cycles and without reference to horizons. The SO_4^{2-} concentrations at the depth of 60.7–61.0 m of the Greenland summit core are 200–260 ng/g vs a background of 10–60 ng/g (Figure 4). This depth interval was dated as 1816 ± 4 , or 1816 ± 0 with respect to the Laki SO_4^{2-} horizon (1783).

Of the known sources of SO_4^{2-} in polar snow and ice, only explosive volcanic eruptions can elevate SO_4^{2-} levels drastically for a period of several years.^{3,4} In April, 1815, the Tambora volcano on Sumbawa Island, Indonesia (8°S , 118°E), erupted violently, causing great devastation. The Tambora eruption is one of the largest since the end of the last glaciation (10,000 years ago), and has been regarded as the greatest in historic time.²⁵ The acidity or SO_4^{2-} signal of Tambora has been found in previous ice cores from both Greenland and Antarctica.^{17,26} Comparison with previous ice core data on Tambora and our relatively accurate dates for the elevated SO_4^{2-} concentrations strongly suggest that the Tambora eruption is responsible for the above SO_4^{2-} horizons found in the Siple and Greenland summit cores.

The flux (mass/area) of an atmospheric chemical species to the surface can be calculated from available ice core data, i.e., the concentration of the species in the liquid sample (mass/volume) and the thickness of the firm or ice sample in water equivalent. For example, the SO_4^{2-} flux (mass/area) for an individual sample is calculated by multiplying the SO_4^{2-} concentration (mass/volume) in a small volume of the melted sample by the thickness or length of the sample in water equivalent. Water equivalent depths are obtained by multiplying the core length by the density at that depth.¹⁵ Subsequently, the annual flux can be obtained by adding the individual sample fluxes for all samples in the year. An ice core "year"

Tambora and Unknown Eruptions

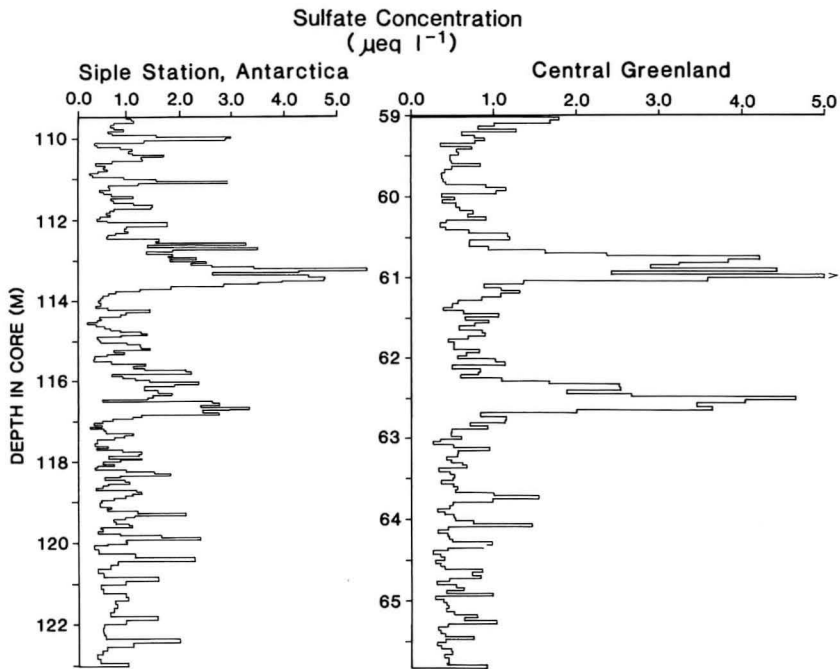


FIGURE 4. Concentrations of SO_4^{2-} in the Siple and the Greenland summit cores in early 19th century.

is defined as the depth interval between two adjacent seasonal minima or maxima (see Figure 1). The annual SO_4^{2-} flux of both cores for 1800 to 1820 is shown in Figure 5. In both cores, the Tambora eruption is associated with the exceptionally high fluxes in 1816 and 1817. At Siple, the 1816 flux ($10.2 \mu\text{g}/\text{cm}^2$) is six times that of the previous year ($1.7 \mu\text{g}/\text{cm}^2$) which is representative of background annual SO_4^{2-} flux in this area. In the Greenland summit core, the Tambora SO_4^{2-} flux is similarly higher than the background (Figure 1).

It is significant that the Tambora eruption is recorded in both Siple and Greenland summit cores. Whether the aerosols of a particular eruption can reach the polar areas and be recorded in the ice strata depends on many factors, such as the magnitude of the eruption, chemical composition of the eruption clouds, and latitude and altitude of the volcano. In Antarctica, due to the lack of large volcanoes on the continent and in the surrounding oceans, few volcanic eruptions have left signals sufficiently large to be detected in ice cores. Only extremely large tropical and southern hemisphere eruptions produce SO_4^{2-} signals detectable above the background level; and eruptions in the middle and high northern latitudes ($\geq 20^\circ\text{N}$) do not produce a detectable signal in Antarctic ice.²⁶ Similarly, eruptions south of 20°S latitude are not likely to be recorded in Greenland ice. Only large explosive eruptions in the low latitudes can significantly perturb

stratospheric sulfur levels in both hemispheres to be recorded in both the Antarctic and Greenland ice sheets.²⁷ Tambora is found in both the Siple and the Greenland summit cores because of its enormous magnitude and its tropical location. In contrast, the 1783 eruption of the Laki volcano in Iceland (64°N), although strongly recorded in Greenland ice, is not found in any Antarctic cores.

VI. UNKNOWN ERUPTION AROUND 1809 A.D.

Figure 5 also reveals another prominent high SO_4^{2-} flux at 1810 in both cores. Sulfate levels return to their respective background concentrations in both cores after 1811. The striking similarity between this event and the Tambora signal in both flux and concentration profiles (Figure 4) strongly suggests that a volcanic eruption is the most probable cause of this high SO_4^{2-} influx to both polar areas. The suddenness of the concentration or flux increase and short duration of the event are apparent evidence of an earlier injection of volcanic sulfur into the atmosphere and the subsequent removal of the extra sulfur burden from the atmosphere; no other natural source has been demonstrated to cause such changes to the atmospheric sulfur reservoir.¹⁸ The coincidence of the increased flux in both polar cores strongly indicates a single eruption as the source for this global increase in atmospheric sulfur. Figure 5 shows that maximum SO_4^{2-} deposition from the 1815 Tambora eruption occurred in 1816, with reduced but still elevated deposition in the following year (1817). The earlier eruption appears to follow a similar 2-year depositional pattern, suggesting a probable eruption time in 1809 (dating is accurate to ± 1 year).

The unknown eruption may be compared with the Tambora eruption just 6 years later. The presence of the SO_4^{2-} signal of the 1809 eruption in both the Greenland and Antarctic cores strongly indicates a low latitude location for this unnamed volcano, probably located between 20°S and 20°N. A more quantitative comparison may be obtained using the calculated fluxes. The net contribution of SO_4^{2-} flux from each eruption is estimated from the total flux corrected for the background. The data are presented in Figure 5 for both cores. The results show that at Siple the net SO_4^{2-} flux from the 1809 eruption is 43% that of Tambora, while in central Greenland it is 58%. Based on these data, the contribution of the 1809 eruption to the global atmospheric sulfur reservoir is estimated to be approximately half that of Tambora. Self et al.²⁵ estimated the ash and tephra volume of Tambora to be 150 km³. Clausen and Hammer,¹⁶ using Greenland ice cores, calculated the 1816 Tambora eruption to have contributed a total of 145 million tons of sulfur (as SO_2) to the atmosphere. The 1809 eruption thus emitted approximately 73 million tons of SO_2 . In comparison, the catastrophic 1883 Krakatau (6°S, 105°E) eruption is estimated to have contributed 19–25 million tons²⁶ or 36 million tons¹⁶ of SO_2 .

If we assume that the ash and tephra volume from the 1809 eruption is also $\approx 50\%$ that of Tambora, then this particular eruption should undoubtedly be ranked with the most explosive eruptions in historic time. An ash and tephra volume of

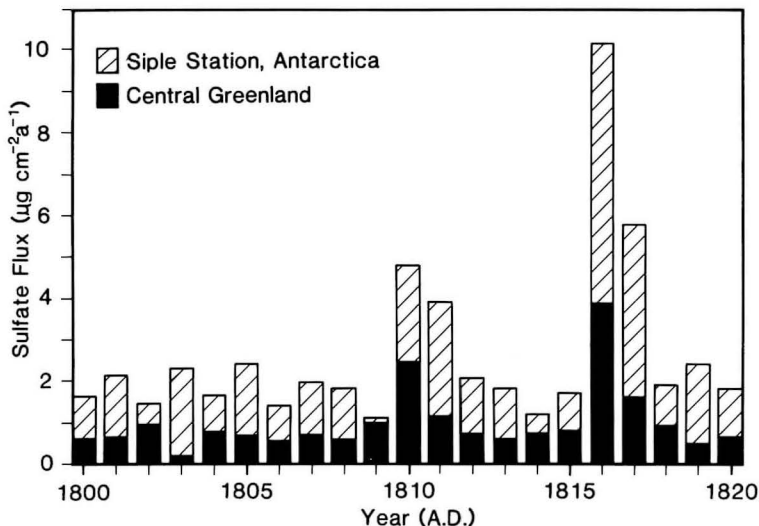


FIGURE 5. Annual SO_4^{2-} flux derived from cores at Siple in West Antarctica and near the summit in Greenland. The method for flux calculation is described in text. Dating is accurate to ± 1 year.

75 km³ would warrant a 5 or 6 on the Volcanic Explosivity Index²⁸ (VEI); and a VEI of 5 or 6 is suggested for this 1809 eruption. In the most recently compiled comprehensive records of global volcanic eruptions dating back to 8300 B.C. by Simkin et al.,²⁹ only Tambora is given the highest VEI, 7. No eruption of >3 VEI is recorded between 1800 and 1812 in this volcanic chronology. Only 11 known eruptions over the last 200 years are given VEI ≥ 5 by Newhall and Self.²⁸ Examples of these types of large explosive eruptions are the 1883 Krakatau eruption (VEI = 6), the 1835 Cosiguina eruption (VEI = 5), and the 1912 Katmai eruption (VEI = 6). Other more recent, but less violent, eruptions are the 1963 Agung eruption (VEI = 4) and the 1980 Mount St. Helen eruptions (VEI = 3, 5). However, the estimate of magnitude of the 1809 eruption and the assigned VEI must be regarded as tentative, for the eruption volume may not be proportionally reflected in the amount of gaseous sulfur emitted. This represents the general difficulty of estimating volcanic eruptions with ice core data.²⁶ Only the amount of sulfur in gases emitted by eruptions can be assessed with ice core acidity or SO_4^{2-} measurements. On the other hand, conventional estimates are usually less accurate for gaseous content than for eruption volumes. Therefore, ice core data can be used to complement other methods of indexing volcanic eruptions. In fact, it has been proposed²⁶ that a glaciological volcanic index be used, based on ice core measurements of explosive volcanic eruptions.

There are several reasons why the 1809 eruption may have escaped earlier detection in Greenland and Antarctic ice cores. High resolution records are not produced for most ice cores because they are not analyzed continuously and in sufficient detail to detect each annual layer. Generally, only selected sections are

analyzed by multiple analytical procedures such as $\delta^{18}\text{O}$, dust, soluble chemical species, and pH. These selected sections are identified by electrical conductivity measurements as possibly containing unusual chemical signals or are suspected to contain specific "known events" such as Tambora or Krakatau. In fact, Hammer³⁰ noted elevated acidity around 1810 in the Crête (Greenland) core which he suggested might be due to unnoticed eruptions. Hammer did not investigate this further in his later work. Legrand and Delmas²⁶ reported two closely spaced (6–8 years) H_2SO_4 or SO_4^{2-} maxima in the early 1800s in several Antarctic ice cores. However, time scale uncertainties arising from the low snow accumulation over East Antarctica (~ 0.04 m H_2O equivalent) made it impossible to determine which was associated with Tambora. In fact, Tambora was first assigned to the older event, and the younger was assigned to Galunggung (7°S , 108°E , $\text{VEI} = 5$) in 1822; however, subsequent work has led to the correct assignment of Tambora to the younger eruption. No later studies have investigated the 1809 eruption, and no interhemispheric comparisons have been explored.

Our data from well-dated cores from both Antarctica and Greenland lead us to propose a major volcanic eruption in the early 19th century (1809 ± 1). The erupting volcano was probably located in the tropics near the equator. The magnitude of the eruption was quite large, with a contribution of ≈ 70 million tons of SO_2 to the global atmosphere. The eruption clouds clearly reached the stratosphere where the sulfuric acid aerosols generated by this unknown eruption were distributed globally. The removal of the volcanic sulfur from the atmosphere occurred over the following 2 years.

VII. CONCLUSION

Ice cores obtained from polar areas of the world contain valuable records of the history of the atmosphere because atmospheric chemical constituents are preserved chronologically in accumulated precipitation. Therefore, chemical analyses of ice cores provide unique and valuable information on histories of atmospheric composition. These records can be integrated to reconstruct the paleoclimatic history on a global scale.

Explosive volcanic eruptions leave signals in polar ice sheets by elevating SO_4^{2-} or acid levels above the natural background. Two such volcanic SO_4^{2-} horizons corresponding to two major eruptions were found in ice cores from central Greenland and West Antarctica. The dates for the SO_4^{2-} horizons, correlated in both cores to within 2 years, were determined to be A.D. 1816–1817 and 1810–1811, respectively. The more recent one (1816–1817) is attributed to the eruption of Tambora volcano in April 1815, the greatest historically recorded volcanic eruption. The earlier eruption probably occurred in 1809 but is not found in published volcanic records. The quantity of SO_4^{2-} deposited in Antarctica and Greenland indicates that the eruption was approximately half the magnitude of Tambora. We suggest that it should be assigned a VEI of at least 5 and probably 6 on the scale of explosivity. For comparison, other large low latitude eruptions

include Tambora (VEI = 7) and the 1883 Krakatau eruption (VEI = 6). The 1809 eruption contributed a total of 62–84 million tons of SO_2 to the atmosphere and affected the stratospheric sulfur budget on a global scale. The distribution of the SO_4^{2-} from this unknown eruption to both hemispheres indicates a tropical location for the erupting volcano, similar to that of Tambora or Krakatau.

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