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PERCHLORATE VARIATIONS OVER 300 YEARS: INFLUENCE OF HUMAN ACTIVITIES, VOLCANIC ERUPTIONS, AND BOLIDE EVENTS

BY

KARI PETERSON

A dissertation submitted in partial fulfillment of the requirements for the

Doctor of Philosophy

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South Dakota State University

2016

PERCHLORATE VARIATIONS OVER 300 YEARS: INFLUENCE OF HUMAN ACTIVITIES, VOLCANIC ERUPTIONS, AND BOLIDE EVENTS

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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TABLE OF CONTENTS

Page

ABBREVIATIONS ix

LIST OF FIGURES xi

LIST OF TABLES xiii

ABSTRACT xiv

1 Introduction 1

1.1 Chemistry of Perchlorate 1

1.2 Perchlorate in the Environment 1

1.3 Sources of Perchlorate 2

1.3.1 Anthropogenic Sources 2

1.3.2 Natural Perchlorate 4

1.4 Environmental Stability of Perchlorate 5

1.5 Health Concerns over Perchlorate 6

1.6 Regulation of Perchlorate 7

1.7 Ice Core Records 8

1.8 Objectives of Research 9

2 Analytical Method Development 13

2.1 Techniques for Measuring Perchlorate 13

2.2 Overview of IC-ESI-MS/MS 14

2.3 Analytical Figures of Merit 15

2.3.1 Selectivity 15

2.3.2 Limit of Detection and Lower Limit of Quantification 16

2.3.3 Accuracy and Precision 17

2.3.4 Inter-laboratory Comparison 18

3 Sample Preparation and Analysis 20

3.1 Ice Core Collection 20

3.2 Ion Chromatography Eluent Preparation 21

3.3 Calibration 22

3.4 Sample Preparation 22

4 Ice Core Dating 25

4.1 Importance 25

4.2 Dating Methods 25

4.2.1 Annual Layer Counting 25

4.2.2 Constant Accumulation Method 27

4.3 Dating SM07C2 27

4.4 Dating the TUNU and Basin 4 Cores 29

5 Long Term Trends in Perchlorate 31

5.1 Pre-Industrial Revolution vs. Modern Concentrations 31

5.2 Perchlorate Concentrations across the Arctic 33

5.3 Possible Anthropogenic Sources 36

5.3.1 Perchlorate as an Oxidizer 36

5.3.2 Perchlorate as an Impurity 39

5.4 Conclusions 41

6 Stratospheric Chlorine 43

6.1 Evidence of Stratospheric Production of Perchlorate 43

6.2 Overview of Chlorine Chemistry in the Stratosphere 43

6.3 Trends in Stratospheric Chlorine and Perchlorate Concentrations 46

6.3.1 Enhanced Chlorine Activation over Antarctica 50

6.4 Mechanisms for Stratospheric Perchlorate Production 52

6.4.1 Chlorine Activation 52

6.4.2 Oxidation 54

6.4.2.1 Ozone-Mediated Oxidation 54

6.4.2.2 Photochemical Oxidation 62

6.4.3 Hydrolysis 64

6.5 Conclusions 64

7 Impact of Volcanic Eruptions 66

7.1 Identification of Volcanic Eruptions in Ice Cores 67

7.2 Elevated Perchlorate Concentrations 68

7.2.1 Correlation between Perchlorate and Sulfate 69

7.3 Volcanoes as a Direct Source 70

7.4 Volcanic Aerosols 71

7.5 Possible Explanations for Increased Perchlorate Concentrations 72

7.5.1 Input of Chlorine to the Stratosphere 73

7.5.2 H_2SO_4 Aerosols 76

7.6 Conclusions 82

8 Unknown Perchlorate Event 85

8.1 Volcanic Impact 86

8.2 Bolide Events 87

8.2.1 Tunguska Event 88

8.2.2 Atmospheric Impacts of Tunguska 90

8.2.2.1 Ozone 91

8.2.2.2 Chlorine 95

8.2.2.3 Aerosols 97

8.3 Future Investigations into the Tunguska Event 99

8.4 Conclusions 101

9 Conclusions and Future Work 103

9.1 Anthropogenic Contributions 103

9.2 Stratospheric Production 104

9.3 Future Work 107

References 111

ABBREVIATIONS

%CV – Coefficient of Variation

2D-IC – Two-Dimensional Ion Chromatography

ANOVA – Analysis of Variance

BD – Bottom Depth

CFA-IC – Continuous Flow Analysis-Ion Chromatography

CFC – Chlorofluorocarbon

CNF – Chilean Nitrate Fertilizer

DWEL – Drinking Water Equivalent Level

ECM – Electrical Conductivity Measurement

EESC – Equivalent Effective Stratospheric Chlorine

EPA – Environmental Protection Agency

ESI – Electrospray Ionization

ESI-MS/MS – Tandem Mass Spectrometry with Electrospray Ionization

FDA – Food and Drug Administration

HCFC - Hydrochlorofluorocarbon

HPLC-ESI-MS/MS – High Performance Liquid Chromatography-Tandem Mass Spectrometry with Electrospray Ionization

IC – Ion Chromatography

IC-ESI-MS/MS – Ion Chromatography-Tandem Mass Spectrometry with Electrospray Ionization

LLOQ – Lower Limit of Quantification

LOD – Limit of Detection

MD – Middle Depth

MRM – Multiple Reaction Monitoring

NAS – National Academy of Sciences

NASA – National Aeronautics and Space Administration

NIS – Sodium/Iodide Symporter

NSS – Non-Sea Salt

OMPS/LP – Ozone Mapping Profiler Suite Limb Profiler

PSC – Polar Stratospheric Cloud

Rfd – Reference Dose

S/N – Signal-to-Noise

SDSU – South Dakota State University

SM07C1 – Summit Station Core 1

SM07C2 – Summit Station Core 2

SWE – Snow Water Equivalent

TD – Top Depth

TTU – Texas Tech University

VEI – Volcanic Explosivity Index

WAIS – West Antarctic Ice Sheet

WOUDC – World Ozone and Ultraviolet Radiation Data Centre

WSS – Water Sample Size

LIST OF FIGURES

Page

Figure 1. Perchlorate Mass Chromatogram 16

Figure 2. Limit of Detection Mass Chromatogram 17

Figure 3. Greenland Core Locations 21

Figure 4. Annual Oscillations in SM07C2 Ions Used for Dating 28

Figure 5. Depth-Age Profiles for Greenland Ice Cores 30

Figure 6. Pre-Industrial Revolution vs. Modern Perchlorate Concentrations 32

Figure 7. Annual Perchlorate Concentrations in Greenland Ice Cores 34

Figure 8. Industrial Perchlorate Production 37

Figure 9. Calcium Concentrations in SM07C2 40

Figure 10. EESC and SM07C2 Perchlorate Concentrations 48

Figure 11. Atmospheric CFC-11 Concentrations 49

Figure 12. EESC and South Pole Perchlorate Concentrations 49

Figure 13. Proposed Oxidation Pathways 54

Figure 14. Perchlorate Seasonal Oscillations in SM07C2 56

Figure 15. Total Ozone at Sondrestrom, Greenland. 58

Figure 16. WAIS Divide Perchlorate Seasonal Oscillations 59

Figure 17. Total Ozone at South Pole 61

Figure 18. Relationship between Radical Chlorine, Ozone, and Perchlorate Concentrations 62

Figure 19. Periods of Elevated Perchlorate Concentrations 67

Figure 20. Perchlorate Concentrations During Volcanic Events 69

Figure 21. Chloride Concentrations During Volcanic Events 74

Figure 22. Chloride Concentrations for El Chichón 75

Figure 23. South Pole Perchlorate Concentrations for Pinatubo 78

Figure 24. Total Ozone at South Pole during Pinatubo 80

Figure 25. Perchlorate Concentrations during Mt. Agung..... 81

Figure 26. Unknown Perchlorate Event..... 86

Figure 27. Nitrate Concentrations during the Tunguska Event 93

Figure 28. Chloride Concentrations during the Tunguska Event..... 96

Figure 29. Perchlorate Concentrations Between 1964 and 1966..... 100

Figure 30. Stratospheric Perchlorate Production 107

LIST OF TABLES

Page

Table 1. Mass Spectrometer Parameters 15

Table 2. Quality Control Data 18

Table 3. Inter-Laboratory Comparison..... 19

Table 4. Sample Decontamination Assessment 24

Table 5. Coefficient Values..... 30

Table 6. The Atmospheric Residence Times of Common CFCs. 44

Table 7. Oxidation Rate Constants..... 54

Table 8. ANOVA Data..... 70

ABSTRACT

PERCHLORATE VARIATIONS OVER 300 YEARS: INFLUENCE OF HUMAN ACTIVITIES, VOLCANIC ERUPTIONS, AND BOLIDE EVENTS

KARI M. PETERSON

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Perchlorate, which derives from both anthropogenic and natural sources in the current environment, constitutes a significant health risk to humans because it competitively inhibits iodine uptake by the thyroid gland. Thus, there has been considerable interest in reducing the human exposure to environmental perchlorate by limiting the release of perchlorate from anthropogenic sources. However, a lack of understanding of the relative contributions from anthropogenic and natural sources has prevented widespread regulation. A 300-year ice core perchlorate record from Summit Station, Greenland (1700-2007 C.E.) that extends beyond the onset of the Industrial Revolution (1850 C.E.) is used to assess the anthropogenic contributions to environmental perchlorate. The perchlorate record shows that the onset of the Industrial Revolution did not impact perchlorate levels in the environment.

Despite remarkably consistent concentrations for at least 280 years (1700-1980 C.E.), perchlorate concentrations begin unexpectedly to increase around 1980, its concentration by the early 21st century approximately tripling pre-1980 concentrations. Perchlorate is manufactured primarily for use as an oxidizer and is also produced naturally in the atmosphere. Post-1980 perchlorate concentrations are most likely

influenced by changing atmospheric conditions that favor the atmospheric production of perchlorate. Rising stratospheric chlorine concentrations resulting from the emission of chlorine-containing compounds, including chlorofluorocarbons (CFCs), are likely indirectly responsible for approximately two-thirds of the perchlorate present in the current environment.

Variations in perchlorate concentrations suggest that natural perchlorate production occurs in the stratosphere and the production rate is dependent on a delicate balance between activated (i.e., radical) chlorine species and ozone concentrations. Furthermore, a link between large, stratospheric volcanic eruptions and brief periods of increased perchlorate concentrations has been discovered. These volcanic eruptions increase stratospheric H_2SO_4 aerosols, which provides a surface for heterogeneous chlorine activation, resulting in increased perchlorate production. Finally, we suggest that a superbolide event, the Tunguska meteor explosion in 1908, may be primarily responsible for extraordinarily high perchlorate levels between 1908 and 1914. The breakup of the Tunguska meteor could have directly released perchlorate, or the increased aerosol/dust from the explosion could have enhanced chlorine activation in the stratosphere leading to elevated perchlorate concentrations.

1 Introduction

1.1 Chemistry of Perchlorate

Perchlorate (ClO_4^-) is a highly oxidized, nonvolatile form of chlorine that consists of a chlorine atom bonded to and surrounded by four oxygen atoms in a tetrahedral geometry[1]. Due to a large kinetic barrier towards reduction, perchlorate is very slow to react despite its potential as an oxidizer. As a result, perchlorate reduction is not common[2] and perchlorate is quite stable under normal conditions. Because the negative charge on perchlorate is delocalized across four oxygen atoms, perchlorate is a poor nucleophile and is a non-complexing anion. Thus, perchlorate is often used as an inert electrolyte in inorganic and electrochemical studies involving metal ions in solution. Finally, as a result of perchlorate's low affinity for cations, perchlorate salts are highly soluble in both water and organic solvents[2].

1.2 Perchlorate in the Environment

Due to its high solubility in water, the environmental reservoir of perchlorate is typically surface water and groundwater systems[1]. Perchlorate has been identified in various water systems including multiple groundwater systems across the southwest United States[3–6], in seawater off the coast of Maine[7], and in the lower Colorado River[8]. As an example, because the lower Colorado River serves as a source of drinking water for more than 15 million people, there is substantial human exposure to perchlorate in the United States. In addition, water from the Colorado River is used to irrigate fields from which produce is shipped across the country[8], introducing perchlorate into the food supply. The Food and Drug Administration (FDA) has reported perchlorate contamination in fruits and vegetables across the United States[9], as well as in dairy

milk[10]. Blount et al.[11] also found measureable quantities of perchlorate in chicken feed and eggs in California and Arizona. Perchlorate contamination, however, is not limited to the United States. El Aribi et al.[12] measured perchlorate in various consumer products from across the world. The authors found measurable levels of perchlorate in bottled water from the United States, Canada, India, and Portugal. Perchlorate contamination was also found in various food products from the United States, Canada, China, and several Latin American and European countries. Finally, El Aribi et al.[12] found perchlorate contamination in beer and wine samples from every continent (except Antarctica). Thus, human exposure to perchlorate is a worldwide problem.

1.3 Sources of Perchlorate

1.3.1 Anthropogenic Sources

In the United States, perchlorate is primarily manufactured as ammonium perchlorate (NH_4ClO_4), and to a lesser extent potassium perchlorate ($KClO_4$), for use as an oxidizer[13]. Ammonium perchlorate is often used in solid fuels due to its ease of handling and manufacturing[14]. As a result, ammonium perchlorate has been used as a primary component of rocket fuel, as well as in the National Aeronautics and Space Administration's (NASA) space shuttle solid rocket boosters[15]. Ammonium and potassium perchlorate are also used as the major component of solid propellants in many national defense applications including tactical and strategic missiles, training munitions, and many underwater explosives[14]. Finally, perchlorate is used commercially in highway flares and fireworks/pyrotechnics[13].

When used as an oxidant, perchlorate undergoes essentially complete conversion to chloride[1,13]. Analysis of space shuttle plumes showed elevated levels of chloride, but

no elevation in perchlorate levels[13]. In addition, the analysis of fully burnt road flares indicate that only about 0.05% of the original perchlorate remains after burning[16]. This suggests that it is unlikely that anthropogenic contribution to environmental perchlorate stems from the dispersal of perchlorate when used for intended purposes. Instead, the primary anthropogenic contribution to environmental perchlorate may result from the disposal or unavoidable release of the solid salts of perchlorate during manufacture and other applications[1].

Perchlorate pollution may also come from sodium chlorate ($NaClO_3$) that is contaminated with perchlorate. Sodium chlorate is produced through the electrolysis of an acidic brine solution, and is primarily used for bleaching pulp in the paper industry. Because the oxidation of brine (NaCl) to chlorate has a similar electrochemical potential as the oxidation of brine to perchlorate, manufactured sodium chlorate is usually contaminated with perchlorate. Studies have reported that laboratory grade sodium chlorate contains as high as 0.2% w/w (2,000 mg kg^{-1}) perchlorate, whereas analytical grade contains anywhere from 200-900 mg kg^{-1} *(ref 1)*. Considering that in 2012 over 3 million tons of sodium chlorate were produced worldwide, and that production is expected to exceed 4 million tons by 2017 *(ref 17*), this may represent a relevant source of environmental perchlorate.

Another possible source of anthropogenic perchlorate is through the historical use of Chilean nitrate mineral[13], which contains approximately 0.1% perchlorate[18]. Chilean nitrate has been used as a fertilizer (CNF), in gunpowder, and other explosives. Chile began exporting its nitrate to the United States and several European countries including England, France, Germany, and Italy in 1830 with maximum exports in 1920 *(ref 18)*.

Chilean nitrate controlled the world nitrate market throughout the nineteenth and early twentieth centuries. However, with the development of the Haber-Bosch process in 1918, synthetic nitrogen became a major competitor to Chilean nitrate. By 1950, Chilean nitrate only represented 15% of the world nitrogen market and by 1980 the share dropped to 0.14% *(ref 18)*. Due to limited data on the import of Chilean nitrate to the United States between 1830 and 1938, it remains difficult to estimate the amount of perchlorate that was presumably imported during this time. However, using the historical information available, Jackson et al.[18] were able to conservatively estimate that approximately 16.1 million kg of perchlorate were imported into the United States through Chilean nitrate between 1938 and 1968. Thus, it is plausible that the use of CNF and explosives containing Chilean nitrate could have represented a significant source of anthropogenic perchlorate in the environment.

1.3.2 Natural Perchlorate

The natural occurrence of perchlorate was thought to be confined to the nitrate deposits in the Atacama Desert, Chile[18], and that perchlorate in the general environment derived exclusively from anthropogenic sources. However, the measurement of perchlorate in pre-anthropogenic groundwater[4–6] has shown that natural sources of perchlorate exist outside the Atacama Desert. Additionally, perchlorate has been detected in the soils of the Dry Valleys, Antarctica[19], an area that is unlikely impacted by human activities.

Non-anthropogenic perchlorate is formed or produced from other forms of chlorine in the natural environment. Although the natural production of perchlorate is not well understood, it is believed to be produced solely in the atmosphere. Perchlorate

found in groundwater systems located in the high plains of Texas and New Mexico demonstrated a high correlation with the atmospherically derived iodate[3] (IO_3^-). Elevated levels of ^{36}Cl in natural perchlorate suggest that the atmospheric production of perchlorate likely occurs in the stratosphere[20], where ^{36}Cl is abundant. Additionally, Furdui and Tomassini[21] noted a strong correlation between perchlorate concentrations in an ice core from Devon Bay, Canada and ozone measurements from nearby Resolute Bay, Canada between 2002 and 2006, further suggesting a likely stratospheric production of perchlorate involving ozone. Finally, the perchlorate deposits in the Atacama Desert demonstrate elevated $\Delta^{17}O$ values[22], which is another strong indication of ozone involvement in atmospheric production.

1.4 Environmental Stability of Perchlorate

Perchlorate is exceptionally stable in the environment and, due to its high solubility in water, persists and accumulates in water systems. Although the reduction of perchlorate to chloride in aqueous solutions is thermodynamically favorable (E_0 = +1.388 V), there is a large kinetic barrier to reduction[1]. Reduction of perchlorate via protonation is also unlikely because perchlorate's conjugate acid, perchloric acid, is a strong acid. Thus, the direct reduction of perchlorate in water systems is considered negligible[1]. Additionally, due to the delocalization of the negative charge across four oxygen atoms, perchlorate is a poor nucleophile and non-complexing anion. As a result, perchlorate is not readily bound to particle surfaces or sorbed by sediments, resulting in its persistence in water systems[2]. Perchlorate that does sorb to sediments can be taken up by plants[23], but it is unclear whether plants metabolize perchlorate[24]. The perchlorate that plants uptake is released again when the plant undergoes senescence[23,25]. Therefore, the only

possibly effective way for perchlorate to be removed from the environment is by reduction via bacteria that use perchlorate as an electron acceptor in anaerobic environments. However, bacteria preferentially use NO_3^- over perchlorate as an electron acceptor[25]. The reason for this is not well understood, but could be because of the much greater availability of NO_3^- compared to perchlorate. Thus, perchlorate readily accumulates in the environment.

1.5 Health Concerns over Perchlorate

The accumulation of perchlorate in groundwater and surface water systems has become a concern due to the negative health effects of perchlorate exposure. Perchlorate competitively inhibits the uptake of iodine through the sodium/iodide symporter (NIS) to the thyroid gland, which compromises the production of thyroid hormones[26–28]. Sustained inhibition of iodine uptake can lead to hypothyroidism causing metabolic problems in adults. In addition, the adequate production of thyroid hormones is vital to the normal growth and development of fetuses and young children. Fetuses and children with compromised thyroid hormone production are more likely to display behavioral problems, attention deficit hypertension disorder (ADHD), reading and language deficits, lower IQs, and are at greater risk to develop cerebral palsy[26]. Therefore, young children and pregnant mothers, in whom ingested perchlorate is transported to the fetus, are particularly vulnerable to perchlorate exposure[27,28]. Furthermore, infants and children generally intake more perchlorate per unit body mass than any other subpopulation due to the consumption of dairy foods and breast milk, which generally contain high levels of perchlorate[29].

1.6 Regulation of Perchlorate

Due to the adverse health effects of perchlorate exposure, there has been considerable interest and effort in regulating perchlorate in drinking water. In 2005 the National Academy of Sciences (NAS) set an official reference dose (Rfd), which is an estimate of the daily exposure level below which no adverse health effects are expected to occur in humans, for perchlorate at 0.0007 mg kg^{-1} day^{-1} *(ref 27)*. The Environmental Protection Agency (EPA) also adopted this Rfd the same year[30]. The Rfd includes a 10-fold uncertainty factor so that the most sensitive populations (pregnant women, young children, and those with low-iodide intake) are protected. In addition to establishing an Rfd, the EPA also set a Drinking Water Equivalent Level (DWEL) at 24.5 μg L^{-1} *(ref 30)*. The DWEL represents the concentration of perchlorate in drinking water below which no adverse health effects are expected to occur, assuming a 70 kg individual consumes 2 L of water per day, and that all perchlorate exposure is from drinking water[26,30]. Both the Rfd and the DWEL are recommended exposure limits, not enforceable limits.

Despite the establishment of an Rfd and a DWEL in the United States, enforceable regulation of perchlorate has been limited to the state level in only a few states. California originally set a maximum perchlorate concentration in drinking water at 6 μg L^{-1} in 2007. In 2015, however, California announced a goal to limit perchlorate concentrations in drinking water to below 1 μg L^{-1} *(ref 31)*. Oregon requires the concentration of perchlorate in drinking water to be less than 4 μg L^{-1} *(ref 3*), while Massachusetts requires the concentration to be less than 2 μg L^{-1} *(ref 32)*. Nationwide regulation of perchlorate in drinking water remains difficult, partly because of a lack of understanding of the relative source contributions of natural and anthropogenic sources to

environmental perchlorate. Currently, it is unknown how much of the perchlorate in the environment derives from anthropogenic sources, which can be controlled and potentially limited through regulation, and how much of the perchlorate in the environment derives from natural sources. Therefore, the knowledge of relative contributions is vital to the effective mitigation of perchlorate exposure by regulation.

1.7 Ice Core Records

Snow, which carries chemical substances from the atmosphere, accumulates continuously on the glaciers in polar regions, such as Antarctica and Greenland. Thus, ice cores from these areas provide a chronological record of the chemical substances in the environment. Ice core records from Greenland, in particular, have been used in paleoclimatology studies[33,34]. Additionally, ice cores from Greenland are often used to study environmental pollutants, including in the assessment of natural and anthropogenic contributions of an environmental pollutant. For example, ice core records have indicated that the current environmental levels of NO_3^- and sulfate (SO_4^{2-}) are elevated due to anthropogenic emissions of these species[35], when compared to the levels prior to the Industrial Revolution. Thus, a similar ice core record of perchlorate in the environment could be very beneficial in the assessment of the natural and anthropogenic sources of perchlorate.

Perchlorate has been measured in selected samples of ice cores from the Canadian Arctic[21,36] and from the Upper Fremont Glacier in Wyoming, USA[36]. Fifteen samples from the Upper Fremont Glacier covering the time period 1726-1993 were analyzed for perchlorate. Perchlorate concentrations in these measurements range from below the method detection limit (0.2 ng L^{-1}) in all pre-1982 samples to 2.6 ng L^{-1} *(ref 36)*. Rao et

al.[36] also collected snow samples from the Eclipse Icefield, Yukon Territory, Canada covering the time periods of 1970-1973, 1982-1986, and 1999-2002. Perchlorate concentrations in these samples ranged from below the method detection limit (0.2 ng L^{-1}) to 8.8 ng L^{-1}, with lower concentrations in the samples dated between 1970 and 1973 than in samples dated after 1982. Furthermore, Furdui and Tomassini[21] analyzed ice samples from the Devon Island Ice Cap, Canada covering the time period of 1996-2005. Perchlorate concentrations in these samples ranged approximately 1-18 ng L^{-1}.

While the ice core perchlorate records discussed above provide insight into the more recent environmental perchlorate levels, and even suggest the influence of anthropogenic activities on environmental perchlorate, the in-depth study of environmental perchlorate would greatly benefit from a comprehensive record of perchlorate in the environment. A continuous, high-temporal resolution ice core perchlorate record that dates prior to the onset of the Industrial Revolution would allow for the assessment of the natural levels of perchlorate and the natural variations in these levels. This would allow for the accurate evaluation of the anthropogenic contribution to perchlorate in the current environment. Such information is valuable to future plans to effectively regulate perchlorate. Furthermore, a continuous perchlorate record with high temporal resolution, in which multiple samples per year are analyzed, could give valuable insight into the natural production of perchlorate, as well as the atmospheric and climatic conditions that influence its production.

1.8 Objectives of Research

The primary objective of this research is to gain a better knowledge of the history of perchlorate in the environment. Accurate measurement of perchlorate in ice cores can

provide data that will aid in this effort. As discussed above, polar ice cores provide chronological records of the chemical substances in the environment, and thus represent an important tool in the study of the past and present environment. Greenland ice core records, in particular, have been proven to be very valuable in the study of the anthropogenic contributions to environmental pollutants, such as NO_3^-, SO_4^{2-} *(ref 35)*, and lead (Pb)[37–39].

In this research, a 150 m ice core from Summit Station, located in central Greenland (72°34'46" N, 38°27'33" W), was used to create a 300-year record of environmental perchlorate. This record represents the longest and most comprehensive record of environmental perchlorate to date. The record provides the opportunity to obtain an accurate measure of the natural environmental perchlorate level, and to assess the variability in the natural level, which allows for a robust estimation of the anthropogenic contributions to environmental perchlorate. Furthermore, the snow accumulation rate at Summit Station, Greenland is relatively high, receiving approximately 0.24 m ice equivalent of snow per year[40]. Therefore, the analysis of multiple samples per year allows for investigation into the intra-annual variation in perchlorate concentrations. Such information allows for the study of how atmospheric conditions impact the natural production of perchlorate. For example, the examination of the seasonal variations in perchlorate could provide insight into the role of sunlight and/or the impact chemically reactive species have on environmental perchlorate concentrations.

The Greenland ice core perchlorate record will be used to achieve additional project objectives. The first of these additional objectives is to determine the relative

contributions of the natural and anthropogenic sources to perchlorate in the current environment. The magnitude of the natural sources of perchlorate, and the variability in these sources, will be established through the examination of the portion of the record prior to the onset of anthropogenic impact. The perchlorate in more recent snow likely represents perchlorate derived from both natural and anthropogenic sources. Thus, the difference between perchlorate levels in recent snow/ice samples and perchlorate levels in ice dated prior to the onset of the Industrial Revolution likely represents the anthropogenic contributions to environmental perchlorate, assuming the natural sources of perchlorate have remained unchanged. This robust estimate of the anthropogenic contributions to environmental perchlorate will be valuable in the efforts to minimize the anthropogenic sources of perchlorate, as well as in the regulation of perchlorate in drinking water.

In addition to the 300-year perchlorate record obtained from the Summit Station (central Greenland) ice core, perchlorate measurements were also made on ice cores from two additional locations in Greenland: TUNU, located in northern Greenland (78.1° N, 34.0° W)[41], and Basin 4, located in southern Greenland (62.31° N, 46.3° W)[42]. Comparison of the three separate perchlorate records allows for exploration into the spatial variability in perchlorate concentrations and trends in these concentrations across Greenland. This could yield information about the atmospheric transport of perchlorate from specific locations, using knowledge of circulation. Furthermore, perchlorate concentrations and trends from these three Greenland cores can be compared with the measurements obtained by Rao et al.[36] and Furdui and Tomassini[21] from Canadian Arctic

locations to gain a greater understanding of the variability in perchlorate concentrations across the Arctic.

Another objective of the project is to explore conditions that possibly impact the atmospheric production of perchlorate. This will be accomplished through the detailed analysis of the various perchlorate records. The high temporal resolution of the records will allow for the assessment of the intra-annual variations in perchlorate concentrations. Such information can give insight into if and how environmental/atmospheric conditions influence perchlorate production. For example, perchlorate has been observed to reach peak concentrations in the spring/summer and minimum concentrations in the winter in the Arctic[21,36], suggesting that the production of perchlorate or perchlorate precursors is dependent on the availability or intensity of solar radiation. Additionally, Furdui and Tomassini[21], through the examination of seasonal variations, noted that perchlorate shows a strong correlation with ozone, suggesting the involvement of ozone in the production of perchlorate. Finally, it has been speculated that perchlorate concentrations may be influenced by volcanic eruptions[21,36]. Prior analysis of Summit, Greenland ice cores has yielded records of volcanic eruptions[43–45]. Because the perchlorate record from Summit, Greenland will include periods when volcanic eruptions occurred, the influence of volcanic eruptions on perchlorate production may be investigated through perchlorate variations during those periods.

2 Analytical Method Development

2.1 Techniques for Measuring Perchlorate

As the work by Rao et al.[36] and Furdui and Tomassini[21] demonstrates, perchlorate concentrations in ice cores from the Arctic are generally at the ng L^{-1}, or even sub-ng L^{-1} level. Thus, the measurement of perchlorate in ice core samples requires an ultra-sensitive technique. Conventional ion chromatography (IC) with conductivity detection can measure perchlorate down to 0.5 μg L^{-1} *(ref 46)*. Two-dimensional ion chromatography (2D-IC) with conductivity detection offers a slightly better limit of detection (LOD) for perchlorate at 12 ng L^{-1} *(ref 47–49)*. However, a lower LOD is still needed to quantify perchlorate in most ice core samples, especially those dated prior to the Industrial Revolution. The use of mass spectrometry has achieved lower LODs than those of conventional chromatography techniques. For example, Koester et al.[50] utilized tandem mass spectrometry with electrospray ionization (ESI-MS/MS) to measure perchlorate down to 10 ng L^{-1}. However, in the presence of non-target ions the LOD increased to 50 ng L^{-1}, indicating the need for chromatographic separation prior to mass spectrometry. A method utilizing high performance liquid chromatography-tandem mass spectrometry with electrospray ionization (HPLC-ESI-MS/MS) was able to measure perchlorate down to 5 ng L^{-1} *(ref 51)*. Finally, the technique of ion chromatography-tandem mass spectrometry with electrospray ionization (IC-ESI-MS/MS) has demonstrated the most success in the measurement of low levels of perchlorate. Furdui and Tomassini[21] were able to achieve a LOD of 0.3 ng L^{-1} without pre-concentration and Jiang et al.[52] were able to obtain a LOD of 0.2 ng L^{-1} utilizing 10-fold online pre-concentration. However, the study of perchlorate, especially the natural levels of

perchlorate, would benefit from a more sensitive technique, as the natural variability in perchlorate is likely at the low sub-ng L^{-1} level. In addition, a rapid technique that does not require pre-concentration procedures is desirable so that a large number of samples can be analyzed quickly.

2.2 Overview of IC-ESI-MS/MS

The separation of perchlorate from other matrix species was accomplished using a ThermoFisher (formerly Dionex, Sunnyville, CA) DX500 ion chromatography system consisting of an IP25 isocratic pump and a CD25 conductivity detector. A Dionex AS40 autosampler was used to load samples from 5 mL vials into a 600 µL injection loop. The samples were subsequently injected onto a Dionex IonPac AS16 (2 x 250 mm) analytical column. Perchlorate was eluted from the column with 60 mM sodium hydroxide (NaOH) at 0.3 mL min^{-1}, which was suppressed using an AERS-500 (2 mm) suppressor. The effluent from the suppressor was mixed with a 90% (v/v) acetonitrile:10% water solution at 0.3 mL min^{-1} to decrease the surface tension and aid in the nebulization of the sample. This mixture was delivered to the electrospray (ESI) inlet/nebulizer of an AB SCIEX (Framingham, MA) QTRAP 5500 triple quadrupole mass spectrometer operating in negative ion mode. In order to analyze both $^{35}ClO_4^-$ (*m/z* 99.0 to 83.0) and $^{37}ClO_4^-$ (*m/z* 101.0 to 85.0), multiple reaction monitoring (MRM) was utilized. The individual mass spectrometry ion source, gas, and compound specific operational parameters can be seen in Table 1 *(ref 53).*

Table 1. Ion source, gas, and compound specific operational parameters for the AB SCIEX QTRAP 5500 triple quadrupole mass spectrometer[53].

Parameter	Optimized Condition
Source Temperature	600° C
Ionspray Voltage	-3,000 V
Curtain Gas	20 psi
Ion Source Gas 1	40 psi
Ion Source Gas 2	15 psi
Collision Gas	Medium
Declustering Potential	-25 V
Entrance Potential	-10 V
Collision Energy	-40 V
Collision Cell Exit Potential	-5 V
Dwell Time	1,000 ms

2.3 Analytical Figures of Merit

2.3.1 Selectivity

The mass chromatogram of a perchlorate sample is shown in Figure 1a. Perchlorate elutes at approximately 10.2 min. The peak area for $^{35}ClO_4^-$ (blue signal) was used for the quantification of perchlorate and the 3:1 peak area ratio between the $^{35}ClO_4^-$ peak and the $^{37}ClO_4^-$ (red signal) peak verifies that the detected species is perchlorate. The method demonstrates excellent selectivity for perchlorate. The common impurities in Greenland snow samples consist mostly of ionic species, including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} at the μg L^{-1} level[54]. Figure 1b shows a typical Greenland sample containing these matrix species, but no perchlorate. No peaks interfere with the perchlorate peak eluting at approximately 10.2 min.

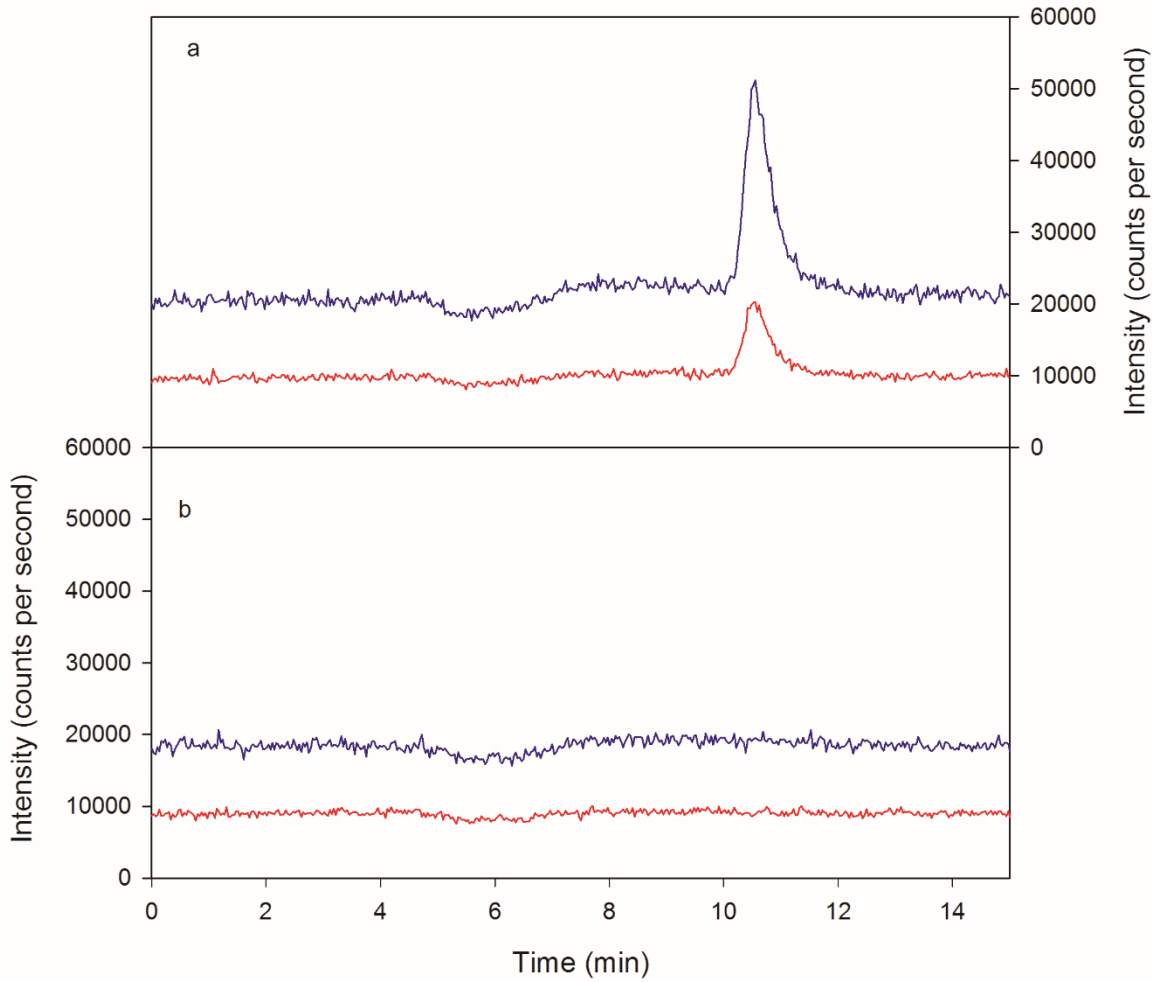

Figure 1. Mass chromatogram of a typical Greenland ice sample containing matrix species along with perchlorate (a) and a typical Greenland ice sample containing matrix species but no perchlorate (b). The blue signal represents $^{35}ClO_4^-$ and the red signal represents $^{37}ClO_4^-$ *(ref 53)*.

2.3.2 Limit of Detection and Lower Limit of Quantification

The LOD, defined as a signal-to-noise (S/N) ratio of three, was determined by analyzing the mass chromatogram and estimating the peak-to-valley baseline noise. The concentration that yielded a S/N ratio of three using this method was 0.1 ng L^{-1} (Figure 2). The LOD was further verified using the standard deviation ($\sigma = 0.04$) of the replicate analysis ($n = 9$) of a 0.75 ng L^{-1} standard. Thus, the LOD of the method described above

was established to be 0.1 ng L^{-1} *(ref 53)*. The lower limit of quantification (LLOQ), defined as a S/N ratio of ten, was determined to be 0.3 ng L^{-1} *(ref 53)*, based upon the analysis of the mass chromatogram. The linear dynamic range was determined as the range of concentrations at which the relative standard deviation and the percent deviation from the nominal concentration for each standard analyzed was within ±20% *(ref 55)*. Using these criteria, the linear dynamic range of the method was determined to be 0.3-10.0 ng L^{-1} *(ref 53)*. When the perchlorate concentration of a sample exceeded this range, the sample was diluted so that its concentration would be within the linear dynamic range and reanalyzed.

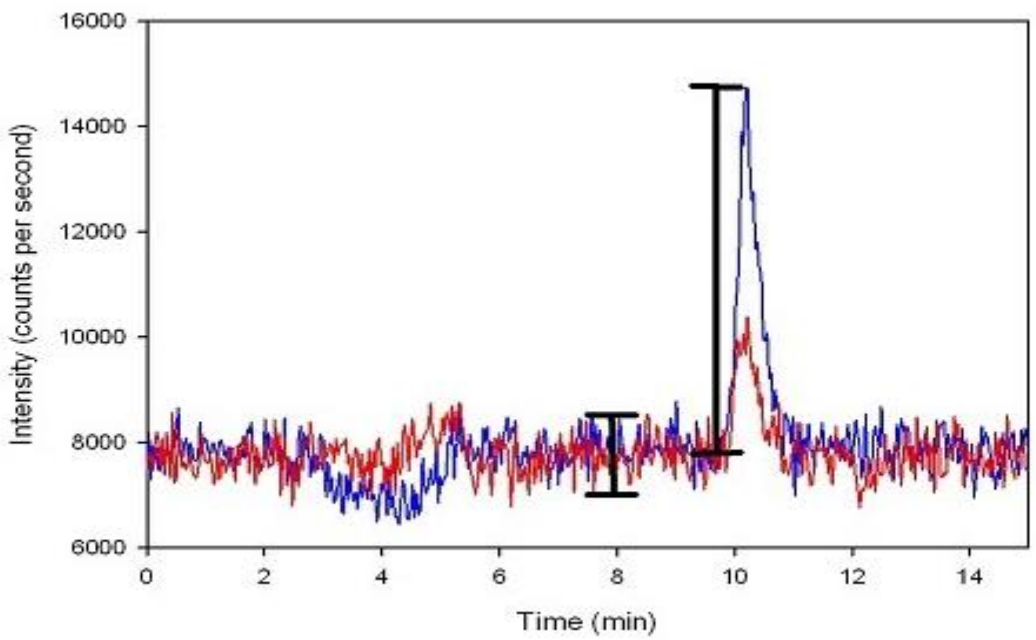

Figure 2. Mass chromatogram of a 0.10 ng L^{-1} standard used to determine the LOD (S/N>3). The blue signal represents $^{35}ClO_4^-$. The red signal represents $^{37}ClO_4^-$ *(ref 53)*.

2.3.3 Accuracy and Precision

The accuracy and precision of the method was determined by intra-assay (1 day of analysis, n = 3) and inter-assay (3 days of analysis, n = 9) analysis of 1.0 and 9.0 ng L^{-1} perchlorate standards. The accuracy was assessed by measuring the recovery of

perchlorate added to deionized water and the precision was assessed by determining the coefficient of variation (%CV). As shown in Table 2, the recovery was between 97.3-98.5% and the precision was between 3.8-12.8%.

Table 2. Quality control data for the analysis of perchlorate by IC-ESI-MS/MS[53]**.**

Nominal Concentration (ng L^{-1})	Intra-assay Recovery (%)[a]	Inter-assay Recovery (%)[b]	Intra-assay Precision (%CV)[a]	Inter-assay Precision (%CV)[b]
1.00	97.38	98.46	7.80	12.76
9.00	97.25	98.27	3.76	6.73

[a]Mean for 1 day of validation (n = 3)
[b]Mean for 3 days of validation (n = 9)

2.3.4 Inter-laboratory Comparison

In order to further validate the method, an inter-laboratory comparison was performed in collaboration with Texas Tech University (TTU) in Lubbock, Texas. Perchlorate standards and meteorite samples were prepared and analyzed by TTU[36], and then independently analyzed at South Dakota State University (SDSU) using the method described above. The results from this study can be seen in Table 3. The percent deviation between the measured concentrations of the standards is less than 10%. There are slightly higher deviations for the two meteorite samples analyzed. This could be due to the measured perchlorate concentrations falling outside the linear dynamic range of the SDSU method. Due to limited sample volume, however, no dilution of these samples could be performed to obtain a more accurate comparison. There also could have been an unknown matrix affect in the meteorite samples that is not present in ice core samples that may have impacted the accuracy of the measurement.

Table 3. Results of an inter-laboratory comparison study between TTU and SDSU[53].

Sample	TTU Concentration (ng L^{-1})	SDSU Concentration (ng L^{-1})	Percent Deviation
Purified water	<1	<LLOQ	N/A
1 ng L^{-1} standard	1.18	1.3	9.2
5 ng L^{-1} standard	5.78	6.0	3.7
10 ng L^{-1} standard	11.3	12.1	6.6
Fayteville 10	52	64.2	19.0
Fayteville 10 fusion layer	140	157.3	11.0

3 Sample Preparation and Analysis

3.1 Ice Core Collection

Three Greenland ice cores, an ice core from the South Pole, and snow pit samples from the West Antarctic Ice Sheet (WAIS) Divide were used over the course of this study. In June-July 2007 four ice cores were drilled near Summit Station, Greenland (72°34'46" N, 38°27'33" W). The primary perchlorate analysis was performed on core 2 (SM07C2) of these cores, which was 150 m deep and 10 cm in diameter. The second Greenland core used for perchlorate analysis (20 m deep, 10 cm diameter) was drilled in 1996 near the TUNU site (78.1° N, 34.0° W)[41]. The third Greenland core was drilled near the Basin 4 site (62.31°N, 46.3° W) in 2002 (~23.65 m deep, 8 cm diameter)[56]. The location of these core sites in Greenland can be seen in Figure 3 *(ref 57)*. The South Pole ice core (10 cm in diameter) was drilled in 2004-2005. After drilling, each meter section of the cores was contained in a plastic bag and placed inside reflective cardboard tubes. The reflective cardboard tubes were packed inside insulated cardboard boxes for transport. All cores were maintained at or below a temperature of -20° C during shipment and storage. The WAIS Divide (79.467° S, 112.085° W) samples were collected in January 2013 from a 2.8 m snow pit. Individual samples were placed inside clean plastic specimen cups and packed inside an insulated cardboard box for transport. Once again the samples were maintained at or below -20° C during shipment and storage.

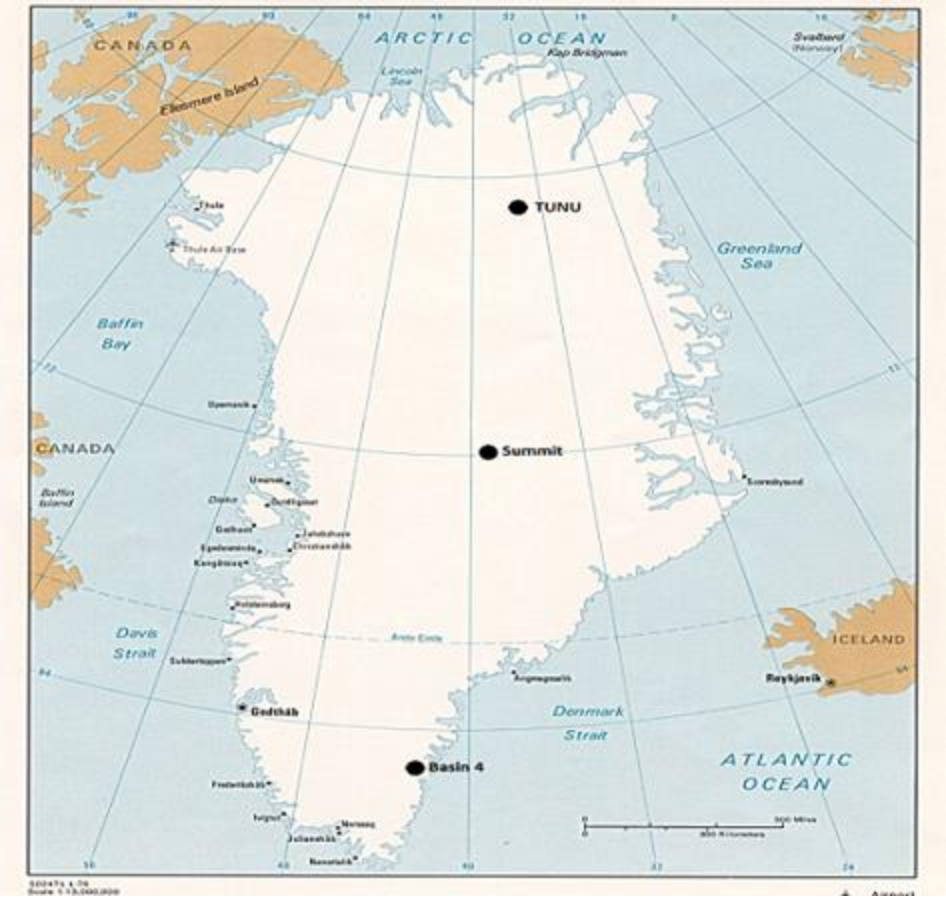

Figure 3. Greenland map showing the location of the Summit, TUNU, and Basin 4 ice core sites. Image adapted from Maps of the World[57].

3.2 Ion Chromatography Eluent Preparation

A 0.5 M NaOH stock solution in ultrapure deionized water was prepared from 50% (w/w) NaOH purchased from Fisher Scientific (Fair Lawn, NJ). The 60 mM NaOH used to elute perchlorate from the column was prepared by dilution of this stock solution with ultrapure deionized water. Following dilution, the 60 mM solution was degassed under vacuum for approximately 45 min. The 90% acetonitrile solution, used to decrease the surface tension and aid in the nebulization of the sample, was prepared by diluting HPLC grade acetonitrile purchased from Fisher Scientific with ultrapure deionized water.

This solution was also degassed under vacuum for approximately 45 min following dilution.

3.3 Calibration

Analytical grade potassium perchlorate ($KClO_4$) purchased from Acros Organics (Geel, Belgium) was used to prepare a 1,000 mg L^{-1} perchlorate stock solution in ultrapure deionized water. A 1.00 μg L^{-1} intermediate stock solution was prepared by dilution of the 1,000 mg L^{-1} stock. Daily perchlorate calibration standards (0.30, 0.75, 2.00, 5.00, and 10.00 ng L^{-1}) were prepared from the intermediate stock solution. Calibration curves were constructed by plotting the $^{35}ClO_4^-$ peak area against the nominal concentration. Linear least squares regression was used to fit the data.

3.4 Sample Preparation

The exposed surfaces of an ice core are assumed to become contaminated during drilling and handling. Therefore, care must be taken to remove all previously exposed surfaces in order to obtain a clean, uncontaminated sample. All samples from the SM07C2, TUNU, and South Pole cores were cut from one-quarter of the 10 cm diameter cores using a band-saw in a -20° C walk-in freezer. Samples from the Basin 4 core were cut from one-half of the 8 cm diameter core. Prior to use, the band-saw blade was washed with ethyl alcohol and then with ultrapure deionized water. Also, sample specimen cups used to melt individual ice samples were thoroughly washed with ultrapure deionized water and allowed to air dry prior to use.

The exposed surfaces of all samples below the core depth of 57 m were removed via washing with ultrapure deionized water. These samples were cut into “ice cubes” (4 x 4 x 3.5 cm) and placed into carrier cups in the -20° C walk-in freezer. These samples

were then transferred from the freezer to the analytical laboratory for washing. Each individual sample was handled with clean tongs and held under the ultrapure deionized water stream until a layer of at least 2 mm of the previously exposed surfaces was washed away. The sample was then placed into a pre-cleaned sample cup, capped, and allowed to melt at room temperature.

Samples above 57 m (firn samples) are too porous to be decontaminated through washing. Therefore, the previously exposed surfaces need to be removed via mechanical means. In the preparation of the firn samples, the operator wore pre-cleaned vinyl gloves to handle the ice core during band-saw cutting. Once an exposed surface was removed, the now clean surface of the sample was not allowed to come into contact with the band-saw bench or any material not explicitly cleaned. After all previously exposed surfaces had been removed, the sample (3.5 x 3.5 x 5.0 cm) was placed directly into a pre-cleaned sample specimen cup, capped, and allowed to melt at room temperature.

The efficacy of the decontamination procedures was assessed through the analysis of operational blanks, which were prepared from frozen ultrapure deionized water. Three different types of operational blanks were prepared: (1) unwashed blanks to estimate the extent of contamination if no decontamination protocols were implemented, (2) washed blanks prepared as ice samples (exposed surfaces removed via washing), and (3) cut blanks prepared as firn samples (exposed surfaces removed using the band-saw). These operational blanks were prepared on three separate days and analyzed in triplicate each day for a total of nine measurements. The results from this study are summarized in Table 4. The relatively high perchlorate concentration (2.2 ng L^{-1}) in the unwashed blanks indicates the need for decontamination protocols. While no perchlorate

contamination was observed in the washed blanks, there was slight contamination in the cut blanks. However, this contamination remained below the LLOQ in all samples analyzed, and is unlikely to affect the accuracy of the perchlorate measurement. The source of the miniscule contamination is difficult to ascertain, but possibly stems from the washed vinyl gloves or the band-saw blade. For quality control, an operational blank was prepared each time samples were prepared for analysis to ensure that contamination was not introduced during sample preparation.

Table 4. Results of the contamination assessment[53].

Blank Type	Average ClO_4^- Concentration (ng L^{-1})	Concentration Range (ng L^{-1})	Standard Deviation (ng L^{-1})
Washed	Below LOD	N/A	N/A
Cut	0.15	0.12 – 0.18	0.02
No Decontamination	2.20	0.35 – 3.85	1.48

4 Ice Core Dating

4.1 Importance

The development of a depth-age scale for, or dating, an ice core is one of the most important aspects of ice core research. An accurate depth-age scale for an ice core is particularly important for investigations into how historical events have impacted the concentrations of various species, such as how human activities or volcanic eruptions have influenced environmental perchlorate levels. The development of a depth-age scale is also necessary for the comparison of data across ice cores from different locations because snow accumulation rates vary from location to location.

4.2 Dating Methods

4.2.1 Annual Layer Counting

One technique often used for dating an ice core is annual layer counting. Certain measured parameters of an ice core oscillate on an annual time scale. For example, the amount of a specific chemical impurity, such as Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}, NO_3^{-}, and SO_4^{2-}, can fluctuate due to variations in source strength and atmospheric transport efficiency. When this fluctuation oscillates on an annual time scale, a yearly peak in concentration is observed. A plot of concentration vs. depth allows for the counting of each yearly peak (or layer). Thus, when the accumulation rate and temporal resolution of measurement is high enough to resolve annual layers, the age at a given depth of snow can be determined by counting the number of peaks between that depth and a depth of a known age (usually the top of the ice core, which would correspond to the year the ice core is drilled).

Chemical impurities are not the only components of an ice core that can oscillate on an annual time scale. Due to increased sublimation during the warmer summer

months, snow in the summer is less dense than in the winter[58]. Thus, density also oscillates on an annual time scale (at the top of the core) and can be used to date an ice core. Density variations may be visually observed within the core itself, making it possible to date the core via visible stratigraphy. Finally, the stable oxygen isotopic composition of the water molecules in snow oscillate on an annual time scale. This is due to the temperature dependence of the preference of $H_2{}^{16}O$ molecules over $H_2{}^{18}O$ molecules when water evaporates or when water vapor condenses. During colder conditions, $H_2{}^{16}O$ molecules are preferentially removed from the atmosphere. Thus, the snow that accumulates during the winter has a higher content of $H_2{}^{16}O$ molecules than the snow that accumulates during the summer. As a result of their annual oscillations, chemical impurities, density, and the stable oxygen isotopic composition of water can all be used to date an ice core via annual layer counting. Often multiple parameters exhibiting annual layers are used to develop the most accurate time scale possible. This technique is particularly useful when an annual signal for one parameter becomes unclear or is temporarily lost. For example, the annual signal for NH_4^+ in Greenland ice cores can become obscured by biomass burning events[59]. Thus, NH_4^+ cannot be used for dating during these events, but the presence of other parameters, such as Ca^{2+}, can be used, allowing for continuous annual layer counting. The age determined for a certain depth can be verified using time stratigraphic markers[60,61], which are events observed in ice core data that correspond to a known year. For example, large volcanic eruptions are represented in ice cores with prominent SO_4^{2-} signals due to the emission of large amounts of sulfur dioxide (SO_2). Therefore, a prominent SO_4^{2-} signal corresponding to

the year of a well-known volcanic eruption can be used to verify that the assigned date for that particular depth is correct.

4.2.2 Constant Accumulation Method

Another technique that can be employed to date an ice core is the use of snow accumulation rates. This technique involves using the average annual snow accumulation rate at a specific location to determine the age at a certain depth. The use of accumulation rates for dating is made more difficult by the compression of annual layers with increased depth by continuous snow accumulation. As a result, annual layer thickness decreases with increasing depth. Thus, the average snow water equivalent (SWE), which is the accumulation measured in amount of liquid precipitation, is often used rather than the actual snow accumulation depth interval to date the ice core.

4.3 Dating SM07C2

The depth-age scale for the portions of SM07C2 used in this study (0 – 98 m) was developed using the method of annual layer counting throughout core 1 from Summit, Greenland (SM07C1) and SM07C2. The concentrations of the major ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+}) in SM07C1 and SM07C2 were determined using continuous flow analysis-ion chromatography (CFA-IC)[62]. The depth resolution of the CFA-IC samples analyzed was slightly less than 3 cm per sample. This resulted in an average of 10.8 samples per year[43], which is sufficient resolution for annual layer counting at this site. As can be seen in Figure 4, Ca^{2+}, which derives from terrestrial dust and peaks in the spring[59], exhibits a very reliable annual signal and was primarily used for annual layer counting. This was complemented by the annual signal in Mg^{2+}, which also derives from terrestrial dust and peaks in the spring. In cases where the annual

signals in Ca^{2+} and Mg^{2+} became unclear, the annual signals in Na^{+}, which derives from sea salt and generally peaks in the winter, and NO_3^{-}, which peaks in the summer, were used to assist in the annual layer counting[40,43].

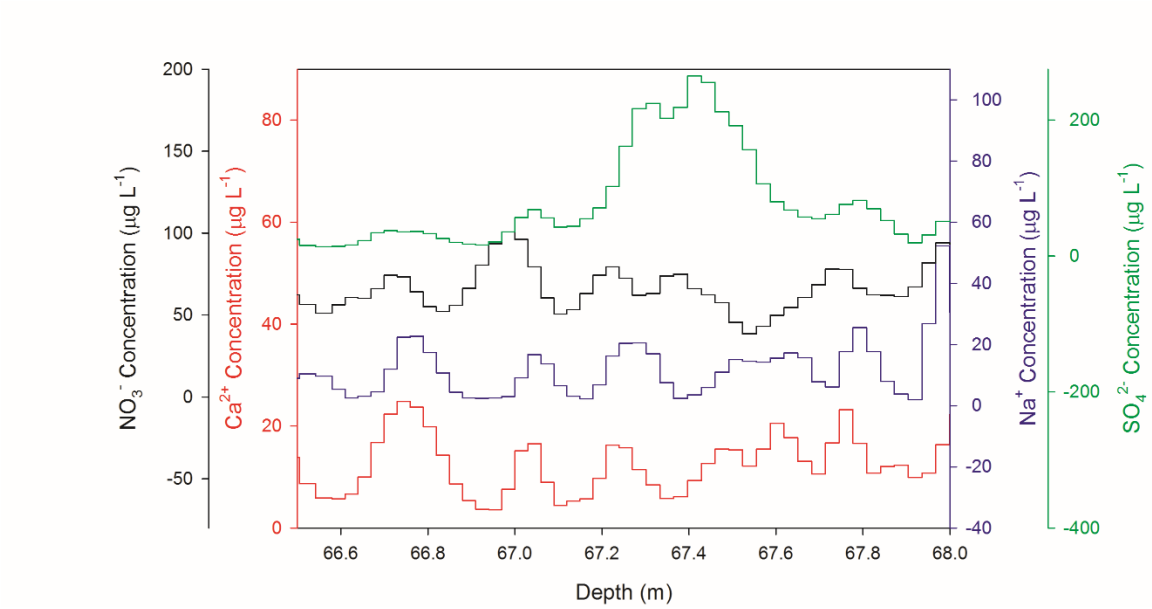

Figure 4. Annual oscillations in Ca^{2+} (red), Na^{+} (blue), and NO_3^{-} (black) from SM07C2, which were used in annual layer counting to develop the depth-age scale for SM07C2. The Tambora SO_4^{2-} (green) volcanic signal was used to adjust SM07C2 depths to SM07C1 depths.

Annual layer counting as described above was used to date the top 66.50 m of SM07C1 to the year 1820 C.E. The top 66.50 m of SM07C2 were not analyzed for major ion concentrations. Thus, the Tambora SO_4^{2-} volcanic signal (Figure 4) was used to establish the corresponding layer in SM07C2. This layer occurred at a depth of 67.44 m in SM07C1 and at 67.62 m in SM07C2. This means that a layer of snow in SM07C2 is 0.18 m deeper than the layer of snow in SM07C1 that fell at the same time of year. Therefore, 0.18 m was subtracted from the SM07C2 depths, which allowed SM07C2 to be appended onto the SM07C1 depth scale, and annual layer counting proceeded on SM07C2 below 66.38 m[40]. Because of occasional ambiguity in the annual signals of the

ions used for dating, there is uncertainty associated with the final time scale of any ice core. The age at the bottom portion of SM07C2 used in this study was determined to be 1700 with an uncertainty of ± 3 years.

4.4 Dating the TUNU and Basin 4 Cores

The ice cores from TUNU and Basin 4 could not be dated via annual layer counting because there was no data available by which annual layer counting could be performed. Thus, these cores were dated using the constant accumulation rate method. The SWEs for TUNU and Basin 4 were 12.5 cm yr^{-1} and 41.1 cm yr^{-1}, respectively. In order to date each core using the accumulation rate method, the density for each sample needed to be determined. The density for each sample (ρ_{sample}) was calculated using Equations 1 (TUNU) and 2 (Basin 4), where the numerical values for coefficients a-h are shown in Table 5. Equation 1 was determined by the polynomial fit of density measurements from a core drilled at 75° N, 30° W and Equation 2 was determined by the polynomial fit of density measurements from a core drilled at 63.1° N, 44.8° W[63]. In Equations 1 and 2, MD is the middle depth for each sample. After calculating the density for each sample, the water sample size (WSS) was calculated by multiplying ρ_{sample} by the sample size. Finally, the water depth for each sample was determined by summing the WSSs for all the samples above the sample of interest. The water depth for each sample was then used to determine the age of each sample based upon average annual SWE for each site. The age at the bottom of the TUNU core (19.96 m) was determined to be 1918 C.E., and the age at the bottom of the Basin 4 core (23.654 m) was determined to be 1972. Figure 5 shows the depth-age profiles of the SM07C2, TUNU, and Basin 4 cores through the year 1915.

Equation 1 $\rho_{sample} = a + (b \times 10^{-2})MD - (c \times 10^{-4})MD^2 - (d \times 10^{-6})MD^3$

Equation 2 $\rho_{sample} = e + (f \times 10^{-2})MD - (g \times 10^{-3})MD^2 + (h \times 10^{-5})MD^3$

Table 5. Numerical values for coefficients a-h in Equations 1 and 2.

Coefficient	Numerical Value
a	0.324
b	2.185
c	2.348
d	9.558
e	0.388
f	4.530
g	2.954
h	7.140

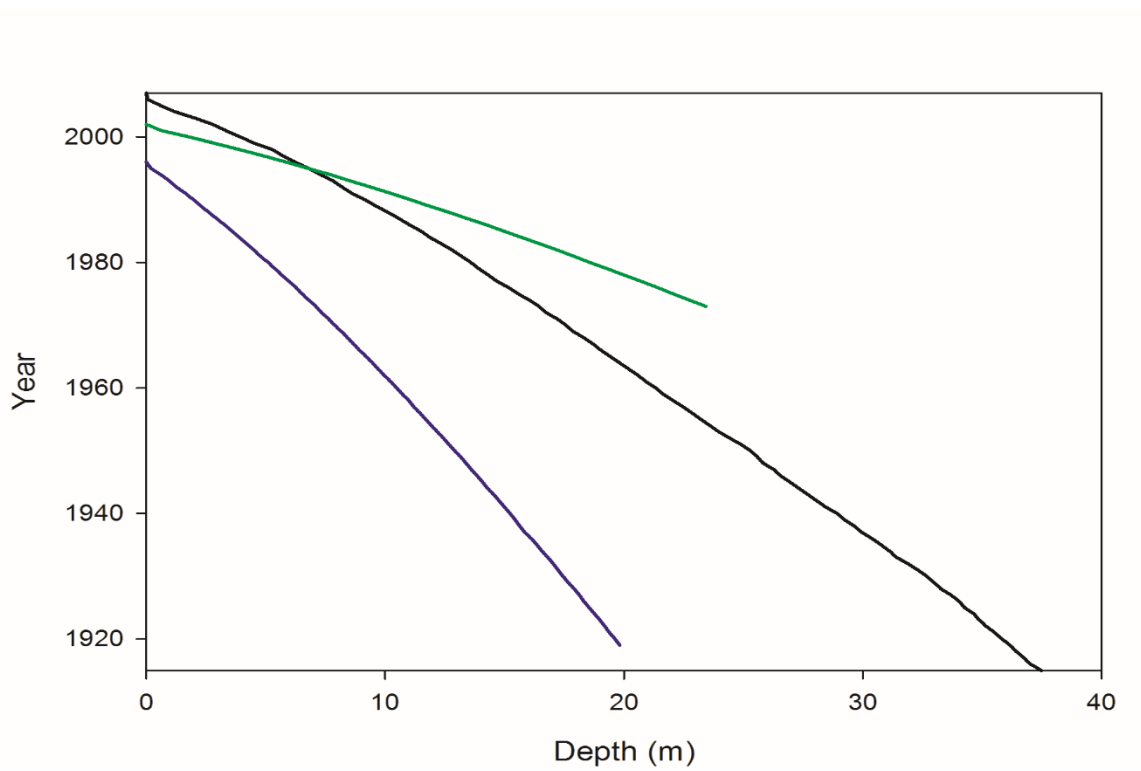

Figure 5. Depth-age profiles through 1915 for the SM07C2 (black), TUNU (blue), and Basin 4 (green) cores.

5 Long Term Trends in Perchlorate

5.1 Pre-Industrial Revolution vs. Modern Concentrations

The 300-year (1700-2007 C.E.) perchlorate record from SM07C2 allows for the comparison of perchlorate concentrations from prior to the onset of the Industrial Revolution (~1850 C.E.), which are assumed to be solely from natural sources, and modern perchlorate concentrations, which likely derive from both anthropogenic and natural sources. This allows for the determination of the anthropogenic contributions to environmental perchlorate, assuming that the contribution from natural sources has remained the same during the entire time period. The average perchlorate concentration prior to the onset of the Industrial Revolution (1700-1850) was 1.0 ± 0.7 ng L^{-1} (n = 801) compared to an average concentration of 1.4 ± 1.4 ng L^{-1} (n = 1,194) between 1850 and 2007. This suggests some anthropogenic contribution to environmental perchlorate following the onset of the Industrial Revolution. However, closer examination of the perchlorate record shows that there is no significant change or trend in perchlorate concentrations during the time period of 1700-1980. The average perchlorate concentration between 1850 and 1980 was 1.0 ± 0.9 ng L^{-1} (n = 930), essentially the same as pre-Industrial Revolution concentrations (Figure 6). Therefore, it can be concluded that the onset of the Industrial Revolution had negligible impact on environmental perchlorate.

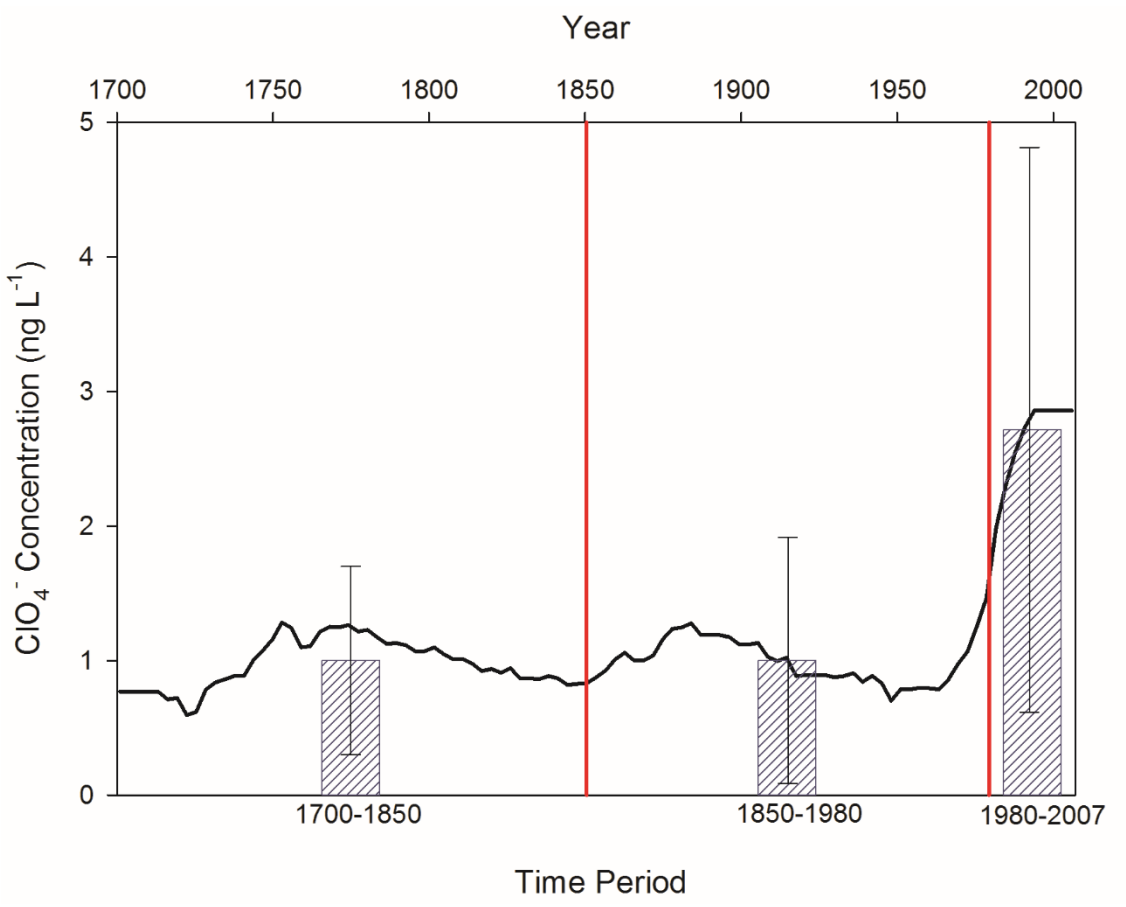

Figure 6. A comparison of average perchlorate concentrations in pre-Industrial Revolution samples, pre-1980 samples, and post-1980 samples (bars). The black solid line is the smoothed annual perchlorate concentrations between 1700 and 2007 from SM07C2. Data was smoothed using a running average with a 0.1 sampling proportion. Error bars represent the standard deviation of the perchlorate measurements.

Perchlorate concentrations increased significantly post-1980. The average perchlorate concentration between 1980 and 2007 was 2.7 ± 2.1 ng L^{-1} (n = 266), nearly a three-fold increase over pre-Industrial Revolution concentrations. A Mann-Whitney Rank Sum Test between annual perchlorate concentrations between 1700 and 1980 and between 1980 and 2007 revealed a statistically significant difference (p = <0.001). The significantly higher perchlorate concentrations post-1980 indicate that an additional source of perchlorate appeared around 1980. This source could be the direct release of

perchlorate from anthropogenic activities, which is discussed in more detail in section 5.3. Another possibility is that conditions changed in favor of the atmospheric production of perchlorate. This possibility is discussed in Chapter 6.

5.2 Perchlorate Concentrations across the Arctic

Analysis of perchlorate concentrations in three different Greenland ice cores allows for the comparison of perchlorate concentrations, as well as a more comprehensive view of trends and fluctuations in these concentrations, across Greenland. Figure 7 shows the average annual perchlorate concentrations between 1972 and 1996 in the SM07C2, TUNU, and Basin 4 cores. In general, perchlorate concentrations, as well as the trends in these concentrations, with the exception of the large peak in the TUNU core between 1983 and 1985, are similar across Greenland, suggesting similar sources and deposition patterns. The average annual concentrations (excluding the large peak in the TUNU core between 1983 and 1985) for SM07C2, TUNU, and Basin 4 between 1972 and 1996 are 2.23, 2.50, and 2.51 ng L^{-1}, respectively.

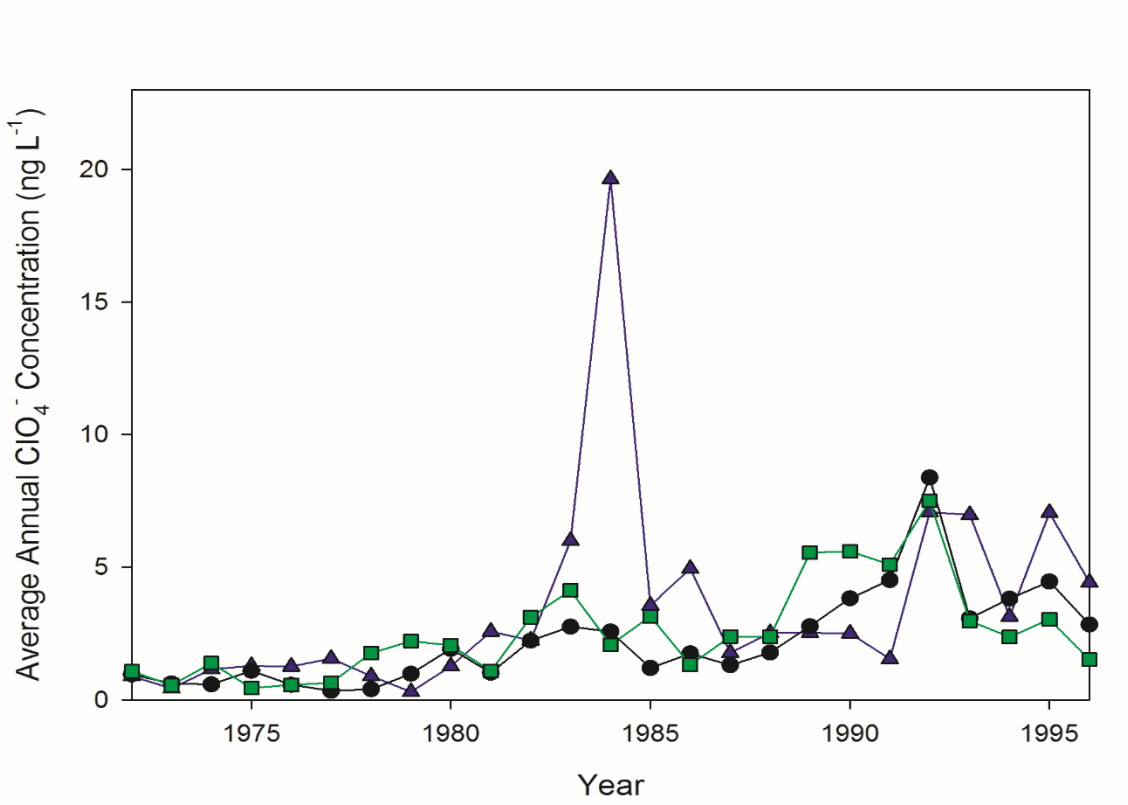

Figure 7. The average annual perchlorate concentrations in the SM07C2 (black circles), TUNU (blue triangles), and Basin 4 (green squares) ice cores covering the time period 1972-1996.

The cause of the large perchlorate peak in the TUNU core between 1983 and 1985 remains unclear. TUNU samples over this time period were analyzed twice, yielding the same result. Furthermore, a second set of samples for this time period was cut from the remaining core and analyzed. The Mann-Whitney Rank Sum Test showed that there was no statistical difference between the two sets of samples (p = 0.445). Thus, the high concentration is not likely a result of errors in sample preparation and analytical measurement, and this perchlorate peak represents the actual environmental perchlorate concentrations across the time period at the TUNU site. There is an increase in perchlorate concentrations during this time period in SM07C2 and Basin 4, although the increase is much smaller in these two cores. The increase in perchlorate concentrations

over this time period could be associated with the volcanic eruption of El Chichón in Mexico in 1982 (this possibility is discussed in detail in Chapter 7). While the El Chichón eruption seems to be a possible explanation for the large peak in perchlorate concentrations in the TUNU core between 1983 and 1985, it remains difficult to explain why these concentrations are significantly higher than those observed in SM07C2 and Basin 4, especially when perchlorate concentrations are so similar during other periods in the records. Data from other Greenland locations would be needed to determine if this anomaly in perchlorate concentrations is localized to the TUNU site, or is an anomaly seen only in northern Greenland locations. If the anomaly was seen in other northern Greenland locations, it could suggest that there was a local event impacting northern Greenland, but not other Greenland locations.

Perhaps the most notable trend in perchlorate concentrations in the TUNU and Basin 4 cores is a marked increase in perchlorate concentrations post-1980, remarkably similar to that observed in SM07C2. The average perchlorate concentrations pre-1980 for TUNU (1918-1979) and Basin 4 (1972-1979) were 1.05 and 0.92 ng L^{-1}, respectively, compared to 3.40 and 2.94 ng L^{-1} post-1980, respectively (excluding the anomaly in the TUNU core). This 3- to 4-fold increase in perchlorate concentrations post-1980 over pre-1980 concentrations is consistent with the increase observed in SM07C2.

The typical perchlorate concentrations and the trends across Greenland are also found in other Arctic locations. Furdui and Tomassini[21] found the average perchlorate concentration in ice samples dated between 1996 and 2005 from Devon Island in eastern Canada to be 5.5 ng L^{-1}, compared to 2.4 ng L^{-1} during the same period in SM07C2. Rao et al.[36] measured perchlorate concentrations in ice core samples dated 1970-1973, 1982-

1986, and 1999-2002 from the Eclipse Icefield, Yukon Territory, Canada. Similar to the trend observed across Greenland, perchlorate concentrations post-1980 at Eclipse Icefield were approximately 3-fold higher than pre-1980 concentrations, as the average perchlorate concentration between 1970 and 1973 was 0.6 ng L^{-1} compared to 2.3 and 2.2 ng L^{-1} between 1982 and 1986 and between 1999 and 2002, respectively.

5.3 Possible Anthropogenic Sources

5.3.1 Perchlorate as an Oxidizer

In the United States perchlorate is considered a strategic chemical due to its use in many military and strategic applications. As a result, accurate production and usage data on perchlorate is not openly and readily available. The lack of such data complicates the process of identifying specific anthropogenic contributors to environmental perchlorate. Despite limited data, Dasgupta et al.[13] were able to develop perchlorate production figures in the United States based upon production data in EPA archives for three perchlorate production plants and estimates for one additional plant. As seen in Figure 8 (from Dasgupta et al.[13]), the industrial production of perchlorate in the U.S. began to increase around 1980 over the annual production of the previous 15 years. This rise in the industrial production of perchlorate likely led to an increase in perchlorate usage in applications, such as its use as a propellant in space shuttle launches.

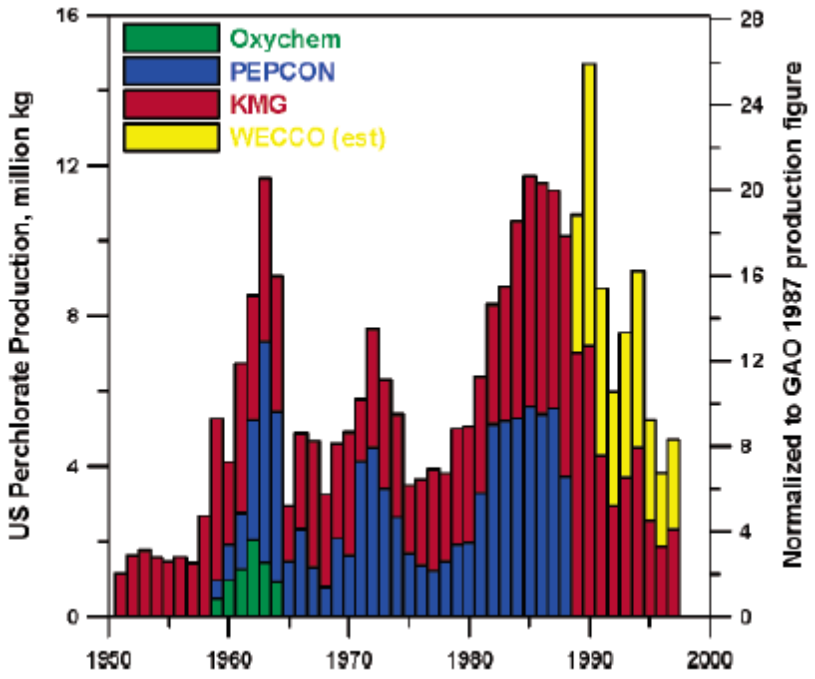

Figure 8. Perchlorate production in the United States based on data from EPA archives for Oxychem, PEPCON, Kerr-McGee, and estimates for WECCO. Figure from Dasgupta et al.[13]

The National Aeronautics and Space Administration's (NASA) space shuttle program began in 1981*(ref 15)*. Between 1981 and 2007, there were 120 space shuttle launches, averaging slightly more than four per year. The advent of space shuttle launches corresponds with the increase in perchlorate levels observed in the ice core record. This seemingly suggests a link between space shuttle launches and increasing perchlorate levels. However, as mentioned in Chapter 1, when perchlorate is used as an oxidizer, as in a space shuttle launch, evidence indicates that essentially no perchlorate residue remains[1,13,16,21]. Thus, it is unlikely that residue from space shuttle launches is a significant direct source of perchlorate, although it may serve as a minor source to environmental perchlorate. Each space shuttle launch utilizes approximately 701,000 kg of ammonium perchlorate[15]. Even if as little as 0.05% of the perchlorate remains, as is the case in road flares[16], each space shuttle launch could release up to approximately 350

kg of ammonium perchlorate to the environment. Thus, during the space shuttle era, it is possible that more than 1,400 kg of perchlorate could have been released to the environment per year, assuming four space shuttle launches per year. Considering the perchlorate concentrations observed in the ice core records are in the low ng L^{-1} range, this could represent a relevant source of perchlorate. However, as pointed out by Dasgupta et al.[13] the temperatures during a space shuttle launch are much higher and sustained much longer than in a road flare, which would presumably result in much less perchlorate residue.

While it seems unlikely that space shuttle launches are a significant direct source of environmental perchlorate since 1980, they may serve as an indirect source. While no significant elevation in perchlorate levels was found in space shuttle plumes, elevated levels of chloride were observed[13]. The chloride release could enhance the level of chlorine in the stratosphere. As will be discussed at length in Chapter 6, stratospheric chlorine is likely a major precursor to perchlorate. Therefore, space shuttle launches could contribute to the enhanced stratospheric production of perchlorate. This assumes, though, that the levels of chloride that reach the stratosphere is significant relative to the typical levels of stratospheric chlorine. The contribution of space shuttle launches to the rising perchlorate concentrations in post-1980 samples remains unclear, but this possibility should considered in future research.

Although perchlorate's usage as an oxidizer in applications may not contribute significantly to environmental perchlorate, the release from disposal when it is no longer needed may be significant. According to Dasgupta et al.[13], the rocket propellant mixture containing perchlorate has a limited lifetime, and often needs to be replaced when not

used immediately. When this occurs the propellant is washed out with high pressure water creating large volumes of perchlorate-contaminated wastewater which is discharged into sewage systems or natural waters. As a result of similar disposal practices by the Department of Defense and manufacturing plants, perchlorate has been found to be present in groundwater in at least 22 states[8]. Similarly, perchlorate pollution in the lower Colorado River has been attributed to disposal at upstream production plants[8]. The lower Colorado River, as a source of drinking water and irrigation water throughout southwestern Arizona and southern California, may pose as a significant potential for human perchlorate exposure[8].

5.3.2 Perchlorate as an Impurity

The presence of perchlorate as an impurity in CNF and in sodium chlorate used in the pulp and paper industry may represent another anthropogenic source of perchlorate. However, these sources of perchlorate are unlikely contributing to the post-1980 increase in perchlorate concentrations in Arctic snow. The import of Chilean nitrate to the United States and Europe declined significantly as the large-scale industrial production of nitrogen fertilizer increased. As a result, imports of Chilean nitrate have remained relatively consistent since the mid-1960s *(ref 13)*. Finally, although the global production of sodium chlorate has been steadily increasing, it remains unclear if this is a significant source of perchlorate pollution. Therefore, perchlorate as an impurity in sodium chlorate may currently exist as a minor anthropogenic source of environmental perchlorate.

The perchlorate pollution resulting from the disposal of perchlorate salts and the release from applications typically remains local. Thus, these sources of perchlorate are likely largely responsible for the perchlorate observed in the groundwater and surface

water systems across the United States. However, in order for perchlorate that is disbursed locally, as is the case in the disposal of perchlorate salts and the use of CNFs, to reach Greenland, it would likely be transported with dust. Dust records from Arctic ice cores have revealed that dust concentrations have not increased since 1980 *(ref 64)*. As an example, calcium concentrations in SM07C2 are provided in Figure 9. Calcium concentrations in ice cores are often used as a proxy for dust[59]. Calcium concentrations do not change significantly around 1980, indicating no increased dust input. Thus, it does not appear the perchlorate concentrations in Greenland snow were impacted by the direct release of perchlorate from anthropogenic sources.

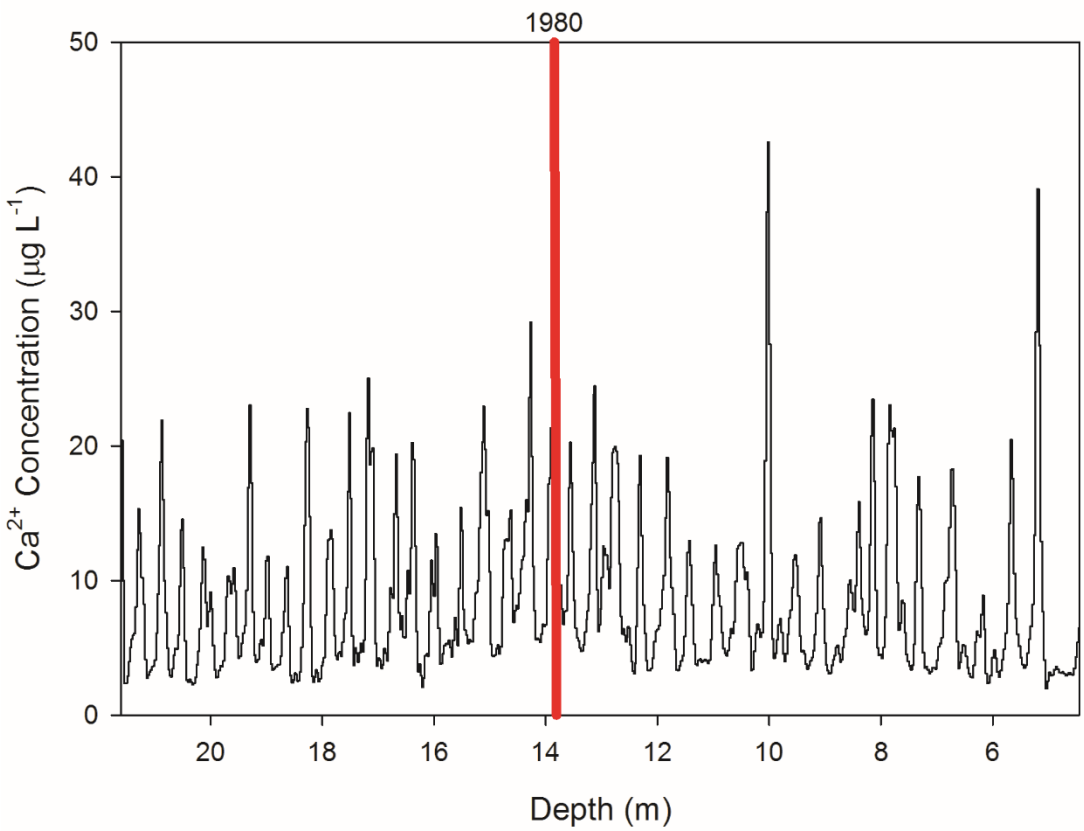

Figure 9. Calcium concentrations (proxy for dust) between 1960 (left) and 2000 (right) in SM07C2.

5.4 Conclusions

The 300-year perchlorate record from SM07C2 reveals that the onset of the Industrial Revolution did not impact environmental perchlorate levels, as typical perchlorate concentrations were remarkably stable between 1700 and 1980. A significant increase in perchlorate concentrations began in 1980, which is observed in all three Greenland ice cores, as well as in other Arctic locations[36], indicating additional perchlorate likely entered the environment. Despite limited available data on perchlorate production, analysis by Dasgupta et al.[13] suggested that more perchlorate may have been released into the environment because the industrial production of perchlorate increased around 1980. The most likely human activities contributing to environmental perchlorate are perchlorate's use as an oxidizer in space shuttle launches and the disposal of unused perchlorate.

The disposal of perchlorate likely contributes to the perchlorate pollution found in groundwater and surface water systems. However, this pollution generally remains localized. Because of the tendency of perchlorate pollution to remain localized to the source of the release, the disposal of perchlorate by the manufacturing plants and perchlorate users unlikely explains the significant increase in observed perchlorate levels in the Canadian and Greenland ice core records. The impact of perchlorate as an oxidizer in large scale activities could be detected in ice core records. This is because when perchlorate is used as an oxidizer it is often released into the atmosphere where it can undergo more widespread distribution. However, as discussed above, it remains debatable whether perchlorate's use as an oxidizer could represent a significant source of environmental perchlorate. Likely, the direct release of perchlorate from anthropogenic

applications is not a significant cause of the increase since 1980. As a result, it seems likely that there is another source of perchlorate, or that atmospheric conditions changed in a way that promotes the atmospheric production of perchlorate and is contributing to the post-1980 increase that is observed across the Arctic.

6 Stratospheric Chlorine

6.1 Evidence of Stratospheric Production of Perchlorate

In addition to the anthropogenic sources discussed in Chapter 5, formation in the atmosphere is expected to be a significant source of environmental perchlorate[3–5,22,65]. The processes leading to perchlorate production, though, are not well understood. Elevated levels of cosmogenic chlorine (^{36}Cl) observed in natural perchlorate deposits suggest that at least some perchlorate is formed in the stratosphere[20]. This is because ^{36}Cl is formed in the stratosphere due to the galactic cosmic-ray spallation of ^{40}Ar, whereas the chlorine present in the troposphere is dominated by marine chlorine, and contains negligible amounts of ^{36}Cl *(ref 20)*. Furthermore, perchlorate has been observed in H_2SO_4 aerosols present in the stratosphere[66]. Thus, it seems likely that stratospheric chlorine is important for the formation of perchlorate, and its role in enhanced perchlorate production post-1980 will be discussed in this chapter.

6.2 Overview of Chlorine Chemistry in the Stratosphere

The only significant natural contributor to stratospheric chlorine is methyl chloride[67], which mainly derives from biogenic sources including salt marsh plants[68], fungal species[69], and marine algae[70]. The other main sources of stratospheric chlorine in the present environment are chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which originate from anthropogenic sources[67]. CFCs were synthesized in the 1930s and were produced to replace the toxic fluids used as coolants in refrigerators. However, they also found uses as solvents, cleaners, propellants for spray cans, and as blowing agents for plastic foam. CFCs are inert in the troposphere. Because CFCs lack hydrogen atoms, they are not reactive to the hydroxyl radical (HO•), a ubiquitous species

in the troposphere that typically initiates oxidation of hydrocarbons by abstraction of hydrogen in C-H bonds[71]. Furthermore, CFCs are not soluble in water, and therefore are not removed via precipitation[72]. As a result, CFCs released into the environment are transported through the troposphere to the stratosphere. Because the transport of CFCs to the stratosphere, where they break down readily, is very slow, the atmospheric residence time of CFCs is on the order of a century[72], allowing for the accumulation of chlorine species in the atmosphere. Table 6 shows common CFCs along with their atmospheric residence times[73].

Table 6. The atmospheric residence times of common CFCs[73].

CFC Formula	Short Name	Lifetime (years)
CCl_3F	CFC-11	45
CF_2Cl_2	CFC-12	100
$CF_2ClCFCl_2$	CFC-113	85
ClF_2CCF_2Cl	CFC-114	300
$CClF_2CF_3$	CFC-115	1700

Once in the stratosphere, CFC molecules are exposed to short wavelength (<220 nm) solar ultraviolet radiation. Exposure to this ultraviolet radiation destroys CFC molecules and causes the release of radical chlorine atoms[72], as shown in Reaction 1.

$$\text{(R1)} \quad CF_2Cl_2 + h\nu\ (<220\ \text{nm}) \rightarrow Cl\bullet + CF_2Cl$$

The chemical and physical processes by which chlorine radicals catalyze the destruction of ozone in the stratosphere leading to the annual appearance of the stratospheric ozone hole over Antarctica has been well documented[74]. Here is a brief summary of the current understanding of the stratospheric ozone loss phenomenon. As first suggested by Molina and Rowland[75], the chlorine atoms react to destroy ozone via the cycle shown in

Reactions 2 and 3, in which the Cl• is regenerated, resulting in the catalytic destruction of ozone.

$$\text{(R2)} \quad Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$
$$\text{(R3)} \quad ClO\bullet + O \rightarrow Cl\bullet + O_2$$

These reactions continue to deplete ozone until the chlorine radicals combine or react to form chlorine reservoir species (HCl and $ClONO_2$) through Reactions 4 and 5, where M is a third body molecule such as N_2 or O_2.

$$\text{(R4)} \quad Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$$
$$\text{(R5)} \quad ClO\bullet + NO_2 + M \rightarrow ClONO_2 + M$$

Under normal conditions, chlorine is sequestered in the reservoir chlorine species and therefore unavailable for ozone destruction reactions. Reactions 6 and 7 can release chlorine from the reservoir[76–79], yielding species (Cl_2 and HOCl) that can easily generate radicals.

$$\text{(R6)} \quad HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$
$$\text{(R7)} \quad H_2O + ClONO_2 \rightarrow HOCl + HNO_3$$

The rates of Reactions 6 and 7 are much faster when they heterogeneously occur on the surface of ice crystals of polar stratospheric clouds (PSCs) than in the gas-phase (homogeneous reactions). For example, experiments performed by Atkinson et al.[80] show that the homogeneous rate constant for Reaction 7 is approximately 2×10^{-21} cm^3 $molecule^{-1}$ s^{-1}, whereas experiments performed by Rowland et al.[81] show that the

heterogeneous rate constant is approximately 1×10^{-19} cm^3 $molecule^{-1}$ s^{-1}, approximately two orders of magnitude higher. The dramatic increase in the rate constant is mainly due to the reactants becoming concentrated on the surface of the PSCs, compared with in the gas phase. PSCs also increase activated chlorine concentrations because Cl_2 gas molecules can escape the surface of PSCs, which shifts the equilibrium of Reaction 6 towards the products[71,80,81]. During the Antarctic winter, the absence of sunlight allows Cl_2 and HOCl to accumulate in the stratosphere. When sunlight returns in the spring, Cl_2 and HOCl undergo photolysis to form Cl• and ClO•, respectively, which then initiate the catalytic destruction of ozone, resulting in the spring ozone hole over most of the high southern latitudes including Antarctica.

As the emission of CFCs increased the amount of chlorine species in the stratosphere, the amount of activated (radical) chlorine, particularly over the poles, increased as well. While stratospheric chlorine chemistry and the enhanced chlorine activation over the poles has mainly been studied in relation to the depletion of ozone, it is possible that these processes lead to increased perchlorate production, because radical chlorine species are important precursors to perchlorate[82,83].

6.3 Trends in Stratospheric Chlorine and Perchlorate Concentrations

The abundance of stratospheric chlorine is estimated by a parameter referred to as equivalent effective stratospheric chlorine (EESC). EESC is essentially the sum of ozone depleting substances, which are primarily chlorine- and bromine-containing chemicals, taking into account their atmospheric residence time and the their ozone destruction efficiency. EESC, which is estimated from the production of ozone depleting substances, is often used to predict the extent and duration of ozone depletion. Equation 3 shows

how EESC is calculated. In Equation 3, a is an arbitrary factor and is often assumed to be 1 *(ref 84)*, n_i is the number of chlorine or bromine atoms in a specific source gas, f_i is the fractional halogen release of a specific source gas at a designated time, ρ_i is the mixing ratio of the source gas, and α accounts for the increased efficiency at which bromine destroys ozone compared to chlorine and is assumed to be 60. Based upon mixing ratios reported by Newman et al.[84] for 2000 and f_i values for 3 and 5.5 years after the release of the source gases, the contribution of chlorine containing source gases to total EESC is calculated to be approximately 70–75%. Furthermore, as EESC concentrations have increased in the recent decades, measurements by Fabian and Borchers[85] show that stratospheric chlorine concentrations have also increased. Thus, EESC is considered a good estimate of stratospheric chlorine concentrations[84].

Equation 3 $$EESC(t) = a(\sum_{Cl} n_i f_i \rho_i + \alpha \sum_{Br} n_i f_i \rho_i)$$

As can be seen in Figure 10, EESC increases rapidly throughout the 1980s and early 1990s before peaking in 1996, a trend that has been attributed primarily to changes in the production and emission of CFCs. To reduce and prevent the destruction of ozone, the production of CFCs was first limited under the Montreal Protocol in 1987, and eventually phased out in the subsequent London and Copenhagen amendments in 1990 and 1992, respectively[72]. As a result, EESC concentrations have been steadily decreasing since 1996. As shown in Figure 11 (from Elkins[86]), these trends are also reflected atmospheric levels of CFC-11, one of the key CFC compounds. The average annual perchlorate concentrations from SM07C2 parallel the increasing trend in EESC throughout the 1980s and early-1990s, followed by decreasing concentrations throughout the late-1990s and early 2000s. Furthermore, a similar trend, increasing concentrations

starting in 1980 followed by decreasing concentrations starting in the mid-1990s, was observed in perchlorate measurements in an ice core drilled at the South Pole (Figure 12). The parallel trends in EESC and perchlorate concentrations in both the Arctic and Antarctic strongly suggest that stratospheric chlorine is likely playing a major role in perchlorate production globally.

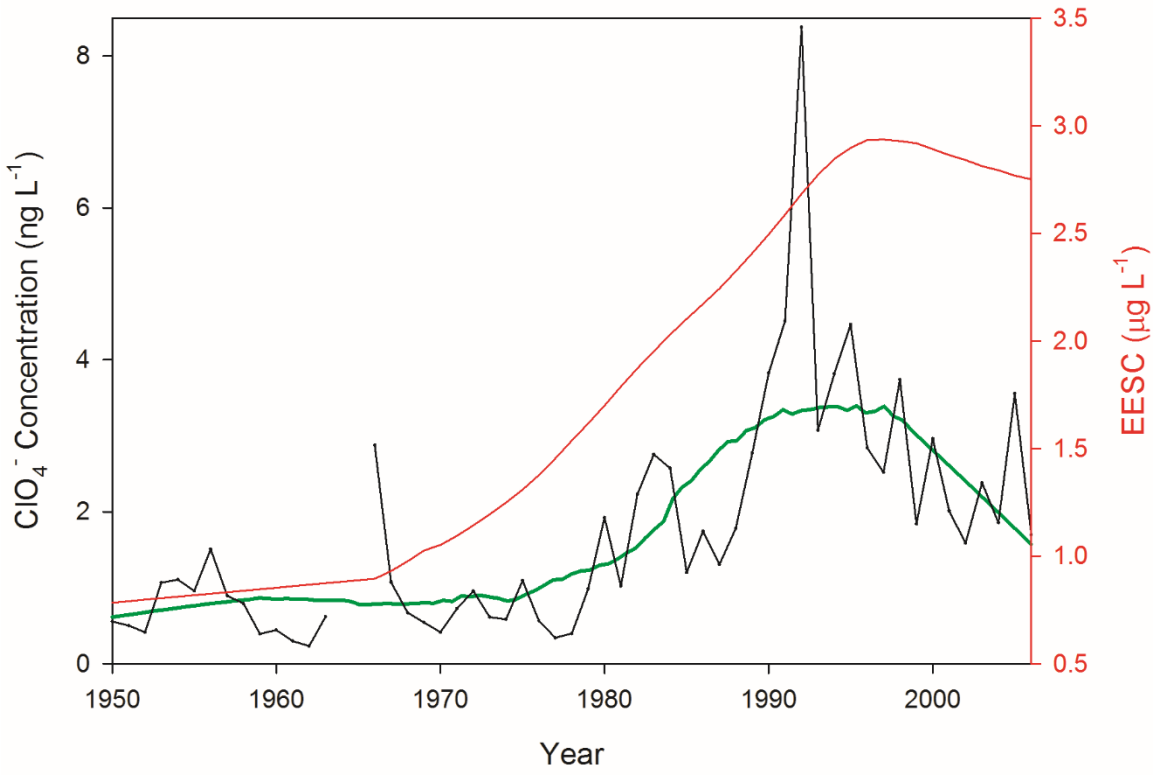

Figure 10. Average annual (black) and smoothed (green) perchlorate concentrations from SM07C2, as well as annual EESC concentrations (red) between 1950 and 2006. Perchlorate concentrations were smoothed in Sigma Plot by taking a running average with a sampling proportion of 0.3. Lack of ice core samples resulted in no perchlorate data for the time period of 1964-1966.

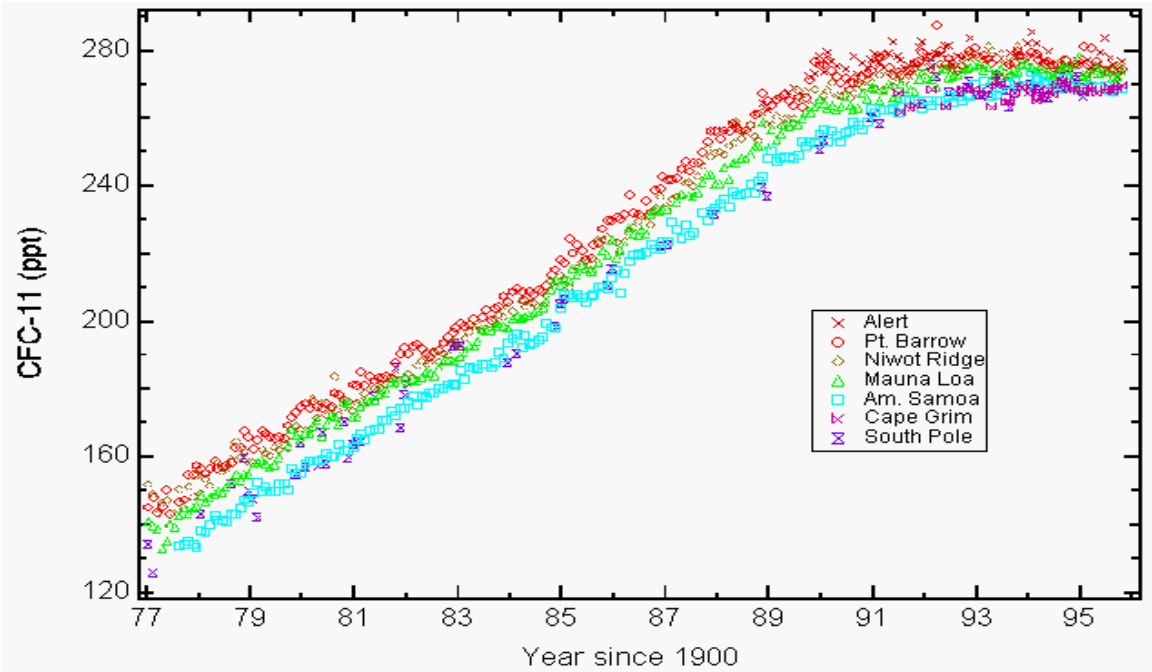

Figure 11. Atmospheric CFC-11 concentrations from various National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostic Laboratory locations (from Elkins[86]).

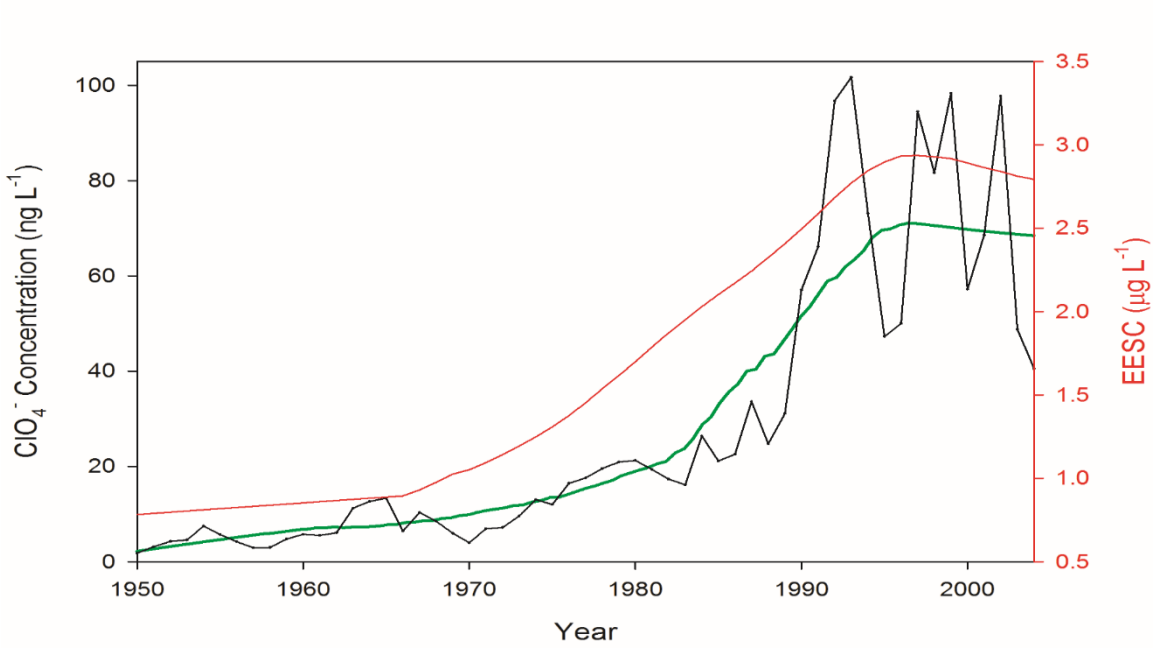

Figure 12. Annual (black) and smoothed (green) perchlorate concentrations from the South Pole, as well as EESC concentrations (red) between 1950 and 2004. Perchlorate concentrations were smoothed in Sigma Plot by taking a running average with a sampling proportion of 0.3.

As can be seen in Figures 10 and 12, perchlorate concentrations are significantly higher in Antarctica than in Greenland, which was unexpected. Initially, it was speculated that perchlorate in recent snow was influenced by anthropogenic activities and, due to the fact that anthropogenic activities are more prevalent in the Northern Hemisphere, higher perchlorate levels would be found in Greenland snow. It was also thought that, in the absence of significant anthropogenic influence, perchlorate levels in Antarctic snow would be similar to those in Greenland snow. The data show that the average annual perchlorate concentration in snow between 1980 and 2004 at the South Pole is 56.7 ± 35.8 ng L^{-1} (n = 134) compared to only 2.8 ± 2.2 ng L^{-1} (n = 245) for the same time period in SM07C2. The average perchlorate concentration at WAIS Divide, Antarctica between 2008 and 2012 is 45.9 ± 31.4 ng L^{-1} (n = 87). This indicates that the difference in snow accumulation between the South Pole (SWE = 8.4 cm yr^{-1} *(ref 87)*) and Summit Station (SWE = 24 cm yr^{-1} *(ref 40)*) cannot account for the difference in perchlorate concentration, as WAIS Divide (22 cm yr^{-1} *(ref 88)*) and Summit Station have similar snow accumulation rates. Perchlorate concentrations at the South Pole are also much higher than concentrations at Summit Station prior to 1980. The average perchlorate concentration between 1950 and 1979 at the South Pole and Summit Station are 8.9 ± 5.4 (n = 126) and 0.7 ± 0.6 ng L^{-1} (n = 243), respectively.

6.3.1 Enhanced Chlorine Activation over Antarctica

The reason for the significantly higher concentrations of perchlorate in Antarctica is unclear. However, assuming activated chlorine in the stratosphere is a significant precursor to perchlorate production, greater chlorine activation over the Antarctic compared to the Arctic[67] could be responsible for the higher perchlorate concentrations in

Antarctica than in Greenland. There are two main reasons why chlorine activation is greater over the Antarctic than over the Arctic, and why stratospheric ozone loss over the Arctic is much less severe than over the Antarctic. First, the Arctic polar vortex is warmer than its Antarctic counterpart because it is weaker, it moves away from the pole, and it becomes more easily distorted in shape[67]. Thus, although PSCs still form over the Arctic[89], temperatures cold enough for their formation are reached less often and do not persist as long, resulting in smaller-sized PSCs. With smaller PSCs, the activation of chlorine is not as massive over the Arctic as it is over the Antarctic, resulting in lower concentrations of radical chlorine species over the Arctic. A second reason there is more activated chlorine over the Antarctic than over the Arctic is that more HNO_3 is removed from the Antarctic stratosphere (denitrification) than the Arctic stratosphere leading to lower NO_2 concentrations[67]. As discussed in section 6.2, NO_2 is responsible for the termination of radical chlorine species. Therefore, more significant denitrification in the Antarctic prevents the deactivation of chlorine radicals, leading to more activated chlorine in the stratosphere over Antarctica[67]. Thus, the combination of larger, longer lasting PSCs and more significant denitrification over Antarctica explains the higher degree of chlorine activation observed over Antarctica. This is likely responsible for the higher perchlorate concentrations in Antarctica, since perchlorate production is strongly influenced by activated chlorine, as discussed previously.

The abundance of stratospheric chlorine appears to be a major factor in perchlorate production. Furthermore, significantly higher perchlorate concentrations in Antarctica compared to Greenland indicate that activated, or radical, chlorine species are important precursors to perchlorate. Therefore, the reactions leading to these precursors

and the subsequent oxidation reactions leading to perchlorate need to be investigated. Most notably, the role of ozone in the formation of perchlorate needs to be given significant attention due to its close relationship with radical chlorine species in the stratosphere.

6.4 Mechanisms for Stratospheric Perchlorate Production

6.4.1 Chlorine Activation

Rao et al.[82] proposed a mechanistic pathway to perchlorate involving the oxidation of chlorine radicals to higher chlorine oxide radicals, such as Cl_2O_4 and Cl_2O_6, via ozone, and their subsequent hydrolysis to form perchlorate. This mechanism is summarized herein. The most efficient precursor to perchlorate was identified to be ClO_2^- followed by Cl^-, HOCl, and OCl^-. The rapid reaction between ClO_2^- and O_3 or HO• in the aqueous phase via Reactions 8 and 9 (k = 8.2 x 10^6 M^{-1} s^{-1} and 4.2 x 10^9 M^{-1} s^{-1}, respectively) forms ClO_2, an activated chlorine species that has been observed in the stratosphere over Greenland[90].

$$\text{(R8)} \quad O_3 + ClO_2^- \leftrightarrow ClO_2 + O_3^-$$

$$\text{(R9)} \quad ClO_2^- + HO \rightarrow ClO_2 + OH^-$$

Chlorine dioxide is also formed in the atmosphere as part of the ClO dimer cycle (Reactions 10-12)[67]

$$\text{(R10)} \quad 2 \times (Cl + O_3 \rightarrow ClO + O_2)$$

$$\text{(R11)} \quad ClO + ClO + M \rightarrow Cl_2O_2 + M$$

$$\text{(R12)} \quad Cl_2O_2 + h\nu \rightarrow ClO_2 + Cl$$

and through coupled BrO/ClO chemistry (Reaction 13)[91].

$$\text{(R13)} \quad ClO + BrO \rightarrow Br + ClO_2$$

In the stratosphere, the ClO dimer cycle and the coupled BrO/ClO chemistry likely play a larger role in the production of ClO_2 than Reactions 8 and 9, because the lack of water in the stratosphere makes aqueous reactions unlikely. Chlorine dioxide can undergo several different oxidation pathways to form higher chlorine oxide radicals, which can then undergo hydrolysis to form perchlorate. These oxidation pathways and hydrolysis reactions are summarized in Figure 13, and the rate constants for several of these reactions are shown in Table 7. One should note that perchlorate often represents a minor product in these reactions. However, considering that observed perchlorate concentrations in snow are only about 1 ng L^{-1}, this still likely represents a significant source of perchlorate. The most likely pathway to perchlorate begins with common chlorine radicals, the formation of ClO_2 via Reactions 10-13, and proceeds through the gas phase oxidation of ClO_2 (Reaction 2a in Figure 13), rather than through the aqueous phase. In addition to these oxidation pathways, ClO_2 can also undergo photolysis to form higher chlorine oxide radicals[92,93].

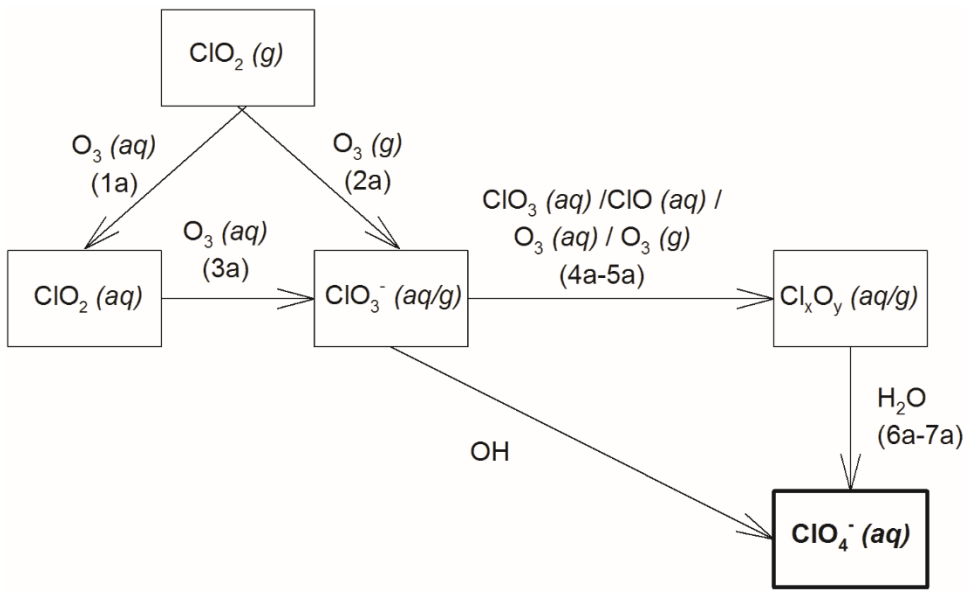

Figure 13. Proposed oxidation pathways for the formation of perchlorate in the stratosphere adapted from Rao et al.[82]. The numbers in parentheses correspond to the reactions listed in Table 7.

Table 7. Reaction rate constants for potential oxidation and hydrolysis reactions leading to perchlorate[82].

Reaction Number	Reaction	Rate Constant
1a	$ClO_2 + O_3^- \rightarrow O_3 + ClO_2^-$	$k = 1.8 \times 10^5\ M^{-1}\ s^{-1}$
2a	$O_3 + ClO_2 \rightarrow ClO_3 + O_2$	$k = 1.05 \times 10^3\ M^{-1}\ s^{-1}$
3a	$O_3^- + ClO_2 \rightarrow ClO_3^- + O_2$	$k = 1.8 \times 10^5\ M^{-1}\ s^{-1}$
4a	$ClO_3 + ClO_3 \rightarrow Cl_2O_6$	$k = 4.5 \times 10^8\ M^{-1}\ s^{-1}$
5a	$ClO_3 + ClO \rightarrow ClO_2O_4$	$k = 7.5 \times 10^9\ M^{-1}\ s^{-1}$
6a	$Cl_2O_6 + H_2O \rightarrow ClO_3^- + ClO_4^- + 2H^+$	$k_h = 180\ M^{-1}\ s^{-1}$
7a	$Cl_2O_4 + H_2O \rightarrow HClO + ClO_4^- + H^+$	$k_h = 180\ M^{-1}\ s^{-1}$

6.4.2 Oxidation

6.4.2.1 Ozone-Mediated Oxidation

In addition to perchlorate production being dependent on the availability and amount of activated chlorine, the mechanism for perchlorate production in the stratosphere proposed by Rao et al.[82] also suggests a dependence on ozone. Previous studies on the isotopic composition of the natural perchlorate found in the NO_3^- deposits

from the Atacama Desert have shown elevated $\Delta^{17}O$ levels[22]. Because perchlorate does not exchange oxygen atoms with the ambient environment, its oxygen isotopic signature retains that of its sources. Atmospheric ozone is known to have a highly positive $\Delta^{17}O$ signature, which can be transferred to products receiving oxygen in reactions. Thus, the elevated $\Delta^{17}O$ signature in perchlorate suggests ozone plays an important role in the oxidation of chlorine species[22]. Further evidence supporting the importance of ozone in the production of perchlorate can be inferred by investigating the seasonal variations in perchlorate concentrations and total column ozone measurements.

The annual oscillations in certain chemical impurities have already been discussed in their use as time markers for annual layer counting and dating ice core records (Chapter 4). These annual oscillations can also be useful in determining the seasonality of other species, such as perchlorate, which may provide clues about their atmospheric formation. Figure 14 shows the oscillations in the Ca^{2+} and perchlorate concentrations in SM07C2. Elevated Ca^{2+} concentrations in Greenland ice cores are associated with high dust content and peak in the boreal (northern hemisphere) spring[59]. As can be seen in Figure 14, although perchlorate does not demonstrate as explicit seasonal signal as Ca^{2+}, it does generally peak at approximately the same time or slightly after Ca^{2+}, indicating maximum perchlorate concentrations are reached in the late spring and early summer.

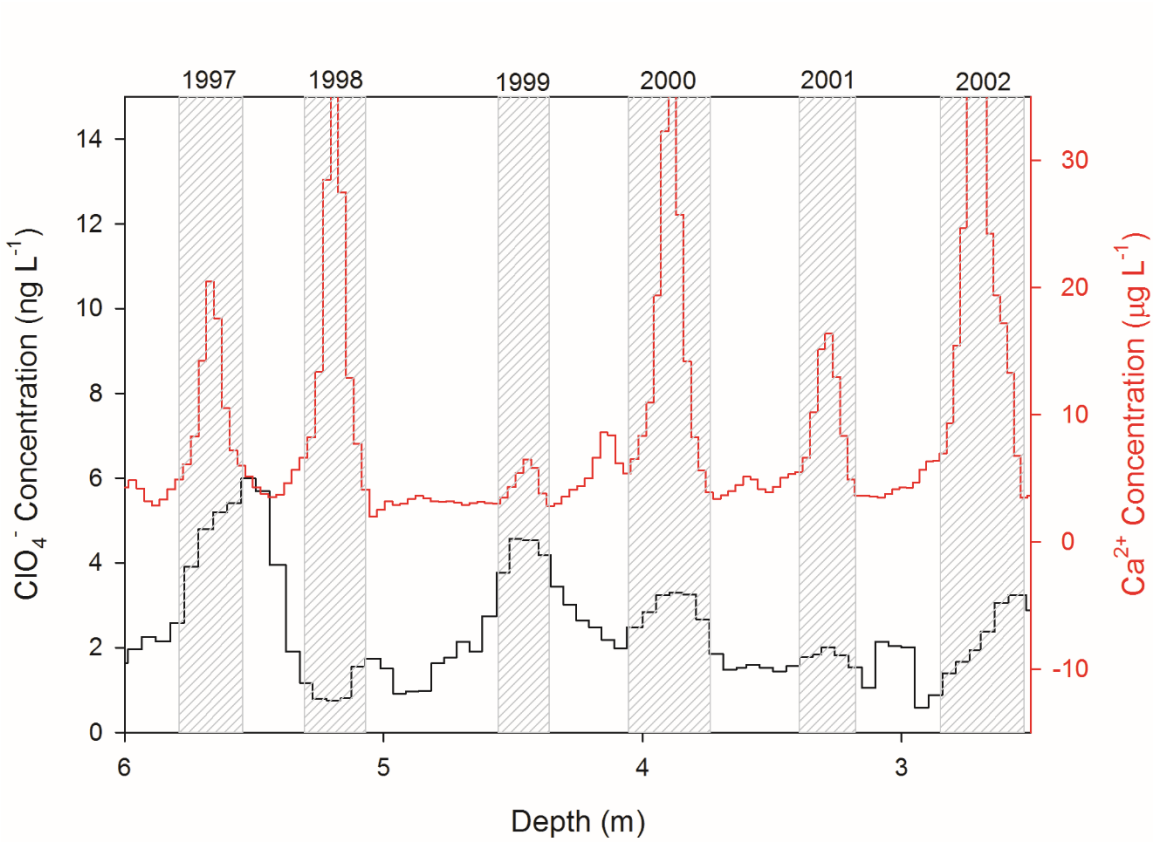

Figure 14. Seasonal oscillations in Ca^{2+} (red) and perchlorate (black) concentrations in SM07C2 between 1997 and 2002. Gray shaded bars (with years labeled on the top axis) highlight the maximum Ca^{2+} concentrations reached during the boreal spring (March-May). The perchlorate and Ca^{2+} concentrations are smoothed with a running average.

Total ozone also exhibits seasonal variations in Arctic locations. Figure 15 shows the monthly total ozone column concentrations at Sondrestrom, Greenland (67°00'38 N, 50°42'33 W) reported by the World Ozone and Ultraviolet Radiation Data Centre (WOUDC)[94] and average monthly perchlorate concentrations between 1997 and 2002 (the same time period shown in Figure 14) in SM07C2. In order to determine the monthly perchlorate concentration, the snow accumulation between Ca^{2+} peaks, which were assumed to peak March 1, was calculated. This value was then divided by 12 to approximate the average monthly snow accumulation. This information was then used to determine an average perchlorate concentration for each month. For example, if the

maximum Ca^{2+} concentration was reached at 2.0 m and the average monthly snow accumulation was 0.05 m, all perchlorate concentrations between 2.0 and 2.05 m were averaged and determined to be the average perchlorate concentration for March. As can be seen in Figure 15, maximum ozone concentrations are generally reached in the late winter and early spring, in which winter is defined as December-February and spring is defined as March-May. Although perchlorate concentrations appear to peak slightly later in the year, they do show a slight correlation with ozone indicating that ozone is involved in the formation of perchlorate. The slightly later peak in perchlorate concentrations could be due to a lack of sunlight in the late winter and early spring. The production of perchlorate also depends on radical chlorine, and the lack of sunlight in the late winter and early spring inhibits the generation of radical chlorine. In addition, the later perchlorate peak could be partially due to the assumption that snow accumulation is the same each month. Furdui and Tomassini[21] also noted a correlation between perchlorate concentrations at Devon Island, Canada and ozone concentrations from nearby Resolute Bay, Canada, and found that both reached maximum concentrations in the spring, further suggesting that ozone plays a key role in the formation of perchlorate.

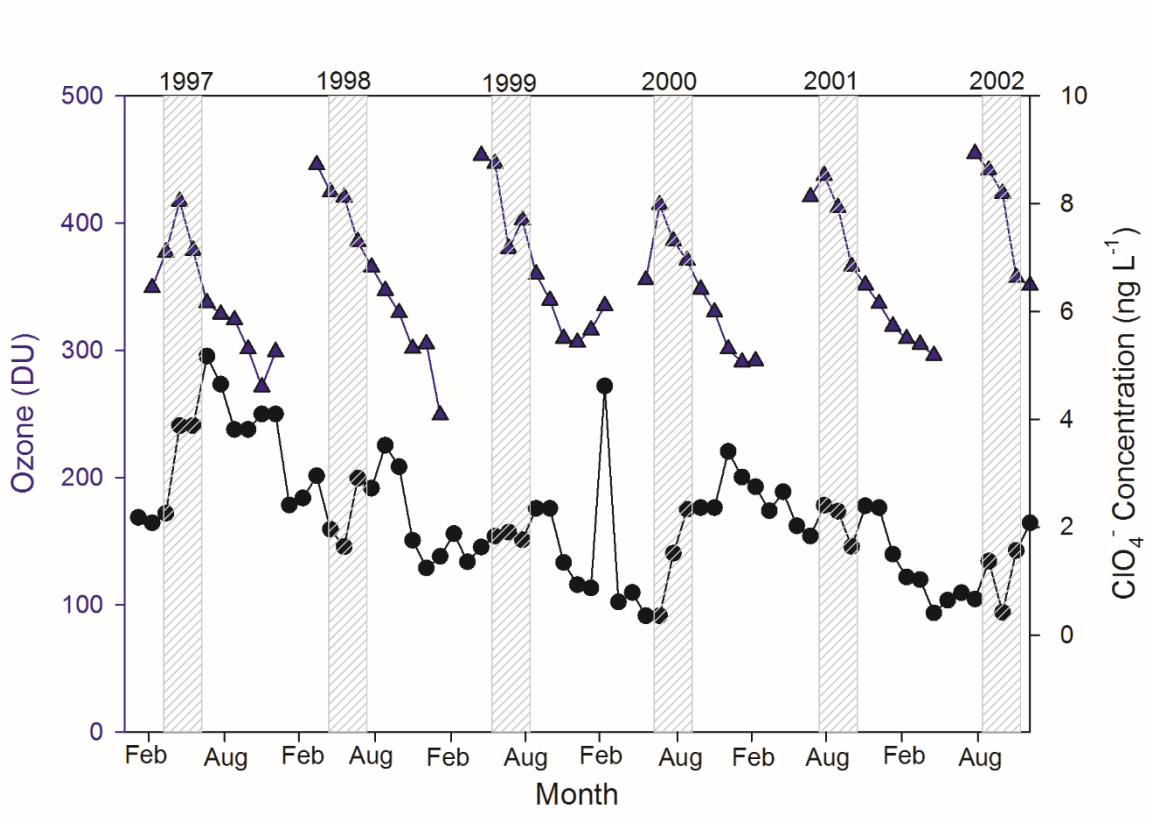

Figure 15. Monthly total ozone column concentrations (blue triangles) from Sondrestrom, Greenland[94] and average monthly perchlorate concentrations (black circles) in SM07C2. The gray shaded bars (with years labeled on the top axis) indicate the boreal spring (March-May).

The analysis of perchlorate in the snow pit samples collected from WAIS Divide, Antarctica has revealed that perchlorate concentrations in recent Antarctic snow exhibit a different seasonal signal than that in Greenland. Figure 16 shows the seasonal oscillations in the concentrations of perchlorate, non-sea salt (nss) SO_4^{2-}, and Cl^-. Sulfate in Antarctica derives mainly from sea salt and marine biogenic sources. The concentration of SO_4^{2-} that originates from marine biogenic sources (nss SO_4^{2-}) is calculated using the ratio of SO_4^{2-} to Na^+ in sea water[95]. Peak concentrations in nss SO_4^{2-} are reached during the austral summer (December-February) at WAIS Divide. Chloride in Antarctic ice cores mainly derives from sea salt and generally exhibits a peak in

concentration during the austral winter (June-August) due to the increased frequency and intensity of storms into Antarctica[95]. As can be seen in Figure 16, perchlorate concentrations reach a maximum slightly after peak SO_4^{2-} concentrations and slightly before peak Cl^- concentrations. Thus, perchlorate concentrations reach a maximum during the austral autumn (March-May) at WAIS Divide.

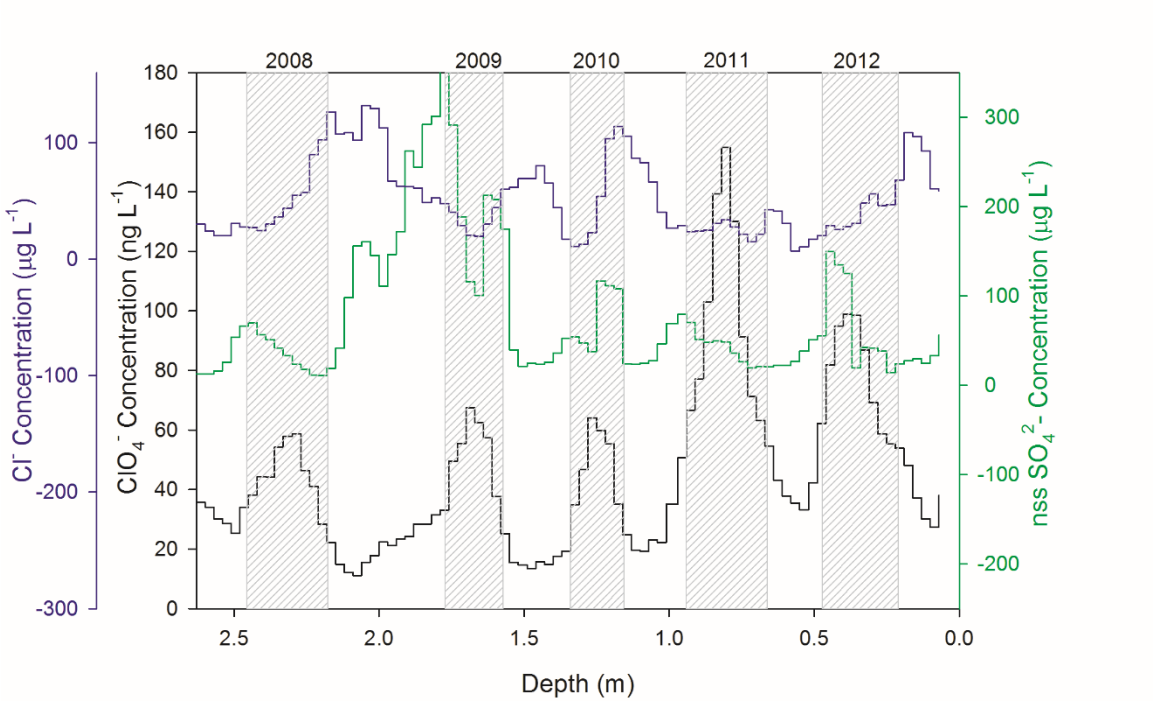

Figure 16. Seasonal oscillations in perchlorate (black), nss SO_4^{2-} (green), and Cl^- (blue) as seen in WAIS Divide snow pit samples between 2008 and 2012. The gray shaded bars (with years labeled on the top axis) highlight the austral autumn season when maximum ClO_4^- concentrations are reached. The data was smoothed with a running average.

The autumn peak in perchlorate concentrations seemingly contradicts the conclusion that activated chlorine is a major contributor to perchlorate production, as chlorine activation is most prominent in the austral spring. However, if the availability of ozone is taken into account, the difference in the seasonality of perchlorate in Greenland and Antarctica, as well as the autumn peak in perchlorate concentration in Antarctica can

be explained. The depletion of ozone over Antarctica during the austral spring over the last three decades has been well documented and is demonstrated in Figure 17, which shows the monthly total ozone column measurements from the South Pole reported by WOUDC[94] and average monthly perchlorate concentrations from WAIS Divide. The average monthly perchlorate concentrations were determined using the method described above, except in this case SO_4^{2-} concentrations were used to determine the annual snow accumulation and SO_4^{2-} concentrations were assumed to peak January 1. These measurements indicate that ozone concentrations reach a minimum during October and are relatively low throughout the austral spring (September-November). Thus, although there is more activated chlorine available for perchlorate production in the spring, ozone concentrations are low due to the significant depletion of ozone during this time; in this scenario it is likely that ozone limits the rate of perchlorate production. Therefore, a maximum in perchlorate concentrations is not observed in the spring in Antarctica as it is in Greenland, where spring ozone concentrations are much higher. As seen in Figure 17, ozone concentrations quickly recover from a spring minimum to reach maximum concentrations during the austral summer (December-February) before decreasing slightly during the autumn. Maximum ozone concentrations during the austral summer seem to suggest that perchlorate concentrations should also peak in the summer. However, warmer temperatures during the summer prevent the formation of PSCs, and thereby decreases the magnitude of chlorine activation. As a result, activated chlorine levels are likely much lower than during the austral spring and limits the rate of perchlorate production during the summer. The slight decrease in ozone concentrations during the austral autumn indicates increased chlorine activation over that during the

summer[96]. Unlike during the spring, though, ozone concentrations may remain sufficiently high to maintain or enhance the production of perchlorate, leading to maximum austral autumn perchlorate concentrations. Ozone concentrations increase again during the austral winter. However, the lack of sunlight over Antarctica during the winter prevents the release of chlorine radicals from their reservoirs, limiting perchlorate production. The relationship between stratospheric chlorine, ozone, and perchlorate concentrations is illustrated in Figure 18. In the end, the austral autumn peak in perchlorate concentrations at WAIS Divide indicates that perchlorate production depends on a delicate balance between activated chlorine and ozone concentrations. This is due to the close relationship between activated chlorine and ozone. As activated chlorine in the stratosphere increases, ozone levels decrease.

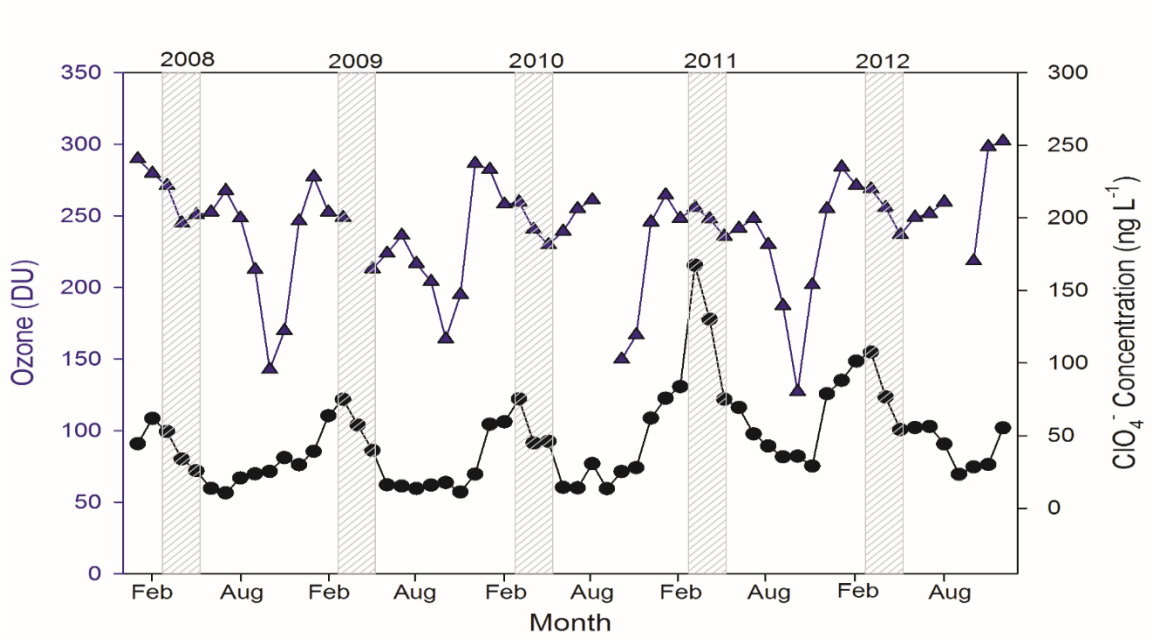

Figure 17. Monthly total ozone column concentrations (blue triangles) from the South Pole[94] and perchlorate concentrations (black circles) from WAIS Divide. The gray shaded bars (with years labeled on the top axis) indicate the austral autumn (March-May).

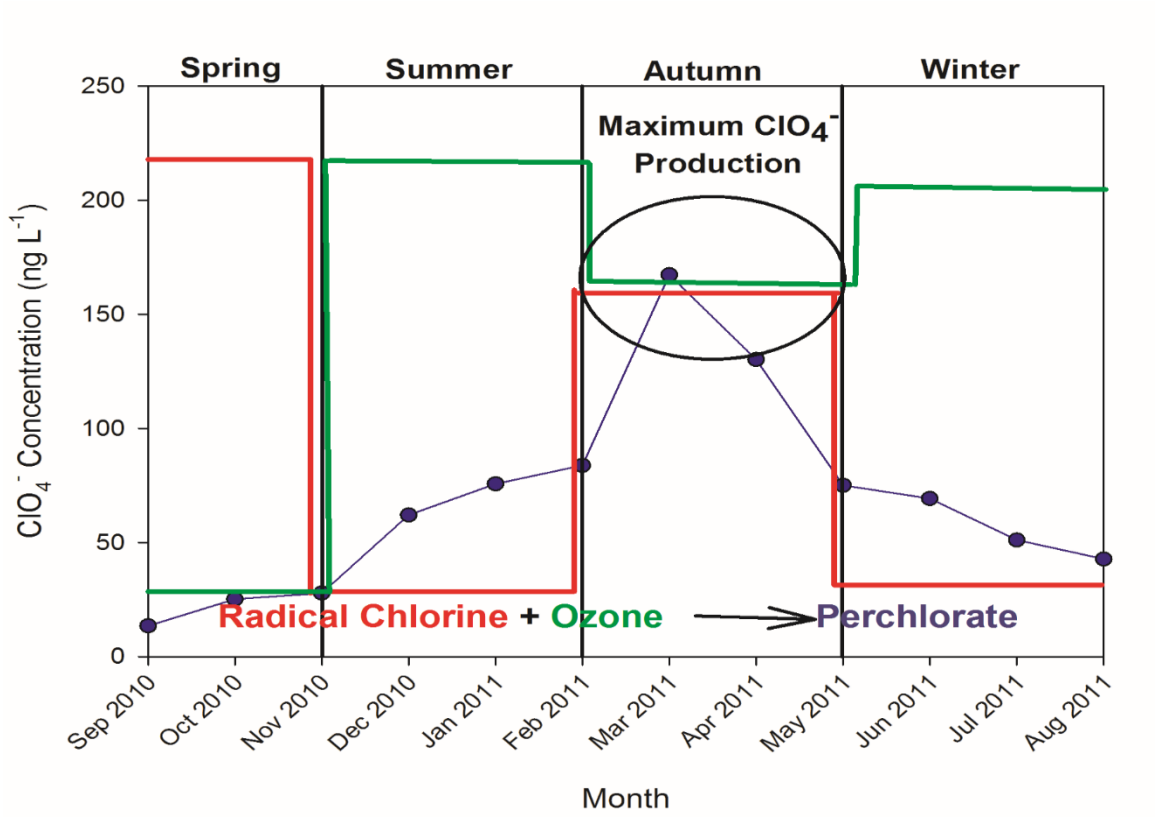

Figure 18. Relationship between radical chlorine (red), ozone (green), and perchlorate (blue circles) concentrations (WAIS Divide). Maximum perchlorate production occurs in the autumn when neither radical chlorine nor ozone concentrations are too low.

6.4.2.2 Photochemical Oxidation

Although there is strong evidence that ozone is directly involved in the oxidation of ClO_2 to higher chlorine oxide radicals, it should be noted that ClO_2 can also undergo photolysis in the presence of an unspecified oxygen source to form higher chlorine oxide radicals[92,93]. Quiroga et al.[93] found that perchlorate forms when ClO_2 undergoes photolysis in the gas phase, but not in the aqueous phase. The authors attributed this to the formation of Cl_2O_5 via photolysis in the aqueous phase as opposed to the perchlorate precursors Cl_2O_4 and Cl_2O_6. When Cl_2O_5 undergoes hydrolysis it preferentially forms

ClO_3, as opposed to perchlorate, via Reaction 14, whereas Cl_2O_4 and Cl_2O_6 form perchlorate, as shown in Reactions 15 and 16, respectively[93].

$$\text{(R14)} \quad Cl_2O_5 + H_2O \rightarrow 2ClO_3^- + 2H^+$$
$$\text{(R15)} \quad Cl_2O_4 + H_2O \rightarrow HClO + ClO_4^- + H^+$$
$$\text{(R16)} \quad Cl_2O_6 + H_2O \rightarrow ClO_3^- + ClO_4^- + 2H^+$$

In the aqueous phase the decomposition of Cl_2O_5 is likely prevented by rapid hydrolysis to ClO_3. On the other hand, in the gas phase, if Cl_2O_5 is formed, it is expected to decompose quickly, as the hydrolysis reaction is slowed due to lack of liquid water in the gas phase. Thus, in the gas phase the formation of Cl_2O_4 and Cl_2O_6 is favored. The absence of gas phase photolysis of ClO_2 is supported by the winter minimum in perchlorate concentrations in both Greenland and Antarctica due to the lack of sunlight over the Arctic and Antarctic during the winter. However, the activation of chlorine also requires sunlight. Therefore, the winter minimum in perchlorate concentrations could also be explained by a lack of activated chlorine. As a result, the data from the perchlorate record cannot determine which mechanism, ozone-mediated oxidation or photochemical oxidation, contributes more to perchlorate production, but it is possible that both processes are involved. Although, the elevated $\Delta^{17}O$ in natural perchlorate deposits[22] does suggest that ozone-mediated oxidation may be the more important contributor to perchlorate formation. Either way, it appears that the availability of sunlight is also an important factor in perchlorate formation as demonstrated by minimum perchlorate concentrations during the winter.

6.4.3 Hydrolysis

The final step in the formation of perchlorate according to the mechanism proposed by Rao et al.[82] is the hydrolysis of higher chlorine oxide radicals. Hydrolysis reactions in the stratosphere often occur on aerosol surfaces[97]. Most likely, gaseous higher chlorine oxide radicals undergo hydrolysis via heterogeneous reactions on H_2SO_4 aerosols, which are ubiquitous in the lower stratosphere[98]. Perchlorate has been observed within stratospheric H_2SO_4 aerosols[66], suggesting that perchlorate is being formed via hydrolysis in these aerosols in the stratosphere. Furthermore, in a series of wall reaction studies, Martin et al.[99], showed that after chlorine radical species were titrated with excess ozone and subsequently passed through H_2SO_4, measurable quantities of perchlorate were formed.

6.5 Conclusions

Based upon perchlorate seasonal patterns in Greenland (Summit, TUNU, and Basin 4), Antarctica (South Pole and WAIS Divide), and in other Arctic locations[21,36], the stratospheric production of perchlorate appears to be a major source of environmental perchlorate. Furthermore, the information from the high temporal resolution perchlorate data from SM07C2 and WAIS Divide strongly supports the stratospheric production mechanism for perchlorate proposed by Rao et al.[82] in which perchlorate production proceeds through ozone-mediated oxidation of radical chlorine species to higher chlorine oxide radicals, followed by hydrolysis of these radicals to form perchlorate. The ice core records also suggest that the production of perchlorate is dependent on a delicate balance between radical chlorine and ozone concentrations.

The apparent influence of the emission of CFCs on the observed trends in the perchlorate records is an example of how human activities can impact natural processes in the environment. As concentrations of stratospheric chlorine increased due to CFC emissions, the abundance of reactive chlorine species, such as ClO_2 and higher chlorine oxide radicals, also rose. This likely led to enhanced perchlorate production in the stratosphere. This enhanced production of perchlorate is likely the major contributor to the observed increase in perchlorate concentrations across Greenland and in Antarctica in the recent decades, as perchlorate concentrations are unlikely to be significantly impacted by the direct emission of perchlorate from manufacture, application, and disposal processes. However, this does not completely rule out a potential contribution from the usage of perchlorate, particularly in applications involving explosives, where perchlorate could reach the stratosphere and be disbursed across a large area.

7 Impact of Volcanic Eruptions

With the exception of the recent increase in concentrations, there appear to be no notable trends in perchlorate over the last 300 years. However, the 300-year perchlorate record does reveal substantially elevated perchlorate levels during brief periods. As seen in Figure 19, although transient, the elevated perchlorate levels are likely from sources that have not been identified or discussed. These sources are either direct sources of perchlorate, or they contribute to the enhanced atmospheric production of perchlorate, similar to how CFC emissions have increased perchlorate production. These peaks in perchlorate concentrations resemble the appearance of SO_4^{2-} peaks seen in ice core records. Because elevated SO_4^{2-} concentrations in ice cores are commonly associated with volcanic eruptions[100], it seems likely that the elevated perchlorate concentrations seen in Figure 19 are also influenced by volcanic eruptions. A potential link between volcanic eruptions and elevated perchlorate concentrations has been suggested by others[21,36], but due to limited data this link has remained speculative. As will be discussed below, the perchlorate record from SM07C2 provides strong evidence that volcanic eruptions do impact environmental perchlorate concentrations.

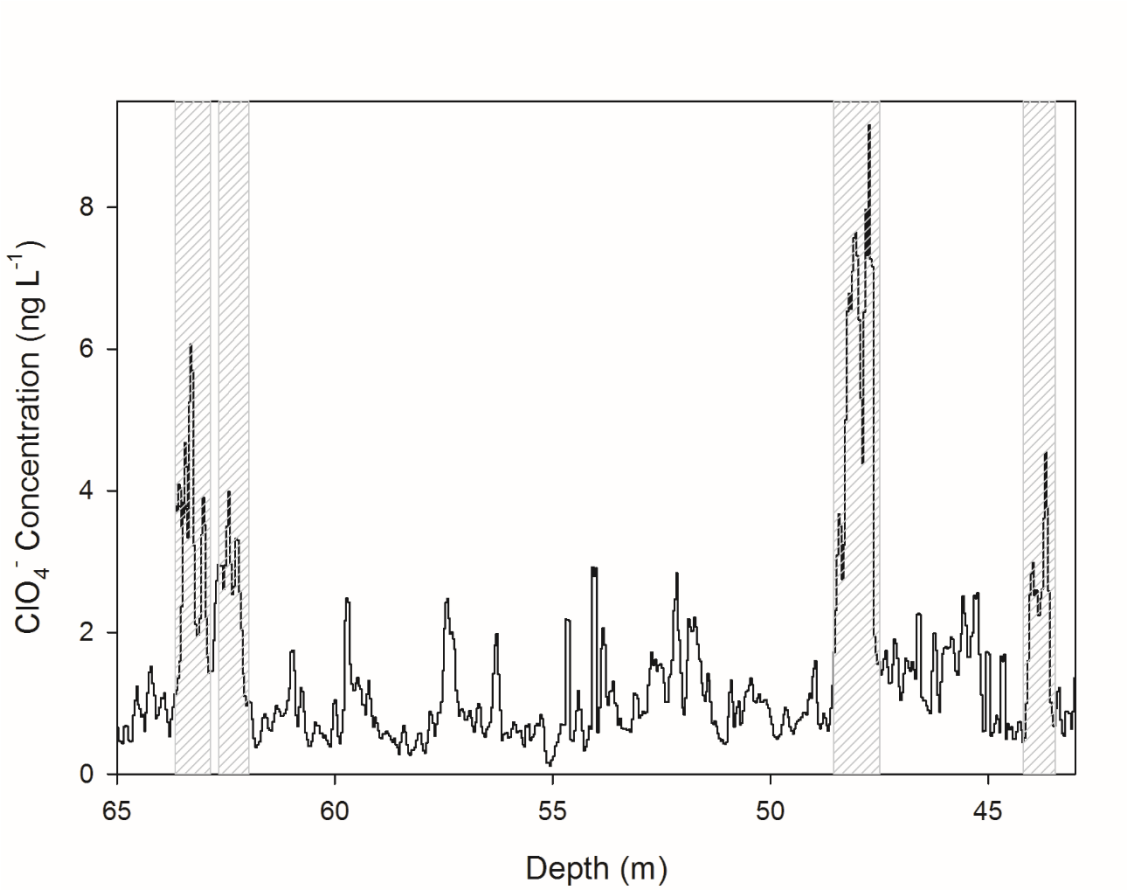

Figure 19. Perchlorate concentrations in SM07C2 between 1825 (left) and 1897 (right). The gray shaded bars highlight episodes of elevated perchlorate concentrations.

7.1 Identification of Volcanic Eruptions in Ice Cores

Volcanic eruptions emit significant quantities of SO_2, which is oxidized to H_2SO_4 in the atmosphere and form H_2SO_4 aerosols. These H_2SO_4 aerosols are eventually deposited from the atmosphere to the Earth's surface. The H_2SO_4 fallout from volcanic eruptions are preserved within the snow layers of ice sheets[101]. As a result, past volcanic eruptions are often identified in polar ice cores by increased SO_4^{2-} concentrations[100]. The volcanic eruptions in this study were identified by periods of increased SO_4^{2-} concentrations that corresponded with known volcanic eruptions. Using this technique, five volcanic events were identified. These volcanic events include Pinatubo

(Phillippines, 1991), El Chichón (Mexico, 1982), Krakatoa (Indonesia, 1883), Cosiguina (Nicaragua, 1835), and Babuyan Claron (Philippines, 1832).

The explosiveness of a volcanic eruption is rated on a scale ranging from 0-8, referred to as the volcanic explosivity index (VEI). Volcanic eruptions with a VEI of at least four are considered sufficiently explosive to have injected gaseous materials into the stratosphere[102]. With the exception of Babuyan Claron, all these eruptions had a VEI of at least five[103]. Although the VEI of Babuyan Claron is unknown, it is estimated to be four[43]. Thus, all five of the eruptions in this study were very large, explosive eruptions in which material was likely injected into the stratosphere.

7.2 Elevated Perchlorate Concentrations

The five volcanic eruptions mentioned above are all associated with elevated perchlorate concentrations in the SM07C2 record. This is demonstrated in Figure 20, which shows both perchlorate concentrations and the volcanic SO_4^{2-} signals in SM07C2 for each event. The volcanic SO_4^{2-} signals for Pinatubo and El Chichón are not readily identifiable in the record due to increased anthropogenic emissions of SO_2 in the 20th century[104] increasing the background levels and fluctuation of SO_4^{2-}. However, an increase in perchlorate concentrations during these two eruptions is still evident.

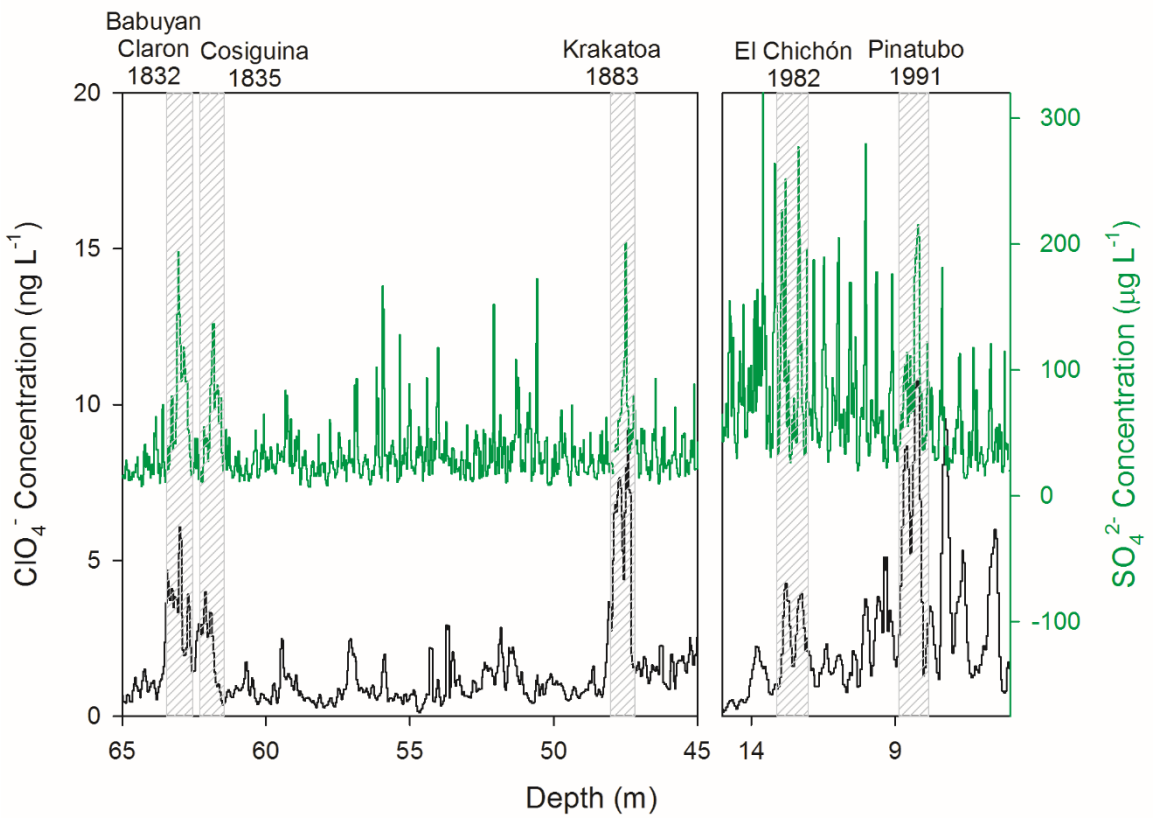

Figure 20. Perchlorate (black) and SO_4^{2-} (green) concentrations in SM07C2 with gray shaded bars highlighting elevated perchlorate and SO_4^{2-} concentrations associated with the volcanic eruptions of Babuyan Claron (1832), Cosiguina (1835), Krakatoa (1883), El Chichón (1982), and Pinatubo (1991).

7.2.1 Correlation between Perchlorate and Sulfate

A statistically significant positive correlation between SO_4^{2-} and perchlorate concentrations would further substantiate a link between volcanic eruptions and elevated perchlorate concentrations. In order to determine if such correlation exists, an analysis of variance (ANOVA) was performed. The correlation between perchlorate and SO_4^{2-} was determined to be statistically significant if the *p* value was less than 0.05. The results of the ANOVA tests for the five volcanic eruptions, as well as two non-volcanic sections are shown in Table 8. The non-volcanic sections were chosen to represent modern times (5-6 m, 1997-1999) and pre-Industrial Revolution times (60-61 m, 1840-1843). The results

from the ANOVA tests indicate that while there is not a correlation between perchlorate and SO_4^{2-} concentrations under non-volcanic conditions, there is a statistically significant positive correlation between the two ions during all five volcanic events. A significant correlation between perchlorate and SO_4^{2-} concentrations remains for the eruptions of El Chichón and Pinatubo, where anthropogenic SO_4^{2-} emissions may have masked a possible correlation. The lack of a statistically significant correlation between perchlorate and SO_4^{2-} concentrations under ambient atmospheric conditions, but the presence of a statistically signifcant correlation under volcanic conditions, is strongly indicative that volcanic eruptions contribute to increased perchlorate concentrations.

Table 8. Results from ANOVA tests for a correlation between perchlorate and SO_4^{2-} concentrations during volcanic events (*n* = number of samples, R = coefficient of determination).

Eruption	*n*	R	*p* value
Pinatubo	19	0.715	<0.001
El Chichón	25	0.489	0.013
Krakatoa	43	0.474	0.001
Cosiguina	26	0.530	0.005
Babuyan Claron	38	0.518	<0.001
Background (5 – 6 m)	19	0.300	0.212
Background (60 – 61 m)	26	0.302	0.396

7.3 Volcanoes as a Direct Source

One possible explanation for increased perchlorate concentrations associated with volcanic eruptions is that perchlorate is being injected into the atmosphere directly by the volcano. This explanation, however, is doubtful. Prior to an eruption, volcanoes have very low oxygen (O_2) concentrations. As a result, their chemistry is typically reducing[105]. However, terrestrial magmas contain volatile chlorine species[106]. During an eruption, the conditions change from reducing to oxidizing[105]. Thus, the volatile chlorine species

could be oxidized to perchlorate. Even if this were to occur, though, perchlorate's high solubility in water would mean it would be quickly scavenged by water droplets in the troposphere. As a result, any perchlorate emitted by a volcano or formed during the eruption would remain local and not be capabable of long-range transport. There were several Icelandic volcanic eruptions between 1870 and 1880 (48.75-52 m in Figure 19). However, as seen in Figure 19, there does not appear to be elevated perchlorate concentrations over the typical background variation across this section. This suggests that (1) perchlorate is not directly emitted by the volcanic eruptions and (2) the volatile chlorine species present in the magma are not oxidized to perchlorate immediately after the eruption. Thus, volcanic eruptions likely influence the atmospheric production of perchlorate by impacting atmospheric chemistry.

7.4 Volcanic Aerosols

Volcanic eruptions emit significant quantities of gas and ash into the atmosphere. In the case of very large, explosive eruptions, the introduction of these materials has been shown to impact climate. Ash clouds from volcanoes can darken skies by blocking visible sunlight and contribute to reduced solar heating. These effects, however, are generally short-lived and limited geographically because ash settles out of the atmosphere by gravity quickly after the eruption has ceased[101]. The main gases emitted by volcanoes include water vapor, CO_2, SO_2, H_2S, and HCl[107]. The contribution of water vapor and CO_2 to the atmosphere from volcanic eruptions are neglible due to large reservoirs of these species in the atmosphere. Therefore, the climatic impacts from these gases are insignificant. The emission of sulfur compounds (mostly as SO_2), on the otherhand, are known to impact climate, especially when these compounds are injected into the

stratosphere. The H_2SO_4 aerosols resulting from the emission of SO_2 can efficiently scatter visible light, reducing the energy that reaches the Earth's surface. Therefore, the presence of H_2SO_4 aerosols contributes to cooling at the Earth's surface[101]. The lifetime of H_2SO_4 aerosols in the troposphere is short, approximately a week. Therefore, as is the case with volcanic ash, any climate impact from these aerosols when they are only present in the troposphere is very short-lived and geographically limited[43]. The lifetime of volcanic H_2SO_4 aerosols in the stratosphere, though, is much longer, ranging from months to a few years[108]. Thus, when SO_2 is injected into the statosphere, H_2SO_4 aerosols can have long-term impacts on global climate. In addition to impacting climate, H_2SO_4 aerosols can also influence atmospheric chemistry, potentially leading to increased concentrations of chemically reactive species, such as reactive chlorine, in the stratosphere[109].

7.5 Possible Explanations for Increased Perchlorate Concentrations

As discussed in section 7.3, volcanoes are unlikely to release perchlorate directly to the environment. Most likely volcanoes are changing atmospheric conditions in a way that favors perchlorate production. One possible way volcanoes could do this is through the emission of chlorine species, such as HCl. If these chlorine species reach the stratosphere, they could enhance the stratospheric production of perchlorate. Another possibility is that H_2SO_4 aerosols from an eruption enhance chlorine activation in the stratosphere resulting in increased perchlorate production. The likelihood of these two explanations are discussed below.

7.5.1 Input of Chlorine to the Stratosphere

Volcanic eruptions could contribute to elevated perchlorate levels by the injection of chlorine species into the stratosphere. Major volcanic eruptions can inject anywhere from 0.5 to 5 Mt (1 Mt = 1 million metric tons) of HCl into the atmosphere[110]. Considering that the the total mass of chlorine in the stratosphere under ambient conditions is approximately 0.5 Mt, if the HCl from a large volcanic eruption reaches the stratosphere, volcanic eruptions could potentially increase stratospheric chlorine concentrations by 2-10 times.

However, there is evidence that very little of the HCl emitted during an eruption reaches the stratosphere. Measurements of stratospheric chlorine by Mankin et al.[111] and Wallace et al.[112] following the eruption of Pinatubo indicated that less than 1% of the total chlorine emitted during the eruption entered the stratosphere. Furthermore, if a significant amount of HCl reached the stratosphere, elevated levels of Cl^- in ice core records would be expected[110]. However, ice core records provide little evidence that Cl^- concentrations increase due to volcanic eruptions[113,114]. This is demonstrated in Figure 21, where there does not appear to be an increase in Cl^- concentrations in the SM07C2 record associated with the eruptions of Babuyan Claron, Cosiguina, or Krakatoa. The reason very little chlorine emitted during a volcanic eruption reaches the stratosphere is because HCl is likely scavenged by supercooled water within the volcanic plume prior to reaching the stratosphere. Tabazadeh and Turco[110] discussed the physical properties of a volcanic plume, as well as how HCl is scavenged prior to reaching the stratosphere.

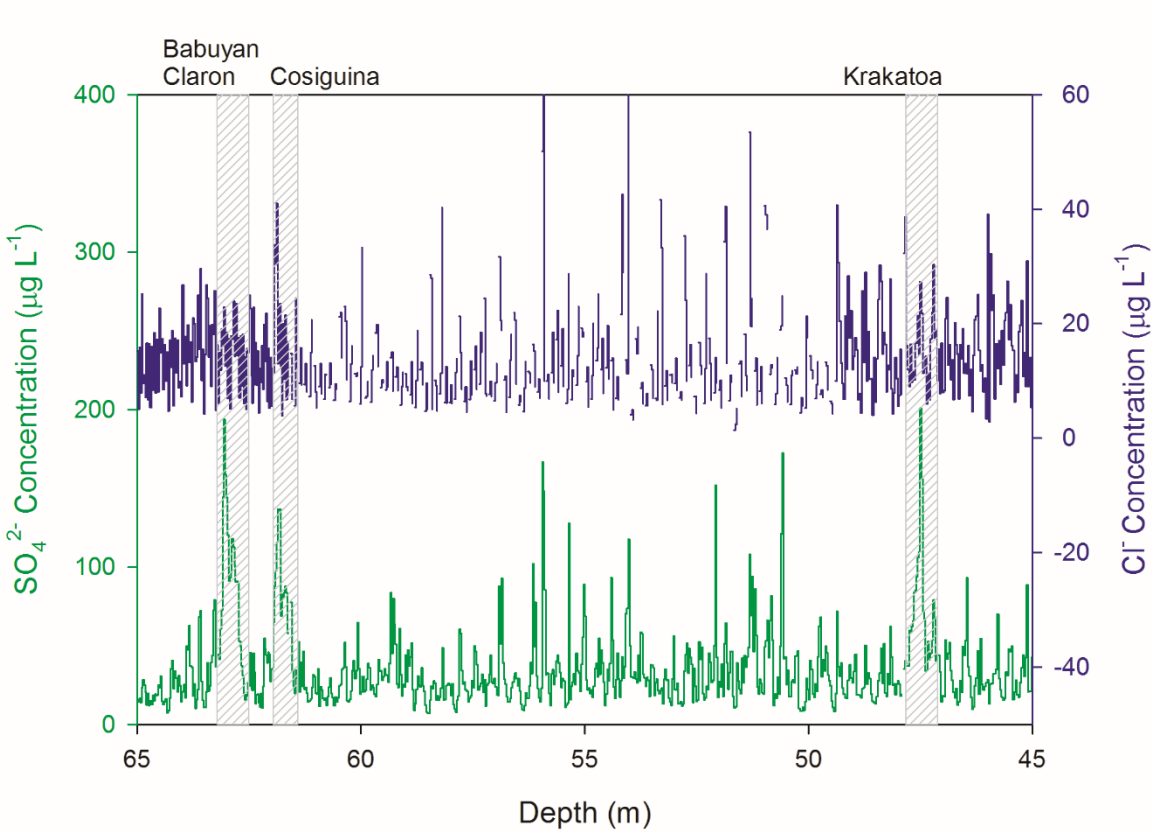

Figure 21. Sulfate (green) and Cl^- (blue) concentration profiles in SM07C2 between 1825 and 1891. Gray shaded bars highlight the Babuyan Claron (1832), Cosiguina (1835), and Krakatoa (1883) volcanic eruptions.

Although the injection of HCl into the stratosphere is usually prevented due to scavenging by supercooled water droplets, models by Textor et al.[115] suggest that as much as 25% of the HCl emitted by a volcanic eruption could become associated with ice particles rather than supercooled water droplets and reach the stratosphere. However, based on Cl^- concentrations, this does not appear to be the case for the volcanic eruptions in this study (Figure 21). Occasionally, unique eruption conditions can contribute to increased chlorine concentrations in the stratosphere. This is believed to be the case in the eruption of El Chichón, where Mankin et al.[116] observed stratospheric HCl levels to increase by 3%. This is also demonstrated in the SM07C2 record (Figure 22), where

there does appear to be a slight increase in Cl^- concentrations associated with the eruption of El Chichón. El Chichón injected a large amount of halites, mostly as NaCl, which reacted with H_2SO_4 in the stratosphere to form gaseous HCl via Reaction 17 *(ref 117)*.

$$\text{(R17)} \quad 2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl$$

Therefore, under unique eruption and atmospheric conditions, the stratospheric loading of HCl could become an important factor in increased perchlorate production. However, it does not appear to be the driving force behind the increased perchlorate levels observed in SM07C2 due to a lack of increased Cl^- concentrations associated with the volcanic eruptions studied (with the exception of El Chichón). Even if stratospheric chlorine concentrations were to increase due to a volcanic eruption, the chlorine would still have to undergo activation in order to produce perchlorate.

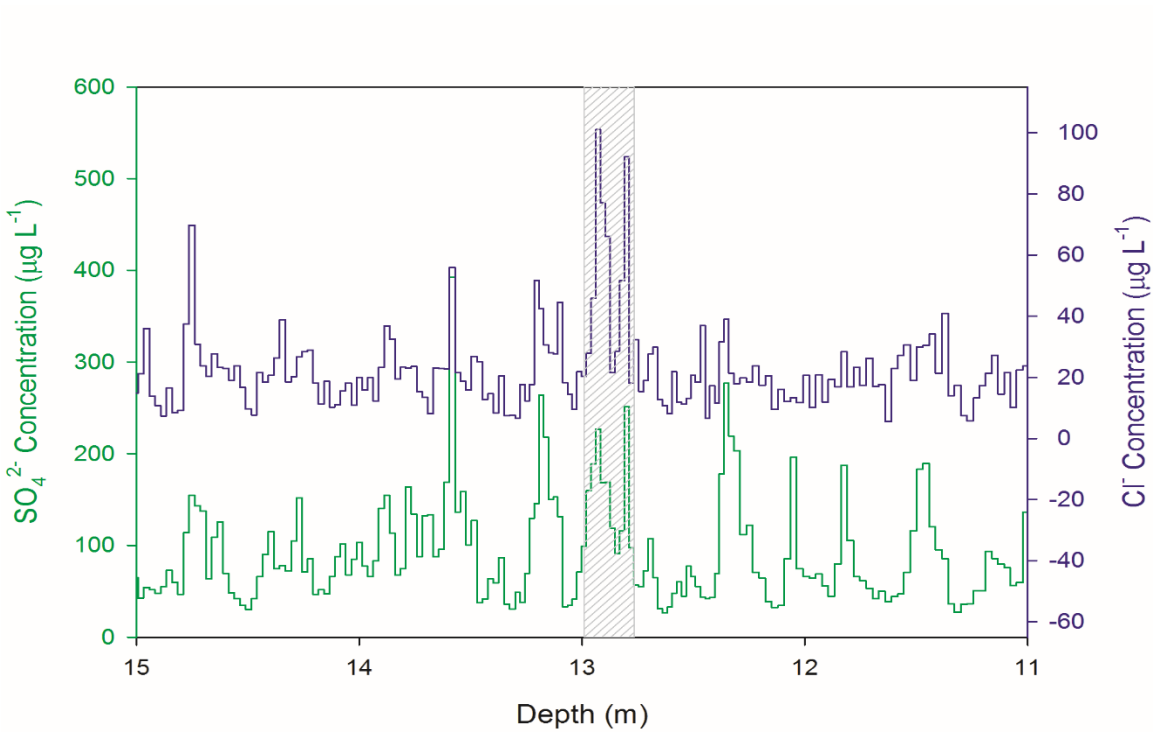

Figure 22. Sulfate (green) and Cl^- (blue) concentration profiles in SM07C2 between 1977 (left) and 1986 (right). The gray shaded bar highlights the El Chichón eruption (1982).

7.5.2 H_2SO_4 Aerosols

Despite the lack of an observed increase in overall stratospheric chlorine concentrations following the eruption of Pinatubo[111,112], Solomon et al.[118] observed increased levels of ClO_2 over Antarctica, which is indicative of enhanced chlorine activation[107]. The increased levels in activated chlorine are likely leading to the increased perchlorate concentrations associated with volcanic eruptions. Therefore, it appears that volcanic eruptions influence chlorine activation. Because the increase in chlorine activation does not seem to stem from increased chlorine concentrations, there must be another factor contributing to the activation of the chlorine that was already present in the stratosphere.

Unlike HCl, SO_2 has a low solubility in water under typical volcanic plume conditions[110] and can therefore reach the stratosphere. This leads to the increase in H_2SO_4 aerosols following a volcanic event. Solomon et al.[118] suggest that the presence of H_2SO_4 aerosols is responsible for the increased chlorine activation observed over Antarctica following the eruption of Pinatubo, as H_2SO_4 aerosol surface area was observed to increase substantially during this time period[119]. The surface provided by H_2SO_4 aerosols can lead to heterogeneous chlorine activation in the same way the surface provided by PSCs does, resulting in enhanced chlorine activation. Furthermore, laboratory studies by Tolbert et al.[120] and Hanson and Ravishankara[121] have shown that Reactions 18 and 19 take place in H_2SO_4.

$$\text{(R18)} \quad N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

$$\text{(R19)} \quad ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$$

Although HNO_3 can undergo photolysis to form NO_2, this reaction is much slower than

the photolysis of N_2O_5 to form NO_2 *(ref 122)*. The HNO_3 formed can also be removed via denitrification preventing its photolysis to NO_2. Thus, the formation of HNO_3 via Reactions 18 and 19 inhibits the formation of NO_2, which, as discussed in Chapter 6, is responsible for the termination of chlorine radicals. As a result, these reactions indirectly contribute to chlorine activation. Also, the HOCl formed in Reaction 19 can rapidly undergo photolysis to form ClO•, which is likely the source of the observed increase in ClO_2, perhaps the most important precursor to perchlorate.

Once chlorine activation occurs, the production of perchlorate likely proceeds through the process outlined in Chapter 6. However, it is important to remember that the formation of perchlorate is not solely dependent on the availability of activated chlorine species. The availability of ozone is also a very important factor, and increased activated chlorine is typically associated with decreased ozone concentrations. Ozone concentrations were observed to decrease over Antarctica following the eruption of Pinatubo[109]. Single day total ozone column measurements in October 1992 and 1993, revealed the lowest ozone concentrations on record, which was attributed to unusually cold temperatures and the presence of H_2SO_4 aerosols from Pinatubo[123]. As can be seen in Figure 23, unlike in SM07C2 (Figure 20), there does not appear to be a significant increase in perchlorate concentrations associated with the eruption of Pinatubo at the South Pole. Furthermore, there is not a statistically significant correlation between perchlorate and SO_4^{2-} concentrations ($R = 0.342$, $n = 12$, $p = 0.276$). The absence of a perchlorate peak associated with the eruption of Pinatubo in Antarctica could be because ozone concentrations became too low to contribute to increased perchlorate production. In the Arctic, however, ozone loss was not observed, despite indications of an

enhancement in H_2SO_4 aerosol surface area and increased levels of activated chlorine species[124]. In order to determine if the absence of a perchlorate peak associated with the Pinatubo eruption in Antarctica is due to lower ozone concentrations, perchlorate and ozone data from Antarctica covering other volcanic eruptions would be needed.

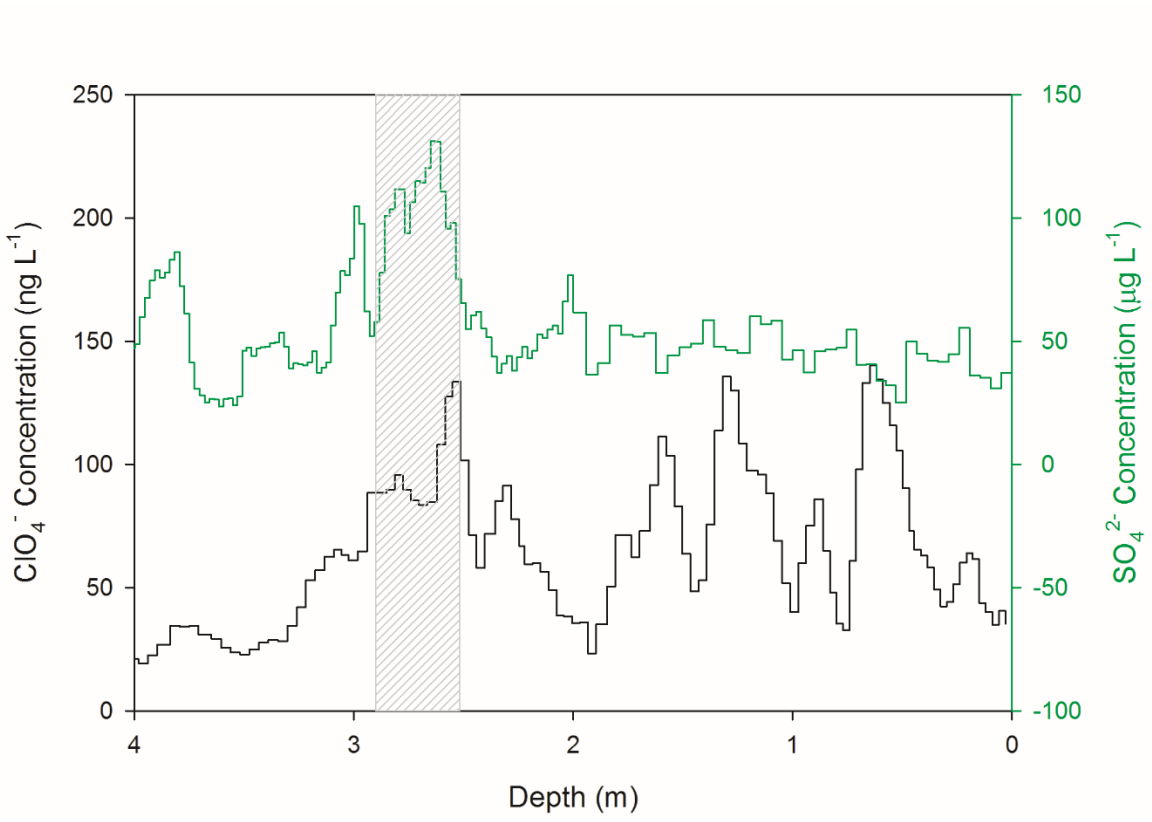

Figure 23. Perchlorate (black) and SO_4^{2-} (green) concentrations in the South Pole ice core associated with the eruption of Pinatubo (highlighted by the gray bar).

Another possible explanation for why there is not a significant increase in perchlorate concentrations observed in Antarctica corresponding with the eruption of Pinatubo could be that the small increase in perchlorate concentrations typically associated with volcanic eruptions is simply not relevant due to higher background concentrations of perchlorate in Antarctica than in Greenland. The perchlorate concentrations in Greenland were only observed to increase approximately 1-6 ng L^{-1}

when associated with a volcanic eruption. As the background perchlorate concentrations in Greenland are on average only about 1 ng L^{-1}, this marks a significant increase. However, the background perchlorate concentrations at the South Pole are approximately 50 ng L^{-1}. The small increase in perchlorate concentrations due to a volcanic eruption may not be detectable in the fluctuation of the high background in Antarctica. In the case of the Pinatubo eruption, this seems to be the more likely explanation for the absence of a perchlorate peak. Despite ozone reaching its lowest recorded concentrations in 1992 and 1993 over the South Pole, these extremely low concentrations appear to have been short-lived (on the order of days). As demonstrated in Figure 24, the monthly ozone concentrations reported by WOUDC were not significantly lower in these years compared to other years. Furthermore, the average ozone concentrations in the three years before (1988-1990) and three years after (1992-1994) the eruption of Pinatubo, 261.9 and 248.2 DU[94], respectively, are very similar. A Mann-Whitney Rank Sum Test indicated that there was no statistical difference between the ozone concentrations for these time periods ($p = 0.518$).

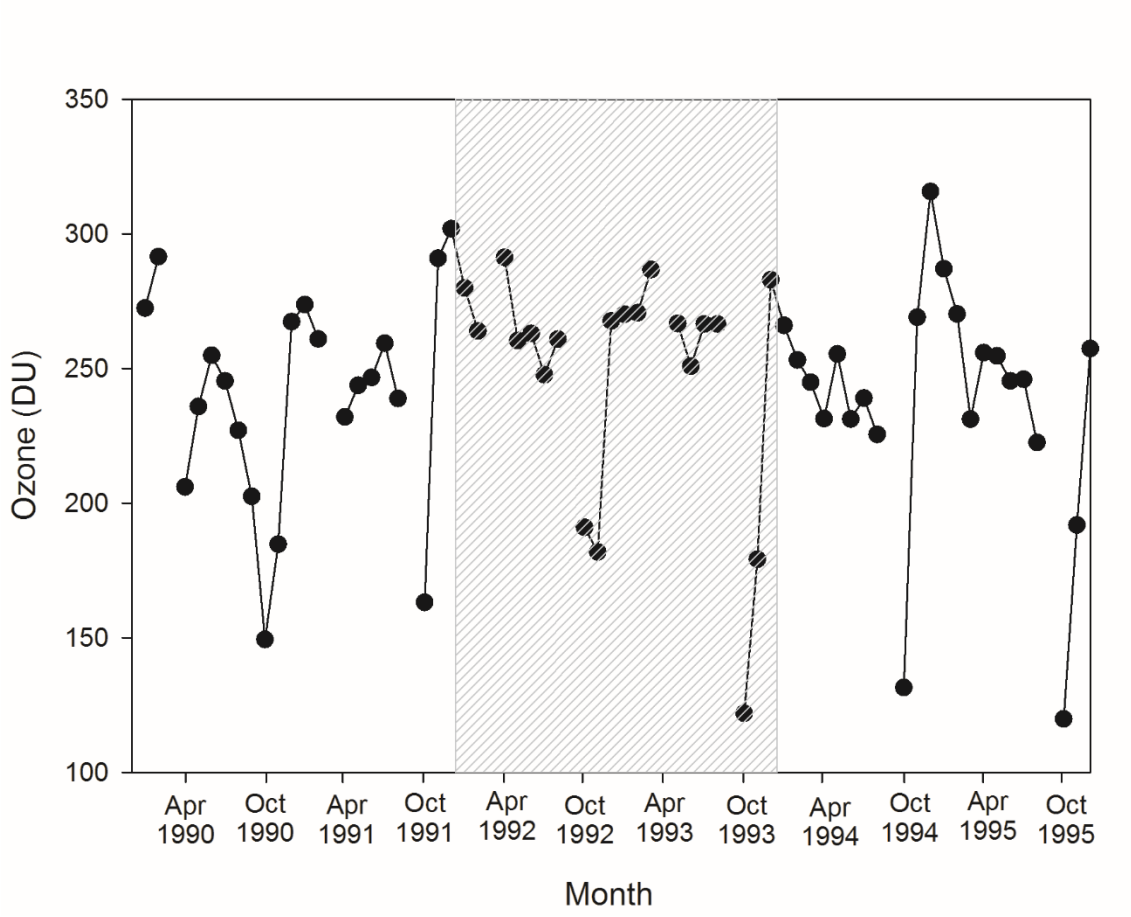

Figure 24. Monthly ozone concentrations at the South Pole[94] between 1990 and 1995. The gray shaded box highlights the years 1992-1993, in which there were short-lived periods of ozone depletion.

As can be seen in Figure 25, there does appear to be a small perchlorate peak in the South Pole record associated with the eruption of Mt. Agung (VEI = 5)[103] in Indonesia in 1963. Like Pinatubo, the eruption of Mt. Agung does not meet the criteria for a significant correlation between SO_4^{2-} and perchlorate concentrations (R = 0.574, *n* = 11, *p* = 0.065). The eruption of Mt. Agung occurred before the formation of the ozone hole. Thus, ozone depletion associated with the eruption would likely have less of an impact than for the eruption of Pinatubo because ozone concentrations were higher. Also, as was the case for Pinatubo there was not a statistically significant difference (*p* =

0.122) between ozone concentrations in the two years prior (1961-1962) and the three years following (1964-1966) the eruption.

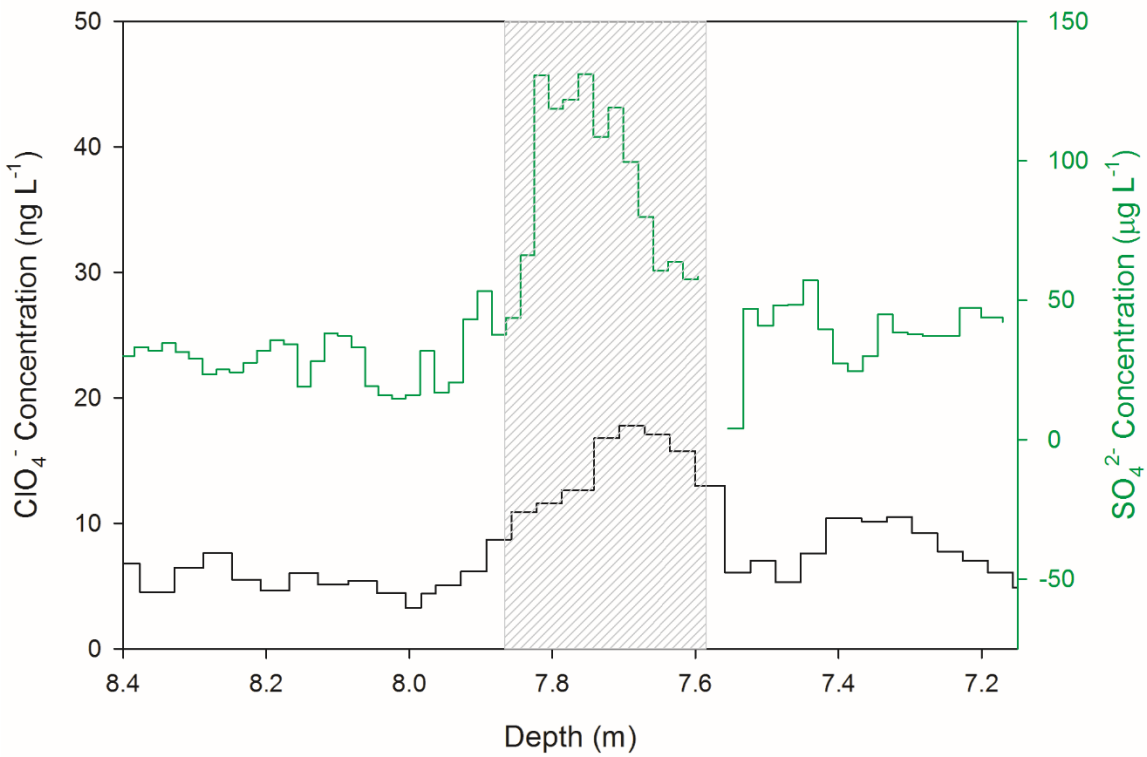

Figure 25. Perchlorate (black) and SO_4^{2-} concentrations from the South Pole associated with the 1963 eruption of Mt. Agung (highlighted by the gray-shaded bar).

The background perchlorate concentrations at the time of the Mt. Agung eruption are much lower (6 ng L^{-1}), than at the time of the Pinatubo eruption (50 ng L^{-1}). Thus, the fluctuation in perchlorate concentrations associated with volcanic eruptions is more relevant to the background perchlorate concentrations at the time of Mt. Agung. This likely explains why there appears to be a small peak in perchlorate concentrations at the time of Mt. Agung. Although, the correlation between SO_4^{2-} and perchlorate did not meet the criteria for a statistically significant correlation, it is much stronger than that for Pinatubo. The lower background perchlorate concentrations at the time of Mt. Agung

likely accounts for the stronger correlation. However, a definitive connection between volcanic eruptions and perchlorate concentrations in Antarctica cannot be made until other evidence is found.

7.6 Conclusions

The 300-year perchlorate record from SM07C2 reveals a connection between perchlorate concentrations in the Arctic and volcanic eruptions. During the periods of volcanic eruptions (Pinatubo, El Chichón, Krakatoa, Cosiguina, and Babuyan Claron), a statistically significant positive correlation is found between perchlorate and SO_4^{2-} concentrations. In contrast, no significant correlation is found between the two ions during typical non-volcanic periods. Whether there is a connection between perchlorate and volcanic eruptions in the Antarctic remains unclear. The Antarctic perchlorate data only covers the eruptions of Pinatubo and Mt. Agung. Neither eruption displayed a significant correlation between SO_4^{2-} and perchlorate concentrations. This could be due to greater ozone depletion over Antarctica preventing the oxidation of activated chlorine, or because the increase in perchlorate concentrations due to the eruption may be undetectable compared to the higher background perchlorate concentrations in Antarctica. Because the eruption of Mt. Agung occurred before the ozone hole, at a time when background perchlorate concentrations were much lower than for Pinatubo, and exhibits a stronger correlation between SO_4^{2-} and perchlorate concentrations, the latter seems to be the more likely explanation. Other volcanic eruptions, particularly eruptions occuring when background perchlorate concentrations are much lower (prior to 1950) than the current levels, need to be investigated to determine if there is a link between perchlorate and volanic eruptions in the Antarctic.

The most important factor contributing to elevated perchlorate concentrations appears to be the volcanic H_2SO_4 aerosols in the stratosphere. These aerosols are believed to be responsible for the elevated levels of reactive chlorine species observed in the stratosphere above Antarctica associated with the eruption of Pinatubo by enhancing the heterogeneous activation of chlorine species already present in the stratosphere. As described in Chapter 6, activated chlorine species are important precursors to perchlorate. Thus, enhanced chlorine activation likely leads to enhanced perchlorate production. In addition, the increased amount of H_2SO_4 aerosols may also contribute to increased hydrolysis of higher chlorine oxide radicals, further enhancing perchlorate production following a volcanic eruption. Although the emission of HCl by volcanic eruptions does not appear to be a major factor in increased perchlorate concentrations due to efficient HCl scavenging in the troposphere[110], it is possible that under unique eruption conditions the injection of chlorine species into the stratosphere may be a minor factor in perchlorate production.

Elevated perchlorate levels are only observed for large, stratospheric volcanic eruptions, not for small tropospheric eruptions, supporting the conclusion that perchlorate production likely occurs only in the stratosphere. Furthermore, the volcano-perchlorate connection supports the conclusion that a key factor in determining perchlorate production appears to be the activation of chlorine species. In the case of volcanic eruptions, activation appears to occur on the surface of H_2SO_4 aerosols in a fashion similar to chlorine activation on PSCs, resulting in elevated levels of reactive chlorine in the stratosphere, and consequently elevated perchlorate concentrations.

The role of H_2SO_4 aerosols on perchlorate production may be even more

pronounced at non-polar latitudes, where temperatures are not cold enough to permit consistent PSC formation. Therefore, chlorine activation is likely controlled by the availability of solid and liquid particles, such as H_2SO_4 aerosols. The concentration of H_2SO_4 aerosols was observed to increase at non-polar latitudes following the eruption of Pinatubo[125]. This is consistent with increased concentrations of ClO• indicating enhanced chlorine activation[125], which likely led to increased perchlorate production. Jaeglé et al.[126] performed balloon-borne measurements of total chlorine species in the stratosphere out of Fort Sumner, New Mexico in September 1993, when H_2SO_4 aerosol concentrations were still high following the Pinatubo eruption. The measurements revealed the observed levels were lower than the predicted levels by 30-40% (approximately 0.2 $\mu g\ L^{-1}$). The authors suggest that the missing fraction of chlorine was in the form of $HClO_4$. If true, the increased presence of H_2SO_4 aerosol due to a volcanic eruption at non-polar latitudes may play a much larger role in enhancing perchlorate production at non-polar latitudes than it does at polar latitudes.

8 Unknown Perchlorate Event

Prior to 1980, perchlorate concentrations in the Summit, Greenland ice core typically ranges from about 0.3-2 ng L^{-1}, with an average concentration of 1.0 ± 0.8 ng L^{-1} (n = 1,763). Brief anomalies with higher perchlorate concentrations, typically associated with volcanic eruptions, are observed, but even during these events the maximum perchlorate concentration reached is only 9.1 ng L^{-1}. Even in post-1980 samples, where perchlorate concentrations are likely influenced by the emission of CFCs, the maximum concentration is 10.7 ng L^{-1}, also likely influenced by the eruption of Pinatubo. The largest anomaly in SM07C2, though, reaches a maximum concentration of 43.7 ng L^{-1}, approximately 4 times higher than concentrations observed anywhere else in the record. This anomaly, which is highlighted in Figure 26, occurs between 1908 and 1914 and remains difficult to explain. Ice core samples over this time period were analyzed twice and the same result was obtained. Therefore, it appears unlikely that this anomaly stems from analytical error or contamination, but rather derives from perchlorate deposition in central Greenland. Although uncertainty about the cause of the anomaly remains, possible explanations, including two potential volcanic eruptions and a superbolide event, are discussed below.

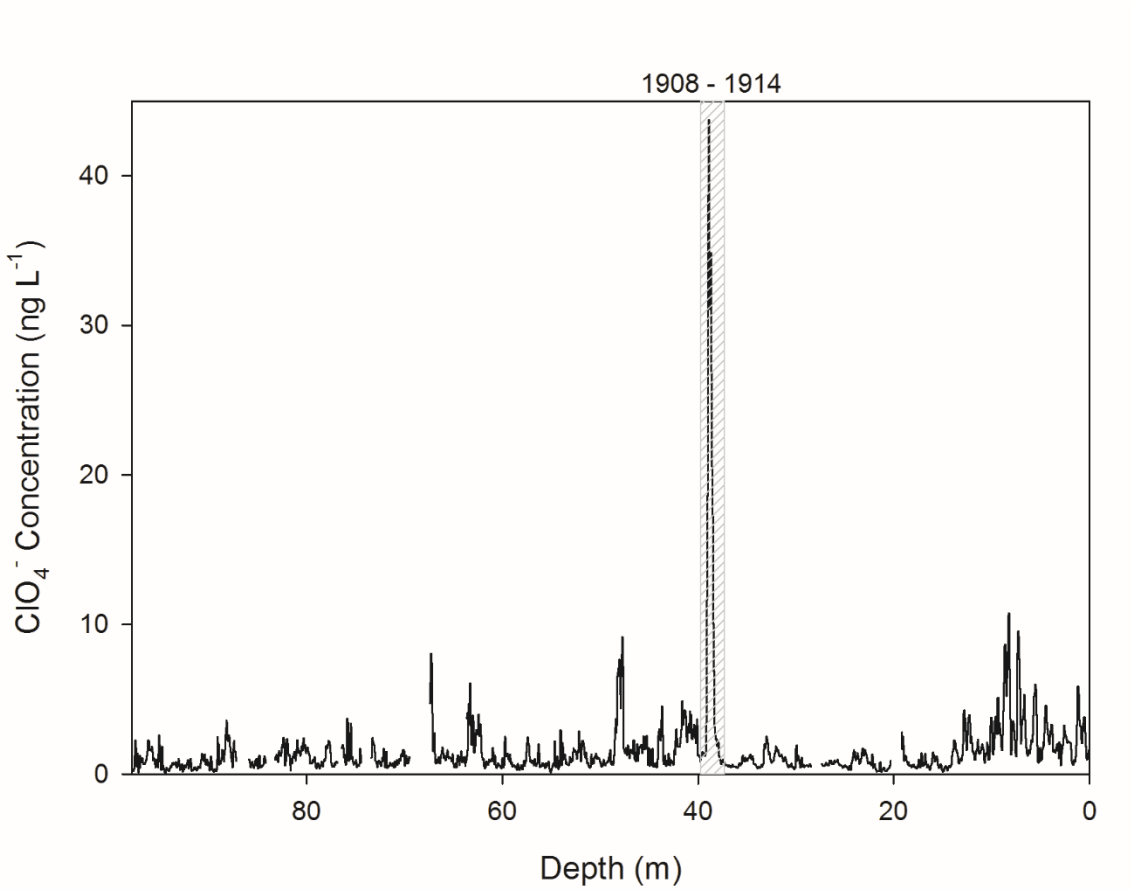

Figure 26. The entire perchlorate record from SM07C2 (1700-2007) with the gray shaded bar highlighting an outstanding perchlorate event occuring between 1908-1914.

8.1 Volcanic Impact

Most brief periods of elevated perchlorate concentrations appear to be connected to volcanic eruptions. In this case, it is possible that volcanic eruptions may be contributing to the high perchlorate concentrations observed between 1908 and 1914, as there were two volcanic eruptions around this time. The first was the March 1907 eruption of Ksudach in Russia (VEI = 5) and the second was the June 1912 eruption of Katmai in Alaska, United States (VEI = 3)[103]. While these two volcanic eruptions probably did contribute to increased perchlorate production to an extent, several pieces of evidence indicate that they are unlikely the sole source behind the elevated perchlorate

concentrations observed between 1908 and 1914. First, as mentioned above, the maximum perchlorate concentrations observed for this anomaly are significantly higher than those observed for any other volcanic eruption. Second, a statistically significant positive correlation between SO_4^{2-} concentrations and perchlorate concentrations was found in each of the five volcanic eruptions studied in Chapter 7, where the eruptions appeared to be the sole contributor to the elevated perchlorate levels. No such statistically significant correlation between SO_4^{2-} and perchlorate concentrations (n = 36, R = 0.198, p = 0.248) is found in this early 20th century event. Finally, closer examination of this anomaly in perchlorate concentrations reveals that the maximum concentrations occurred in 1911. The maximum concentrations, therefore, occur at a time when it would be expected that perchlorate concentrations would no longer be elevated due to Ksudach, and before concentrations would be influenced by the eruption of Katmai. Thus, other factors which could contribute to the elevated perchlorate levels need to be considered.

8.2 Bolide Events

A bolide is a large cosmic body, such as part of a comet or an asteroid, that explodes within the Earth's atmosphere resulting in the emission of a bright light and release of a large amount of energy. Due to the release of a large amount of energy bolides can have significant atmospheric impacts. The atmospheric impact of a bolide depends heavily on its density[127]. Occasionally, superbolides, bolides with an apparent magnitude (measure of brightness) of at least -17 (brightness increases with decreasing apparent magnitude), explode in the atmosphere. These superbolides can have even more devastating physical and atmospheric effects than typical bolides. The most recent

superbolide was the Chelyabinsk meteor that exploded over Russia in 2013. Another superbolide, which exploded over Russia in 1908 and is referred to as the Tunguska Event, may be partially responsible for the large peak in perchlorate between 1908 and 1914.

8.2.1 Tunguska Event

On June 30, 1908 a meteor entered the Earth's atmosphere and exploded approximately 9 km above the Tunguska River basin in Siberia[127]. The explosion was so massive that it was heard over 1,000 km away[128]. The energy released from the explosion is estimated to be 5×10^{16} J, approximately 60 times the energy released by the atomic bomb dropped on Hiroshima at the end of World War II. The force from the explosion killed hundreds of reindeer[129], knocked men 60 km away from their feet[128], and downed 2,200 km^2 of forest[127]. The airwave disturbance caused by the explosion circled the Earth twice[128]. In the days following the the explosion, Europe experienced bright nights caused by the scattering of sunlight by dust particles during which there was enough light to read outdoors at midnight[130]. The Tunguska Event is the largest meteor impact event in recorded history[128].

Despite being classified as a meteor impact event, the Tunguska Event does not appear to have generated a crater[128,130–132]. Some suggest that Lake Cheko in Siberia may be a crater from the event, but these claims are heavily disputed[130]. The lack of a crater and any fragments of a substantial size, coupled with the fact that the first scientific investigation into the Tunguska Event did not occur until 1927, 19 years after the event, have led to considerable debate over the nature of the event. A wide range of theories have been suggested, some more plausible than others. Perhaps the most extraordinary

theory about the Tunguska Event was suggested by Alexander Kazantsev in 1946 *(ref 130)*. Kazantsev suggested that a nuclear powered alien spaceship exploded, an idea that was earnestly pursued for several decades. Another interesting theory was proposed by Jackson and Ryan[133], in which the Tunguska Event was caused by a black hole passing through the Earth. One idea that garnered significant attention was first suggested by Lincoln Lapaz. Lapaz proposed that the Tunguska explosion was due to a meteor containing antimatter[130]. The antimatter theory seemed to gain support when elevated carbon-14 levels were observed in tree rings dated at 1909, suggesting the release of radiation when the antimatter was annihilated as it hit the atmosphere[134]. However, elevated levels of carbon-14 have not been observed from antimatter annihilation in nearby cosmos. Thus, this theory has lost favor.

Several theories about the nature of the Tunguska event have revolved around the idea that it was an exploding comet. This idea was first proposed in 1930 when Harlow Shapely suggested that the explosion was due to a very low density comet. Shapely argued that due to the low density of the comet, it exploded and burned up at altitude, explaining the lack of a crater[130]. The idea of an extremely low density comet was accepted by others including Turco et al.[135], who in 1982 suggested that the comet had a density of 0.003 g cm^{-3}. Another theory, proposed in 1989 and not as widely accepted, was that a deuterium-rich comet was turned into a hydrogen bomb when it was exposed to extreme heat and pressure as it entered Earth's atmosphere[130]. The final theory involving a comet is that the exploding body was a fragment of Comet Encke. A meteor shower derived from the dust from Encke reportedly occurred around the time of the Tunguska Event[130].

Originally, the idea that the Tunguska Event could be due to a stony asteroid was neglected because of the lack of a crater. Turco et al.[135] suggested that the atmosphere could only overcome the momentum of a low-density object to slow it down enough to cause complete vaporization prior to reaching the ground. However, as more information was collected about the event, it was discovered that a comet would likely explode at too high of an altitude to account for the ground observations, such as the downing of the Siberian forests. This led Chyba et al.[136] to model the entry of different types of cosmic bodies, such as comets, carbonaceous asteroids, iron asteroids, and stony asteroids, into Earth's atmosphere. The authors found that comets and carbonaceous asteroids would likely explode at too high of an altitude, and iron asteroids would likely not be completely burned in the atmosphere and would reach the Earth's surface resulting in a crater. Based upon the results from the model, the authors concluded that the Tunguska Event was most likely caused by a stony asteroid approximately 30 m in diameter with a density of 3.5 g cm^{-3} and mass of 560,000 Mg, traveling at about 15 km s^{-1}, and exploding at an altitude around 9 km *(ref 136)*.

8.2.2 Atmospheric Impacts of Tunguska

Because the first investigations into the Tunguska Event did not occur until 19 years after the event, much of what is assumed about the atmospheric impacts of the event is based on models as opposed to actual measurements of the direct impact of the event. Also, most of the investigations into the Tunguska Event have been into the nature of the meteor itself. Therefore, there have been only a few investigations into the atmospheric impacts of the event. However, the effort has been complicated by the fact that the atmospheric impacts of a bolide event depend heavily on the nature of the bolide.

Because of the debate over the nature of the bolide responsible for Tunguska, there have been conflicting reports on the atmospheric impacts of the event, most notably on how ozone was affected. Below, the possible atmospheric effects of the Tunguska Event are discussed in the context of the most important factors leading to perchlorate formation: ozone, chlorine, and aerosols.

8.2.2.1 Ozone

The energy generated from the ablation of a bolide passing through the atmosphere can break the triple bond in N_2 molecules. This is followed by the formation of active nitrogen species, including NO *(ref 137)*. Thus, a bolide event can result in the production of a tremendous amount of NO_x ($NO + NO_2$). As shown in Reactions 20 and 21 *(ref 71*), NO_x can lead to the destruction of ozone through a catalytic cycle.

$$\text{(R20)} \quad NO\bullet + O_3 \rightarrow NO_2\bullet + O_2$$

$$\text{(R21)} \quad NO_2\bullet + O \rightarrow NO\bullet + O_2$$

However, NO_x can also prevent ozone destruction by reacting with other ozone depleting substances, such as HO• and ClO•, converting them to unreactive reservoir species, as seen in Reactions 22 and 23, respectively[71].

$$\text{(R22)} \quad HO\bullet + NO_2\bullet \rightarrow HONO_2$$

$$\text{(R23)} \quad ClO\bullet + NO_2\bullet \rightarrow ClONO_2$$

Whether NO_x contributes more to ozone destruction or more to the prevention of ozone destruction depends mostly on altitude. NO_x mainly contributes to ozone destruction above an altitude of 25 km, but because of higher radical chlorine concentrations in the lower stratosphere, NO_x typically prevents ozone destruction below an altitude of 25 km *(ref 71)*. However, in an atmosphere with low halogen concentrations, NO_x can

contribute significantly to ozone loss[71], as NO_x is not consumed by reactions with ClO•, allowing it to enter the catalytic ozone destruction cycle.

Turco et al.[128] predicted that as much as 30 Tg of NO could have been formed in the atmosphere as a result of the Tunguska Event. Assuming that 30 Tg of NO was injected into the stratosphere, the authors modeled that stratospheric ozone could have been depleted by as much as 45% across the entire Northern Hemisphere within the first year following the event, with significant depletion persisting for 3 or more years. Turco et al.[128] also modeled ozone depletion over a limited latitude band ranging from 55-65° N. The results from this model suggested that ozone depletion was as high as 96% above an altitude of 10 km within the first month. This depletion, though, was only expected to last a few months, rather than years.

The possible ozone depletion described by Turco et al.[128] relies on the generation of a significant amount of NO in the atmosphere. However, no evidence of such a large production of NO associated with the Tunguska Event has been found. Because NO_3^- is an oxidative product of NO_x, it has served as a proxy in ice cores of atmospheric NO_x *(ref 133)*. Thus, a significant generation of NO would be reflected by elevated NO_3^- in ice cores. As can be seen in Figure 27, NO_3^- concentrations in SM07C2 during the Tunguska Event are not elevated. Furthermore, Rasmussen et al.[132] also measured NO_3^- concentrations associated with the Tunguska Event in ice cores from Camp Century, (77.18°N, 61.11°W) and Dye-3 (65.18°N, 43.83°W), Greenland. As in SM07C2, no elevated levels of NO_3^- were observed. Because no elevated levels of NO_3^- were observed, Rasmussen et al.[132] estimated that the total NO resulting from the Tunguska Event could not exceed one standard deviation of the average annual global NO fallout.

Thus, the authors suggest that the maximum NO formed from Tunguska could only be about 0.6 Tg *(ref 132)*, as opposed to 30 Tg. As a result, it is very unlikely that stratospheric ozone underwent the significant depletion described by Turco et al[128].

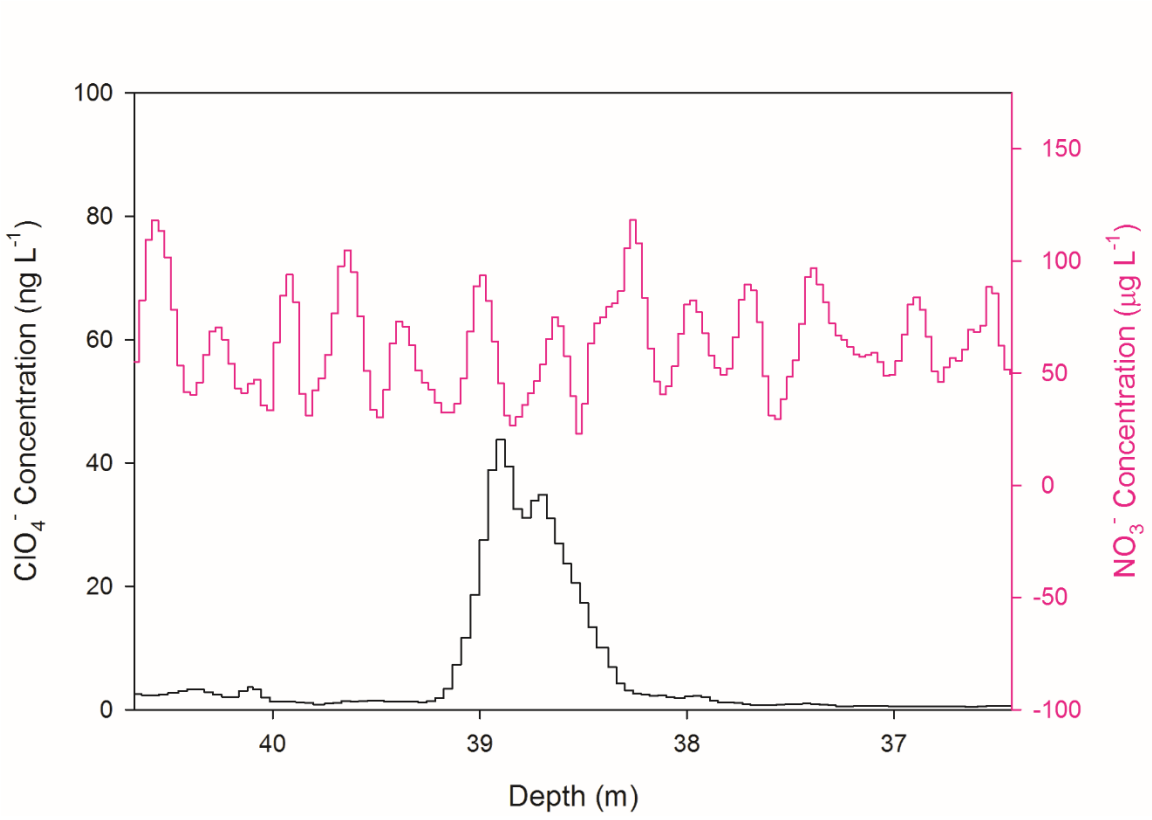

Figure 27. Perchlorate (black) and NO_3^- (pink) concentrations between 1906-1918 in SM07C2.

The estimate made by Turco et al.[128] that 30 Tg of NO was produced by the Tunguska Event, was based on the assumption that the Tunguska meteor was a low density comet (0.003 g cm^{-3}) entering the atmosphere with approximately 10^{18} J of kinetic energy. In this case, NO would be efficiently produced throughout the mesosphere and stratosphere due to ablation of the comet, and only about 1% of its energy would be released at the time of explosion approximately 9 km above the surface[127]. However, if the Tunguska meteor was a stony asteroid, significantly less NO

would be produced. Due to its higher density, a stony asteroid would not undergo significant ablation. As a result, nearly all of its energy (assumed to be 5×10^{16} J)[127] would be released at the point of explosion. Operating under these assumptions, and that the NO production efficiency is 1.5×10^{17} molec J^{-1} (same value assumed by Turco et al.[127]), Curci et al.[127] predicted that only about 0.4 Tg of NO were produced by the Tunguska Event. This is much more consistent with the 0.6 Tg of NO predicted by Rasmussen et al[132].

Assuming that the Tunguska meteor was a stony asteroid and that 0.4 Tg of NO were produced in the troposphere, Curci et al.[127] also modeled ozone depletion associated with the Tunguska event. The modeling results suggest that ozone was nearly completely scavenged from the troposphere 3-4 days after the event, but then concentrations increased briefly by about 30% compared to the ozone levels prior to the Tunguska Event. Despite the near complete scavenging from the troposphere immediately after the event, the model shows that the monthly mean ozone concentrations would only drop by, at most, a few percent[127], consistent with models performed by Melott et al[137]. Based upon these models, the ozone depletion associated with Tunguska was very short-lived and constrained in the troposphere. Because perchlorate is assumed to be formed in the stratosphere, the short-lived depletion of ozone in the troposphere would not likely inhibit perchlorate production. On the other hand, as ozone does not appear to increase over this time period, it would not have led to enhanced perchlorate production. As a result, it appears that changes in ozone associated with the Tunguska Event would not have played a role in the highly elevated perchlorate levels.

8.2.2.2 Chlorine

The explosion of the Tunguska meteor was so powerful that debris from the explosion has been claimed to be found in ice cores from the South Pole, indicating that the debris was injected into the stratosphere[131]. Therefore, if the meteor contained a substantial quantity of chlorine, it is possible that a large amount of chlorine was injected into the stratosphere, which could lead to enhanced perchlorate production. Unfortunately, investigations into the mineralogical and chemical compositions of the Tunguska meterorite have not reported chlorine content.

A rough estimate of the chlorine content of the Tunguska meteor may be inferred based upon chlorine measurements from other meteorites. However, this inference may not be completely valid due to the uncertainty over the identity of the Tunguska meteor. Even with the assumption that the Tunguska meteor was a stony asteroid, chlorine content may vary significantly among different classifications of stony asteroids. Garrison et al[138]. studied the total chlorine content in 94 different types of meteorites and found that the chlorine concentrations differ greatly both between classes of meteorites, and within the same class of meteorites. Chlorine concentrations for stony asteroids ranged from 1-653 mg kg^{-1}, with an average of 82 ± 111 mg kg^{-1} (n = 124)[137]. If a chlorine concentration of 82 mg kg^{-1} is used to calculate a rough estimate of the mass of chlorine released from the explosion of the Tunguska meteor, the total amount of chlorine released would only be approximately 4.6×10^{-5} Mt. This mass of chlorine is insignificant when compared to the ambient mass of chlorine in the stratosphere (0.5 Mt). Finally, as shown in Figure 28, the chloride concentrations in SM07C2 throughout the

Tunguska Event remain unchanged from the background levels, suggesting that stratospheric chlorine concentrations were not impacted by the event.

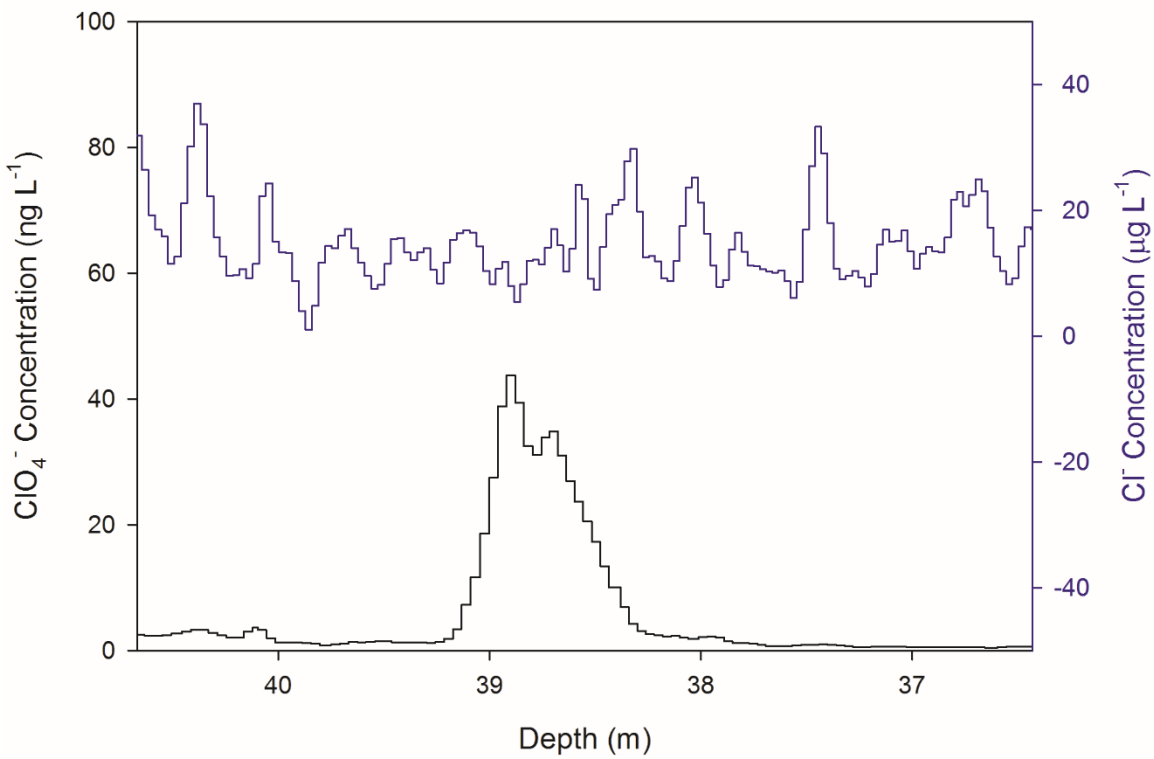

Figure 28. Perchlorate (black) and Cl^- (blue) concentrations between 1906-1918 in SM07C2.

Although it does not appear that meteorites contribute enough chlorine to the stratosphere to greatly impact the production of perchlorate, a recent study by Jackson et al.[139] suggests that a fraction of the chlorine content of meteorites could be in the form of perchlorate. A series of perchlorate measurements on two different chondrite meteorites (a class of stony asteroid) showed that perchlorate concentrations ranged from 0.06-6.0 mg kg^{-1} with an average concentration of 2.4 ± 1.9 mg kg^{-1} (n = 8)[139]. If the average perchlorate concentration observed by Jackson et al. is applied to the Tunguska meteor, approximately 1.3 Mg of perchlorate would have been released by the explosion.

Therefore, it is possible that the Tunguska meteor itself served as a direct source of perchlorate. However, this estimation is based on two major of assumptions. First, this assumes that the Tunguska meteor is a stony asteroid. Secondly, the estimation assumes that perchlorate concentrations in the chondrite meteorites are representative of all classes of stony asteroids. The variation of perchlorate concentrations observed by Jackson et al.[139] range over two orders of magnitude, demonstrating that perchlorate concentrations are not consistent within a single class of meteorite, much less among different classes of meteorites. Jackson et al. also found perchlorate to be present in lunar samples[139] and Catling et al.[140] found perchlorate on Mars, suggesting that it may be ubiquitous throughout the Solar System. Therefore, it is not unreasonable that the Tunguska meteor contained perchlorate, which was released on explosion in the atmosphere. Although intriguing, this explanation for the increased levels of perchlorate that seem to be associated with the Tunguska Event is speculative at this stage of research.

8.2.2.3 Aerosols

Similar to the case for volcanic eruptions, the increased perchlorate levels may be due to increased aerosol or dust surface in the stratosphere during the Tunguska Event. Once again, little information is available on the impact the Tunguska Event had on stratospheric aerosols. However, studies on more recent bolide events, such as the Chelyabinsk meteor explosion over Russia in 2013, can provide some insight into the potential impact of the Tunguska Event.

The 18 m diameter, 11,000 ton Chelyabinsk bolide is one of only two bolide events over the last century to release energy comparable in magnitude to the Tunguska Event, releasing approximately the equivalent of 570 kt of TNT[141], or 2.4×10^{15} J

(Tunguska = 5×10^{16} J). Most of the debris from the explosion was transported upward in a mushroom cloud. The Ozone Mapping Profiler Suite Limb Profiler (OMPS/LP) identified a meteor dust belt in the stratosphere with a vertical depth of approximately 5 km following the explosion of the Chelyabinsk meteor. Although the Tunguska meteor exploded at a much lower altitude than the Chelyabinsk meteor (9 km compared to 23.3 km)[142], there is evidence that meteoric debris still entered the stratosphere. Ganapathy[131] estimated that approximately 7×10^{6} tons of debris was injected into the stratosphere by the explosion of the Tunguska meteor. As suggested by the studies on the Chelyabinsk meteor, the meteoric debris injected into the stratosphere could have formed dust belts.

The effects the meteor dust belt from the Chelyabinsk meteor on stratospheric chemistry have yet to be studied. However, it is known that meteoric debris can serve as a condensation nuclei for the formation of stratospheric clouds[142]. Thus, it is possible that in addition to providing a surface for heterogeneous chlorine activation itself, the meteoric debris/dust could also promote the formation of stratospheric clouds, providing additional surface for heterogeneous chlorine activation. Thus, it seems plausible that the presence of dust particles in the stratosphere from the Tunguska Event, could have led to enhanced chlorine activation. This enhanced chlorine activation, if it did occur, could be responsible for the increased perchlorate concentrations observed in SM07C2 following the Tunguska Event. Future studies on the impact bolide events have on stratospheric chemistry could contribute to evaluating the significance of this mechanism for enhanced perchlorate production.

8.3 Future Investigations into the Tunguska Event

Although the hypothesis that the Tunguska Event is mainly responsible for the elevated perchlorate levels observed in SM07C2 appears plausible, more research is needed before a definitive conclusion can be made. First, the elevated perchlorate concentrations will need to be verified, probably through replication measurements in other ice cores. Because the Tunguska Event was unusually powerful, with claimed effects seen as far away as the South Pole, the elevated perchlorate levels would be expected in ice cores from other Arctic locations and perhaps even from Antarctica. Also, perchlorate records covering other bolide events could be helpful in establishing a link between such events and perchlorate. As can be seen in Figure 29, there are elevated perchlorate levels between 1964 and 1966 in both SM07C2 and TUNU. This could be associated with a bolide event off the coast of South Africa that occurred on August 3, 1963. This bolide event is the only other bolide event, besides the Chelyabinsk bolide, over the last 100 years to release a comparable amount of energy (1.11×10^{15} J)[143] as the Tunguska Event[141]. However, it is important to note that the perchlorate concentrations between 1964 and 1966 in the SM07C2 and TUNU ice core records may also be influenced by the eruption of Mt. Agung in 1963. Measurement of perchlorate in polar or Arctic snow covering the Chelyabinsk bolide event could help in verifying the link between bolide events and perchlorate concentrations.

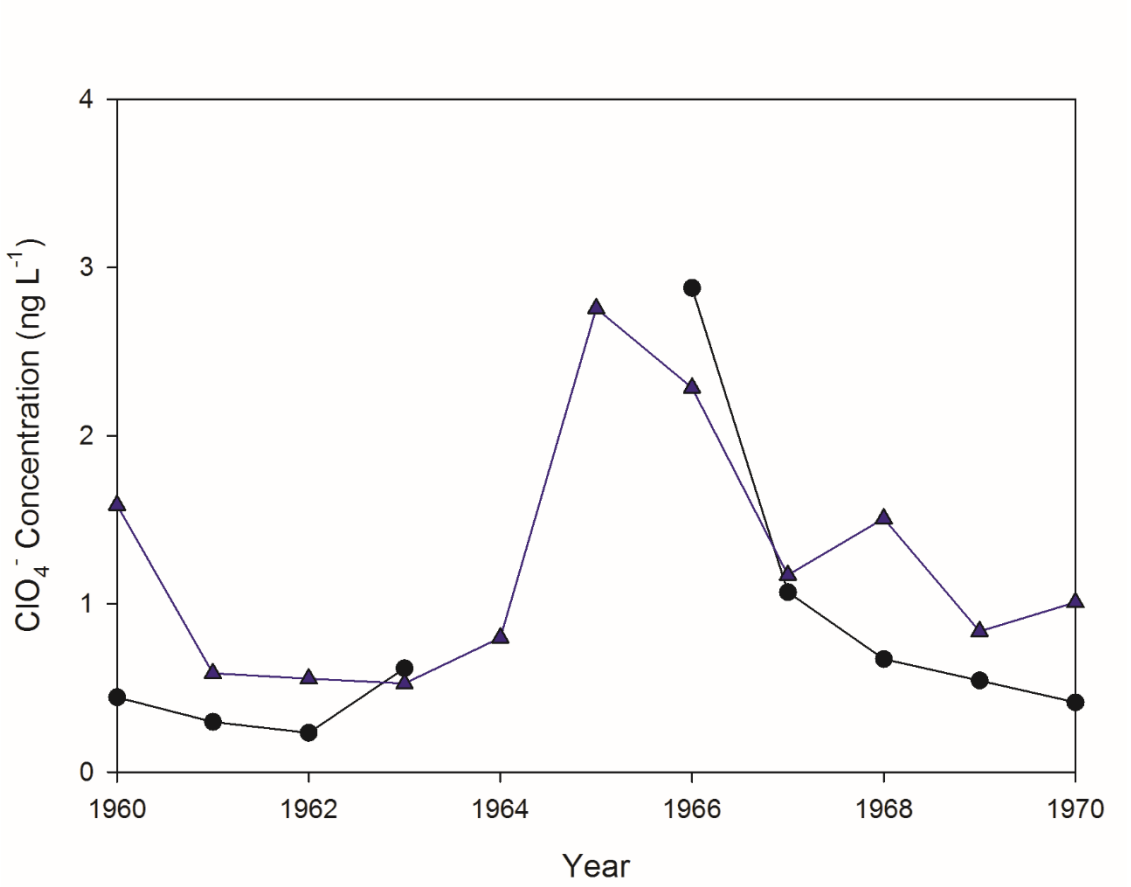

Figure 29. Average annual ClO_4^- concentrations in the SM07C2 (black circles) and TUNU (blue triangles) cores. Elevated perchlorate concentrations between 1964 and 1966 may correspond to the 1963 bolide event off the coast of South Africa. Lack of ice core samples resulted in no perchlorate data for the time period of 1964-1966.

Future investigations into bolide events should also focus on how these events affect atmospheric chemistry. The injection of a tremendous amount of debris into the atmosphere when a bolide explodes likely has a significant impact on the chemical processes occuring in the atmosphere. Understanding the impact can improve our knowledge of atmospheric chemistry. For example, a better understanding of how bolide events may affect chlorine activation could provide insight into if and how these events lead to significant natural fluctuations in stratospheric ozone. Finally, understanding of the origin of perchlorate in bolide events may shed light on the occurrence of perchlorate

in the Solar System. If perchlorate is indeed ubiquitous in extraterrestrial material, the entry of these materials into Earth's atmosphere could represent a previously unrecognized source of terrestrial perchlorate.

8.4 Conclusions

The anomaly in perchlorate concentrations between 1908 and 1914 contains perchlorate concentrations that are more than four times higher than any other anomaly observed in the 300-year SM07C2 perchlorate record. These significantly elevated perchlorate levels appear to be due to the combined effect of two volcanic eruptions and a superbolide event. The first volcanic eruption was that of Ksudach, which occurred in Russia in 1907. However, it is unlikely that elevated perchlorate levels from this eruption persisted until the eruption of Katmai, which occurred in Alaska in 1912. Furthermore, although volcanic eruptions have been shown to contribute to increased perchlorate levels, the increase is only a few parts per trillion, not the tens of parts per trillion observed over this time period. Therefore, although still hypothetical at this point, another contributor to the elevated perchlorate levels is the Tunguska Event in 1908. The presence of perchlorate in other stony asteroids suggest that it is possible that the Tunguska meteor could have served as a direct source of perchlorate. Also, the injection of significant amounts of debris could have contributed to the heterogeneous activation of chlorine in the stratosphere. The debris injected into the stratosphere could have also promoted the formation of stratospheric clouds, which could also enhance chlorine activation. Perhaps both mechanisms contributed to the extraordinarily high perchlorate levels. However, it is important to note that the atmospheric impacts of the Tunguska Event, and bolide events in general, are not well understood at this point. Thus, much

more research is needed to make a verified connection between, not only the Tunguska Event and elevated perchlorate levels, but also between bolide events in general and perchlorate.

9 Conclusions and Future Work

9.1 Anthropogenic Contributions

Human exposure to environmental perchlorate is widespread. Thus, there has been considerable interest in the regulation of perchlorate. The widespread regulation of perchlorate, though, has remained difficult due to a lack of understanding of the relative contribution of the anthropogenic sources of perchlorate compared to the natural sources. The 300-year perchlorate record from SM07C2 shows that perchlorate levels remained relatively consistent between 1700 and 1980 C.E, suggesting that the source(s) of perchlorate did not change over this time period, and that the Industrial Revolution (beginning around 1850 C.E.) did not impact environmental perchlorate levels. However, average perchlorate concentrations increased from approximately 1 ng L^{-1} between 1700 and 1980 to nearly 3 ng L^{-1} post-1980, a trend that was observed, not only at two other Greenland locations (TUNU and Basin 4), but also in the Canadian Arctic[36] and the South Pole. While the industrial production of perchlorate, and presumably usage and disposal, increased in the 1980s, these anthropogenic sources that directly release perchlorate to the environment are unlikely responsible for the trend seen in the ice core perchlorate records, as the dispersal of this type of pollution tends remain local. However, as perchlorate pollution enters rivers and other water systems that are used for irrigation purposes, human exposure to perchlorate from direct anthropogenic sources can become more widespread.

Perchlorate concentrations in modern snow have most likely been indirectly influenced by increased stratospheric chlorine concentrations. Increased stratospheric chlorine concentrations enhanced the stratospheric production of perchlorate, resulting in

the approximate 3-fold increase in perchlorate concentrations post-1980 when compared to pre-1980 concentrations. Rising stratospheric chlorine concentrations throughout the 1980s and early-1990s have largely been attributed to the emission of CFCs. Thus, human activities appear to be indirectly responsible for about two-thirds of the current environmental perchlorate. However, as stratospheric chlorine concentrations continue to decrease due to the phasing-out of the use of CFCs and other chlorine compounds, perchlorate concentrations in polar snow will also likely decrease.

9.2 Stratospheric Production

The data from our various ice core perchlorate records suggests that perchlorate is produced naturally in the stratosphere and then deposited to the Earth's surface. The stratospheric production of perchlorate appears to be largely dependent on three factors: stratospheric chlorine, aerosol surfaces, and ozone. The parallel trends between increasing perchlorate and EESC concentrations starting in 1980 and continuing through the mid-1990s indicates that stratospheric chlorine is the main driving force of inter-annual variability in perchlorate. The key step in the production of perchlorate seems to be the conversion of reservoir chlorine to radical chlorine species. One of the most important factors in the activation of chlorine species is the availability of particle surface for heterogeneous activation reactions, which proceed much faster than homogeneous activation in the gas phase. This is supported by higher perchlorate concentrations observed in Antarctica than in Greenland. Mainly due to colder temperatures, larger, longer lasting PSCs form in the stratosphere above Antarctica than the Arctic. Thus, there is more prominent chlorine activation over Antarctica, which presumably leads to enhanced perchlorate production. The increased perchlorate concentrations associated

with large, stratospheric volcanic eruptions further supports the role of heterogeneous chlorine activation in perchlorate production. These volcanic eruptions produce H_2SO_4 aerosols in the stratosphere, which provide additional particle surface for chlorine activation. Finally, heterogeneous chlorine activation could also occur on the surface of dust particles, which may have occurred in the case of the Tunguska Event.

Events such as volcanic eruptions and superbolide explosions may have a greater impact on enhanced perchlorate production at non-polar latitudes than at the polar latitudes. This is because at non-polar latitudes it is too warm for the formation of PSCs. As a result, chlorine activation at non-polar latitudes often relies on the presence of aerosol surfaces. Thus increased aerosol suface area resulting from volcanic eruptions or bolide events could potentially lead to the production of a significant amount of perchlorate, as was suggested by Jaeglé et al[126].

The second step in the stratospheric production of perchlorate is likely the ozone-mediated oxidation of radical chlorine species to higher chlorine oxide radicals. This is demonstrated by the intra-annual variations observed in SM07C2, as both perchlorate and ozone concentrations peak during the spring, a trend also observed by Furdui and Tomassini[21] in the Canadian Arctic. At WAIS Divide, Antarctica, peak perchlorate concentrations were not reached until the autumn. In the spring over Antarctica, the rate of perchlorate production is likely limited by ozone levels which reach annual minimum in the austral spring due to its well documented destruction during this time of year. Although ozone levels recover quickly by the beginning of the summer, perchlorate production does not fully rebound, since, during the summer, chlorine activation is inhibited due to warmer temperatures preventing the formation of PSCs. With the onset

of autumn, temperatures become cold enough to allow for the formation of PSCs, leading to increased chlorine activation, as suggested by a slight decrease in ozone concentrations during this time. Despite the slight decrease in ozone concentrations during the autumn, they appear to remain high enough to allow for the formation of perchlorate. In the end, the autumn concentration maximum in perchlorate observed at WAIS Divide suggests that perchlorate production relies on a delicate balance between activated chlorine and ozone concentrations in the stratosphere.

The final step in the stratospheric production of perchlorate appears to be the hydrolysis of higher chlorine oxide radicals, such as Cl_2O_6 and Cl_2O_4. Once again the presence of aerosols is important in this aspect of perchlorate production, as hydrolysis reactions in the stratosphere often occur within aerosols, most notably H_2SO_4 aerosols. The observation of perchlorate within H_2SO_4 aerosols in the stratosphere by Murphy et al.[66] further suggests that the hydrolyis of higher chlorine oxide radicals to form perchlorate occurs in these aerosols.

In the end, the information from the perchlorate records from Greenland and Antarctica strongly indicates a stratospheric production mechanism of perchlorate with dependence on stratospheric chlorine levels, the presence of PSCs or other aerosol surfaces for chlorine activation, and the availability of ozone (Figure 30). The records also demonstrate how unusual phenomena such as volcanic eruptions, and perhaps superbolide events, can affect stratospheric chemistry, leading to increased perchlorate production. Furthermore, this research also reveals the impact of human activities on atmospheric processes. Although CFCs are not a direct anthropogenic source of perchlorate, it is evident from the increasing perchlorate concentrations starting in 1980

and continuing through early-1990s, that they have impacted the stratospheric production of perchlorate.

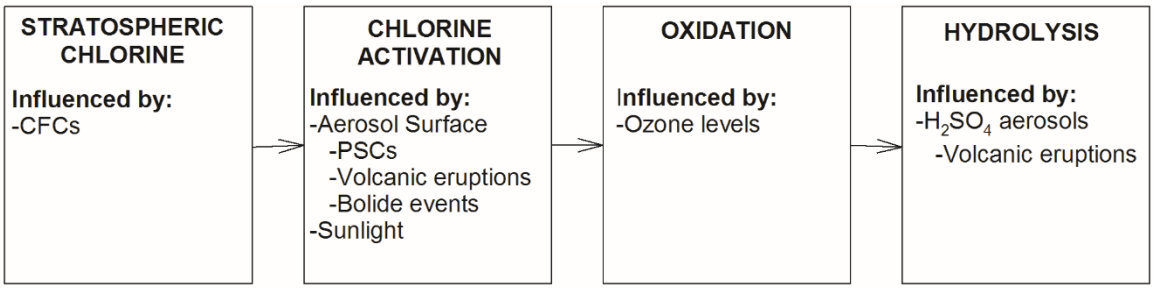

Figure 30. Overview of the stratospheric production of perchlorate.

9.3 Future Work

In summary, our polar ice core records of environmental perchlorate strongly support, with mechanistic understanding, the stratospheric production of perchlorate. Future work can build upon this knowledge and seek to gain a better understanding, or a more quantitative description of how atmospheric and climatic conditions impact perchlorate production. More specifically, attention should be given to the roles of chlorine activation and ozone.

Radical chlorine and ozone are closely related because radical chlorine participates in the catalytic destruction of ozone. Consequently, as the concentration of radical chlorine increases, the concentration of ozone typically decreases. Thus, as demonstrated by the WAIS Divide perchlorate record, the production of perchlorate depends on a delicate balance between ozone and radical chlorine concentrations. In order to better understand this relationship, the reactions between radical chlorine species and ozone over varying concentrations (yet still relevant to stratospheric concentrations) need to be studied. This will be important in identifying at which concentrations ozone

limits the rate of perchlorate production, and at which concentrations the availability of activated chlorine limits the rate of perchlorate production. This understanding will be key in building models for perchlorate production. Furthermore, the formation of other chlorine species, such as chlorate, should be studied under these conditions. As mentioned in Chapter 6, perchlorate is often the minor product of oxidation reactions. Thus, studying the formation of not only perchlorate, but also other chlorine species, could help identify conditions that favor perchlorate production as opposed to the formation of other chlorine species.

The role of volcanic eruptions in perchlorate production over Antarctica and non-polar latitudes also need further investigation. A connection between volcanic eruptions and increased perchlorate concentrations in Antarctica has not been established beyond doubt. One obstacle to establishing a connection between volcanic eruptions and perchlorate concentrations in Antarctica is the higher perchlorate concentrations in Antarctica than in Greenland. An increase of a few parts per trillion in perchlorate concentrations, as is typically associated with a volcanic eruption, may not be readily detectable in recent Antarctic snow. One way to determine if this is the case, is to study volcanic eruptions in Antarctic samples prior to 1950, when average perchlorate concentrations are much lower (approximately 3 ng L^{-1}). If, even at lower background perchlorate concentrations, a lack of significant increase in perchlorate concentrations following volcanic eruptions could indicate that ozone concentrations may be too low to promote perchlorate production. The H_2SO_4 aerosol surface resulting from volcanic eruptions promotes chlorine activation in the stratosphere, and, as a result, ozone destruction. Thus, because average ozone concentrations are generally lower over

Antarctica than over Greenland (241 and 344 DU, respectively, between 1995-2000), ozone concentrations following a volcanic eruption may become too low to promote the production of perchlorate. Such information could also improve our understanding of the stratospheric production of perchlorate. Finally, it has been suggested that volcanic eruptions could contribute to the production of a significant amount of perchlorate at non-polar latitudes[126]. This could be verified by studying volcanic eruptions and perchlorate concentrations in mountain glaciers located at non-polar latitudes. Increased perchlorate concentrations associated with volcanic eruptions would further substantiate the role of H_2SO_4 aerosols promoting chlorine activation and consequently perchlorate production.

Finally, the role of superbolide events, such as the Tunguska Event, in perchlorate production/deposition need to be further investigated. The first step in such investigations should be to determine if there are significantly higher perchlorate concentrations in ice cores from other locations, including Antarctic locations, over the time period associated with the Tunguska Event (1908-1914). Significantly higher perchlorate concentrations in ice cores from other Arctic locations, but not Antarctic locations, could suggest that the Tunguska meteor may have served as a direct source of perchlorate. On the other hand, if perchlorate concentrations also increase at Antarctic locations, this could implicate the role of dust/debris in enhancing chlorine activation, leading to increased perchlorate production. In addition, other superbolide events, such as the 2013 Chelyabinsk Event, should be studied in relation to perchlorate concentrations. The connection between increased perchlorate concentrations and superbolide events is still speculative due to, not only a lack of data on the Tunguska Event itself, but also the lack of an understanding of the atmospheric effects of bolide

events in general. Thus, studying other superbolide events would be very beneficial in determining if there is a connection between these events and perchlorate, or if it was an unique occurrence.

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