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Joseph Gibson
South Dakota State University

Amanda Shea
South Dakota State University

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INCREASED PERCHLORATE IN THE ENVIRONMENT FOLLOWING THE 1600 C.E. HUAYNAPUTINA VOLCANIC ERUPTION

Authors: Joseph Gibson, Amanda Shea

Faculty Sponsor: Jihong Cole-Dai

Department: Chemistry and Biochemistry

ABSTRACT

Perchlorate is an environmental contaminant that can have adverse health effects on humans. Although our knowledge about how natural perchlorate is formed is very limited, volcanic eruptions are believed to play an important role. An ice core obtained from Summit Station, Greenland was used to study the effects of the Huaynaputina eruption on the amount of perchlorate in the environment. The section of ice core sampled was determined to span the years 1594 through 1610. The results indicate that the Huaynaputina eruption caused a temporary but significant increase in the amount of perchlorate in the atmosphere.

INTRODUCTION

The perchlorate anion (ClO_4^-) is an environmental contaminant that can be harmful to humans by inhibiting uptake of iodine to the thyroid gland.¹ It is both naturally occurring and manufactured for industrial purposes.² Perchlorate salts are strong oxidizing agents, and are used in rocket fuel, munitions, fireworks, matches, signal flares, and airbag initiators.³ Although it has strong oxidizing properties, perchlorate is

generally nonreactive in aqueous systems.² Due to the nonreactive tendencies and high solubility of perchlorate, it is commonly found in surface and ground water.^{2,4} The United States Environmental Protection Agency currently recognizes perchlorate as a contaminant in public water systems, although official national standards have yet to be implemented.^{3,5} In order to impose proper regulations on the use and disposal of manufactured perchlorate, it is necessary to evaluate the contribution of all sources to the amount present in the environment. Research has shown a significant increase in the amount of perchlorate in the environment beginning in the early 1980s, indicating environmental perchlorate has both anthropogenic and natural sources.⁶ Although the mechanisms of natural perchlorate formation are not fully understood, volcanic eruptions are believed to play an important role.⁷ The main objective of this study is to determine if a well-known volcanic eruption in the early seventeenth century impacted perchlorate in the environment.

Volcanic eruptions have a major impact on the chemical composition of the atmosphere and can have dramatic effects on the global climate.⁸ The sulfur dioxide released by volcanic eruptions is oxidized in the atmosphere and combined with water to form sulfuric acid aerosols. Large eruptions, such as the 1600 C.E. eruption of the Huaynaputina volcano (VEI 6) in Peru (16° S, 70° W), are capable of injecting sulfur gasses directly into the stratosphere, and the resulting aerosols can spread globally.⁹ The Huaynaputina eruption is the largest recorded volcanic eruption in South America. The eruption began on February 19 and did not cease until March 6 of that year.¹⁰ Records indicate that many regions of the world experienced abrupt cooling following the eruption, which led to poor crop yields, causing famine and epidemics.¹¹ Elevated sulfate concentration resulting from the Huaynaputina eruption has been observed in ice from both Greenland and Antarctica,¹² but no investigation has been made on the eruption impact on environmental perchlorate.

Ice core analysis is one way to assess chemical species in the environment and how they change over time. When precipitation is formed, it contains a sample of the chemical

composition of the atmosphere. In polar regions, the snow continues to build, and a chronological record of the atmospheric chemistry is preserved. The resulting ice can be drilled and extracted in the form of ice cores. Polar ice cores are a useful tool in the study of the effect of volcanic eruptions the atmosphere and climate. Through the chemical analysis of polar ice cores, volcanic eruptions can be identified based on the link between elevated sulfate concentrations in snow and the amount of volcano-derived sulfuric acid in the atmosphere when the snow was deposited.¹³ By comparing the concentrations of sulfate and perchlorate in ice core samples, the impact of volcanic eruptions on perchlorate can be investigated.

METHODS

Sample Preparation

Four meters, in the depth interval of 120.39-124.37 meters, of a 2007 ice core obtained near Summit Station, Greenland (SM07C4) were sampled for chemical analysis. The depth interval was selected to include the time period when the Huaynaputina eruption occurred, which was determined by examining sulfate ion data in a previously dated core (SM07C2), which was retrieved from the same location as SM07C4. Each meter of the ice core was cut into samples approximately 4 cm long using a band saw and placed into temporary containers for transfer from the freezer to the lab. Each ice core sample was then washed thoroughly with ultrapure deionized water to melt away the outermost layer of the ice, which removed surface contaminants. The samples were placed in clean containers and allowed to melt at room temperature. All sample containers were washed five times with ultrapure deionized water prior to use for ice core samples. A total of 101 samples were prepared, and each one was separated into two vials for chemical analysis. Ultrapure deionized water was used to make ice blanks for quality control. Ice blanks were prepared using the same procedure as for samples to ensure that the samples

were not being contaminated during the preparation process.

Ion Concentration Measurement

The concentrations of Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^+ , and Ca^{2+} in the ice core samples were measured using a Thermo Fischer (formerly Dionex) ICS-1500 ion chromatography system. Perchlorate in Arctic ice cores occurs at significantly lower concentrations than the other ions of interest and falls below the detection limit of conventional ion chromatography.⁷ Ion chromatography tandem mass spectrometry techniques can be used to measure the concentration of ions that are present in sub-ng L^{-1} levels.⁷ Perchlorate concentration was measured using an AB Sciex 5500 Q-trap tandem mass spectrometer connected to a Thermo Fischer ICS-1500, as described in Peterson et al.¹⁴ Calibration curves were prepared using external standards.

Ice Core Dating

Dating of the ice core was accomplished by examining the Cl^- and Na^+ concentrations of the samples. The ratio (Cl^-/Na^+) of these ions shows well-defined seasonal oscillations, reaching its lowest point during the winter of every year.¹³ These seasonal minima represent January of each year, and were used to count the number (16) of annual layers within the depth interval sampled. A sulfate response to the eruption of Huaynaputina had been identified in SM07C2, an ice core retrieved from the same location as SM07C4.⁶ SM07C2 was previously dated by (Cole-Dai et al.)¹⁵ using an annual layer-counting method, which showed that the sulfate response to Huaynaputina occurred at a depth corresponding to the year 1601. Aligning the sulfate signals in the two data sets allowed for the identification of the year 1601 in the 16-year time period. This allowed for the exact year of each annual layer to be determined. The results of the dating, shown in Figure 1, indicate that the four meters of ice span the years 1594 to 1610.

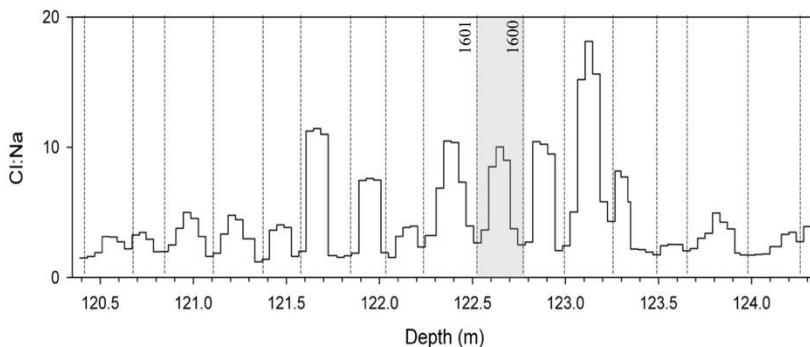


Figure 1. Cl^-/Na^+ concentration ratio used to date the ice core. Dashed lines represent the beginning of a new year.

RESULTS AND DISCUSSION

Perchlorate Response to Huaynaputina

The sulfate concentration increased drastically beginning in the year 1601 (Figure 1) and remained at elevated levels through 1602. This peak corresponds to the 1600 Huaynaputina eruption. The concentration response beginning one year after the eruption is expected, due to the atmospheric transport time of the volcanic aerosols from Huaynaputina (16° S , 71° W) to Summit Station (72° N , 38° W). The poleward dispersion of the aerosol cloud created by large volcanic eruptions is a relatively slow process compared to dispersion in the longitudinal directions.^{8,9} Because the Huaynaputina eruption was large enough to inject sulfur dioxide directly into the stratosphere, the delay in response can also be attributed to the extra time required for aerosols to be removed from the stratosphere.¹⁶ The increase in perchlorate concentration at approximately the same depth range as that of sulfate indicates that the eruption of Huaynaputina caused a significant increase in the amount of perchlorate in the atmosphere. Although the mechanism of perchlorate formation is

unknown, the data may provide some hints. The similarities between the perchlorate and sulfate signals could indicate that the two chemical species form through similar processes.

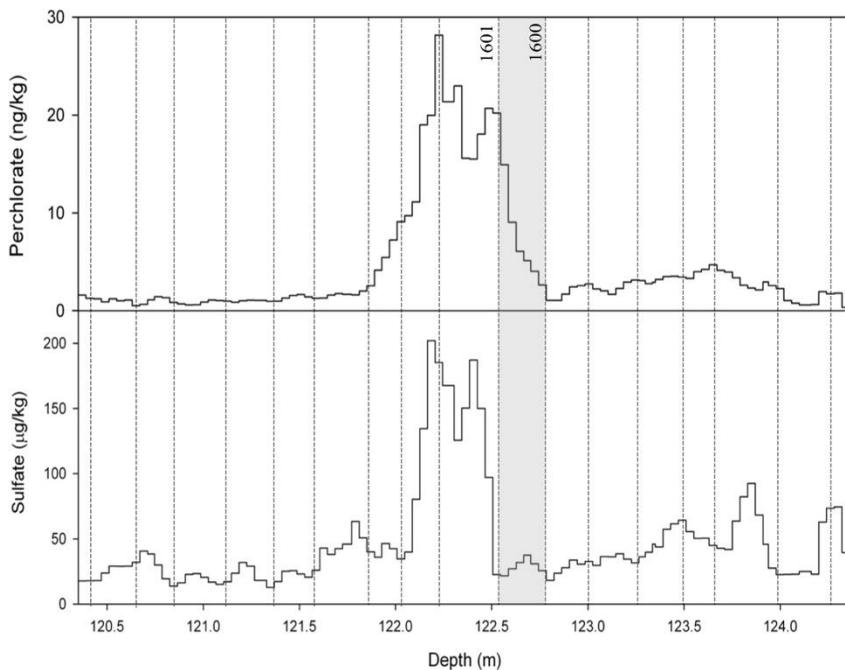
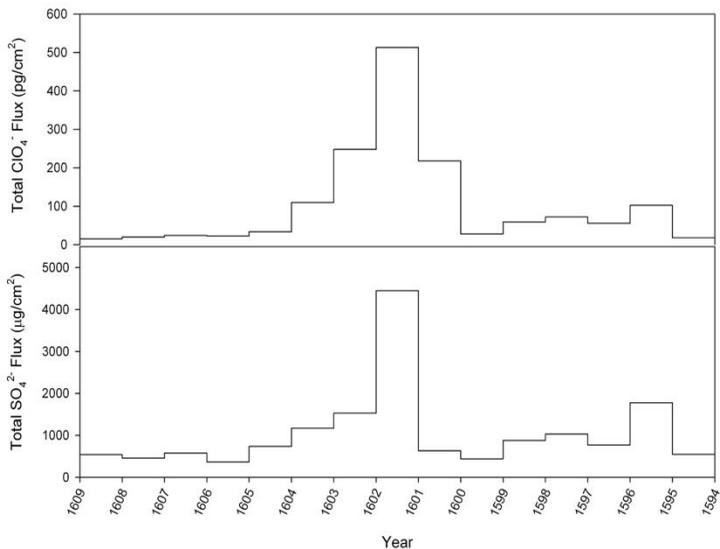


Figure 2. Sulfate and perchlorate concentration data (smoothed with a 3-sample running mean) from 120.35 m to 124.37 m spanning the years 1594 to 1610.

The annual perchlorate flux was calculated using the process described in Ferris et al.¹⁷ The flux data (Figure 3) show that perchlorate deposition attributed to the Huaynaputina eruption began in 1600, peaked in 1601, and did not cease until 1604. The large increase in perchlorate deposition begins approximately one year before the sulfate flux begins to increase. It appears (Figure 2) that perchlorate concentration

begins to increase gradually in the latter half of 1600 and reaches a high plateau in 1601 (when sulfate concentration begins to rise sharply). The plateau lasts until 1602 (when sulfate begins to decrease rapidly) and is followed by a gradual decrease which lasts until 1604. The gradual increase and decrease before and after the plateau in perchlorate concentration from 1601 to 1602, when sulfate concentrations are elevated, seem to suggest that high perchlorate concentration from the 1601-1602 section may have diffused to adjacent (1600, 1603 and 1604) snow layers.¹⁸ This is speculative, because there is no evidence that perchlorate or other ions can diffuse in ice significantly in the time span of hundreds of years.



Comparison of Huaynaputina to Other Major Eruptions

Sulfate and perchlorate concentrations in samples of Summit ice cores containing

several volcanic events were measured in previous research.¹⁴ Four volcanic events that occurred prior to 1980 were used for comparison to the Huaynaputina eruption. For each eruption the total volcanic perchlorate flux was plotted against the total volcanic sulfate flux and a linear regression analysis was performed. The value of the regression coefficient ($R^2= 0.91$) suggests a linear relationship between volcanic perchlorate flux and that of volcanic sulfate. However, the linear relationship is dominated by the very high fluxes of the Novarupta eruption (58°N, 155°W, VEI 6) in Alaska and of the Huaynaputina eruption. The eruptions of Krakatoa (6°S, 105°E, VEI 6), Cosigüina (12°N, 88°W, VEI 5), and Babuyan Claro (20°N, 122°E, VEI 4) all have much smaller perchlorate and sulfate flux values; no correlation is apparent between perchlorate and sulfate of these three eruptions. Therefore, a conclusion of a positive and linear correlation between sulfate and perchlorate from volcanic eruptions is not warranted by the data of these eruptions. Perchlorate data for more volcanic eruptions would be needed to investigate the possible correlation between sulfate and perchlorate flux.

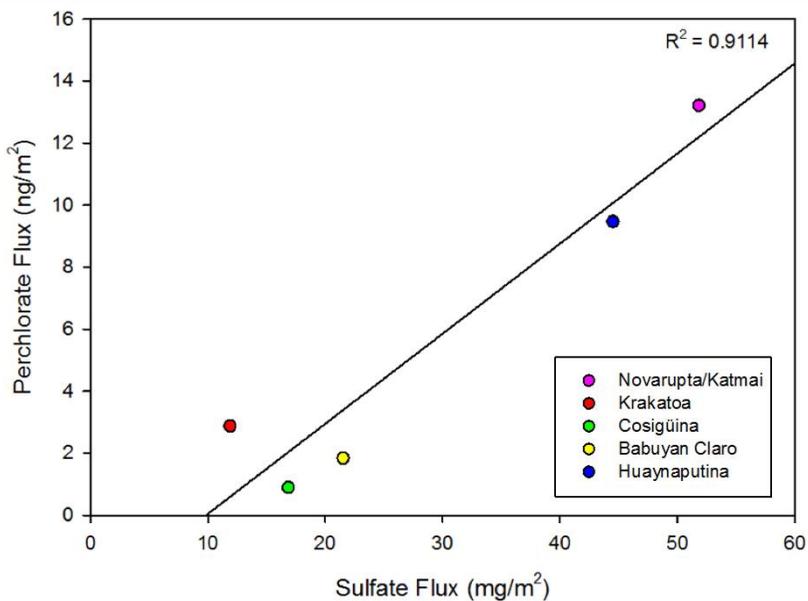


Figure 3. Total perchlorate and sulfate flux values for Huaynaputina, Novarupta/Katmai, Krakatoa, Cosigüina, and Babuyan Claro.

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