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Alex Georgiev

*South Dakota State University*

Collin Livingston

*South Dakota State University*

Cody Ward

*South Dakota State University*

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# **Determination of Volcanic Impact on Perchlorate Using Polar Ice Cores**

Authors: Alex Georgiev, Collin Livingston, Cody Ward

Faculty Sponsor: Jihong Cole-Dai

Department: Chemistry and Biochemistry

## **ABSTRACT**

Arctic (Greenland) ice core samples covering the time period of 1638 to 1646 were analyzed for perchlorate and sulfate concentrations. The sulfate data shows a signal corresponding to the 1640 eruption of the Komaga-Take volcano in Japan. Perchlorate concentrations show a significant increase at the time of the Komaga-Take eruption. It is concluded that a positive correlation likely exists between stratospheric volcanic eruptions and perchlorate concentration in the environment. When a volcano has enough explosive force to inject substances into the stratosphere, some of the substances, such as sulfate, can remain in the stratosphere for months and spread all over the global atmosphere. The sulfate aerosols in the stratosphere may enhance the formation of perchlorate from chlorine species commonly present in the atmospheric environment.

**Keywords:** Volcanoes, perchlorate, Arctic, ice cores

## **INTRODUCTION**

Polar ice cores contain chronological records of chemical substances in the environment and are basically, naturally occurring archives. These cores are obtained from ice sheets that are made from the accumulation of snow over many years. A timeline can be constructed based on the depth of the snow and ice in the core, much like geologists date fossils based on their depth in the ground. A lot of information can be found about the atmospheric and environmental conditions of the past by looking at the different concentrations of chemical substances in the ice (Wolff, 2010).

One chemical that is of interest, and found in trace amounts in polar snow and ice, is perchlorate. Studies have shown that perchlorate has the ability to inhibit the uptake of iodine by the thyroid gland, which has the potential to cause a variety of metabolic problems in humans (Blount, et al., 2006). In addition to posing health risks, perchlorate also poses a risk to the environment. Being highly resistant to change and degradation, perchlorate is very stable in the environment. The anion is water-soluble and is mainly housed in aquatic environments such as surface and ground water (Peterson, 2015). This leads to the risk of contaminating drinking water and furthers the possibility of causing problems to human (Lutter, 2014). Knowledge about the sources and levels of perchlorate in the environment is needed to determine the risk to humans through exposure.

One potential source of perchlorate is volcanic activity. Volcanic eruptions disperse an abundance of gas and ash into the atmosphere. Sulfur dioxide is a major component of the gaseous emission and is chemically converted in the atmosphere to sulfate, which falls out of the atmosphere gradually and can be found in accumulating polar snow (Cole-Dai and Mosley-Thompson, 1999).

The objective of this research is to determine if volcanic activity contributes to perchlorate in the environment. Specifically, we measure perchlorate concentration in Arctic snow deposited during the time period when volcanic sulfate is present in snow, in order to evaluate the impact of volcanic eruptions on perchlorate level.

## **METHODS**

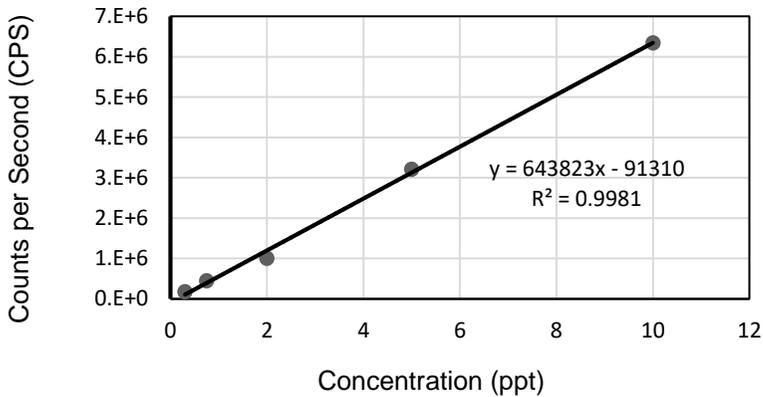
A 150 m ice core was obtained from Summit Station, Greenland in 2007 and the tubes of 112 and 113 of the core were dated from 1638 to 1646 using annual layer counting methods described by Cole-Dai et al. (2013). During this time, the volcano Komaga-Take in Japan had a violent eruption in 1640 and emitted many contaminants into the atmosphere. When preparing samples from the ice cores, plastic gloves were used in order to prevent contamination. A vertical section from Tubes 112 and 113 was cut into 4.0×4.0×4.0 cm cubes and the ice samples were left in the freezer until chemical analysis.

Plastic cups with lids were washed multiple (at least 10) times with ultra-pure deionized water and then allowed to air-dry. The ice samples were moved from the freezer and washed on all sides with ultra-pure deionized water. The ice samples were then placed in

the clean cups with lids to melt. Standards were made in order to make calibration curves for sulfate and perchlorate concentration. The standards used with ion chromatography had sulfate concentrations of 50, 100, 150, and 200 parts per billion (ppb). The perchlorate standards had concentrations of 0.3, 0.75, 2, 5, and 10 parts per trillion (ppt). Once the ice in the clean cups was melted, the meltwater and standards were poured carefully into autosampler vials, which had been cleaned by rinsing repeatedly with ultra-pure deionized water. Clean caps were applied to the vials. Resulting samples were loaded in chromatographic instruments for measurement of sulfate and perchlorate. For sulfate determination, a ThermoFisher DX500 ion chromatograph with conductivity detection was used. Because perchlorate exists at very low concentrations, it could not be analyzed using ion chromatography with conductivity detection. A recently developed method was used for perchlorate determination (Peterson, 2015). In this method, an AB Sciex triple quadrupole mass spectrometer with electrospray ionization (ESI-MS/MS) interfaced with a Dionex DX500 ion chromatograph was used to quantify perchlorate in the meltwater samples at the parts-per-trillion level.

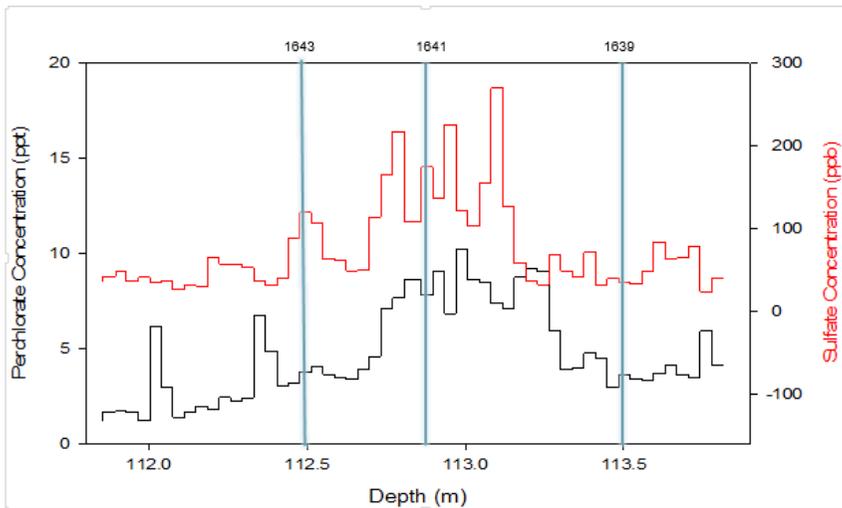
## **RESULTS AND DISCUSSION**

The calibration curve for perchlorate is shown in Figure 1. The correlation coefficient of 0.998 and the y-intercepts close to 0 indicate a linear signal response to perchlorate concentration without blank contribution.



**Figure 1:** A perchlorate calibration curve. The equation of that line was used to relate mass spectrometer signal (counts per second) to perchlorate concentration of the ice samples.

Volcanic eruptions result in emission of sulfur compounds, such as  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , which are converted to sulfate in the atmosphere. When an eruption has a Volcanic Explosivity Index (VEI) of 4 or greater, on a 0-8 scale (Peterson, 2016), it has enough force to put the sulfur compounds into the stratosphere. Once in the stratosphere, these compounds in the form of sulfate will remain for months, and spread around the world. The sulfate aerosols are gradually removed from the atmosphere and deposit onto snow surface at the poles, where they become trapped in accumulating polar ice. Elevated sulfate concentrations in ice core indicate explosive volcanic eruptions (Cole-Dai, et al., 2013). It is with this knowledge, and previous data collected by others (Cole-Dai, et al., 2013), that we decided to measure sulfate and perchlorate in Tubes 112 and 113 in the Greenland ice core. The increase in the sulfate concentration, as shown in Figure 2 (red line), was caused by the eruption of Komaga-Take in 1640. The eruption leads to sulfate concentrations averaging 159.5 ppb in the depth interval of 112.7 m to 113.1 m. This is elevated, compared to the averages of 51.76 ppb and 58.46 ppb before and after the eruption event, respectively. The perchlorate concentration (Figure 2, black line) has a similar pattern to that of sulfate. The average perchlorate concentration of 7.94 ppt between 112.7 m and 113.3 m is significantly higher than the averages of 1.16 ppt and 4.09 ppt before and after the volcanic event interval.



**Figure 2:** Concentrations of perchlorate and sulfate relating to depth in the ice core. Sulfate concentrations are depicted on red, and perchlorate concentrations in black. The vertical lines show the approximate dates associated with ice core depth.

Volcanic eruptions could contribute to the increased perchlorate found in polar snow in several ways. The simplest would be that perchlorate is directly released from the volcano during the eruption; however, there are several reasons that this is unlikely. First, volcanos in general provide a reducing environment, which would not be conducive to formation of perchlorate, the most oxidized form of chlorine. Second, perchlorate is very water soluble, so water vapor in the troposphere would likely scavenge the perchlorate from the eruption plume and remove it through precipitation, which will keep the perchlorate from being transported to the polar regions.

Another possibility is that large volcanic eruptions have an environmental impact that enhances the formation of perchlorate in the atmosphere. Common species of chlorine (chloride and chlorine oxides) can be oxidized to perchlorate in atmospheric reactions (Peterson, 2016). In the stratosphere, chlorine radicals are oxidized by ozone. Under normal conditions, chlorine does not exist as radicals and, therefore, little chlorine is

oxidized to perchlorate. On the other hand, chlorine radicals form readily when the formation reaction or activation takes place on particle surfaces. When sulfate is in the stratosphere, it exists in the form of aerosol particles and provides surface area resulting in accelerated chlorine activation (Peterson, 2016). This leads to enhanced perchlorate formation. This is a possible way volcanic eruptions lead to more perchlorate formed in the stratosphere and, eventually, in polar snow.

## CONCLUSIONS

It is known that volcanic eruptions emit large amounts of sulfide dioxide and hydrogen sulfide into the atmosphere. Samples in Tubes 112 and 113 of the Summit Station, Greenland ice cores were analyzed for sulfate and perchlorate, because previous data indicated that a major volcanic eruption had taken place during the time period covered by these ice core samples. An increased amount of sulfate was found at the time period following the 1640 eruption of the Komaga-Take volcano in Japan. Perchlorate concentration is also significantly elevated during this time period.

The comparison between sulfate and perchlorate levels ( Figure 2) suggests that volcanic activity can have an impact on the amount of perchlorate in the environment. Perchlorate is probably not, however, released directly into the atmosphere by a volcanic eruption. Rather, it is postulated that the volcanic eruption produces an atmospheric environment that makes the formation of perchlorate much more favorable.

## ACKNOWLEDGEMENTS

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