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Depletion of atmospheric nitrate and chloride as a consequence of the Toba volcanic eruption

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Abstract. Continuous measurements of SO_4^{2-} and electrical conductivity (ECM) along the GISP2 ice core record the Toba mega-eruption at a depth 2590.95 to 2091.25 m (71,000 \pm 5000 years ago). Major chemical species were analyzed at a resolution of 1 cm per sample for this section. An ~6-year long period with extremely high volcanic SO_4^{2-} coincident with a 94% depletion of nitrate and 63% depletion of chloride is observed at the depth of the Toba horizon. Such a reduction of chloride in a volcanic layer preserved in an ice core has not been observed in any previous studies. The nearly complete depletion of nitrate (to 5 ppb) encountered at the Toba level is the lowest value in the entire ~250,000 years of the GISP2 ice core record. We propose possible mechanisms to explain the depletion of nitrate and chloride resulting from this mega-eruption.

Introduction

The eruption of Toba, Sumatra, between 68,000 and 75,000 years ago is the largest known explosive volcanic eruption in the late Quaternary [Rose and Chesner, 1987; Chesner et al., 1991; Rampino and Self, 1992]. During the Toba eruption, the large amount of volcanic ash and sulfur gases (about 10^{15} g each of fine ash and sulfur gases that rose to heights of 27-37 km [Rampino and Self, 1992]) emitted into the stratosphere formed a blanket that may have significantly reduced sunlight to a state of darkness [Chesner et al., 1991; Rampino et al., 1988]. Previous assessments of the atmospheric impact of the Toba eruption have been relied on estimates of the amount of sulfur (10^{16} g H_2SO_4) emitted as approximated by mineralogical studies of the eruptive products [Rose and Chesner, 1990] or have been based on the gas emitted/volume of erupted magma ratio for several historical eruptions [Rampino et al., 1988; Rampino and self, 1992]. Now, estimates from the GISP2 ice core are that 2-4 10^{15} g of H_2SO_4 aerosol were emitted into stratosphere [Zielinski et al., 1996]. All of these estimates are within an order of magnitude, especially considering the different approaches used. This single volcanic eruption is believed to have caused a several year decrease of ~3-5°C in annual surface temperature for northern hemisphere [Rampino and Self, 1992].

Historical volcanic eruptions can be identified in ice cores through the preserved high concentrations in the continuous measurement of SO_4^{2-} and electrical conductivity [e.g. Hammer, 1977; Taylor et al., 1992; Zielinski et al., 1994]. The Toba event was identified at ~2591.10 m (71,000 \pm 5000 years ago) in the

GISP2 ice core (3053.44 meter deep) from central Greenland (76.6°N; 38.5°W) [Zielinski, et al., 1996]. It was suggested that magnitude and longevity of the atmospheric loading during the Toba eruption may have led directly to enhanced cooling during the initial two centuries of an ~1000-year cooling event [Zielinski et al., 1996].

In addition to the climatic impact of volcanic eruptions, atmospheric photochemistry can be severely influenced by the release of large amounts of sulfur and fine ash into the atmosphere [Hofmann, 1987; Hofmann and Solomon, 1989; Brasseur and Granier, 1992]. Based on a one dimensional sulfate aerosol model and recent laboratory data, Bekki (1994) suggested that substantial denitrification of the lower polar stratosphere occurred during the Toba eruption. In the work presented here, the Toba horizon preserved in the GISP2 ice core was utilized to investigate the influence of this mega-eruption on changes in the concentration of several chemical species (SO_4^{2-} , Cl^- and NO_3^-).

Results and Discussion

Continuous measurements of SO_4^{2-} and electrical conductivity (ECM) along the GISP2 ice core record a large volcanic signal at a depth 2590.95 to 2091.25 m (71,000 \pm 5000 years ago). It is believed that this signal is from the Toba mega-eruption [Zielinski et al., 1996]. Major chemical species were analyzed at a resolution of 1 cm per sample for this section. Details on the analytical procedures were given in Mayewski et al. (1987) and Buck et al. (1992). Concentrations of Na^+ , Cl^- , NO_3^- , non-seasalt SO_4^{2-} , and the ratio of Cl^-/Na^+ of the section covering ± 20 years around the Toba signal are plotted on Figure 1. The non-seasalt SO_4^{2-} peak value of 1935.3 ppb (40.57 $\mu\text{eq/kg}$) is the highest concentration detected in the entire ~250,000 years of the GISP2 ice core record. A mean NO_3^- concentration of 5 ± 1.0 ppb at this level persists for ~6 years (~1.5 years/sample [Zielinski et al., 1996]), the lowest level in the entire GISP2 record. A mean value of 83.4 ± 5.5 ppb of NO_3^- characterizes the period prior to the eruption. In addition, Cl^- concentration during the eruption is 24.7 ± 4.23 versus a pre-eruption mean of 66.4 ± 3.0 ppb and the ratio of Cl^-/Na^+ is 0.75 ± 0.06 versus a pre-eruption mean of 1.87 ± 0.09 . Thus NO_3^- , Cl^- and Cl^-/Na^+ are all dramatically decreased in section of the ice core containing high amounts of volcanic SO_4^{2-} .

However, no volcanic glasses have been found from the Toba horizon in the GISP2 ice core [Zielinski et al., 1996] despite the suggestion that Toba eruption may force climatic cooling on century time scales [e.g., Rampino and Self, 1992; Zielinski et al., 1996]. This drastic climatic disturbances in the northern hemisphere due to the explosive eruption was preserved in the GISP2 ice core [Zielinski et al., 1996]. The large amount of

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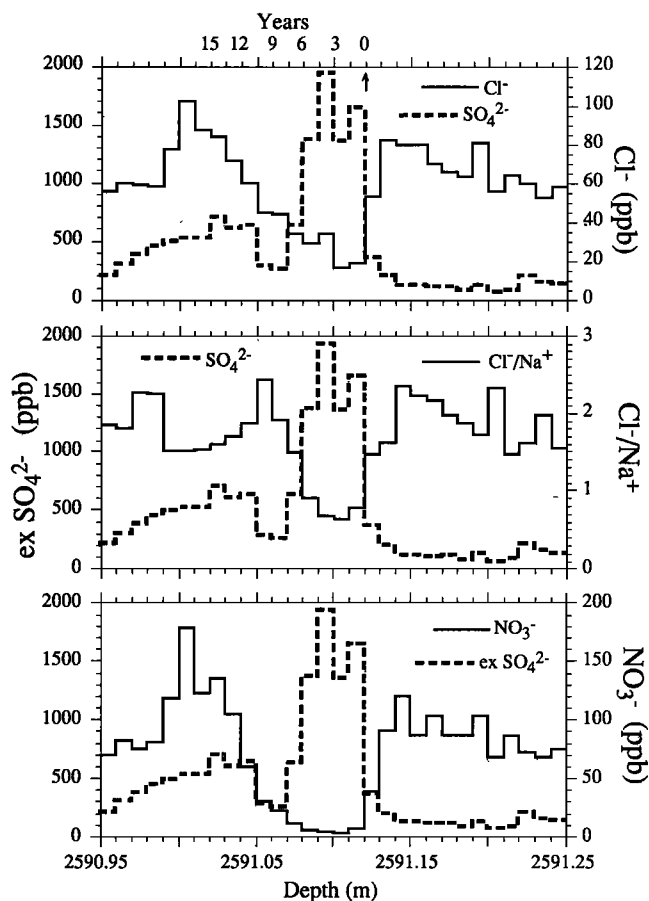


Figure 1. Concentrations (ppb) of Cl⁻, NO₃⁻, and the ratio of Cl⁻/Na⁺ plus non-seasalt SO₄²⁻ for the Toba signal in the GISP2 ice core at 2590.95–2591.25 m (71,000 ± 5000). Time scales are after Zielinski et al. [1996]

volcanic H₂SO₄ with no volcanic glass suggests that H₂SO₄ aerosols play a more important role than ash in climatic disturbances [Rampino and Self, 1992].

To investigate the possible causes for depletion Cl⁻ and NO₃⁻ in this section core, we first considered whether the depletion of Cl⁻ and NO₃⁻ results from diffusion taking place in the core as De Angelis and Legrand [1994] suggested for fluoride. The fluoride was observed to be subsequently excluded from a volcanic acidic layers in the ice cores from Greenland ice sheet [Angelis and Legrand, 1994]. The amount of volatile HCl released from a major volcanic eruption can be of the same order of magnitude as modern anthropogenic emissions of Cl⁻ into the atmosphere [Legrand and Delmas, 1988; Tabazadeh and Turco, 1993]. Explosive volcanic eruptions (e.g., Krakatoa, 1883 AD; Tambora, 1815 AD) have released several teragrams (10⁶ t) of HCl into the atmosphere [Legrand and Delmas, 1988; Devine, 1984]. However, elevated levels of Cl⁻ associated with these volcanic events are not observed in Antarctic ice cores and levels in Greenland ice cores are insignificant despite the distinct elevated concentrations of SO₄²⁻ [Legrand and Delmas, 1988; Laj, 1993]. The absence of volcanic Cl⁻ in these ice cores has been attributed to the rapid scavenging of HCl in the local troposphere. Plume dynamics and thermodynamics modeling suggest that water released from a major volcanic eruption will remove most of the volcanic emissions of HCl from the troposphere, thus preventing substantial contributions of HCl into the stratosphere [Tabazadeh and Turco, 1993].

Above arguments suggest that volcanic eruptions may be not marked by elevated Cl⁻ concentrations in ice core records. Those arguments do not, however, explain the remarkable reduction of Cl⁻ related to the Toba SO₄²⁻ increase (Figure 1). The post-depositional movement of HCl in a volcanic layer in ice cores has never been observed and Cl⁻ spikes are considered to be indicators of volcanic signal in ice cores [Lyons et al., 1990]. Therefore it is clear that Cl⁻ depletion in the GISP2 horizon must have occurred, at least in part, prior to deposition.

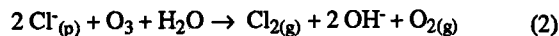
Reduction of NO₃⁻ has been observed along with volcanically deposited SO₄²⁻ in Greenland [Laj et al., 1993] and Antarctic ice cores [Legrand and Kirchner, 1990]. The magnitude of NO₃⁻ reductions is, however, not comparable to the nearly complete ~6-year depletion observed in this study. It has been reported that surface snow over Greenland contains elevated concentrations of both NO₃⁻ and SO₄²⁻ [Laj et al., 1992; Whitlow et al., 1992; Yang et al., in press]. These observations suggested that high concentrations of NO₃⁻ and SO₄²⁻ can be preserved in the snow so that a direct chemical interaction between these two anions may be ruled out [Laj et al., 1993]. Even though we do not rule out the possibility of depletion of Cl⁻ and NO₃⁻ due to the extremely acidic condition in the Toba horizon, there must be an atmospheric photochemistry perturbation during such an explosive volcanic eruption. Since both Cl⁻ and NO_x (a precursor of NO₃⁻) are important species in atmospheric photochemistry, we propose a possible mechanisms for the atmospheric depletion of the Cl⁻ and NO₃⁻ as evidenced by the minima of two species in the GISP2 ice core.

Sea-salt is the primary source of Cl⁻ deposited in polar snow and ice [Legrand and Delmas, 1988]. Heterogeneous reactions involving sea-salt aerosol in the marine troposphere are the major global source for volatile inorganic chloride [Keene et al., 1990]. The reaction between sea-salt aerosol and H₂SO₄ is believed to produce most of the volatile HCl in the atmosphere [Legrand and Delmas, 1988; Brimblecombe and Clegg, 1988]



This mechanism causes a Cl⁻ deficit in transported sea-salt aerosols so that the Cl⁻/Na⁺ ratio in ice cores can be lower than that in mean seawater (1.8 by weight) [Legrand and Delmas, 1988]. Since SO₄²⁻ emissions from Toba lasted ~6 years and were global in extent [Zielinski et al., 1996], equation (1) may explain part of the Cl⁻ deficit related to this event (Figure 1).

Following the Toba eruption, direct surface reactions between sea-salt aerosol and O₃ in the marine troposphere may have occurred through the reaction [Keene et al., 1990]:

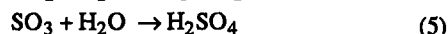
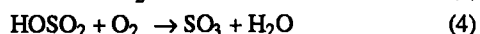
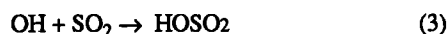


Under nonvolcanic conditions, Cl₂ is rapidly converted to HCl via Cl atoms (Cl[•]) photochemically and with the eventual recapture of HCl by sea-salt aerosols. During the Toba eruption, a decrease in sunlight to near darkness may have prevented Cl₂ from converting to HCl [Rampino et al., 1988; Chesner et al., 1991]. There is, however, as indicated in Figure 1, a Cl⁻ peak following the eruption. This may suggest that after the Toba eruption, the atmospheric reservoir of Cl₂ built up during the Toba eruption was photolyzed to HCl. Thus, depletion of the Cl⁻ may have resulted from the combined effects of loss of Cl⁻ through reaction (1), reduced sunlight preventing chlorine recycling in the atmosphere (Equation 2).

Although sources and deposition pathways of NO₃⁻ in Greenland snow are not well understood [Dibb et al., 1994; Yang et al., 1995], it is clear that the OH radical and NO_x play

important roles in the formation of HNO₃ in the ambient atmosphere over Greenland [Logan, 1983; Yang et al., 1995].

It is estimated that ~3 × 10¹⁵ g of H₂S and SO₂ were released into the atmosphere during the Toba eruption [Rampino and Self, 1992]. Potential SO₂ oxidants include the radicals OH, HO₂, RO₂, and H₂O₂. OH may have been consumed through the reaction [Warneck, 1988]:



During nonvolcanic periods, there is no net consumption of OH since it is recycled through the reaction [Calvert and Stockwell, 1984]:



However, it has been suggested that OH recycling is interrupted following a large volcanic eruption since the atmosphere is overwhelmed by SO₂ [Laj et al., 1993]. Rampino and Self (1992) and Zielinski et al. (1996) suggested that the Toba eruption produced as much as 10¹⁶ g H₂SO₄ aerosol in the stratosphere. Therefore, OH was presumably consumed via oxidation with SO₂. In fact, reaction (6) may have been eliminated following the Toba eruption because HO₂ is also a potential oxidant which may have been consumed by the large amount of SO₂ released from the Toba eruption [Warneck, 1988]. On the other hand, the state of reduced sunlight following the eruption may have caused changes in the stratosphere's radiative field. Thus, there may have been subsequent loss of OH resulting in a decrease in UV radiation [Legrand and Kirchner, 1990].

Following the Toba eruption, thermal convection may have decreased dramatically due to reduced heating in the atmosphere. As a consequence the NO_x formed by lightning and from soil microbial activities at low latitudes would not be as easily incorporated into the atmosphere and levels near Greenland could have been decreased notably. In this case, subsequent loss of OH due to changes in UV radiation and OH consumed by SO₂ following the eruption in the atmosphere, in addition to reduced NO_x sources at low latitudes, may have caused a near complete depletion of HNO₃ in the atmosphere over Greenland as eventually recorded in the GISP2 ice core (Figure 1).

Ozone destruction was observed through heterogeneous chemistry following a volcanic eruption [Hofmann, 1987; Hofmann and Solomon, 1989; Brasseur and Granier, 1992]. It was also suggested by Bekki (1994) that denitrification (i.e., the irreversible removal of nitrogen species from the higher to lower altitude in the polar stratosphere) is enhanced by sulfate aerosol released from the volcanic activities. Bekki (1994) used a one dimension sulfate aerosol model to predict that substantial denitrification of the polar lower stratosphere occurred during the Toba eruption. If this is the case, HNO₃ derived from such denitrification would be eventually scavenged by snow flakes. Consequently, elevated HNO₃ concentration should have been found in the Toba horizon of the GISP2 ice core. Our data in Figure 1, however, do not provide evidence to support Bekki's hypothesis, at least, the denitrification was not as strong as predicted (Figure 1).

Summary

Our data provide an atmospheric reconstruction of the chlorine and nitrogen cycling response to the impact of the Toba mega-volcanic eruption. We agree that the Toba eruption not only caused a volcanic winter effect [Rampino et al., 1988], but

that it also disturbed photochemical reactions in the atmosphere. Further, due to the evidence that extremely acidic SO₄²⁻ layer with no volcanic glasses in the GISP2 ice core, we suggest that SO₄²⁻ aerosols influence the climate disturbance. Although Cl⁻ and NO₃⁻ in a volcanic layer have never been reported to be removed due to their association with strongly acidic layer, we cannot rule out the possibility that Cl⁻ and NO₃⁻ were removed by post-deposition process related to this extremely acidic layer. We suggest that the depletion of Cl⁻ and NO₃⁻ observed in the Toba horizon in the GISP2 ice core was a result of changes in the atmospheric chemistry and removal from the ice layer due to the extreme acidic condition. This and other research on the impact of volcanic aerosols on changes in atmospheric photochemistry and dynamics provide further information to assess the impact of climatic and atmospheric environmental changes following volcanic eruptions.

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