

# Nitrate Generation in the Earth's Atmosphere by Cosmic Rays

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## Abstract

The yearly averaged data on nitrate ( $\text{NO}_3$  ions) concentration in polar ice carry unique information about the cosmic rays intensity in the past. Nitrates can be generated in the Earth's stratosphere due to its ionization by cosmic rays. But the chemical composition of the atmosphere also influenced the nitrate generation. The chemical content of the atmosphere can be changed by human activity. So, in order to investigate the behaviour of cosmic rays intensity, we should take these factors into account. In the present paper the calculation was made of the rate of nitrate generation by cosmic rays at different altitudes taking into account the changes of chemical composition of the atmosphere. It is shown that the nitrate concentration is significantly influenced not only by cosmic rays but by the abundance of nitrate oxides in atmosphere also. The concentration of nitrate oxides increases due to human activity.

## 1 Introduction

Yearly averaged concentration of nitrates in polar ice is the unique source of information on solar activity in the past. Dreschhoff and Zeller (1994) have shown that the nitrate concentration in Greenland ice increases during the strong solar proton events. This is explained by the increase of the rate ionization of the Earth's atmosphere by solar cosmic rays that lead to the generation of free electrons and ions. These electrons are captured by neutral atoms and in the chain of following chemical reactions the  $\text{NO}_3^-$  ions are generated. After the hydration  $\text{NO}_3^-$  ions precipitate on the Earth's surface. Abundance of nitrates in polar ice also depends on climatic changes - variations in the atmosphere temperature and chemical composition of the atmosphere. The long-term trend of nitrate series measured in Greenland ice for 1575-1991 (Figure 1) is similar to that of temperature in Northern Hemisphere (Lamb H.H., Mitchell J.M., jr., 1961), concentration of stable isotope  $^{13}\text{C}$  in Northern Finland (Sonninen E., Jungner H., 1996), annual tree ring growth (La Marche V.C., jr., 1974). The decrease of  $^{13}\text{C}$  trend during last 100-150 years reflects the increase of  $\text{CO}_2$  input into the atmosphere due to fuel burning. The decrease of nitrate trend before the beginning of XIX century probably is connected with the decrease of atmosphere temperature and the following increase is connected with input of burning products into atmosphere.

The aim of present paper is the determination of influence of changes in the atmosphere's chemical composition on the generation of nitrates in the Earth's atmosphere. It is well known that in process of fuel burning the  $\text{NO}_2$  is escaped into the atmosphere. Besides this,  $\text{NO}_2$  can be input in the atmosphere due to denitrification of fertilizations. Now anthropogenic contribution to the sources of  $\text{NO}_2$  attains 20% of their summary intensity. Probably, this leads to the rise in concentration of  $\text{NO}_2$  on 0.15-0.4% per year, observed after the middle of the seventeen hundreds (M.I. Budyko, Yu. Israel, 1987). In the stratosphere and upper troposphere  $\text{NO}_2$  oxidized to  $\text{NO}$  and  $\text{NO}_2$ . Another source of  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) is the pollution, produced

by plane motors. The intensity of anthropogenic sources of NO<sub>x</sub> achieved 4% during 1966-1973 and 1% after 1973.

## 2 Formulation of the Problem.

In order to clarify the influence of increase of CO<sub>2</sub> and NO<sub>x</sub> on the rate of NO<sub>3</sub><sup>-</sup> generation let us consider the scheme of origination of this ion with the participation of thermal electrons, created due to ionization of atmospheric gases by cosmic rays. So, we will not consider the avalanche beginning of ionization but we'll begin to study the reaction after the appearance of thermal electrons and singly charged ions. Also we will not take into account the photochemical reactions.

It is possible to separate two steps in the process of generation of NO<sub>3</sub><sup>-</sup> ion (Table 1.)  
At first step the capture of electron by oxygen and nitrogen molecules and origination of O<sub>3</sub><sup>-</sup> takes place.

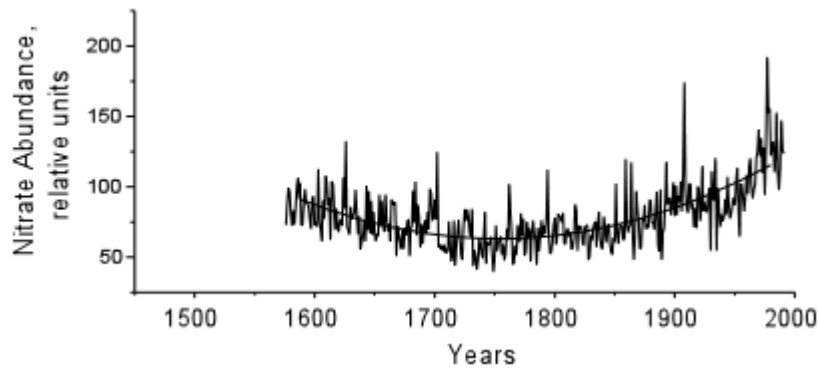
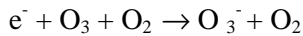
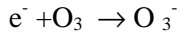
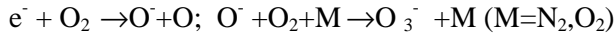
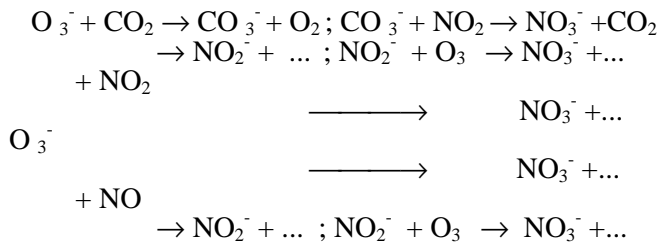


Figure 1: Abundance of nitrates in Greenland ice

At second step the interaction between ion O<sub>3</sub><sup>-</sup> and molecules NO<sub>x</sub> takes place. This interaction leads to the origination of the ions NO<sub>3</sub><sup>-</sup> and molecules CO<sub>2</sub>.



These reactions are described by the following kinetic equations for electrons:

$$\frac{dn_e}{dt} = Q_e - \sum_i \alpha_i^+ n_e n_i^+ - \sum_j \alpha_j n_e n_j - \sum_{j,k} \alpha_{jk} n_e n_j n_k$$

where n<sub>e</sub>-is the concentration of free electrons, t - time, Q<sub>e</sub> - number of thermal electrons generated in 1 cm<sup>3</sup> per second when atmosphere is ionized by cosmic rays, n<sub>i</sub><sup>+</sup> - concentration of positive ions of type i, n<sub>j</sub> - concentration of neutral molecules, α<sub>i</sub><sup>+</sup> and α<sub>j</sub> - constants of the rate of electron capture by positive ions of type i and neutral molecules of type j; α<sub>jk</sub> - constants of the rate of electron capture in collisions with molecules of type j and k simultaneously.

For positive and negative ions we have a similar equation which describes the reactions given in Table 1.

For the ion  $\text{NO}_3^-$  we will analyze the rate of generation of this ion in unit of volume and we will not consider its concentration, because the mechanism of sink of this ion needs to be investigated in more detail.

For normal conditions  $Q_e=10^3 \text{ cm}^{-3} \text{ s}^{-1}$ , but during the strong proton events it can attain the value of more than  $10^5 \text{ cm}^{-3} \text{ s}^{-1}$ . Rates of the atmosphere ionization and concentrations of gases depend on the altitude. For  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , we have used the following functions:

$$n_i(h) = n_i(h=0) \exp(-h/H), \quad H = 8,4 \text{ km};$$

$$n_{\text{O}_2}(h=0) = 5,6 * 10^{18} \text{ sm}^{-3}; \quad n_{\text{N}_2}(h=0) = 2,1 * 10^{19} \text{ sm}^{-3}; \quad n_{\text{CO}_2}(h=0) = 8,7 * 10^{15} \text{ sm}^{-3}$$

Concentrations of ozone,  $\text{NO}$ ,  $\text{NO}_2$  are not constant, in the past their values were smaller. So, calculations were made for different values of these parameters and for different altitudes.

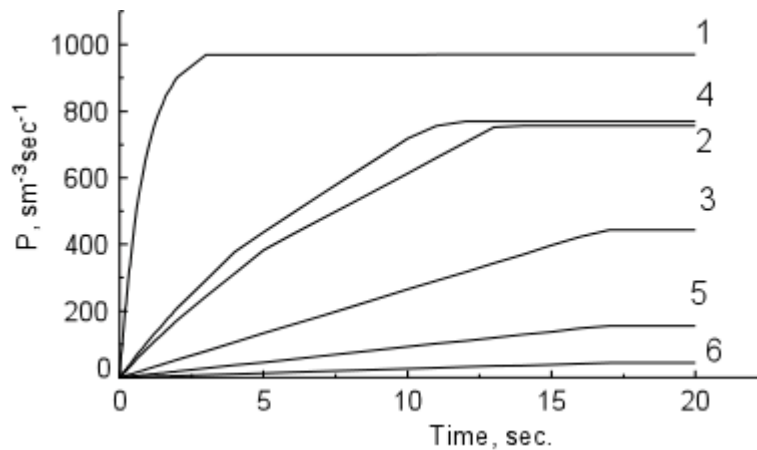
### 3 Results of Calculations

In Figure 2 the time dependence of the rate of generation of  $\text{NO}_3^-$  ion is plotted. The values of ionization are  $Q_e=10^3 \text{ cm}^{-3} \text{ s}^{-1}$  for the altitudes of 20-50 km, for different concentrations of  $\text{NO}_2$ .

As it is seen from Figure 1, generation of  $\text{NO}_3^-$  is more intensive in the dense layers of atmosphere and decreases in more rarefied layers. This is connected with a decrease of rates of chemical reactions when the altitudes increases due to the atmosphere rarefaction. The stationary value is achieved few seconds after the invasion of cosmic rays into the atmosphere.

Calculations also were carried out for other values of concentrations of ozone,  $\text{CO}_2$ ,  $\text{NO}$  and for other values of  $Q_e$ . But changes in concentrations of  $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{NO}$  by the factor 10 does not influence the rate of  $\text{NO}_3^-$  generation. Only a change in the  $\text{NO}_2$  concentration influences the rate of  $\text{NO}_3^-$  generation. The increase of  $\text{NO}_2$  concentrations leads to an increase of  $\text{NO}_3^-$  generation. This effect takes place at different rates of the atmosphere ionization.

Summarizing all stated above we can make the following conclusion: the increase of abundance of oxygen oxides in the Earth's atmosphere should lead to the increase of nitrate generation and hence to the increase of their concentration in polar ice. Such behavior of long-term nitrate trend really takes place in Greenland ice during the last 50 years.



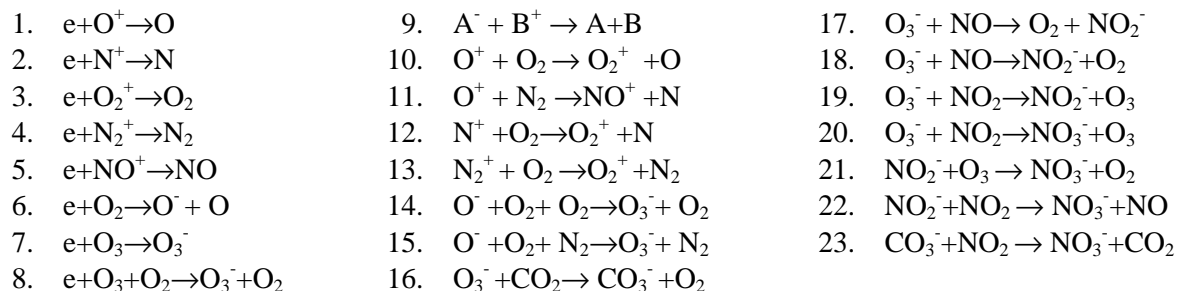
**Figure 2:** Rate of generation of  $\text{NO}_3^-$  ion at different altitudes, when the rate of atmosphere ionization is  $Q_e=10^3 \text{ cm}^{-3} \text{ s}^{-1}$ ,  $n_{\text{NO}} = 5 * 10^9 \exp(-h/H) \text{ sm}^{-3}$ ;  $n_{\text{CO}_2} = 8,7 * 10^{15} \exp(-h/H) \text{ sm}^{-3}$ ;  $n_{\text{O}_3} = 5 * 10^{11} \exp(- (h-30 \text{ km})^2 / 100 \text{ km}^2) \text{ sm}^{-3}$ ;  
 1.  $h=20 \text{ km}$ , 2.  $h=40 \text{ km}$ , 3.  $h=50 \text{ km}$  for  $n_{\text{NO}_2} = 7 * 10^{10} \exp(-h/H) \text{ sm}^{-3}$   
 4.  $h=20 \text{ km}$ , 5.  $h=40 \text{ km}$ , 6.  $h=50 \text{ km}$  for  $n_{\text{NO}_2} = 7 * 10^9 \exp(-h/H) \text{ sm}^{-3}$   
 The modern concentration of  $\text{NO}_2$  at sea level is  $7 * 10^{10} \text{ cm}^{-3}$ .

## 4 Conclusions

1. Generation of nitrates in the Earth's atmosphere by cosmic rays takes place mainly at the altitudes of 20-50 km. The lower line is determined by the depth of cosmic rays penetration in the atmosphere. When the altitude increases the rates of reactions decrease due to decrease of the atmosphere density.

2. The increase of the input of nitrogen oxides due to industrial activity leads to increase of rate of generation of  $\text{NO}_3^-$  ion in the atmosphere and to the increase of the abundance of nitrates in polar ice.

**Table 1:** Reactions used in calculation (Raiser Yu.P.,1992, H.Kawamoto,1984, Brasseur G., Chatel A.,1981, Ferguson E.E.,1987, Boyarchuk, K.A.,1999)



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