

Review

A Study of Chemical Processes of Nitrate in Atmospheric Aerosol and Snow Based on Stable Isotopes

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Abstract: Nitrate (NO_3^-) is a prominent atmospheric pollutant and a key chemical constituent of snow and ice, which plays a crucial role in the atmosphere and significantly impacts regional climate and environment conditions through a series of complex chemical processes. By summarizing the recent research progress on the nitrate chemical process (particularly on the isotopic measurements of NO_3^- ($\delta^{15}\text{N}$, $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$)) in atmosphere and glacier snow, this study mainly investigated the chemical compositions and chemical processes, formation pathways, and photochemical reactions of nitrate in snow and atmosphere. Our results identified that the main ways of atmospheric nitrate formation are the hydrolysis of N_2O_5 and the reaction of $\cdot\text{OH}$ with NO_2 ; the spatial distribution of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of atmospheric nitrate have a significant latitudinal trend between 30°N – 60°N ; the study of stable isotopes ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and the oxygen isotope anomaly ($\Delta^{17}\text{O}$) of nitrate have mainly been carried out over the densely populated and coastal mega cities; there exist significant gaps in the study of chemistry processes of nitrate in snow and ice and the air–snow interfaces across glaciated regions. This study provides a basic reference for more robust observations and research of nitrate in glacier areas in the future.

Keywords: nitrate; isotope composition; oxygen isotope anomaly; snow; formation pathway

1. Introduction

Nitrates are widely present in the surface environment and are an essential mineral of terrestrial ecosystems. They play a crucial role in the nitrogen cycle of the Earth system [1–4]. As one of the important components of atmospheric deposition, nitrate (NO_3^-) has a profound impact on the environment and ecosystem. Nitrate ion in the atmosphere is a key component of fine particulate matter ($\text{PM}_{2.5}$), accounting for more than 20% of the total mass of $\text{PM}_{2.5}$. In addition, nitrates are one of the key factors in the formation of acid rain, which has adverse effects on water quality and ecosystems [5–8]. The precursor of nitrate, NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$), is an important component of atmospheric pollutants. In recent years, with the rapid social and economic development, the content of nitrogen oxides (NO_x) in the atmosphere emitted by motor vehicle exhaust, fossil fuel combustion, thermal power plants, etc., has significantly increased. NO_x not only exacerbates global atmospheric pollution but also gradually becomes a scientific focus of international atmosphere and environmental science community [9–11]. In the atmosphere, the majority of NO_x undergoes various transformations to form nitric acid (HNO_3), and this process has a significant impact on the pH of atmospheric rainfall. The NO_x has a strong relation with ozone (O_3) and hydroxyl radicals ($\cdot\text{OH}$) in the atmosphere [1,12–15]. Therefore, it is crucial to study the formation pathways and chemical processes of atmospheric nitrate to

improve our understanding of nitrate chemistry and advance the field of atmospheric environment. Nitrogen (N) and its cycling in nitrates in atmospheric environment and glacier snow play important roles in the natural nitrogen cycle of the Earth system, offering valuable insights into the impacts of human activities on the atmospheric environment and ecosystem.

The stable isotopes of nitrate and the oxygen isotope anomaly of nitrate are essential parameters and analysis channels in investigating atmospheric nitrate and their sources, formation pathways, and chemical processes [14,16]. The stable isotopes, including ^{18}O , ^{17}O , ^{16}O , ^{15}N , and ^{14}N (Table 1), can be measured within the NO_3^- anion. Given the relatively lower abundance of heavier isotopes, the utilization of δ values is widespread for expressing the relative isotopic ratios, which is defined by the formula $\delta(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$ (Table 1), and according to the Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, the reference is gaseous N_2 for $\delta^{15}\text{N}$ [17]. In various biological, physical, and chemical reactions, the phenomenon where isotopes of a specific element distributed in different substances in varying proportions is referred to as isotope fractionation. Isotope fractionation related to mass is called mass-dependent fractionation (MDF). In this phenomenon, there is a linear relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, which is expressed as $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ [18,19]. This phenomenon is widely observed and identified in oxygen and water bodies. However, this linear relationship does not exist in the formation process of O_3 , which is known as mass-independent fractionation (MIF) of isotope [20–24]. The degree of MIF is generally determined and expressed by employing the oxygen isotopic anomaly ($\Delta^{17}\text{O}$): $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ (Table 1).

Table 1. Stable isotopes and isotopic anomalies of nitrate ion.

Name	Notation	Formula	Parametric
Stable isotope	$\delta^{18}\text{O}$	$\delta(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$	$R = ^{18}\text{O}/^{16}\text{O}$
Stable isotope	$\delta^{17}\text{O}$		$R = ^{17}\text{O}/^{16}\text{O}$
Stable isotope	$\delta^{15}\text{N}$		$R = ^{15}\text{N}/^{14}\text{N}$
Oxygen anomaly of nitrate ion	$\Delta^{17}\text{O}$	$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$	-

The current scientific understanding of atmospheric and snow/ice chemistry remains incomplete. A large number of relevant studies primarily rely on numerical isotopic fractionation model, chemistry box model, and chemical transport model. These models have investigated oxygen isotopic anomalies in the atmosphere, the photolysis of nitrate in Antarctic ice/snow, and the formation processes of nitrate [14,25,26]. In addition, many studies on the chemical processes and formation pathways of atmospheric nitrates have been conducted in coastal cities of North America [12,13,27–29], some mega cities in Europe [28,30], and over the eastern coastal region of Asia [8,31–33]. The investigation of chemical processes of nitrate in glacier regions has significant implications for understanding atmospheric nitrogen oxide levels in the past. However, studies on nitrate chemical processes in glacier snow/ice and its formation pathways at the air–snow interface have been primarily carried out in the Antarctic ice sheet and Greenland ice sheet, while little relevant studies have been performed over mountain glaciers, leaving large gaps in understanding well the nitrate chemical processes over the cryosphere area. This study provides a comprehensive review of atmospheric nitrate chemistry and snow chemistry. Additionally, we propose the current study limitation and highlight the future research needs of nitrate chemistry of snow/ice.

2. Measurement Methods for Stable Oxygen Isotope

Currently, there are several methods available for determining the N and O isotopes of nitrates, including ion-exchange- AgNO_3 method [34], pyrolysis method [35], azide method [36], and denitrification bacteria method [24,37].

The ion-exchange- AgNO_3 method: The nitrate (NO_3^-) samples were individually combusted in a furnace and subjected to a high-temperature pyrolysis to produce N_2 and CO . The separated gases were introduced into an isotope ratio mass spectrometer (IRMS) through a chromatographic column for the analysis of $\delta^{15}\text{N}$ [38]. The oxygen isotopes ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) were determined using the pyrolysis method. After purifying the nitrate (NO_3^-) samples, they were converted into AgNO_3 solution through ion exchange column and Ag_2SO_4 . The dried AgNO_3 powder was then heated in a high-temperature quartz reaction tube ($550\text{ }^\circ\text{C}$) to generate O_2 , NO_2 , Ag , and trace amounts of N_2 and NO . The generated gases were directed into a liquid nitrogen trap for enrichment, purification, and separation. Finally, the obtained oxygen gas (O_2) was introduced into an IRMS for the testing of oxygen isotope ratios [35].

The azide method: The first step involves using cadmium metal to reduce the amount of NO_3^- converted to NO_2^- . The second step is to reduce the generated NO_2^- to N_2O with the assistance of sodium azide and a weak acid buffer environment. Subsequently, the N_2O gas is thermally decomposed into N_2 and O_2 through a high-temperature metal tube, and then, they enter an IRMS for the determination of N and O isotopes [36].

The denitrification bacteria method: This method involves the direct conversion of NO_3^- to N_2O by denitrifying bacteria. Firstly, the cultivation of denitrifying bacteria requires the preparation of culture medium, cultivation liquid, and rinsing solution. The freeze-dried powder of golden pseudomonas bacteria is activated, followed by sealed cultivation. Afterwards, well-grown individual colonies with a golden yellow appearance are isolated and cultivated separately. Then, the cultivated denitrifying bacterial solution undergoes a series of processes, such as centrifugation, fractionation, and nitrogen blowing to remove N_2O gas from the culture liquid. Finally, the sample is injected into sample vials containing the bacterial solution for reaction. The obtained gas samples are purified, concentrated, and separated, and subsequently, their $\delta^{15}\text{N}$, $\delta^{17}\text{O}$, and $\delta^{18}\text{O}$ values are determined using an IRMS [37,39].

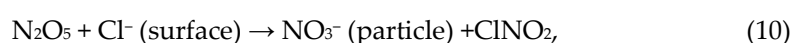
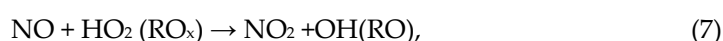
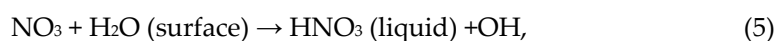
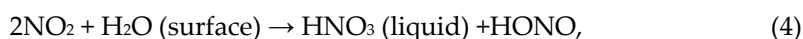
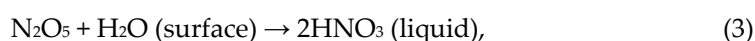
Among the four pre-treatment methods, the ion-exchange- AgNO_3 method and the azide method require a larger quantity of sample volume (with a higher detection limit) and involve a cumbersome process. Additionally, the azide method has a shorter pre-treatment time and higher accuracy, but it involves the use of highly toxic hazardous substances in the reaction. However, the denitrification bacteria method is simple to operate but has a low detection limit and can meet the required experimental accuracy. Thus, the denitrification bacteria method is one of the most widely applied methods for the detection of stable oxygen isotope of nitrate ion (NO_3^-).

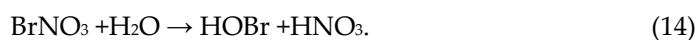
3. Chemical Processes of Atmospheric Nitrate

On a global scale, the photolytic reactions of NO and $\cdot\text{OH}$, along with the hydrolysis of N_2O_5 , are commonly acknowledged as the dominant pathways for the formation of nitrates (Equations (1) and (2)) [26,40]. Chemical Equation (1)–(8) encompass the primary formation pathways of atmospheric nitrate (NO_3^-), whereas M in Equation (1) represents oxygen (O_2) and/or nitrogen (N_2) in the atmosphere, HC in Equation (3) represents hydrocarbons, and DMS stands for dimethyl sulfide. An improved GEOS-Chem simulation, incorporating $\Delta^{17}\text{O}$ of nitrate from various sites, revealed that both $\text{NO}_2 + \text{OH}$ (Equation (1)) and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ (Equation (2)) contribute approximately 41% to global nitrate formation, and other mechanisms contribute less than 6% to near-surface nitrate levels globally [40]. The reaction between NO_2 and $\cdot\text{OH}$ primarily occurs during daylight hours. The reaction between NO_2 and O_3 generates N_2O_5 , which subsequently hydrolyzes to form HNO_3 , primarily taking place at night [26]. The contributions of different reactions vary greatly in

different regions and periods. Due to the significant emissions of hydrocarbon compounds (HCS) in the atmosphere, the reaction between NO_3 and HC (Equation (3)) becomes an important pathway for the formation of industrial nitrates in industrial areas [41]. In non-coastal areas, the lower mixing ratio of DMS leads to a smaller contribution to the reaction of NO_3 + DMS [42]. Studies have shown that in low temperature and heavily polluted weather conditions, the absorption of N_2O_5 in aerosols and clouds is the primary pathway of nitrate formation [8,43]. Experiment-based research has indicated that the hydrolysis of NO_2 and NO_3 (Equations (4) and (5)) is not the main pathway for the formation of HNO_3 in the atmosphere due to their low reaction probabilities [44–46]. However, recent model simulations have reported that the hydrolysis of NO_2 (Equation (4)) is also an important source of HNO_3 formation in winter haze weather [47]. Additionally, it has been found that the heterogeneous reactions of NO_3 and N_2O_5 on the surface of aerosols are the main factors controlling the generation of nitrate in particulate matter during polluted weather conditions [48].

In general, there are two main oxidation pathways for NO to form NO_2 in the atmosphere. One is through the reaction of NO with O_3 (Equation (6)), and the other is through the oxidation of NO with OH/ RO_2 (Equation (7)), followed by hydrolysis to form HNO_3 . HO $_2$ / RO_2 represents peroxy radicals, which typically refer to a group of substances produced by reaction between certain organic groups (R) or hydrogen atoms with O_2 in the atmosphere [31]. NO_2 can also react with O_3 and generates NO_3^- radical (Equation (8)). The NO_3^- radical can react directly with hydrocarbons (HC) and dimethyl sulfide (DMS) and then generate HNO_3 , or it can undergo hydrolysis on the surfaces of aerosols to form HNO_3 [40,41]. The reaction of NO_3 with HC/DMS predominantly occurs during the night, because NO_3 is easily prone to photolysis during the daytime [49]. Nitrogen pentoxide (N_2O_5) is an active NO_x reservoir during the night, which can react at the surfaces of airborne particles, generating HNO_3 or both NO_2 and nitryl chloride (ClNO_2) (Equation (10)) [50]. Moreover, there are other potential mechanisms for the formation of nitrate particles, such as the hydrolysis of organic nitrates (RONO_2) and halogen nitrates (XNO_3), which play an important role in the formation of atmospheric nitrates in coastal areas and tropical rainforest [33]. Additionally, some halogens (X, such as Cl, Br, I) in polar regions can participate in photochemical reactions with NO_x , oxidizing and producing HNO_3 [51,52]. Taking bromine (Br) as an example, the halogen components typically undergo many reactions with nitric oxide and nitrate according to processes presented in Equation (11) – (14) to form nitric acid eventually [51].





Reactions indicated by Equations (7) and (12) represent the oxidation and photolysis of NO_x by O_3 , HO_2 , and RO_x after NO is emitted into the atmosphere. The cycle/transfer between NO and NO_2 occurs quite rapidly, allowing them to establish a photochemical steady state during the day. The conversion of NO_x to nitrates is at least three orders of magnitude slower than the formation of NO and NO_2 . The primary daytime reaction for the conversion of NO_x to nitrates involves the oxidation of NO_2 by $\cdot\text{OH}$ to form HNO_3 (reaction 12, Equation (1)). Processes 5 to 11 in Figure 1 represent the formation pathways of nitrates during the nighttime. NO_2 reacts with O_3 (reaction 5, Equation (8)) to form NO_3 , which then reacts with hydrocarbons (HC) to generate HNO_3 (reaction 8, Equation (3)). Alternatively, NO and NO_2 can inter-react to form N_2O_5 (reaction 7, Equation (9)), which undergoes heterogeneous reactions on the surfaces of aerosol to form HNO_3 (reaction 9, Equation (2)). Reactions 7 to 9 mainly occur at night since NO_3 is highly unstable during the day and rapidly undergoes photolysis, resulting in low concentrations [19,26].

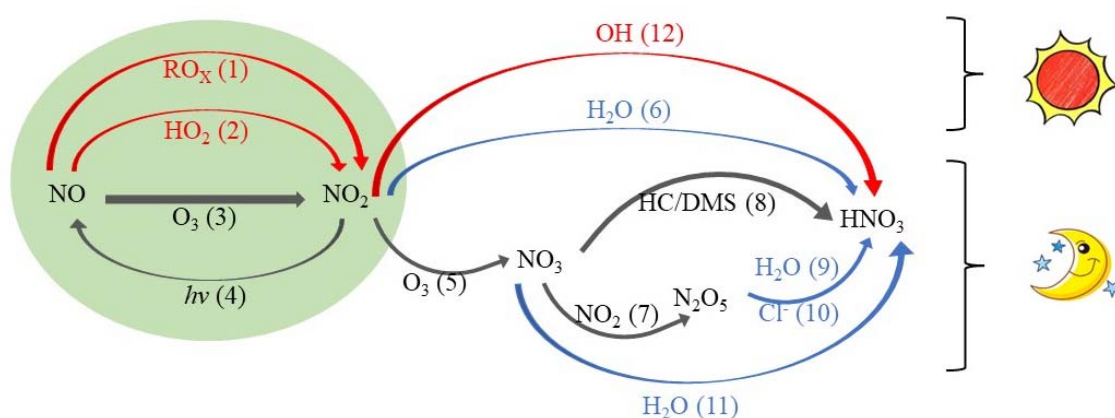
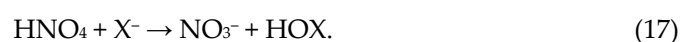
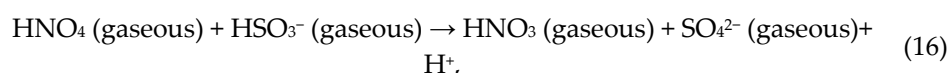
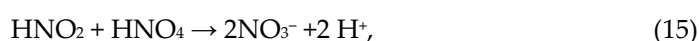


Figure 1. Schematic diagram illustrating main pathways of NO_3^- formation in the atmosphere (reaction 1–reaction 12). Red font indicates reactions where the $\Delta^{17}\text{O}$ of the oxidants is close to zero, and blue font indicates processes of heterogeneous reactions in the atmosphere. (The figure was modified from [19].)

It is worth noting that heterogeneous reactions are also one of the main pathways to produce HNO_3 . Simulations of atmospheric chemistry in the coastal areas of California using a chemistry box model have shown that over 50% of the nitrates in the summer atmosphere are generated from the reaction of NO_2 and $\cdot\text{OH}$, while over 90% of the nitrates in the winter atmosphere are produced through the heterogeneous reaction of N_2O_5 [14]. Nitrates in snow pits in Greenland are almost entirely generated from the reaction of NO_2 and $\cdot\text{OH}$ in the summer, while in the winter, they are mainly produced through the reaction of NO_2 and O_3 . Nitrates formed from the reaction of NO_3 and hydrocarbons account for about 40% of the total nitrate in the atmosphere, while the hydrolysis of N_2O_5 accounts for 60% of nitrate formation [19]. In addition, the reaction between N_2O_5 and Cl^- is a heterogeneous reaction. Studies have shown that N_2O_5 reacts with Cl^- released from coal-fired power plants to form ClNO_2 (reaction 10, Equation (9)), resulting in high concentrations of ClNO_2 in the atmosphere of North China [49,53,54]. Therefore, the reaction between N_2O_5 and Cl^- is also noteworthy in severe polluted regions. Moreover, a higher

relative humidity of atmosphere during nighttime than daytime creates favorable conditions for heterogeneous reactions, such as the hydrolysis of NO_3 (reaction 11, Equation (5)). These processes are crucial for the formation of nitrates during nighttime, with the pathways of $(\text{NO}_3 + \text{H}_2\text{O}/\text{HC})$ and $(\text{N}_2\text{O}_5 + \text{H}_2\text{O}/\text{Cl}^-)$ being the primary contributors. However, it should be emphasized that the heterogeneous reactions, especially the reaction $(\text{NO}_2 + \text{H}_2\text{O}/\text{OH})$, make comparable contributions to nitrate formation during both daytime and nighttime [31]. In wintertime, the low concentration of $\cdot\text{OH}$ [55,56] and the high concentration of N_2O_5 in field measurements [57–59] highlight the significant contribution of N_2O_5 heterogeneous reactions to nitrate formation in haze weather [60,61]. Additionally, during haze periods in North China, higher relative humidity and larger aerosol surface area facilitate the heterogeneous reactions of nitrogen oxides. Therefore, the reaction pathway of $(\text{NO}_2 + \text{H}_2\text{O})$ also serves as an important potential pathway for nitrate formation during haze events [55,62,63]. Moreover, it has been identified that the reactions among biogenic volatile organic compounds (BVOCs) and NO_x and NO_3 produce organic nitrates (e.g., RONO_2 , RO_2NO_2) [64]. Organic nitrate aerosols have the ability of absorbing sunlight, particularly in the ultraviolet (UV) range. Intense solar radiation and high temperature can lead to the increase of NO_x from nitrate photolysis, and a reduced source from organic nitrates can result in a short lifetime in the warmer air [40,65]. The formed RONO_2 undergoes oxidation reactions, yielding second-generation RONO_2 species. The photolysis and oxidation of those species can contribute to the recycling of NO_x [66]. Additionally, particle-phase RONO_2 ($p\text{RONO}_2$) contributes to the formation of organic aerosols. RONO_2 in the atmosphere is usually removed through dry/wet deposition or by subjecting it to hydrolysis to form inorganic nitrates and alcohols [67–69].

In polar regions, cold temperatures maintain/preserve the stability of HNO_4 formed from the reaction between HO_2 and NO_2 [70,71]. The presence of liquid HNO_4 enables further reactions with various chemical substances (such as HNO_2 , HSO_3^- , Cl^- , Br^- , and I^-) to form nitrates [51]. Therefore, heterogeneous chemical reactions play a crucial role in the formation of nitrates in polar regions. The specific reaction processes are illustrated by Equation (15)–(17), and Equation (17) specifically represents the reaction of halogens (X , such as Cl , Br , I) with HNO_4 [72–74].



4. Spatial Distribution of Isotopes of Atmospheric Nitrate

Nitrates is a significant form of nitrogen in the natural environment and can be readily utilized by organisms [75]. The values of $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ of nitrates have significant differences due to their different origins and sources. It has been demonstrated that the $\delta^{15}\text{N}(\text{NO}_x)$ in automobile exhaust is typically around -5‰ [76], while the $\delta^{15}\text{N}(\text{NO}_x)$ in atmospheric deposition ranges from -13‰ to 13‰ [77]. Synthetic fertilizers generally have $\delta^{15}\text{N}$ values ranging from -4‰ to 4‰ [78]. However, $\delta^{15}\text{N}$ alone cannot accurately indicate the different sources of nitrates. As such, the analysis of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in nitrates becomes crucial in accurately identifying their sources. Integrating the data of $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ allows a more precise identification of the origins, formation conditions, and transfer pathways of nitrate formation.

Study of stable isotopes and isotopic anomalies of atmospheric nitrates is mainly focused on the coastal cities of Asia and North America and the western coast of Australia (Figure 2). However, there is a lack of investigation of atmospheric nitrates in glacier areas. High $\delta^{15}\text{N}$ values of atmospheric nitrate are distributed in the eastern coastal areas of Asia, the eastern coastal areas of North America, and the western coast of Australia. This is

likely related to intensive anthropogenic emissions [76,77,79]. High $\Delta^{17}\text{O}$ values of atmospheric nitrate could also be found in the eastern coastal areas of Asia, the western coast of Australia, and the northern regions of North America, while high $\delta^{18}\text{O}$ values of atmospheric nitrate are spatially distributed along the western coast of Australia and the eastern United States. The different $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of atmospheric nitrate are greatly influenced by atmospheric O_3 concentration and the pathways involved in its formation [12,24,80–83].

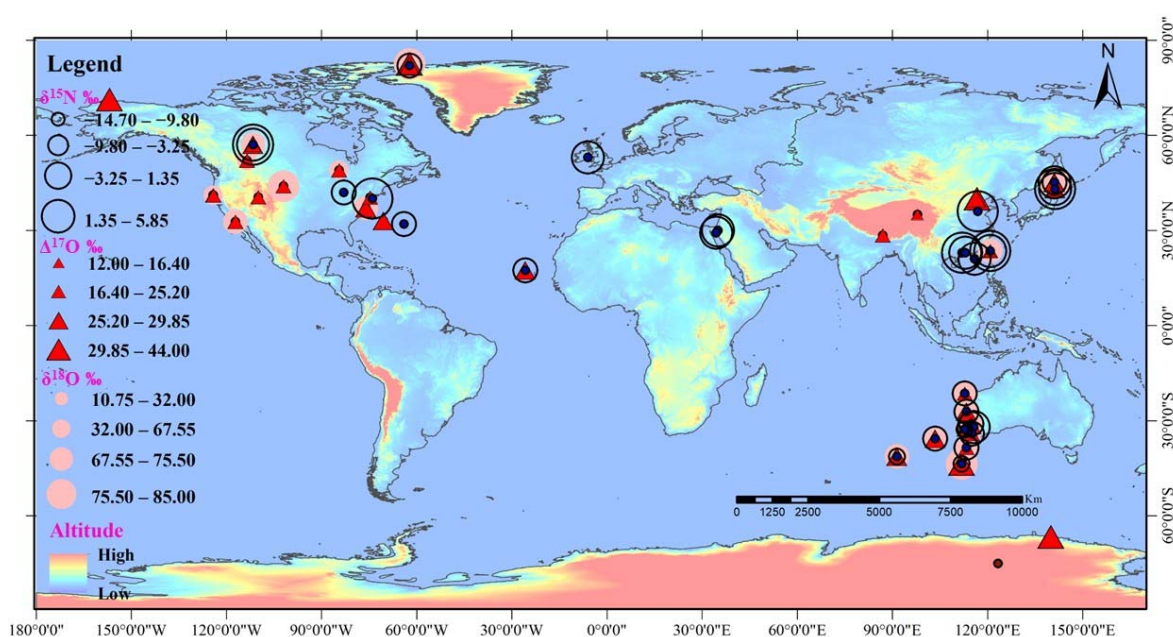


Figure 2. Spatial distribution of stable isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) and oxygen isotope anomaly ($\Delta^{17}\text{O}$) in atmospheric nitrate.

4.1. Investigation of $\delta^{15}\text{N}$ in Atmospheric NO_x

Formation of NO_3^- in the atmosphere primarily occurs through the oxidative reactions of NO_x . Atmospheric NO_x has both natural and anthropogenic sources. Natural sources include lightning, wildfires, microbial activities, and stratospheric transport. Anthropogenic sources primarily consist of the following: (1) fossil fuel combustion, such as emissions from coal-fired power plants and vehicle and aircraft exhaust emissions, (2) biomass burning emissions from agricultural waste (e.g., straw, sugarcane residue, rice husk) and household heating or cooking, and (3) agricultural activities, particularly fertilizer application, which significantly impacts the release of NO_x into the atmosphere [84]. Moreover, the dry and wet deposition of atmospheric NO_x is the main pathway/source of nitrate content in snow and ice. Stable nitrogen isotope of nitrate can be used to determine the origins and chemical processes of atmospheric nitrogen. The calculation method of nitrogen isotope ratios is as follows:

$$\delta^{15}\text{N}_{\text{sample}} (\text{‰}) = \left[\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{sample}} / \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{standard}} - 1 \right] \times 1000 \quad (18)$$

Different sources of NO_x have different $\delta^{15}\text{N}$ values, and emissions from fossil fuel combustion are the primary sources of NO_x in the atmosphere (e.g., automobile emission and coal combustion and power plant emissions) [79,85,86]. Stable nitrogen isotopes from natural sources (such as lightning and coal combustion) typically exhibit positive values [87–89]. Generally, NO_x from anthropogenic sources generated during the combustion process can be categorized into two types. The first is “thermal decomposition NO_x ,” which occurs at very high temperatures ($>2000^\circ\text{C}$). Under high oxygen and pressure conditions in the combustion chamber, nitrogen and oxygen inter-reaction occurs, resulting

in a typically negative $\delta^{15}\text{N}$ value. Examples of fuels that undergo thermal decomposition NO_x include diesel, gasoline, and natural gas. The second type is “combustion NO_x ”, which is formed during the combustion of nitrogen oxides in the fuel itself. As the reaction temperatures are not very high (1300–1400 °C), the resulting $\delta^{15}\text{N}(\text{NO}_x)$ value is typically positive [90–92]. The $\delta^{15}\text{N}(\text{NO}_x)$ values contributed from the combustion of fossil fuels ranged from -17.9‰ to 19.8‰ (Figure 3) [79,85,86,93–95]. The $\delta^{15}\text{N}$ values of nitrogen-containing particles generated from fuel combustion are relatively small, mostly having negative values (-19.4‰ to 2.9‰) [95]. On the other hand, the $\delta^{15}\text{N}$ values of NO_x produced from coal combustion are relatively high (5.2‰ to 19.8‰) [79,86,93]. Different combustion conditions (temperatures of combustion, pressures, oxygen levels, biomasses, fossil fuels, etc.) of fossil fuels significantly influence nitrogen isotopes and their composition [86,95]. For example, diesel and gasoline have similar chemical properties, but their nitrogen isotope values are quite different (diesel: $+4.6\text{‰} \pm 0.8\text{‰}$; gasoline: $-7.5\text{‰} \pm 8.3\text{‰}$), which is due to their different combustion processes in terms of combustion temperature and oxygen content [95]. Moreover, the $\delta^{15}\text{N}$ values of NO_x in vehicle exhaust are lower (-13‰ to -2‰) compared to the values detected from power plant emitted exhausts (6‰ to 13‰). This is primarily due to the reaction ($\text{N}_2 + \text{O}_2 \leftrightarrow 2\text{NO}$) ($>2000\text{ °C}$) that favors the formation of lighter ^{14}N molecules, resulting in negative $\delta^{15}\text{N}(\text{NO}_x)$ values in vehicle exhaust [86]. In power plants, the reaction temperature is relatively low (1300–1400 °C), resulting in the low production of NO and a positive $\delta^{15}\text{N}(\text{NO}_x)$ value [86]. Notably, there exist significant differences in stable isotope values of nitrate from different sources. Factors contributing to these differences include combustion form, fuel type, chamber structure, and testing method. Therefore, it is necessary to conduct a detailed stable isotope analysis of nitrogen to better understand the exact sources, chemical processes, and formation pathways of nitrogen in atmosphere.

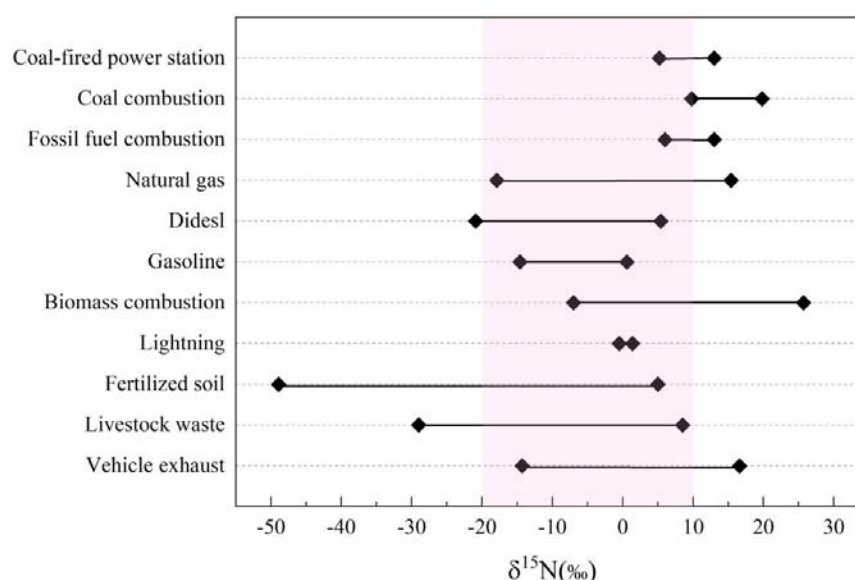


Figure 3. Distribution of $\delta^{15}\text{N}$ (‰) of atmospheric nitrate contributed from different sources.

4.2. Variability of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of Atmospheric NO_3^-

The main oxidants that promote the conversion of NO_x to NO_3^- in the atmosphere are O_2 , O_3 , OH, HO_2/RO_2 , and XO. Figure 4 presents the spatial variations of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of nitrates in the atmosphere across different latitudes at the global scale. There are two distinct patterns in both hemispheres. In the Northern Hemisphere, the $\delta^{18}\text{O}$ values of nitrate in the atmosphere significantly increase according to latitude gradients. The variation of $\delta^{18}\text{O}(\text{NO}_3^-)$ in the atmosphere is more obvious with notable fluctuations in low latitude regions (30°N – 60°N). The variation of $\delta^{18}\text{O}(\text{NO}_3^-)$ with latitudes is primarily due to

the gradient differences of oxygen isotope of O_3 in the atmosphere [80–82]. It is also caused by significant spatial differences in the formation pathways of NO_3^- [80,81]. The variation pattern of $\Delta^{17}O(NO_3^-)$ with latitude is similar to that of $\delta^{18}O(NO_3^-)$ in the atmosphere. The $\Delta^{17}O(NO_3^-)$ values in the atmosphere significantly increase along high latitudes ($60^\circ N$ – $80^\circ N$) in the Northern Hemisphere. The latitude variation of $\Delta^{17}O(NO_3^-)$ in the atmosphere is likely influenced by different formation pathways of nitrate [1,12,13,24,35,81].

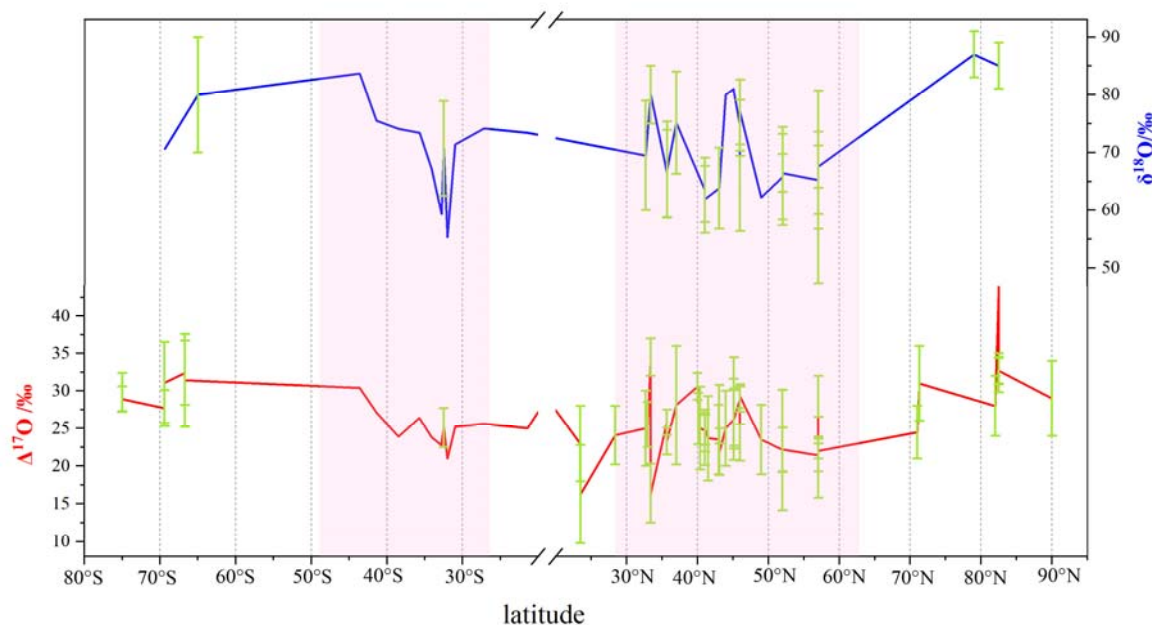


Figure 4. Latitude variations of $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ in the atmosphere.

The characteristic values of $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ in the atmosphere are both positive, with $\Delta^{17}O$ values being smaller than $\delta^{18}O$ values (15–30‰) (Figure 4). $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ in the atmosphere exhibit clear seasonal variations [96]. The $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ values in summer/spring are lower than those in winter. The seasonal variations of ozone content in the atmosphere have significant impacts on the $\Delta^{17}O$ and $\delta^{18}O$ values [1,15,97]. The correlation between $\Delta^{17}O$ and $\delta^{18}O$ values mainly lies in their similar seasonal variations. However, the driving factors behind the seasonal variations of $\Delta^{17}O$ and $\delta^{18}O$ are different [97]. The seasonal variation of $\delta^{18}O(NO_3^-)$ in the atmosphere is primarily influenced by the different oxidation pathways of NO_3^- in winter and summer, and the seasonal variation of O_3 concentration and light intensity. The $\delta^{18}O$ value of the O_3 pathway is higher than that of the $\cdot OH$ pathway. In the summer months, there is strong solar radiation, leading to a high degree of decomposition of volatile organic compounds (VOCs). As a consequence, the O_3 production rate decreases, leading to a greater generation of NO_3^- through the $\cdot OH$ pathway in the summer atmosphere. Conversely, during the winter months, there is relatively weaker solar radiation and a lower degree of VOCs decomposition, and the O_3 production rate increases, causing a higher proportion of NO_3^- produced through the O_3 pathway in the winter atmosphere [12–14]. The seasonal variation of $\Delta^{17}O(NO_3^-)$ values is due to seasonal differences in the oxidation pathways of NO_x [15,19]. Due to the photolysis of N_2O_5 , NO_3^- is primarily generated through the ($NO_2 + \cdot OH$) pathway during the day, while at night, it is mainly produced through the hydrolysis of N_2O_5 or the reaction of NO_3^- radicals with HC/DMS. Notably, the $\Delta^{17}O$ values in the N_2O_5 hydrolysis or the reaction of NO_3^- radicals with HC/DMS to form NO_3^- are higher than those in the $\cdot OH$ pathway [14,31]. In summer, there is a stronger radiation intensity and a longer duration of sunlight compared to winter, which results in the significant photolysis of N_2O_5 and indirectly leads to higher concentrations of $\cdot OH$. Consequently,

lower $\Delta^{17}\text{O}$ values are observed in summer, while higher $\Delta^{17}\text{O}$ values are observed in winter. In addition, the seasonal variation of atmospheric water vapor content can impact the oxidation formation of NO_3^- . Higher water vapor content can facilitate the generation of NO_3^- through the hydrolysis pathway of N_2O_5 , thus influencing the value of $\Delta^{17}\text{O}$ [32]. Currently, our understanding of the reaction processes involving NO_3^- in the atmosphere is still limited. The relative contributions of each process may vary; thus, more in-depth research employing chemical models is necessary to investigate the underlying mechanisms of the seasonal variations in $\Delta^{17}\text{O}(\text{NO}_3^-)$ and $\delta^{18}\text{O}(\text{NO}_3^-)$.

The generation process of nitrate ion (NO_3^-) in the atmosphere is rather complex. It is difficult to accurately determine the chemical pathways of nitrate solely through measuring $\Delta^{17}\text{O}$ of atmospheric nitrate. Currently, many studies combined measured $\Delta^{17}\text{O}(\text{NO}_3^-)$ with atmospheric chemistry models to further analyze the chemical pathways and formation mechanisms of atmospheric nitrate in various regions and seasons. Atmospheric chemistry models usually include chemistry box models, GEOS-Chem chemical transport models, and photochemical steady-state (PSS) [14,26,33,97]. For example, a chemistry box model has been employed to simulate the presence of nitrate in coastal aerosols in California, USA, and its simulation results were in good agreement with the experimental data during the spring and winter seasons [14]. However, a divergence emerged during the late summer and autumn, where the simulated values were found to be 2‰–4‰ higher than the experimental measurements. This discrepancy can be attributed to the oversight of nitrate transport in the box model, highlighting the importance and necessity of considering the transport processes in precisely predicting atmospheric nitrate in coastal aerosols [14]. The results simulated from the chemistry box model indicate that during the spring season, the formation of nitrate primarily occurs through the hydrolysis of N_2O_5 and with high $\Delta^{17}\text{O}$ values, whereas during the summer, the higher oxidation of HO_2/RO_2 results in lower $\Delta^{17}\text{O}$ values. Simulations of $\Delta^{17}\text{O}$ values in the tropical marine boundary layer show that PSS more accurately stimulates $\Delta^{17}\text{O}$ variations, while GEOS-Chem still suffers from some errors due to the utilization of the photochemical steady-state equation at night [33,97].

5. Characteristics of Nitrogen–Oxygen Isotopes of Nitrates in Snow and Ice

Research on nitrates in snow and ice is primarily focused on the Antarctic region [25,81,98,99]. The concentration of NO_3^- in surface snow and ice in Antarctica ranges from 0.5 to 4.0 $\mu\text{eq L}^{-1}$. It increases gradually from coastal regions towards the interior of Antarctica. The NO_3^- concentration in snow and ice from Southwestern Antarctic is lower compared to that of the Southeastern Antarctic region. Emerging evidence from earlier research suggests an inverse correlation between NO_3^- concentration in Antarctic snow/ice and the rate of snow accumulation [100]. In addition, as the thickness of snow increases, NO_3^- concentration gradually decreases, which is attributed to wind drift and sastrugi formation in the vicinity of the sampling site [25]. The concentration changes of NO_3^- after deposition and isotopic fractionation is influenced by the evaporation of HNO_3 , the photolysis of NO_3^- , and the wind-driven redistribution of surface snow, causing a rapid decrease in the surface concentration of NO_3^- [101]. However, $\delta^{15}\text{N}(\text{NO}_3^-)$ values displayed an inverse trend with snow thickness and NO_3^- concentration. Strong enrichment of $\delta^{15}\text{N}(\text{NO}_3^-)$ in snow with increasing snow depth due to isotopic fractionation is caused by the mass loss of NO_3^- in the upper snowpack [102]. The variations of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ along the vertical profiles of snow layer are opposite, as the snow depth increases, $\delta^{18}\text{O}$ values gradually decrease. The variation of $\Delta^{17}\text{O}$ along the depths of snow has a similar trend to that of $\delta^{18}\text{O}$, which is due to the fact that in NO_3^- deposition, the NO_3^- is formed secondarily after NO_3^- photolysis, and the isotopes of $\cdot\text{OH}$ and H_2O are exchanged, resulting in a decrease in $\delta^{18}\text{O}$ values, whereas the $\Delta^{17}\text{O}$ values of $\cdot\text{OH}$ and H_2O are close to zero, and the $\Delta^{17}\text{O}$ value decreases during the secondary NO_3^- formation [25,98]. This trend of NO_3^- and its isotopic composition usually can be observed in the low-accumulation regions of interior Antarctica and is mainly driven by the photolysis and recycling processes of NO_3^- .

[25,81,98,99,102] Isotope analysis suggested that $\delta^{15}\text{N}(\text{NO}_3^-)$ in Antarctic snow ranges from -19.4‰ to 36.6‰ . The significant variation of $\delta^{15}\text{N}(\text{NO}_3^-)$ values likely indicates the fractionation of nitrogen isotopes in the snow of Antarctica [81,103]. The NO_3^- and its $\delta^{15}\text{N}(\text{NO}_3^-)$ values exhibit similar spatial variation, namely, their values gradually increase from the coasts of East Antarctica towards/to the inland of Antarctica [81,99]. The $\delta^{18}\text{O}(\text{NO}_3^-)$ values in Antarctic snow and ice range from 12‰ to 101‰ (Table S1). The spatial variation of $\delta^{18}\text{O}(\text{NO}_3^-)$ is different compared with that of $\delta^{15}\text{N}$, and in areas with high snow accumulation rates along the Antarctic coast, the $\delta^{18}\text{O}(\text{NO}_3^-)$ values are higher, whereas in areas with lower accumulation rates in the inland, the $\delta^{18}\text{O}$ values are lower [99]. The spatial variation of $\delta^{18}\text{O}$ values of nitrate in Antarctic snow/ice is primarily influenced by the formation pathways of NO_3^- in snow layers. Additionally, once NO_x is deposited in snow layers, they will undergo consequent physical and chemical transformations. The products of NO_3^- photolysis undergo secondary oxidation reactions, leading to the regeneration of NO_3^- in surface snow and ice [103,104]. Moreover, it was reported that the $\Delta^{17}\text{O}(\text{NO}_3^-)$ values in Antarctic snow range from 13.2‰ to 44‰ [99,105]. The variation amplitude of $\Delta^{17}\text{O}(\text{NO}_3^-)$ is smaller compared to those of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, suggesting that the spatial variation of $\Delta^{17}\text{O}(\text{NO}_3^-)$ in Antarctic snow is not obvious. The trend of $\Delta^{17}\text{O}(\text{NO}_3^-)$ is similar to that of $\delta^{18}\text{O}$, i.e., it gradually decreases from coastal areas to inland Antarctica [106].

6. Optical Properties of Nitrate in Snow and Ice

Higher concentrations of nitrate in snow and ice can lead to increased light absorption, affecting the albedo of surface snow/ice, which in turn can impact the energy exchange and flux between the Earth's surface and the atmosphere [25,107]. The deposition of NO_3^- from the atmosphere onto the surface of snow layers causes a series of complex physical and chemical reactions, which occur at the air–snow interface. During this process, in addition to NO_3^- concentration changes, the fractionation of nitrogen and oxygen isotopes in NO_3^- also takes place. The photochemical processes of NO_3^- in snow and ice can be described as follows, with reactions (19) and (20) being the main reactions of photolysis [108].



These photochemical reactions significantly affect NO_3^- concentrations in snow and play an important role in the transformation of nitrogen species and impact snowpack chemistry [108,109]. The nitrogen and oxygen isotope fractionation coefficients ($^{18}\epsilon = -34\text{‰}$ and $^{15}\epsilon = -48\text{‰}$) of NO_3^- photo-decomposition in Dome C ice core have been quantified [25,110]. Comparative results with the Raleigh fractionation model indicate that $^{15}\epsilon$ has been underestimated. Snow samples exposed to ultraviolet radiation and placed in a closed laboratory environment greatly impact the photolysis and photo-decomposition of NO_3^- in snow. In this setting, the photolytic products such as NO_2 and OH were involved in subsequent NO_3^- generation and deposition, leading to the dilution of the isotopic ratios [102]. The secondary production of NO_3^- , as a result of the photolysis of NO_3^- , and the by-products (such as NO_2 and NO) of photolysis react with oxidants in the atmosphere, results in the variation of nitrogen isotopes [104,111]. Additionally, the photochemical decomposition of NO_3^- significantly affects the isotope changes in snow. Investigating and understanding the photochemical processes of NO_3^- in snow and ice is crucial for evaluating its environmental fate and impact on atmospheric composition.

7. Conclusions

The stable isotopes and isotopic anomalies of nitrate can be used to robustly trace the sources of NO_3^- and determine the oxidation pathways of NO_3^- and to understand the chemical cycle of NO_3^- in multiple environmental media. This study mainly reviewed and synthesized the chemical processes of nitrate in atmosphere and snow/ice. The conclusions that can be drawn are as follows:

- (1) The formation of nocturnal atmospheric nitrates primarily occurs through the hydrolysis of N_2O_5 . During the daytime, the nitrates are mainly generated through the oxidation of NO_2 by OH radicals, resulting in the formation of HNO_3 . In summer, nitrates are mainly formed through the reaction of OH radicals with NO_2 , while in winter, the hydrolysis of N_2O_5 is the main process for the formation of atmospheric nitrate.
- (2) Research on stable isotopes and isotopic anomaly of atmospheric nitrate in glacier regions is scarce, especially in high-altitude glacier regions.
- (3) The $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of nitrate in the atmosphere increase with latitude. The variation of $\delta^{18}\text{O}(\text{NO}_3^-)$ is more obvious with notable fluctuations in low-latitude regions (30°N – 60°N).
- (4) From the coastal areas to inland Antarctica, $\delta^{18}\text{O}(\text{NO}_3^-)$ values in snow and ice gradually decrease and $\delta^{15}\text{N}(\text{NO}_3^-)$ values increase. Photochemical reactions significantly facilitate the interaction of NO_x and NO_3^- at the air–snow interface, and greatly affect the NO_3^- concentration.

A study of the chemical processes of atmospheric nitrate and snow–ice nitrate in mountain glaciers is very rare and is currently in its initial stage. The study on the oxidation process of nitrate at the air–snow interface and in snow and ice of mountain glaciers has not been performed yet. Stable isotopes and isotopic anomaly of nitrate, as emerging techniques for the study of formation pathway and chemical processes of nitrate in atmosphere and snow/ice, can be used to examine/investigate the contribution of oxidation pathways of nitrate in high-altitude mountain glaciers. The study of nitrate isotopes in ice cores has not been conducted yet, which is an obvious research gap of cryosphere chemistry and can be bridged with the fields of climate study and environmental records. The study of chemical processes of nitrate in snow pits, ice cores, and the air–snow interface on glaciers needs a combination of numerical model simulation and extensive field observations of nitrate. Further study on the chemical processes of nitrate in the atmosphere and snow/ice is also needed to improve the understanding of its sources, formation mechanisms, and spatial–temporal variations.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atmos15010059/s1>, Table S1: Summary of values of $\Delta^{17}\text{O}(\text{NO}_x)$, $\delta^{18}\text{O}(\text{NO}_x)$, and $\delta^{15}\text{N}(\text{NO}_x)$ in Antarctic snow [81,99,112].

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