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# JGR Solid Earth

## RESEARCH ARTICLE

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# Geological Record of Atmospheric Nitrogen Fixation During Explosive Supereruptions: The Case of Tecopa Basin, California



### Key Points:

- Use of nitrogen and oxygen isotopic signatures of nitrate to investigate atmospheric nitrogen fixation by volcanic lightning
- Evidence for atmospheric nitrate enrichment in volcanic deposits relative to sediments in the same geological archive
- Confirmation and quantification of atmospheric nitrogen fixation by volcanic lightning during explosive supereruptions

### Supporting Information:

Supporting Information may be found in the online version of this article.

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**Abstract** Nitrate in dry sedimentary records has long been associated with long-term atmospheric deposition and biological activity. Recent discoveries of nitrate with an atmospheric origin in volcanic deposits from large eruptions have been tentatively linked to volcanic lightning. Lightning can break the chemical bonds of stable molecules like dinitrogen, releasing NO, which is rapidly oxidized by ozone, forming atmospheric nitrate with a high <sup>17</sup>O-anomaly. Another possible source of nitrate in volcanic deposits is atmospheric long-term deposition. To confirm and quantify the origins of nitrate in volcanic deposits, we compare for the first time the multi-isotopic (O, N) signatures of nitrate in sediments and volcanic deposits from supereruptions. Samples were taken in the Tecopa Basin (California), where the dry conditions have been favorable to sample preservation. The mean O and N isotopic compositions in nitrate from sediments ( $\Delta^{17}\text{O} = 12 \pm 1\text{‰}$  and  $\delta^{15}\text{N} = 2 \pm 2\text{‰}$  ( $2\sigma$ )) and volcanic ash layers ( $\Delta^{17}\text{O} = 19 \pm 5\text{‰}$  and  $\delta^{15}\text{N} = -5 \pm 3\text{‰}$  ( $2\sigma$ )) are substantially different. Only a massive and fast production of atmospheric nitrate during supereruptions can explain the higher  $\Delta^{17}\text{O}$  values in volcanic ash layers. The most plausible N-fixation mechanism of this atmospheric nitrate is volcanic lightning. Our results indicate that volcanic lightning from supereruptions such as Lava Creek Tuff (0.64 Ma, Yellowstone) could fix up to  $\sim 100$  Tg of N. Alteration and erosion of nitrate-rich volcanic deposits are expected to free large quantities of nitrate into the environment, which living organisms assimilate and could play a significant role in developing the local biosphere.

**Plain Language Summary** Volcanic lightning, a powerful phenomenon associated with explosive eruptions, has recently been proposed as a source of reactive nitrogen (nitrate) available for living organisms. While its role seems clear, some questions remain regarding the geological archive where this nitrate is found. Indeed, in some volcanic deposits containing nitrate, it is difficult to distinguish their source—volcanic lightning or daily atmospheric deposition—due to their similar isotopic composition. In our study, we compare the origin of nitrate found in volcanic deposits and sediments from the same geological record. This comparison reveals that the large quantity of nitrate in volcanic deposits can only be explained by lightning associated with the explosive eruption. Therefore, we demonstrate that volcanic deposits can be a geological archive of the production of reactive nitrogen by volcanic lightning. Furthermore, the quantity of nitrate in this archive allows to quantify this process and assess its role in the development of life on Earth.

## 1. Introduction

Nitrogen makes up about 78% of atmospheric molecules in the form of the highly stable dinitrogen (N<sub>2</sub>). Nitrogen is also present in the biosphere and is a crucial element of biological molecules such as DNA and proteins. Most living organisms cannot use N<sub>2</sub> directly because of its stability; it must first be transformed (often referred to as “fixed”) into assimilable nitrogen compounds. This process, known as N-fixation, converts N<sub>2</sub> into reactive N-compounds such as oxidized nitrate (NO<sub>3</sub><sup>-</sup>) or reduced ammonium (NH<sub>4</sub><sup>+</sup>). This N-fixation requires high-energy or bio-mediated mechanisms to break the triple bond of atmospheric N<sub>2</sub>. Certain bacteria can fix atmospheric nitrogen, making biological activity a major source of reactive nitrogen.

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Before the appearance of life 3.8 Ga ago (Dodd et al., 2017), natural abiotic processes such as storm lightning (Drapcho et al., 1983; Noxon, 1976) and mineral-catalyzed nitrogen reduction in hydrothermal systems (Brandes et al., 1998) must have driven the production of reactive nitrogen compounds (reduced or oxidized forms) (Miller, 1957; Navarro-González et al., 1998). Nowadays, anthropogenic activities contribute to ~45% of global N-fixation (Gruber & Galloway, 2008), biological activity accounts for ~50% of the total fixation, and lightning (a natural abiotic phenomenon) contributes 5% (Gruber & Galloway, 2008). During Earth's early history, N-fixation should have been secured by abiotic mechanisms before the initial expansion of life on our planet. In an oxidative atmosphere, these atmospheric processes produce nitrogen oxides NOx (NO + NO<sub>2</sub>), eventually forming nitrate the end product of atmospheric N-fixation.

Due to these processes, nitrate can accumulate on Earth's surface, participate in biogeochemical cycles, and be found in geological records within sediments in dry areas after atmospheric long-term deposition (Jackson et al., 2010; Lybrand et al., 2013; Michalski, Böhlke, & Thiemens, 2004; Reich & Bao, 2018). Biological activity can also produce nitrate that can be preserved in sediments. The isotopic composition ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$ ) of these molecules provides a reliable way to distinguish and quantify the different nitrate sources.

Atmospheric nitrate shows a significant excess in <sup>17</sup>O, an isotopic anomaly noted  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5305 * \delta^{18}\text{O}$  (Dauphas & Schauble, 2016; Thiemens, 2006). Tropospheric ozone has a large <sup>17</sup>O-anomaly with a bulk composition of  $\Delta^{17}\text{O}_{\text{O}_3\text{-bulk}} = 26 \pm 1\text{‰}$  (1 $\sigma$ ) (Vicars & Savarino, 2014) due to isotopic mass independent fractionation processes occurring during its formation. However, while the bulk  $\Delta^{17}\text{O}$  of tropospheric ozone is  $26 \pm 1\text{‰}$  (1 $\sigma$ ),  $\Delta^{17}\text{O}_{\text{O}_3\text{-trans.}}$ , the  $\Delta^{17}\text{O}$  actually transferred to NO<sub>2</sub> during the oxidation of NO by tropospheric ozone, is  $39 \pm 1.5\text{‰}$  (1 $\sigma$ ) because the O atom preferably abstracted from ozone by NO is an isotopically enriched terminal O (Vicars & Savarino, 2014). Reactive nitrogen released into the environment by high-energy phenomena or soil/bacteria emissions (Davidson & Kingerlee, 1997), is overwhelmingly oxidized by tropospheric ozone. In most cases, about 2/3 of the nitrate oxygen atoms derives from ozone (Alexander et al., 2020; Michalski et al., 2003), resulting in an expected  $\Delta^{17}\text{O}$  value of about 26‰ (2/3 \*  $\Delta^{17}\text{O}_{\text{O}_3\text{-trans.}}$ ) for atmospheric nitrate. In addition, breaking the triple chemical bonding by lightning generates N-isotope fractionation and leads to a <sup>15</sup>N depletion in the fixed nitrogen produced; the resulting nitrate has a  $\delta^{15}\text{N}$  isotopic ratio between -6 and -15‰ (Barth et al., 2023). Oxygen atoms in nitrate from biological activities originate mainly from ambient O<sub>2</sub> ( $\Delta^{17}\text{O} = -0.4\text{‰}$ ) and H<sub>2</sub>O ( $\Delta^{17}\text{O} = 0\text{‰}$ ), which are essentially isotopically mass-dependent molecules (Dauphas & Schauble, 2016; Thiemens, 2006; Wostbrock et al., 2020); the resulting nitrate has a mass-dependent signature ( $\Delta^{17}\text{O} \approx 0\text{‰}$ ). In addition, during biological processes, the N-isotope fractionation leads to nitrate with a  $\delta^{15}\text{N}$  between 0 and 10‰ (Kendall et al., 2007).

In arid areas like the Atacama Desert, atmospheric nitrate of background origin accumulates from the continuous long-term atmospheric deposition (Michalski, Böhlke, & Thiemens, 2004; Reich & Bao, 2018), with large nitrate deposits exhibiting  $\Delta^{17}\text{O}$  of up to 21‰ and  $\delta^{15}\text{N}$  down to -5‰. Where aridity is less severe than in the Atacama Desert, nitrate from sediment deposits originate from both long-term atmospheric deposition and biological mechanisms. In this case, the isotopic signature of nitrate ranges between that of biological nitrate ( $\Delta^{17}\text{O} \approx 0\text{‰}$ ) and atmospheric nitrate ( $\Delta^{17}\text{O} \approx 26\text{‰}$ ) depending on the proportions of these two sources. Such source mixing has already been observed in the Mojave and Death Valley Desert, where the nitrate's  $\Delta^{17}\text{O}$  is around 13‰, indicating that the two sources appear to balance each other out (Jackson et al., 2010; Lybrand et al., 2013).

Numerous studies have investigated volcanic ash leachates all around the world (Witham et al., 2005), but only very few of them have reported on nitrate and only in low concentrations <50 ppm (Christenson, 2000; Taylor & Lichte, 1980; Witham et al., 2005). The isotopic composition of sulfate from ash leachates has already been measured, revealing a volcanic origin (Bao et al., 2003; Martin, 2018; Martin & Bindeman, 2009; Martin et al., 2014). However, such isotopic measurements had never been performed on nitrate from ash leachates until recently. Aroskay et al. (2024) discovered high concentrations of nitrate in 1.6–20 Ma volcanic deposits from caldera-forming eruptions preserved in arid environments worldwide nitrate concentrations up to 2,700 ppm in Turkey, up to 1,130 ppm in Peru and up to 450 ppm in Ischia, Italy (Aroskay et al., 2024). Nitrate's isotopic composition ( $\Delta^{17}\text{O}$  up to 20‰ and  $\delta^{15}\text{N}$  down to -6‰) was found to be consistent with a formation in the atmosphere. They attributed the atmospheric-like isotopic signature to volcanic lightning generated by plume dynamics during large explosive eruptions (Aplin et al., 2014; Cimarelli et al., 2014; Cimarelli & Genareau, 2022; James et al., 2000; Miura et al., 2002; Nicoll et al., 2019; Van Eaton et al., 2020).

Overall, the volcanic origin of the nitrate was established for most samples. Actually, large concentrations of nitrate with high O-isotope anomalies are found in welded ignimbrites and in deposits from recent eruptions in non-arid environments (450 ppm of nitrate in 70,000–55,500 years old volcanic deposits from Italy (Aroskay et al., 2024)), where long-term atmospheric deposition cannot account for such concentrations. For other samples, exposed in arid environments where atmospheric deposition can be significant, the incorporation of atmospheric nitrate with a large isotopic anomaly by this phenomenon cannot be ruled out (Aroskay et al., 2024).

An important limitation of the Aroskay et al. (2024) study was the focus on volcanic deposits without characterizing as well, the sedimentary layers between the volcanic deposits. Only a comparative analysis between sediments and volcanic deposits from the same environment would allow to conclude unambiguously whether the nitrate present in volcanic deposits originates from long-term atmospheric deposition or rapid deposition of nitrate generated by volcanic lightning. As NO produced by volcanic lightning which also can break the O<sub>2</sub> and N<sub>2</sub> molecules (Pérez-Invernón et al., 2022) is oxidized in the atmosphere (Barth et al., 2023; Navarro-González et al., 2001), the resulting nitrate is expected to exhibit an isotopic signature similar to other atmospheric nitrate ( $\Delta^{17}\text{O} \approx 26\text{‰}$  and  $\delta^{15}\text{N}$  between  $-6$  and  $-15\text{‰}$ ). However, the relative contributions of other nitrate sources, particularly biological ones, with distinct isotopic signatures, are likely to vary depending on the type of layer (volcanic vs. sediments) and the amount and origin of atmospheric nitrate (atmospheric deposition vs. volcanic lightning) they contain.

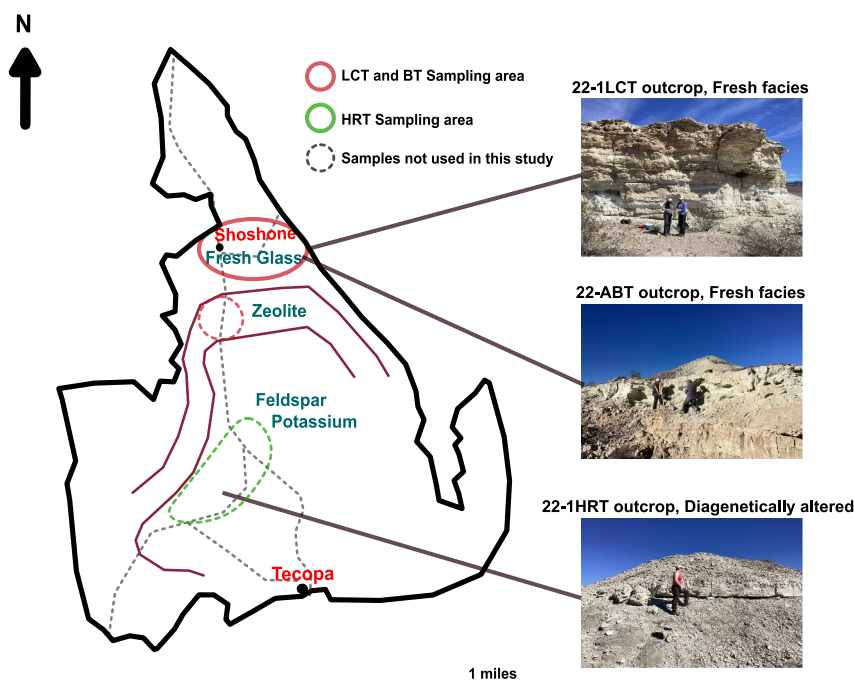
Our study compares the multi-isotope composition of nitrate in both volcanic deposits and sediments preserved in the same arid environment over the last million years, in the Tecopa Basin (California, USA). One of the aims of this study is to distinguish and assess nitrate of atmospheric ( $\Delta^{17}\text{O} \approx 26\text{‰}$ ;  $\delta^{15}\text{N} < -6\text{‰}$ ) and biological ( $\Delta^{17}\text{O} \approx 0\text{‰}$ ;  $\delta^{15}\text{N} > 0\text{‰}$ ) origin. If the isotopic signal in nitrate does not vary significantly across the geological record with multiple layers, this would suggest that nitrate from volcanic layers has the same origin as nitrate in sediments, most likely a mix of long-term atmospheric deposition and biological activity. However, if the isotopic anomaly in nitrate is significantly higher in volcanic deposits than in sediments, it would confirm that the proportion of atmospheric nitrate is higher in volcanic deposits, confirming that volcanic lightning is likely to be an efficient atmospheric N-fixation process during explosive eruptions.

### 1.1. Geological Settings

Tecopa Basin, located in southeastern California (USA), lies at the southern end of Death Valley and north of Mojave Desert. Once an alkaline lake (Larsen, 2008; Sheppard & Gude, 1968), the area is now characterized by a near-hyperarid climate, with a mean annual temperature of about 19°C and about 7 cm of rainfall (Morrison, 1999). Despite its arid climate today, this area episodically hosted a large alkaline lake during wetter periods of at least the last 2 million years (White, 2022).

The sedimentary record of Tecopa Basin spans from 2.54 to 0.185 Ma, primarily consisting of mudstone, sandstone, siltstones, and some calcite-cemented layers (Reheis et al., 2020; White, 2022). Lake Tecopa was a combination of several lakes of varying depths. The oldest lake identified was a shallow one, mainly in basin's southern part. The area then alternated between shallow lakes and beach conditions until 1 million years ago, when the Amargosa River entered the north part of the basin, which had been previously closed. The influx of water from the Amargosa river increased the water volume and sedimentation rate in the basin—between 0.0086 and 0.1 mm yr<sup>-1</sup> over the exposed history of the Tecopa Basin (Morrison, 1999; Reheis et al., 2020; White, 2022). This was followed by two of the deepest lake cycles in the basin's history, around 630 and 500 ka ago, with maximum depths of about 40 and 35 m, respectively (Reheis et al., 2020). The lake systems eventually drained via the Amargosa Canyon 185 ka ago.

The Tecopa Basin's sedimentary record includes up to 15 volcanic deposits (Sheppard & Gude, 1968). Most volcanic deposits are thin (10–30 cm) and discontinuous ash layers scattered across the basin (Reheis et al., 2020; Sheppard & Gude, 1968). However, three volcanic deposits are thicker than 50 cm and present throughout the entire basin: Lava Creek Tuff (LCT: 0.631 Ma, Matthews et al., 2015), Bishop Tuff (BT: 0.767 Ma, Chamberlain et al., 2014), and Huckleberry Ridge Tuff (HRT: 2.079 Ma, Rivera et al., 2014). Sedimentary and ash layers tend to be generally horizontal with slight tilting toward the basin's center, where diagenetic processes have been most advanced. The impact of diagenesis fades toward the basin margin, from “K-feldspar” in the basin's center to “zeolite” and finally “fresh-glass” facies in the northern edge, as shown in Figure 1 (Sheppard & Gude, 1968). In the “fresh-glass” facies, volcanic deposits consist of unaltered volcanic glass shards. In contrast, in the basin's



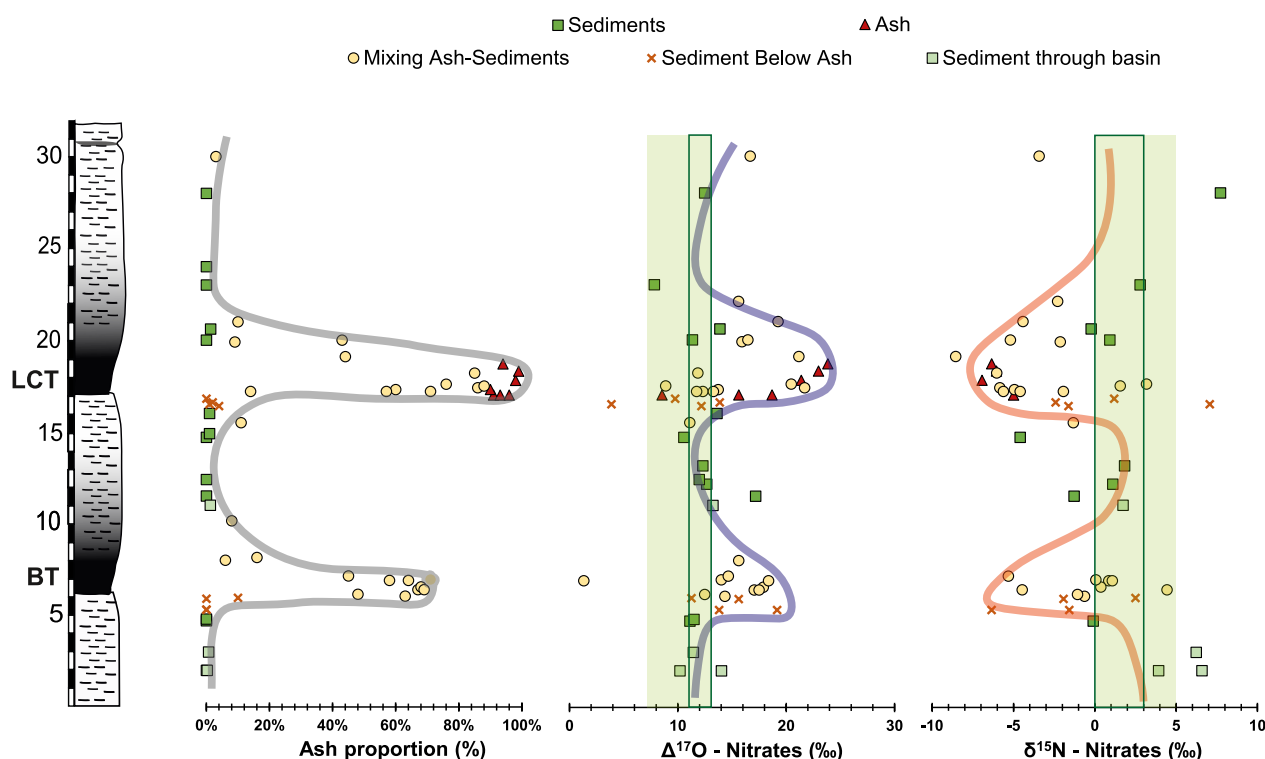
**Figure 1.** Map of the Tecopa Basin indicating the sampling areas of Lava Creek Tuff (LCT), Bishop Tuff (BT) and Huckleberry Ridge Tuff (HRT). The diagenetic facies (fresh glass, zeolite, and K-feldspars) are based Sheppard and Gude (1968). All samples from this study are from the fresh glass facies in the northern part of the basin and correspond to LCT and BT, with no samples from the HRT included. All the samples are compiled in the global stratigraphic column in Figure 2.

center, the glass has been altered into clay minerals and the formation of these authigenic minerals (Larsen, 2008; Martin & Gaillou, 2018) leads to the induration of the deposit. As diagenetic processes, including fluid circulation, can significantly affect the nitrate budget and its isotopic composition, this study focuses only on the sedimentary record from the northern basin in the “fresh-glass” facies, where the effect of diagenetic processes in the volcanic ash should be minimal, and the nitrate record is likely to be well preserved.

The HRT deposit is quite deep in the sedimentary record and is only exposed in outcrops in the southern basin, in the “K-feldspar” facies (Figure 1). Since the isotopic signal at the HRT deposit may also have been affected by fluid circulation, samples from this site were excluded from the study to focus on the “freshest” and least-altered samples. LCT and BT volcanic ash layers have outcrops in the “fresh-glass” facies in the north, near the town of Shoshone. Combining a dozen outcrops, about 30 m of the Tecopa basin facies were sampled, including LCT and BT ash layers (Figure 1). Samples have been taken every ~30 cm throughout the volcanic ash beds and in the first meter below and above them. For the rest of the record, samples were taken in sediments on a meter scale (Figure 2). In total, around 60 samples from this 30 m thick sedimentary record have been collected and analyzed.

The Tecopa Basin's arid climate and low water level during wet periods, are not favorable conditions for fluid circulation in the sedimentary record, which would promote leaching, alteration and homogenization of the nitrate isotopic composition.

Furthermore, relatively high concentration of nitrate and low organic content are also observed in present-day alkaline lakes. The high nitrate concentrations measured in Tecopa sediments could be explained by alkaline lake conditions in Tecopa, with a pH possibly greater than 8 in the past, as reported by Starkey and Blackmon (1979), that reduced biological denitrification (Pan et al., 2023). As a result, the sample's nitrate and their isotopic compositions are expected to be as preserved as possible and most likely reflect their primary origin. This area, characterized by alternating sediments and volcanic deposits preserved in arid conditions for over 180 ka, has already provided evidence of volcanic sulfate production (Martin & Bindeman, 2009). Like atmospheric nitrate, sulfate produced during explosive eruptions is characterized by a  $^{17}\text{O}$ -anomaly provided by the ozone involved in the oxidation of sulfate precursors (e.g.,  $\text{SO}_2$ ).



**Figure 2.** Stratigraphic column of Tecopa Basin with volcanic ash proportion, nitrate  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$ . The log is a synthetic log representing sediments and volcanic deposits. Visually, since the volcanic deposits are less indurated than the surrounding sediments, they tend to be more easily eroded, causing the outcrop to recess at their level. The green areas represent the  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  measured in nitrate in sediments in Death Valley and Mojave Desert (Jackson et al., 2010; Lybrand et al., 2013; Michalski, Böhlke, & Thiemens, 2004; Michalski, Meixner, et al., 2004). The green boxes represent the values for the sediments in this study lying between the first and third quartiles. In the log, the variations in the “front line” represent the proportion of volcanic ash while the dotted areas represent sediments. “Ash,” “Sediments,” “Mix Ash-Sediments,” and “Sediments below Ash” correspond to the sample groups (see text Section 3.1 for further explanations).

## 2. Materials and Methods

Volcanic ash and sediment samples were collected in the spring of 2022. A 10 cm surface layer was removed at each site before sampling to avoid surface contamination prior collecting ash and sediments samples. Each sample was leached with deionized water with a 1/10 sample/water ratio in the laboratory. The leachate solution was then filtered down to 0.45  $\mu\text{m}$  before chloride, nitrate and sulfate concentrations were measured using Ionic Chromatography (ICS 1100) at the ALIPP6 geochemical analytical laboratory (Sorbonne University; Paris, France). The concentration measured in the leachates from this study are reported relative to the mass of rock that has been leached (mg/kg of rock leached). These measurements show discrepancies that could result from measurement reproducibility issues or sample heterogeneity. Due to a calibration for a wide range of concentrations (0.1–150 ppm) the relative reproducibility obtained on the same sample leachates is  $\leq 2\%$ . However due to heterogeneity in the samples, the relative reproducibility obtained from different leachates of the same sample exhibit much larger variations ( $\leq 15\%$ ).

The nitrate multi-isotopic composition ( $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$ ) was measured at the Institut des Geosciences de l’Environnement (IGE; Grenoble, France) using the *Pseudomonas Aureofaciens* method (Casciotti et al., 2002; Christensen & Tiedje, 1988; Sigman et al., 2001). The formed nitrous oxide is subsequently decomposed to  $\text{N}_2$  and  $\text{O}_2$  gases by gold catalysis and then separated by gas chromatography before being directed to an isotope ratio mass-spectrometer (ThermoFisher, MAT253) for the determination of  $^{15}\text{N}/^{14}\text{N}$ ,  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$ . Overall, the  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  ( $= \delta^{17}\text{O} - 0.5305 * \delta^{18}\text{O}$ , Dauphas & Schauble, 2016) and  $\delta^{15}\text{N}$  were determined with a reproducibility of 4, 1.2 and 0.6‰ ( $2\sigma$ ) respectively.

To determine the volcanic ash proportion, the samples were deconsolidated in deionized water, treated with 10% HCl to remove carbonates and finally, sifted at 63  $\mu\text{m}$ . Over 400 grains larger than 63  $\mu\text{m}$  were counted and classified under a binocular magnifier into two categories: “volcanic ash” (including glass chards and pumice

fragments) and “sedimentary grains.” The ash proportion (in %) was calculated by dividing the number of volcanic ash particles by the total number of particles counted. Replicate measurements indicated that the ash proportion determination has a reproducibility  $\leq 2\%$ . It is worth noting that this estimation is only possible visually on particles larger than  $63\ \mu\text{m}$  and uncertainties remain on the unaccounted fraction of smaller particles ( $<63\ \mu\text{m}$ ). The proportions of volcanic ash in each sample are available in Data Set S1 or at Contamine et al. (2025).

### 3. Results

#### 3.1. Ash Proportion

Samples from volcanic deposits consist overwhelmingly ( $>90\%$ ) of pure “volcanic ash,” whereas sediments far from BT and LCT layers contain small ( $<2\%$ ) amounts of ash. However, as shown in Figure 2, the ash content exhibits a cyclic variation across the 30 m sedimentary record. Below BT, the sediments contain less than 2% of ash, with a sharp transition at the BT interface, where ash content rises to 70%–75% in the 1-m thick volcanic deposit. The measured ash proportion in the BT deposits shows a slight decrease compared to the LCT fallout. The reduction may be due to mild diagenetic processes that led to the transformation of volcanic glass into authigenic minerals. In the 3–4 m above this layer, the ash proportion progressively decreases to less than 2%. The ash content stays low in the sediments up to LCT, where it sharply increases to over 90% across the 2 m volcanic deposit. Finally, in the 2 m above LCT, the ash content progressively decreases again to below 2% and stays low in sediments above. These processes are explained by the ash deposition on the landscape after each supereruption and its relatively rapid and progressive redeposition on top of the ash deposited in the lake. This small amount of detritus in ash is from the surface sediments that are coeval with ash deposition.

The ash content in the samples can be used to classify them into four categories:

- “Ash”: Samples with an ash content greater than 90%, corresponding to the fallout of tephra during the volcanic eruption, which was rapidly deposited in the basin.
- “Sediments”: Samples with less than 2% ash, corresponding to sediments deposited in the lake between volcanic events. These are accumulated at a rate about  $0.1\ \text{mm yr}^{-1}$ .
- “Mix Ash-Sediments”: Samples with ash content between 2% and 90%, typically found on top of ash (see explanations above).
- “Sediments below ash”: Samples taken from the base of a tephra layer to about 70 cm below. Within this 70 cm layer, the potential influence of fluid percolation is expected to be most pronounced (Martin & Bindeman, 2009).

While the boundary between a volcanic layer and an underlying sediment layer is often visually sharp (and confirmed by ash content, Figure 2), it does not mean that the chemical compositions of these layers are necessarily independent. Indeed, after the volcanic deposit is laid down, downward fluid percolation may occur through this lithologic boundary, transporting part of soluble chemical compounds (e.g., nitrate and sulfate) from the volcanic layer into the sediments just below. This is illustrated by the precipitation of gypsum pseudomorphs under volcanic ash beds in Nebraska (Bao et al., 2003) and sulfate O-isotopes composition in the Tecopa Basin (Martin & Bindeman, 2009). Therefore, we prefer to treat separate sediments directly beneath ash layers as they may have inherited chemical compounds from the volcanic deposits above.

#### 3.2. Nitrate Concentration

Chloride, nitrate and sulfate concentrations relative to the mass of leached rock were measured on 60 samples (available in Data Set S1 or at Contamine et al. (2025)), revealing high variability across the different sample categories. The average concentrations and standard deviation for the different categories were calculated and are presented Table 1. For chloride, the concentrations are respectively  $877 \pm 1,361\ \text{ppm}$  ( $2\sigma$ ),  $2,263 \pm 1,614\ \text{ppm}$  ( $2\sigma$ ),  $3,496 \pm 2,511\ \text{ppm}$  ( $2\sigma$ ), and  $2,966 \pm 2,213\ \text{ppm}$  ( $2\sigma$ ) for “Ash,” “Mix Ash-Sediments,” “Sediments below ash,” and “Sediments.” Nitrate and sulfate are respectively  $219 \pm 235\ \text{ppm}$  ( $2\sigma$ ) and  $273 \pm 281\ \text{ppm}$  ( $2\sigma$ ) for “Ash,”  $731 \pm 727\ \text{ppm}$  ( $2\sigma$ ) and  $2,396 \pm 1,741\ \text{ppm}$  ( $2\sigma$ ) for “Mix Ash-Sediment,”  $288 \pm 328\ \text{ppm}$  ( $2\sigma$ ) and  $2,385 \pm 2,065\ \text{ppm}$  ( $2\sigma$ ) for “Sediments below ash” and  $1,871 \pm 1,067\ \text{ppm}$  ( $2\sigma$ ) and  $2,535 \pm 1,648\ \text{ppm}$  ( $2\sigma$ ) for “Sediments.” There is no clear correlation between these species across the sample categories.

**Table 1**  
Concentration and Isotopic Composition of Samples From Tecopa Basin, California, USA

Sample	$n_{\text{conc}}$	Concentration (ppm)			$n_{\text{is}}$	Nitrate isotopic composition (‰)		
		$\text{Cl}^- (2\sigma)$	$\text{NO}_3^- (2\sigma)$	$\text{SO}_4^{2-} (2\sigma)$		$\delta^{18}\text{O} (2\sigma)$	$\Delta^{17}\text{O} (2\sigma)$	$\delta^{15}\text{N} (2\sigma)$
Ash	7	$877 \pm 1,361$	$219 \pm 235$	$273 \pm 281$	6	$51 \pm 14$	$19 \pm 5$	$-5 \pm 3$
Sediments	18	$2,966 \pm 2,213$	$1,871 \pm 1,067$	$2,535 \pm 1,648$	16	$33 \pm 3$	$12 \pm 1$	$2 \pm 2$
Mix Ash-Sediments	27	$2,263 \pm 1,614$	$731 \pm 727$	$2,396 \pm 1,741$	23	$40 \pm 5$	$15 \pm 2$	$-2 \pm 1$
Sediments below Ash	8	$3,496 \pm 2,511$	$288 \pm 328$	$2,385 \pm 2,065$	8	$34 \pm 8$	$12 \pm 3$	$0 \pm 3$

Note.  $n$  represents the number of samples from each category.  $n_{\text{conc}}$  is the number of samples whose concentration was measured, while  $n_{\text{is}}$  is the number of samples whose isotopic composition has been determined. Concentrations have been measured by Ionic Chromatography and are reported relative to the mass of rock that has been leached (in ppm).

### 3.3. Nitrate Isotopic Composition

Isotopic signatures were measured on 53 samples (available in Data Set S1 or at Contamine et al. (2025)) and their mean value and standard deviation are shown in Table 1. The mean values for “Sediment” are  $33 \pm 3\text{‰}$  ( $2\sigma$ ) for  $\delta^{18}\text{O}$ ,  $12 \pm 1\text{‰}$  ( $2\sigma$ ) for  $\Delta^{17}\text{O}$  and  $2 \pm 2\text{‰}$  ( $2\sigma$ ) for  $\delta^{15}\text{N}$ . For “Ash” nitrate, the mean values are  $51 \pm 14\text{‰}$  ( $2\sigma$ ),  $19 \pm 5\text{‰}$  ( $2\sigma$ ) and  $-5 \pm 3\text{‰}$  ( $2\sigma$ ) for  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{15}\text{N}$  respectively. The nitrate from “Mix Ash-Sediment” and “Sediments below ash” is characterized by mean values of for  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{15}\text{N}$  of  $40 \pm 5\text{‰}$  ( $2\sigma$ ),  $15 \pm 2\text{‰}$  ( $2\sigma$ ) and  $-2 \pm 1\text{‰}$  ( $2\sigma$ ) and  $34 \pm 8\text{‰}$  ( $2\sigma$ ),  $12 \pm 3\text{‰}$  ( $2\sigma$ ) and  $0 \pm 3\text{‰}$  ( $2\sigma$ ) respectively. The range of values including median, maximum and minimum values and first and third quartiles are shown in Figure 3. Figure 4 compares the isotopic signatures of all samples ( $\Delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  vs.  $\delta^{15}\text{N}$ ). Sediment samples from zeolite and potassic facies were also analyzed. As their isotopic signature falls within the range of sediments measured in fresh facies, they were included in the “Sediments” category.

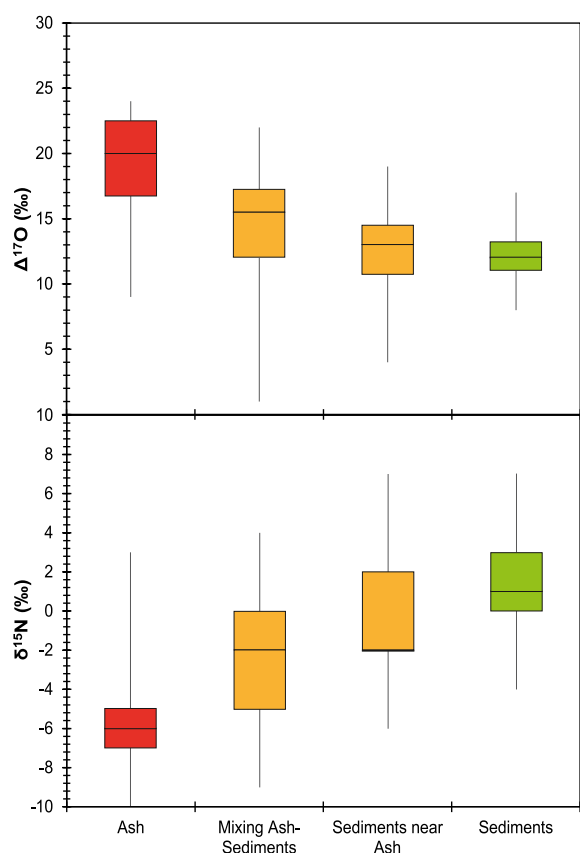
Overall, the isotopic compositions of nitrate in “Ash” and “Sediments” samples appear clearly distinct, though there is a more pronounced variability in ash samples. As seen in Figure 3, the median “Ash”  $\Delta^{17}\text{O}$  is  $20\text{‰}$ , significantly higher than “Sediments,” which stands at  $12\text{‰}$ . Nitrate from “Mix Ash-Sediments” and “Sediments below ash” have intermediate  $\Delta^{17}\text{O}$  values with medians of  $15$  and  $17\text{‰}$  respectively. The value of “Sediments below ash” is close to that of “Sediment,” which can be interpreted as an absence of significant fluid percolation. Similarly, nitrogen isotopic signatures show distinct values for “Ash” and “Sediment” samples with  $\delta^{15}\text{N}_{\text{Ash-median}} = -6\text{‰}$  and  $\delta^{15}\text{N}_{\text{Sediments-median}} = 1\text{‰}$  (Figure 3). As for  $\Delta^{17}\text{O}$ , the  $\delta^{15}\text{N}_{\text{median}}$  of “Mix Ash-Sediment” and “Sediments below Ash” fall between these extremes, with medians of  $-2\text{‰}$  and  $-1\text{‰}$ , respectively. These distinct O- and N-isotopic signatures for different sample categories may likely reflect variations in processes of nitrate production in the various sample categories.

Figure 2 presents the isotopic composition of nitrate according to the sample location in the 30 m stratigraphic record.  $\delta^{15}\text{N}$  values are the lowest in volcanic deposits, ranging from  $-5\text{‰}$  in BT to  $-10\text{‰}$  in LCT while the highest values ( $6\text{--}8\text{‰}$ ) are found in sediments. A similar trend is observed in the oxygen isotopic composition, with the maximum  $\Delta^{17}\text{O}$  values reached in volcanic layers ( $\Delta^{17}\text{O} = 24\text{‰}$  in LCT and  $18\text{‰}$  in BT) and minimum values of about  $10\text{--}12\text{‰}$  in sediments below and above the volcanic deposits. Note that the transition in  $\Delta^{17}\text{O}$  between volcanic deposits and sediments is sharp at the bottoms of BT and LCT but is more gradual at the tops of the volcanic layers; the same pattern is observed in the ash content at the transitions and, to a lesser extent, in  $\delta^{15}\text{N}$  (Figure 2).

## 4. Discussion

### 4.1. Nitrate Origins in Tecopa Basin and Mass Balances of Its Sources

The isotopic composition and concentration of nitrate leached from Tecopa Basin samples show significant differences between volcanic deposits ( $\Delta^{17}\text{O}_{\text{median}} = 20\text{‰}$ ;  $\delta^{15}\text{N}_{\text{median}} = -6\text{‰}$ ) and sediments ( $\Delta^{17}\text{O}_{\text{median}} = 12\text{‰}$ ;  $\delta^{15}\text{N}_{\text{median}} = 1\text{‰}$ ; Figures 3 and 4). The  $\Delta^{17}\text{O}_{\text{median}}$  of  $20\text{‰}$  and  $\delta^{15}\text{N}_{\text{median}}$  of  $-6\text{‰}$  of “Ash” are comparable to values typically found in purely atmospheric nitrate  $\Delta^{17}\text{O}$  between  $20$  and  $26\text{‰}$  and  $\delta^{15}\text{N}$  between  $-6$  and  $-11\text{‰}$  (Barth et al., 2023; Michalski et al., 2003). In contrast, the  $\Delta^{17}\text{O}_{\text{median}}$  of  $12\text{‰}$  and the  $\delta^{15}\text{N}_{\text{median}}$   $1\text{‰}$  of “Sediment” nitrate from Tecopa are perfectly consistent with values reported for nitrate in sediments from Death Valley



**Figure 3.** Whisker Diagram of  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  measured in nitrate from Tecopa Basin, California, USA. The median, first and third quartiles and maximum and minimum values are used to generate these whisker diagrams. In both diagrams, “Ash,” “Sediments,” “Mix Ash-Sediments,” and “Sediments Below Ash” represent the categories of samples (see text Section 3.1 for further explanation). The samples belonging to “Ash” and “Sediments” categories are clearly distinct, while those from the “Mixing Ash-Sediments” and “Sediments Below Ash” categories are situated between the first two.

and the Mojave Desert, two nearby sedimentary basins  $\Delta^{17}\text{O}$  around 12‰ and  $\delta^{15}\text{N}$  around 0‰ (Jackson et al., 2010; Lybrand et al., 2013; Michalski, Böhlke, & Thiemens, 2004; Figure 4). Thermal nitrogen fixation at volcanic vent (Mather et al., 2004) cannot explain the amount of nitrate measured in volcanic deposits. Indeed, in contrast with lava lake conditions where the 1000–1100°C lava is in direct contact with the atmosphere for a long period of time, during large explosive eruption the initial lava temperature is much lower (800–900°C) and the exposure time of atmospheric  $\text{N}_2$  to lava is extremely short. Consequently, our results show that the nitrate found in volcanic deposits has been overwhelmingly formed in the atmosphere and confirm that the nitrate from sediments is a mixture of atmospheric and biological nitrate.

To estimate the contribution of atmospheric nitrate in each sample, we use  $\Delta^{17}\text{O} = 26‰$  for atmospheric nitrate and a  $\Delta^{17}\text{O} = 0‰$  for biogenic nitrate in the mass balance Equation 1 where  $p_{\text{atm}}$  and  $p_{\text{bio}}$  represent the proportions of nitrate from atmospheric deposition and biological activity respectively (with  $p_{\text{atm}} + p_{\text{bio}} = 1$ ).

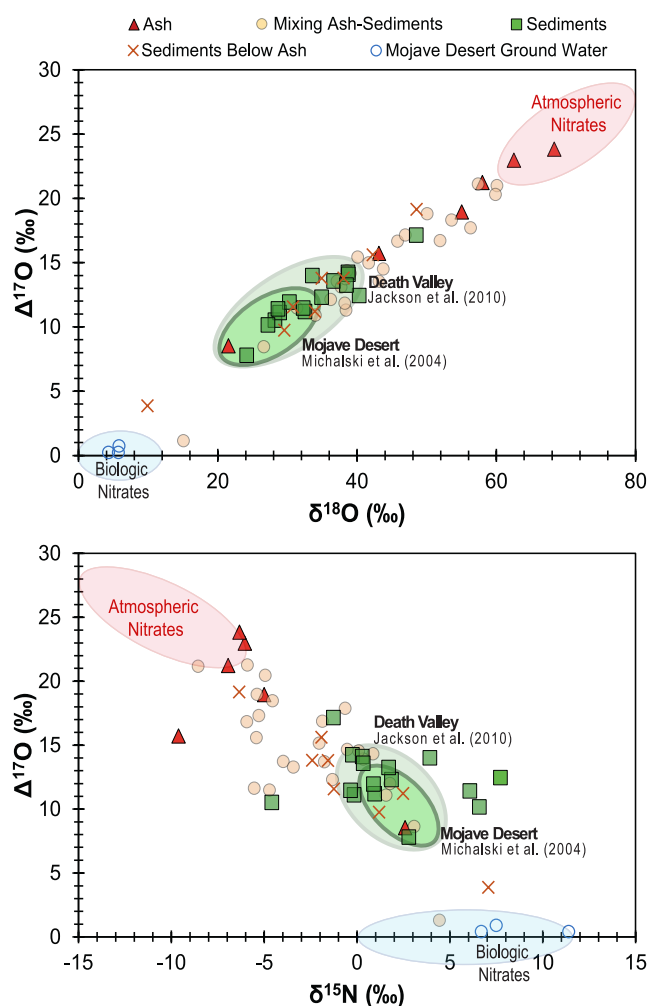
$$\Delta^{17}\text{O}_{\text{sample}} = \Delta^{17}\text{O}_{\text{bio}} * p_{\text{bio}} + \Delta^{17}\text{O}_{\text{atm}} * p_{\text{atm}} \quad (1)$$

For “Ash,” the concentration of atmospheric nitrate ( $220 \pm 300$  ppm ( $1\sigma$ )) mirrors the concentration of total nitrate. For “Mix Ash Sediments,” “Sediments below ash,” and “Sediments,” the concentrations of atmospheric nitrate are respectively  $416 \pm 1,184$  ppm ( $1\sigma$ ),  $122 \pm 185$  ppm ( $1\sigma$ ) and  $925 \pm 953$  ppm ( $1\sigma$ ). This atmospheric nitrate represents  $47 \pm 8\%$  of the total nitrate in Tecopa “Sediments,” with the remaining  $53 \pm 8\%$  coming from biological nitrification. In contrast, the  $\Delta^{17}\text{O}$  value of 20‰ in volcanic deposits indicates that more than 90% of this nitrate is of atmospheric origin and hence <10% is of biological origin. For the nitrogen isotopes, using typical  $\delta^{15}\text{N}$  values for volcanic and biological nitrate and the measured median values ( $\delta^{15}\text{N}_{\text{volcanic}} = -10‰$  and  $\delta^{15}\text{N}_{\text{biogenic}} = 10‰$ ), the proportion of atmospheric nitrate in “Ash” is estimated to be around 80% whereas it is 45% in “Sediments,” which aligns with the  $\Delta^{17}\text{O}$  results.

The isotopic composition of “Mix Ash Sediments” samples appears to line up between nitrate measured in the “Sediments” and those in “Ash” (Figure 4). 80% of our samples can be explained by mixing nitrate from volcanic deposits

and nitrate from sediments situated between the atmospheric end-member and the sedimentary background (Jackson et al., 2010; Michalski, Böhlke, & Thiemens, 2004). Around 15% of the samples cannot be fully explained by simply mixing sedimentary and atmospheric nitrate alone (Figure S1). Possible explanations for this include post-depositional processes such as biological activity leading to nitrification, which may significantly alter the isotopic composition of the total nitrate and/or fluid percolation leading to the transfer of nitrate from volcanic deposits to underlying sediments and the reverse (i.e., transfer from overlying sediments to volcanic deposits).

Biological nitrification during sediment formation generates nitrate with  $\Delta^{17}\text{O} = 0‰$ , which mixes with atmospheric nitrate, continuously deposited on the Earth’s surface, explaining the 12‰ observed in sedimentary nitrate. However, it is also possible that, for a few samples, post-deposition biological activity alters the overall isotopic composition after deposition. This process would also affect the isotopic composition of “Sediments” nitrate but to a lesser extent than for “Ash” nitrate because the difference in  $\Delta^{17}\text{O}$  between biological and “Sediment” nitrate is almost a factor of 2 smaller than the difference between biological and “Ash” nitrate. Another potential factor affects the extent of biological activity in volcanic deposits. Since the ash deposits analyzed here are not at all indurated, water can generally circulate through parts of the volcanic layers much more quickly than in indurated sediments. This generates spatial heterogeneity and favors the input of “sedimentary” nitrate from the watershed, thus reducing the initial atmospheric isotopic signature in the affected domains. It is



**Figure 4.** Multi-isotopic ( $\Delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  et  $\delta^{15}\text{N}$ ) signature of Nitrate from Tecopa Basin samples. Nitrate in samples from the Tecopa Basin are lying both for oxygen and nitrogen between two end-members: atmospheric nitrate ( $\Delta^{17}\text{O} \approx 26\text{‰}$ ,  $\delta^{18}\text{O}$  between 60 and 80‰ and  $\delta^{15}\text{N}$  between  $-6$  and  $-11\text{‰}$ ) and biologic nitrate ( $\Delta^{17}\text{O} \approx 0\text{‰}$ ,  $\delta^{18}\text{O}$  between 0 and 5‰ and  $\delta^{15}\text{N} > 5\text{‰}$ ). Nitrate from Ash are near the atmospheric nitrate end-members whereas those from Sediments have a higher portion of biological nitrate. These are also mainly in the sedimentary background measured by Michalski, Böhlke, and Thiemens (2004), Michalski, Meixner, et al. (2004), and Jackson et al. (2010) in Mojave Desert and Death Valley respectively. Mix Ash-Sediments are mainly between the atmospheric and the sedimentary end-members as for some of Sediments Below Ash. Mojave groundwaters are from the study of Michalski, Böhlke, and Thiemens (2004), Michalski, Meixner, et al. (2004) and show a major biological component.

(Holland et al., 1999), it would have taken about 5.5 ka of atmospheric deposition to accumulate the amount of nitrate observed in the volcanic deposits. In the case of the maximum nitrate concentration of 823 ppm measured in the LCT deposit, it would have taken 19.3 ka. These accumulation times are unrealistic, given that volcanic ash layers typically form in less than a year and possibly in a few years for supereruptions. Note that even N deposition rates estimated nowadays for large and polluted cities (e.g., Los Angeles), with intensive NO<sub>x</sub> emissions deposition rates between  $3.5 \times 10^3$  and  $4.5 \times 10^3$  kg of N km<sup>-2</sup> yr<sup>-1</sup> (Michalski, Meixner, et al., 2004), would be vastly insufficient to accumulate  $1.4 \times 10^5$  kg of N km<sup>-2</sup> in a few years. Therefore, consistent with the conclusion drawn from nitrate isotopic composition, nitrate concentrations in volcanic deposits are found to be too high to be attributed to long-term atmospheric deposition.

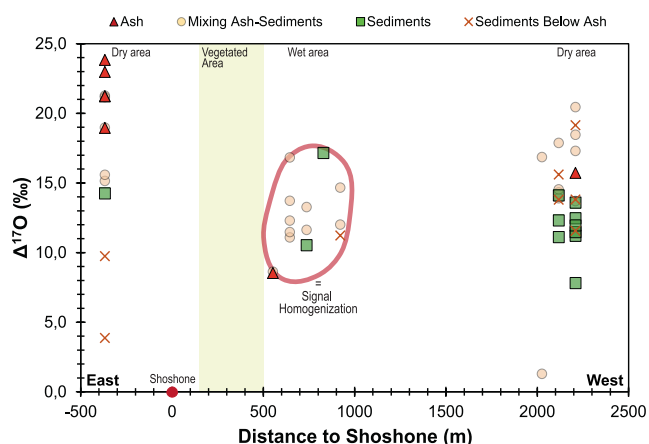
consistent with the greater dispersion of nitrate isotopic composition in the “Ash” category than in “Sediments.” This phenomenon is well illustrated in the northern part of Tecopa Basin, by the Shoshone village, where some vegetation attest to the presence of water, the remains of the Amargosa river. In this area, the  $\Delta^{17}\text{O}_{\text{ash}}$  decreases down to 9‰ while it is up to 20–25‰ a few hundred meters west and up to 15–20‰ on the east (Figure 5).

We have to bear in mind that the isotopic transition can be progressive beneath the volcanic deposits, though, the petrological transition is sharp between sediment and volcanic ash (Figure 2, visible under BT). It means that sediments in the first meter below the volcanic deposits can have intermediate isotopic values ( $\Delta^{17}\text{O} = 12\text{--}18\text{‰}$ ) between the nitrate from pure sediment end-member and that from pure volcanic deposit end-member (sediments below BT, Figure 2). A change in the sedimentary rate in the basin could increase the atmospheric nitrate proportion compared to the biological nitrate. Indeed, a decrease in the sedimentation rate could potentially favor the long-term atmospheric deposition compared to the biogenic nitrate, leading to sediments with higher  $\Delta^{17}\text{O}$  than expected. However, the sedimentation rate was relatively constant, with a rate of about 0.08 mm yr<sup>-1</sup> before BT and about 0.1 mm yr<sup>-1</sup> from BT to LCT (Morrison, 1999). It is more likely that some nitrate from the volcanic deposits were transferred down into the sediments below. As nitrate are rather soluble, this transfer can be driven by fluid percolation from the volcanic layer down toward the sediments below. This process is also suggested by the gypsum precipitates observed beneath the ash bed in Nebraska (Bao et al., 2003).

#### 4.2. Long-Term Atmospheric Deposition of Nitrate

Atmospheric nitrate is produced continuously in the atmosphere by thundercloud lightning (and human activities in the past ~150 years) and deposited onto the Earth's surface by dry or wet deposition processes (Seinfeld & Pandis, 2016), referred to as atmospheric long-term deposition. According to our measurements, about half of the total nitrate in “Sediments” layers is of atmospheric origin into the Tecopa Basin. This corresponds to an average atmospheric nitrate concentration of about 960 ppm in “Sediments” samples, which can be accounted for by a long-term atmospheric rate of about 43 kg of N km<sup>-2</sup> yr<sup>-1</sup> considering a sedimentation rate of 0.1 mm yr<sup>-1</sup> (Morrison, 1999). This deposition rate is in the order of magnitude of the average deposition rate of 26 kg of N km<sup>-2</sup> yr<sup>-1</sup> estimated for the northern hemisphere deserts during the pre-industrial period (Holland et al., 1999).

On the other hand, the long-term atmospheric deposition cannot at all account for the nitrate concentrations observed in volcanic deposits. For example, the average atmospheric nitrate concentration measured in the 1.5 m thick LCT “Ash” deposit is 235 ppm, corresponding to the equivalent of an atmospheric nitrate deposition of about  $1.4 \times 10^5$  kg of N km<sup>-2</sup>. With a preindustrial deposition rate of 26 kg of N km<sup>-2</sup> yr<sup>-1</sup> for the northern hemisphere desert



**Figure 5.** Nitrate  $\Delta^{17}\text{O}$  variation in samples from the West to East transect near Shoshone. While in sediments the  $\Delta^{17}\text{O}$  remains relatively constant it decreases in ash samples toward the center, where a humid area is present due to what is left from the Amargosa river (See the text Section 5.1 for further discussion). “Ash,” “Sediments,” “Mix Ash-Sediment,” and “Sediments below ash” represent the categories of samples (see text Section 3.1 for further explanation).

The only plausible origin for the high nitrate concentrations in volcanic ash deposits is the production of nitrate during the volcanic eruption itself. The only known volcanic process able to produce such an amount of nitrate during explosive eruptions is volcanic lightning (Aroskay et al., 2024; Navarro-González et al., 1998; Navarro-González & Segura, 2001). Lightning produces first  $\text{NO}$ , which is expected to be rapidly oxidized by ozone to form  $\text{NO}_2$ ;  $\text{NO}_2$  is then oxidized into nitrate (Alexander et al., 2020). As a result, this process produces nitrate with a distinct isotopic signature, high  $\Delta^{17}\text{O}$  and negative  $\delta^{15}\text{N}$  values (Barth et al., 2023), which concur with the nitrate characteristics observed in the “Ash” layers of Tecopa Basin.

## 5. Summary and Conclusion About the Origin and the Deposition of Nitrate in Tecopa Basin

Figure 6 illustrates the scenarios inferred from this study to explain the concentrations and multi-isotopic composition of nitrate in the sedimentary record of the Tecopa Basin over the last 2 million years.

### 5.1. Nitrate Deposition During a Non-Eruptive Period

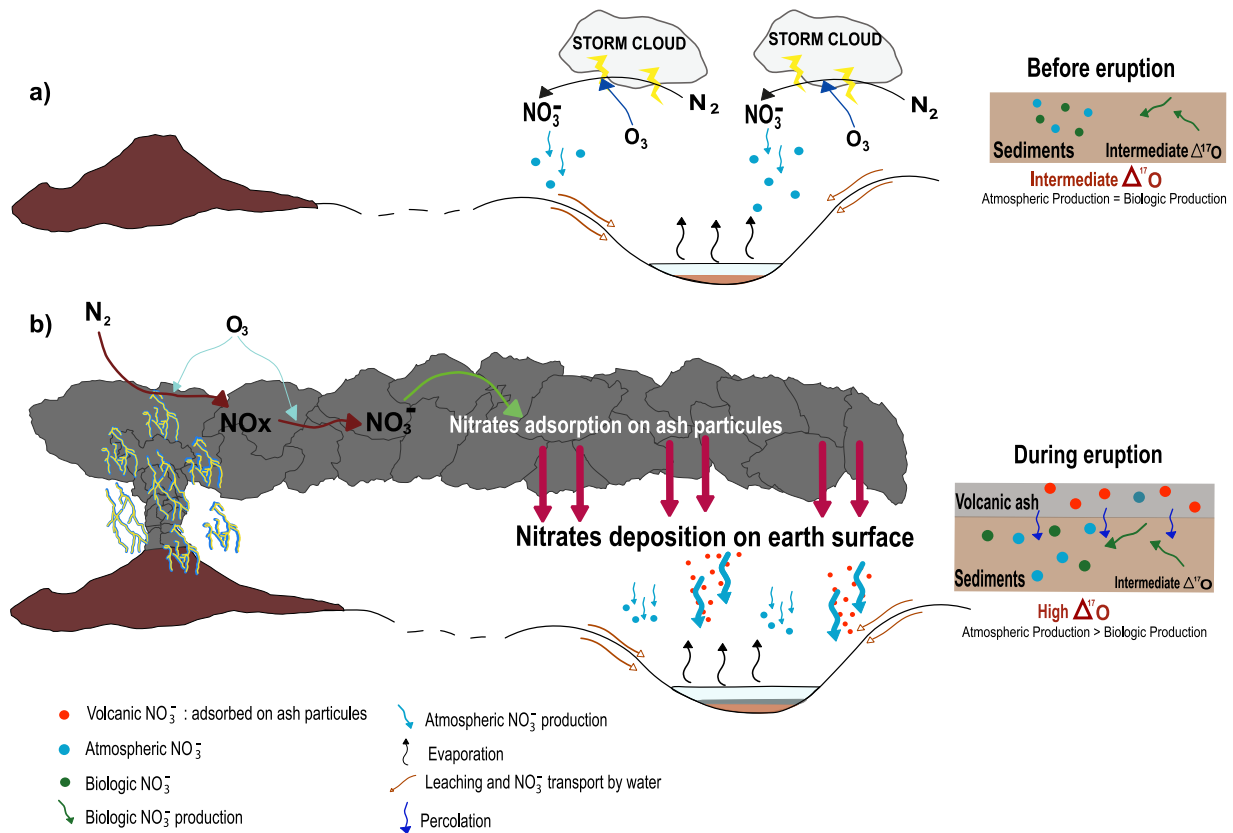
During non-eruptive periods (i.e., absence of powerful explosive volcanic activity), atmospheric nitrate in the Tecopa Basin originates primarily from storm lightning and hence have  $\Delta^{17}\text{O} \approx 26\text{‰}$  and  $\delta^{15}\text{N} \approx -10\text{‰}$ . This nitrate

is slowly but continuously deposited on the Earth’s surface across the whole catchment area of the Tecopa basin, making a very significant contribution to the basin’s nitrate budget. Once nitrate is in the basin, slow sedimentary processes (sedimentation rate between  $0.0086$  and  $0.1 \text{ mm yr}^{-1}$ ) drive their integration into the forming sediments. At the same time, biological nitrification also produced nitrate but at  $\Delta^{17}\text{O} = 0\text{‰}$ , altering substantially the overall isotopic composition of the total nitrate. On average, about half of nitrate is found to be of biological origin in the “Sediments” samples. These non-volcanic nitrate formation processes are illustrated by scenario (a) in the first part of Figure 6.

### 5.2. Nitrate Deposition During Supereruptions

Extreme explosive eruptions represented by scenario (b) in Figure 6, known as “supereruptions” resulted in the formation of very thick volcanic layers in the Tecopa basin, that is, eruptions at Yellowstone (1,000 km from Tecopa) for the LCT ash layer and eruptions at Long Valley Caldera (300 km from Tecopa) for the BT ash layer. During such explosive eruptions, intense volcanic lightning occurred within and on the edges of the volcanic plumes. This lightning fixes atmospheric  $\text{N}_2$  and ultimately produces nitrate with a  $\Delta^{17}\text{O} \approx 26\text{‰}$  deposited alongside the ash. The deposition of volcanic material (ash and associated nitrate, sulfate...) is massive and rapid, occurring over a period of up to a few years in the case of a supereruption. For example, the total volume of the LCT and BT deposits over the USA has been estimated at  $\sim 1,000$  and  $600 \text{ km}^3$ , respectively (National Research Council, 1984; Southworth, 2012). When scaled down to the Tecopa Basin area, the LCT and BT deposits would correspond to volumes of about  $0.35$  and  $0.24 \text{ km}^3$ , respectively. Although these deposits were emplaced over a geologically brief period (a few years), they account for approximately 8% of the total volume of the studied Tecopa sedimentary sequence. This is based on a thickness comparison:  $\sim 2.5$  m for the combined LCT and BT layers, versus  $\sim 30$  m for the entire sedimentary column. Thus, while the volcanic deposits represent only a tiny fraction ( $\sim 2 \times 10^{-6}$ ) of the 2-million-year time span recorded in the stratigraphy, they contribute a disproportionately large share of its total volume.

For the volcanic nitrate-rich deposits, the volcanic lightning source vastly outweighs the biological sources, considerably limiting the dilution of the volcanic nitrate isotopic signature by biological nitrate. Therefore, nitrate in volcanic ash layers retains a predominantly atmospheric signature ( $\Delta^{17}\text{O} \approx 20\text{--}23\text{‰}$ ). This massive production of nitrate with an atmospheric signature during a supereruption explains the considerable variation in the nitrate isotopic signal between volcanic deposits and sediments. If supereruptions had not produced nitrate, the nitrate isotopic signal would change little throughout the stratigraphic record, regardless of the nature of the layer



**Figure 6.** Processes of nitrate deposition in the Tecopa Basin during a non-eruptive period and large explosive eruption. Two scenarios (a and b) are proposed to explain the variations in isotopic signatures between Ash and Sediments. During a non-eruptive period (scenario a), nitrate are from atmospheric long-term deposition with a  $\Delta^{17}\text{O}$  around 26‰ which is slowly deposited on earth surface. Those atmospheric nitrate can be diluted by biological activity including the formation of nitrate with a  $\Delta^{17}\text{O}$  around 0‰. This leads to a decrease of the  $^{17}\text{O}$ -anomaly, around 12–14‰ in sediments. During an explosive eruption (scenario b), a massive N-fixation by volcanic lightning takes place near the vent. Nitrate produced by the oxidation of N-fixed by ozone is then adsorbed on ash particles and deposited on Earth surface at the same time. As this deposition is “instantaneous” and massive, biological activity does not have the time to take place. So, there is no dilution by biological activity and the atmospheric signal ( $\Delta^{17}\text{O}$  around 26‰) is preserved.

(volcanic or sedimentary). The variation supports the hypothesis that atmospheric nitrogen fixation during supereruptions, most likely through volcanic lightning, can be a very significant source of bioavailable nitrogen.

### 5.3. Proportion of Nitrogen Fixation During a Supereruption

Although most of the nitrate in volcanic deposits originates from volcanic lightning, a small fraction may also be of sedimentary origin. To account for this small sedimentary contribution when estimating the amount of nitrate produced by volcanic lightning, we apply a more refined mass balance approach (see Equations 2 and 3) using two end-members: “sediment nitrate” ( $\Delta^{17}\text{O}_{\text{sed}} = 12\text{‰}$ ) and “volcanic nitrate” ( $\Delta^{17}\text{O}_{\text{vol}} = 26\text{‰}$ ). This allows us to estimate the concentration of volcanic (atmospheric) nitrate in the ash samples:

$$\Delta^{17}\text{O}_{\text{sample}} = \Delta^{17}\text{O}_{\text{sed}} * p_{\text{sed}} + \Delta^{17}\text{O}_{\text{vol}} * p_{\text{vol}} \quad (2)$$

$$[\text{NO}_3^-]_{\text{volc}} = p_{\text{volc}} * [\text{NO}_3^-]_{\text{sample}} \quad (3)$$

With  $p_{\text{sed}}$  and  $p_{\text{vol}}$  being the proportions of nitrates from sediment and volcanic ash respectively ( $p_{\text{sed}} + p_{\text{vol}} = 1$ ).

Thus, we can determine  $p_{\text{vol}}$  for each  $\Delta^{17}\text{O}_{\text{sample}}$  by solving Equation 2 and then use it in Equation 3 to derive the volcanic nitrate concentration  $[\text{NO}_3^-]_{\text{volc}}$  in LCT samples. Focusing on the freshest samples: 22-1LCT, the inferred  $[\text{NO}_3^-]_{\text{volc}}$  ranges from 63 to 247 ppm, with a mean value of 170 ppm. Assuming a LCT deposit density of 1.8 ( $\text{g cm}^{-3}$ ) and volume of 1,000  $\text{km}^3$ , the total nitrogen fixed during the LCT eruption is estimated at

approximately  $\sim 305$  Tg of nitrate, corresponding to  $\sim 70$  Tg of N. If the maximum nitrate concentration (247 ppm) is taken as representative of the most preserved samples, up to  $\sim 450$  Tg of nitrate could have been produced, corresponding to a fixation of about 100 Tg of N.

In comparison, human activities produce globally  $200 \text{ Tg N yr}^{-1}$  of reactive nitrogen, while biological activity contributes  $140 \text{ Tg N yr}^{-1}$  nowadays (Gruber & Galloway, 2008). This nitrogen is distributed across the entire surface of the Earth. The LCT eruption represented a very significant regional source of reactive nitrogen, releasing more than half of the nitrogen produced globally by biological processes, but over an area 68,000 times smaller than the Earth's total surface area.

The erosion of the LCT deposits over time in the USA can release significant amounts of nitrate into the environment, which are readily assimilable by living organisms and thus can play a significant role in the development of the local biosphere.

## 6. Conclusions

Tecopa Basin provides the first geological archive of volcanic nitrogen fixation. The variation in the isotopic signature of nitrate between volcanic deposits and sediments, with volcanic deposits having a much higher proportion of atmospheric-like nitrate, confirms that nitrogen fixation by volcanic lightning during supereruptions is most likely the primary source of the large amounts of nitrate present in the volcanic ash layers.

It is worth pointing out that the amount of nitrogen fixed by supereruptions, particularly LCT (0.64 Ma, Yellowstone), represent a very significant input of reactive nitrogen (with a mean value of 90 Tg of N), of the order of at least half of the actual annual source of anthropogenic nitrogen fixation (Gruber & Galloway, 2008). The subsequent alteration of explosive eruption deposits rich in volcanic lightning nitrate is expected to free and scatter this fixed nitrogen that living organisms can assimilate. On early Earth, before the atmosphere became oxidized, volcanic lightning may have produced reduced forms of nitrogen species such as  $\text{NH}_4$  (Miller, 1957) or, alternatively, more oxidized forms via thermal dissociation of  $\text{CO}_2$ , creating transient oxygen-rich conditions (Navarro-González et al., 1998; Navarro-González & Segura, 2001; Yung & McElroy, 1979). Overall, our findings support the hypothesis that volcanic lightning could have played an important role in nitrogen fixation on the primitive Earth, potentially contributing to the development of life (Aroskay et al., 2024; Bada, 2023; Miller, 1953).

## Data Availability Statement

The data set for this study is available at Contamine et al. (2025).

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