



Geological evidence of extensive N-fixation by volcanic lightning during very large explosive eruptions

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Most of the nitrogen (N) accessible for life is trapped in dinitrogen (N₂), the most stable atmospheric molecule. In order to be metabolized by living organisms, N₂ has to be converted into biologically assimilable forms, so-called fixed N. Nowadays, nearly all the N-fixation is achieved through biological and anthropogenic processes. However, in early prebiotic environments of the Earth, N-fixation must have occurred via natural abiotic processes. One of the most invoked processes is electrical discharges, including from thunderstorms and lightning associated with volcanic eruptions. Despite the frequent occurrence of volcanic lightning during explosive eruptions and convincing laboratory experimentation, no evidence of substantial N-fixation has been found in any geological archive. Here, we report on the discovery of a significant amount of nitrate in volcanic deposits from Neogene caldera-forming eruptions, which are well correlated with the concentrations of species directly emitted by volcanoes (sulfur, chlorine). The multi-isotopic composition ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) of the nitrates reveals that they originate from the atmospheric oxidation of nitrogen oxides formed by volcanic lightning. According to these first geological volcanic nitrate archive, we estimate that, on average, about 60 Tg of N can be fixed during a large explosive event. Our findings hint at a unique role potentially played by subaerial explosive eruptions in supplying essential ingredients for the emergence of life on Earth.

N-fixation | volcanic lightning | nitrate | O-isotopes

Nitrogen (N) is an essential element for life and its main atmospheric form today is dinitrogen (N₂), the most stable atmospheric molecule. In order to be metabolized by living organisms, N₂ has to be converted into biologically assimilable forms, so-called fixed N. Nowadays, N-fixation is dominantly achieved through biological and anthropogenic processes (1). In early prebiotic environments on Earth, N-fixation, which supported the emergence of life, must have occurred only via natural abiotic processes. Several hypotheses have been proposed including photochemical reactions, hydrothermal reduction, lightning discharges, thermal reduction over magma, and meteoric impact-induced shocks (2–4). So far, the lack of identified geological archives of fixed N corroborating the existence of such processes has prevented the confirmation and quantification of these possible abiotic mechanisms on Earth. One of the most invoked processes is lightning from thunderstorms but also lightning associated with volcanic eruptions (3). Due to the electrification of the ash- and water-rich volcanic plumes, volcanic lightning (VL) occurs systematically during explosive eruptions (5); Fig. 1). Lightning strokes detection in volcanic regions also serves nowadays as a potential eruption alert indicator (6, 7). Experimental laboratory studies and thermodynamic models suggest that VL can contribute significantly to N-fixation over the Earth's history (8, 9). However, no geological evidence of substantial N-fixation by VL has ever been found so far. We report here the discovery in volcanic deposits of significant amount of nitrate, which multi-oxygen and nitrogen isotopes composition points toward atmospheric N-fixation induced by VL.

In search for volcanic fixed N, we targeted nitrates (NO₃⁻), the nitrogen oxidation end-product, in volcanic deposits from very large eruptions (for which VL is expected to be extensive) in arid to semi-arid environments, which are most favorable to the preservation of deposit integrity. We considered volcanic deposits from Neogene caldera-forming eruptions (1.6 to 20 Ma; volcanic explosivity index VEI of about 7), in Turkey (Anatolia) and Peru (North of the Andean Central Volcanic Zone) (10, 11). Samples were collected from volcanic tephra fallout deposits and large-volume pyroclastic density current (PDC) deposits called ignimbrites. For comparison, three samples were also collected in a nonarid environment and more recent tephra fallout deposits of two large explosive eruptions from Ischia, Italy (the Tischiello eruption: ~75 kyrs; VEI of about 3 to 4 and the Monte Epemeo Green Tuff eruption—MEGT: ~55 kyrs; VEI of about 5 to 6 (12)). Indeed, atmospheric (nonvolcanic) nitrate deposition and accumulation over time in volcanic deposits could

Significance

Nitrogen (N) fixation is an essential process for life as it converts atmospheric dinitrogen into biologically assimilable forms. Experimental and theoretical studies have proposed that volcanic lightning could have contributed to N-fixation in early prebiotic environments on Earth but geological evidence are still lacking. For the first time, significant amount of nitrate have been discovered in volcanic deposits from very large explosive eruptions. Geochemical analyzes, including oxygen multi-isotopes, indicate that this nitrate is the oxidation end-product of atmospheric N-fixation by volcanic lightning. These findings provide geological support for a unique role played by subaerial explosive eruptions in high energy-demanding processes, which were essential in supplying building blocks for life during its emergence on Earth.

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at first be considered possible (13). Such mechanism could contribute significantly to the nitrate budget of volcanic samples in an arid environment (for the sake of nitrate conservation over time) and over a long period of time (few Myrs typically). Therefore, the contribution of long-term atmospheric nitrate deposition and accumulation overtime is unlikely to be efficient for young volcanic deposits (about tens of kyrs old) in a nonarid environment like Ischia.

Results and Discussion

Nitrate from Volcanic Deposits Is Linked to the Explosive Eruption Events. The most remarkable finding is the unexpectedly high NO_3^- concentrations in all volcanic deposits from this study, comparable to SO_4^{2-} concentrations in most samples, including fully welded ignimbrites. Nitrate in volcanic deposits has hardly been reported in previous studies and yet several features indicate that most of this NO_3^- was formed during the volcanic eruptions.

First, NO_3^- , SO_4^{2-} , and Cl^- contents are found to be well correlated in all samples (Fig. 2), which suggests that they share a common origin. As large volcanic eruptions directly release large amounts of sulfur and halogens in the atmosphere, their origin in volcanic deposits is overwhelmingly volcanic. Second, the two types of analyzed volcanic deposits (ignimbrite and fallout) show similar elemental compositions (Fig. 2), indicating that the incorporation of external NO_3^- by long-term atmospheric deposition and accumulation since the eruptions (few millions of years) cannot be dominant in most samples. Indeed, such a post-depositional process should affect more fallout deposits than ignimbrites because ignimbrites are generally less porous and much denser than fallout deposits, particularly some of the fully welded ignimbrites units which become quasi-impermeable by welding typically a decade after deposition (14). Therefore, if a contribution of long-term atmospheric deposition followed by fluid percolation and accumulation over long timescales (millions of years) could not be ruled out for the most

porous volcanic deposits, this mechanism cannot explain large amounts of nitrate found within the fully welded ignimbrites. Finally, in these regions, volcanic deposits are covered by other deposits, which reduce their exposure time to the atmosphere and their nitrate deposition over time. The effect of long-term atmospheric deposition is expected to be much less effective in the youngest deposits from a nonarid environment (Ischia samples). Nevertheless, large amounts of nitrates (up to 450 ppm) are also measured in these young volcanic deposits. The absence of a positive correlation between the age of the deposit and its concentration in nitrate suggests that the nitrate found in volcanic deposits is not related to a slow mechanism operating on very long timescales after the deposit emplacement but rather to the volcanic eruption itself. Third, Anatolian samples collected in different stratigraphic layers in a fallout deposit of a single volcanic event show a quasi-systematic increase in NO_3^- , SO_4^{2-} , and Cl^- concentrations from the top to the base of the deposit. Note that a similar pattern is also observed in the fallout deposits from the younger Tischiello eruption (Ischia). Fluid circulation (rainwater percolating through the deposit) can affect the repartition of anions in the deposits, but at least two observations do not support the prevailing role of this process in our volcanic deposits. i) the concentration enrichments of the salts (NO_3^- , SO_4^{2-} , and Cl^-) from the top to the base of the deposits is higher for chlorine, than for nitrate and then sulfate which is not in full accordance with their relative solubilities and hence mobilities in the deposits. ii) The concentration profiles are not found to be dependent on the deposit thickness (from 0.7 to ≈ 10 m; *SI Appendix, Fig. S1*), contrary to what would be expected, i.e., the thinnest deposits being more washed out than the thickest. Such vertical zoning, also typically observed in major and trace elements concentrations in volcanic clasts is explained by a stratified magma reservoir (15). The most volatile-enriched part of the reservoir that is discharged in the early stage of the eruption is deposited first and forms to the base of the volcanic fallout deposit. The vertical zoning for nitrate may have been



Fig. 1. Intense volcanic lightning during the Calbuco eruption (VEI 4), Chile, in 2015. Photograph by Francisco Negroni.

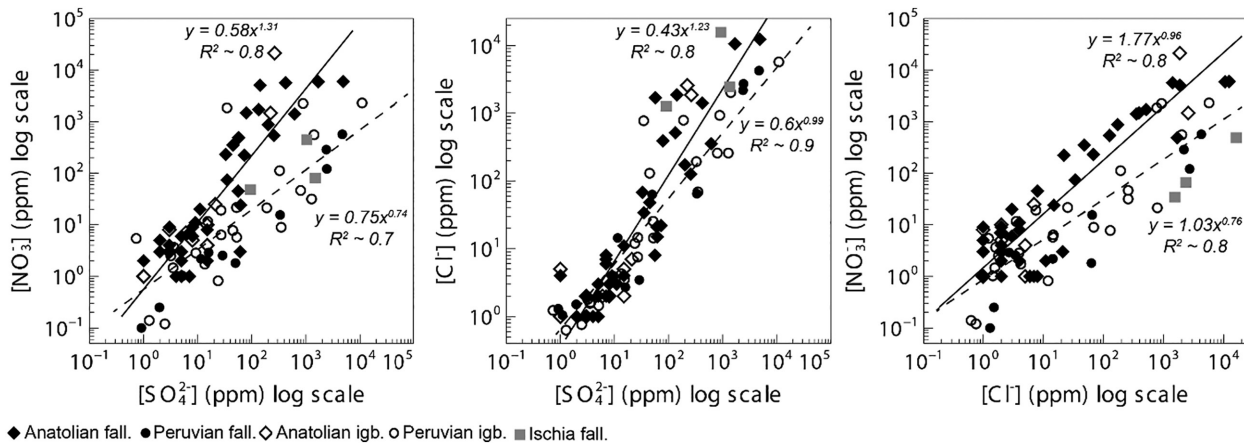


Fig. 2. Correlation between NO_3^- , SO_4^{2-} , and Cl^- measurements in Anatolian (diamonds), Peruvian (circles), and Italian (squares) samples. Filled and empty symbols represent tephra fallout and ignimbrite samples, respectively. Dash lines and regular lines represent the correlation line for Peruvian ($n = 36$) and Anatolian ($n = 55$) samples, respectively. Correlation coefficients are indicated for each plot.

accentuated by the general decreasing intensity of the volcanic explosivity as an eruption goes on, and hence decreasing volcanic lightning and associated fixed N generation, as discussed below.

Nitrate Generated by NO_x Oxidation via O_3 . We use the multi-isotopic composition ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) of nitrate extracted from the volcanic deposits by sample leaching to characterize their origins. Isotopic composition of compounds provides insights into emission sources and formation processes. In particular, triple oxygen isotope ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) measurements allow us to trace back the oxidation pathways leading to the formation of NO_3^- or sulfate (SO_4^{2-}) (16). The measurements show that the nitrate in the majority of the samples exhibit large positive oxygen isotopes mass-independent signature ($\Delta^{17}\text{O} > 0\text{‰}$) (Fig. 3). Such isotopic anomaly can only be inherited from the atmospheric ozone molecule (O_3), revealing the atmospheric origin of nitrate (17). Indeed, NO formed or emitted in the atmosphere acquires an oxygen mass-independent isotopic anomaly during its oxidation to NO_2 via its reaction with O_3 , the $\Delta^{17}\text{O} > 0\text{‰}$ source molecule; then NO_2 is partly oxidized to nitrate via reactions involving O_3 again (17). In contrast, biological nitrate systematically exhibit a $\Delta^{17}\text{O} \approx 0\text{‰}$ (18). In the same way, significant positive ($>2\text{‰}$) $\Delta^{17}\text{O}$ signatures in volcanic SO_4^{2-} can only be present if S-bearing gases are oxidized by atmospheric O_3 or certain O_3 -derived oxidants (19). $\Delta^{17}\text{O}_{(\text{NO}_3^-)}$ and $\Delta^{17}\text{O}_{(\text{SO}_4^{2-})}$ are found to be somewhat correlated (SI Appendix, Fig. S2) with a slope of ~ 2.9 , which is consistent with atmospheric oxidation of precursor gases (e.g., NO , SO_2) involving ozone.

About 83% of the samples display $\Delta^{17}\text{O} > 0\text{‰}$ and line up between two endmembers EM1 and EM2 in a $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ diagram (Fig. 3). EM1- NO_3^- results necessarily from the NO_x oxidation by O_3 [$\Delta^{17}\text{O} \approx 35\text{‰}$ (20)]. EM2- NO_3^- is characterized by $\Delta^{17}\text{O}$ close to zero and small positive $\delta^{18}\text{O}$ values, which are rather indicative of NO_3^- from NO_x oxidation by oxidants carrying a $\Delta^{17}\text{O} = 0\text{‰}$ [e.g., tropospheric OH-radicals (21)], though a contribution of biological NO_3^- cannot be ruled out. The lining up between EM1 and EM2 reflects the varying contributions of different pathways to NO_x oxidation, possibly reflecting the range of emissions and environmental conditions covered by the various volcanic events considered here. For instance, the conditions in a PDC (dense cloud moving along the ground level; high temperatures) are drastically different from the conditions in a Plinian column (volcanic plumes rising, expanding, and mixing with the background atmosphere; ambient temperatures). Even for a single

volcanic plume, the composition evolves rapidly, with oxidation pathways changing between the core and the edge of the plume depending on atmospheric dispersion and mixing, and the presence of highly effective ozone-destroying halogens (22). Biologically produced nitrate, represented by the EM3- NO_3^- end-member (Fig. 3 and SI Appendix, Fig. S3 and Supplementary Text), appear to slightly contribute to the total nitrate content in our samples (17%). On the whole, the multi-isotopic composition of our samples implies that most of the NO_3^- in the volcanic deposits originates from NO oxidation in the atmosphere.

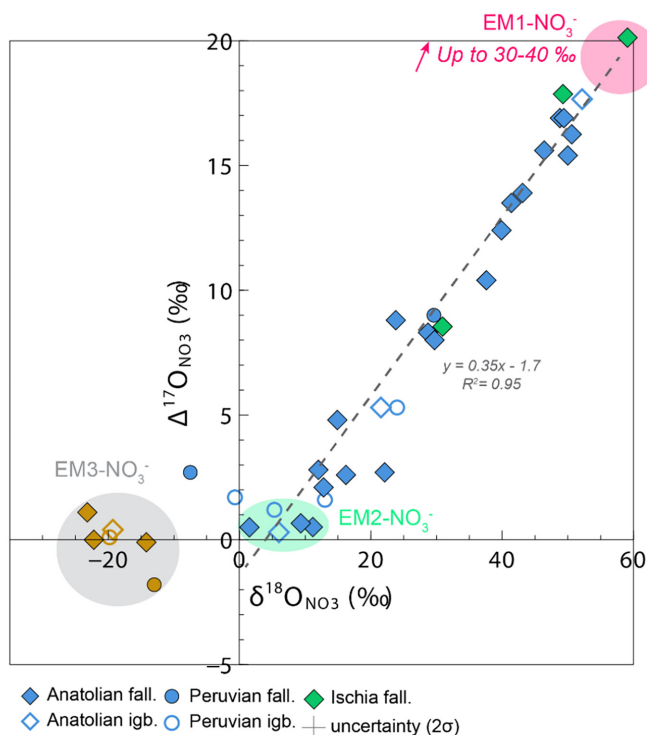


Fig. 3. $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ in Anatolian ($n = 27$), Peruvian ($n = 8$), and Italian ($n = 3$) volcanic deposits. Analytical uncertainties (in 2σ) are 1.5 and 0.4 for $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, respectively. EM1 represents nitrate generated by NO_x oxidation via ozone. EM2 represents atmospheric nitrate formed via the oxidation of NO_x by an atmospheric oxidant with $\Delta^{17}\text{O} = 0\text{‰}$ and possibly biological nitrate. Blue symbols, which are well correlated, correspond to nitrate with co-varying $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ isotopic compositions, they line up along with the EM1-EM2 mixing line (dotted line). EM3- NO_3^- (light brown) represents biological nitrate.

The remaining question concerns the sources of NO_x in the volcanic plumes and PDCs. N₂ can be released from the magma but only in very low quantities [$\approx 10^9$ to 10^{10} mol y⁻¹ (23)], which cannot account for the nitrate amount measured in our samples. Gaseous fixed N species (HNO₃, NH₃, and NO_x = NO + NO₂) have been detected in passive degassing volcanic plumes (not due to explosive eruptions, (24, 25)) but again at very low concentrations, generally at least two orders of magnitude lower than sulfur concentrations (24). Some of these detections were attributed to the thermal fixation of N₂ above hot lava lakes (26). This mechanism requires a relatively long exposure of N₂ to lava with high temperatures (>1,000 °C). During explosive caldera-forming eruptions, the lava typically displays lower temperatures (800 to 900 °C) and as highly fragmented, the lava cools down very quickly in contact with the atmosphere (27, 28). Therefore, it is unlikely that N₂ thermal fixation can account for the very high NO₃⁻ concentration measured in our samples.

NO_x Production by Volcanic Lightning. The most plausible mechanism able to produce vast amounts of NO_x during large explosive eruptions appears to be volcanic lightning (3, 29). Several electrification mechanisms are thought to play a role in VL. This includes ice charging, the primary mechanism for ordinary storm lightning, which is particularly effective when a volcanic plume, rich in water, rises up high into the air (5). Other mechanisms more specific to volcanic eruptions can also contribute to the electrification of volcanic plumes, notably mechanisms for which the main carriers of electrical charges are rock/ash particles instead of hydrometeors. Note that the quantification of electrification mechanisms at play in volcanic plumes, including interactions between volcanic particles and hydrometeors, remains relatively poor. The potential intensity of volcanic lightning has been well illustrated by the recent 2022 Hunga Tonga Plinian eruption where about 400,000 lightning strikes were detected in only 6 h during the main hydro-magmatic explosive phase of the eruption (30). Different electrification mechanisms are expected to dominate depending on the surrounding conditions, composition of the volcanic jet, and dynamics, typically a rising convective plume versus a pyroclastic flow. For instance, the intensity of ice-charging lightning should largely depend on the plume water content and

height, whereas the volcanic particle lightning should depend, among other factors, on the plume ash content. Although lightning in PDCs is far less studied, the lightning activity is generally more intense in volcanic plumes because they reach higher altitudes than in PDCs where most of the lightning occurs in the ash cloud/plume above the flow (31).

NO produced by lightning is oxidized to NO₂ in a few minutes and NO_x (NO + NO₂) is oxidized to HNO₃ or NO₃⁻ in hours/days following different oxidation pathways (32, 33). Considering the high particle concentrations and water content often found in large volcanic plumes, heterogeneous chemical pathways for NO_x-to-nitrate conversion, though uncertain, should prevail. A large part of the produced nitrate is subsequently adsorbed onto settling volcanic clasts. Ultimately, the volcanic lightning nitrate, referred as vLNO₃ thereafter, ends up archived in volcanic deposits over geological times in dry environments (Fig. 4). Overall, our data show that volcanic lightning during caldera-forming eruptions can be an efficient abiotic N-fixation process and that the presence of vLNO₃ in dry volcanic deposits is probably more frequent than previously thought.

Quantification of N-Fixation during Caldera-Forming Eruptions.

The amounts of vLNO₃ produced during the very large explosive volcanic eruptions analyzed here can be crudely estimated by considering the density and volume of each volcanic deposit layer and its mean NO₃⁻ concentration. The mean mass of N per single caldera-forming eruption varies strongly from 0.02Tg to 282Tg, with an average of 60Tg over the nine volcanic events from this study (*SI Appendix, Table S3*). Some of this variability is certainly caused by the high spatial heterogeneity of nitrate concentration in the deposits and by the varying electrifying plume conditions. Note that one such large explosive eruption can possibly deliver up to about 1 y of biological and anthropogenic global present-day fixed-N production (1) over a limited area. This range estimated from our data can be compared to theoretical calculations (3) that derive electrical power generated by volcanic lightning based on the volcanic ash output assuming that all electrical charges are only carried by ash particles. Since other electrification mechanisms of volcanic plumes are ignored, in particular, the ice-driven mechanism, the electric power available in explosive

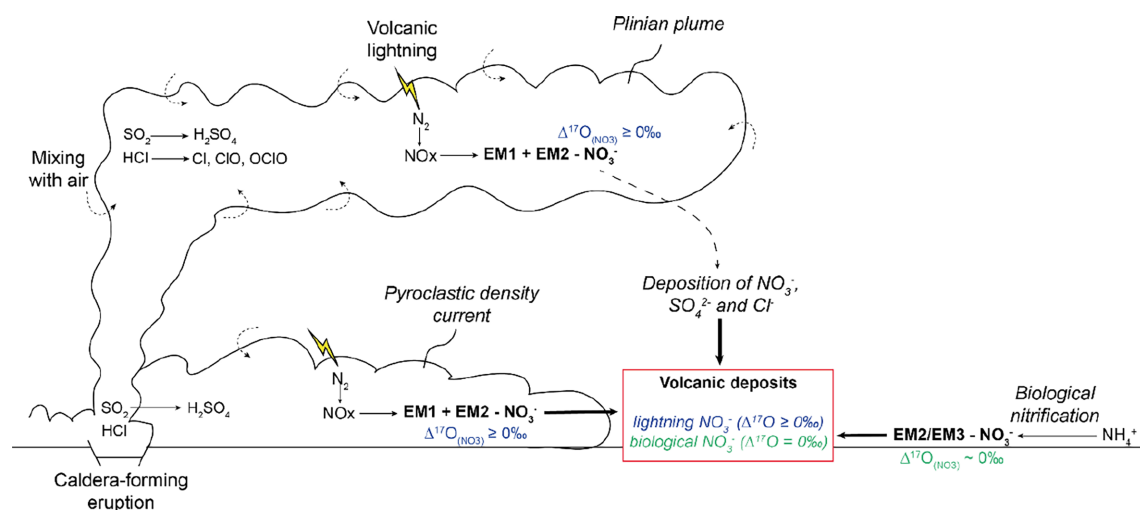


Fig. 4. The different formation pathways of nitrate collected in our volcanic deposits are summarized in this schema. Lightning occurring in volcanic plumes and in PDCs produces NO_x from atmospheric N₂. They are then oxidized into nitrate by O₃ leading to EM1-NO₃⁻ with a $\Delta^{17}\text{O} \sim 30$ to 40‰. Some NO_x can be oxidized by compounds such as OH radicals in the troposphere leading to EM2-NO₃⁻ with a $\Delta^{17}\text{O} = 0$ ‰. It cannot be ruled out that biological nitrate that has a $\Delta^{17}\text{O} = 0$ ‰ also contribute to EM2-NO₃⁻. In both cases, nitrate coming from EM1 + EM2-NO₃⁻ show a $\Delta^{17}\text{O} \geq 0$ ‰ whose value depends on the relative proportions of the nitrate sources. Biological nitrate resulting from bacterial nitrification with $\Delta^{17}\text{O} = 0$ ‰ (EM3-NO₃⁻ and possibly part of EM2-NO₃⁻) are identified in few volcanic deposits.

volcanic eruptions can be considerably underestimated in these calculations. The NO production by VL was estimated at 5.10^{12} g (equivalent to 1.10^{15} g of nitrate) for $1.3.10^{15}$ kg of volcanic ash, which corresponds to a nitrate concentration in ash deposit of about 10 ppm (10 μ g of nitrate per g of volcanic ash). Interestingly, this estimate of 10 ppm falls in the lower end of our range (1 to 2,700 ppm, see *SI Appendix, Table S3* for the nine analyzed eruptive events), which is consistent with this calculation being a conservative estimate, only N-fixation from injected ash is considered.

Implications. The discovery of nitrate in volcanic deposits makes them the first field evidence and geological archive of N-fixation by volcanic lightning, and this can have important implications. First, volcanic activity had already been mentioned as a possible source of the Atacama Desert nitrate deposits, but this possibility has been mostly discounted recently in favor of an atmospheric origin (13, 34). One of the main arguments was that volcanism could not generate nitrate with $\Delta^{17}\text{O} > 0\text{‰}$, as measured in the Atacama's deposits. Our results indicate that, on the contrary, volcanic lightning during large explosive eruptions produces νLNO_3 with positive $\Delta^{17}\text{O}$. A possible contribution of the intense Miocene-Quaternary volcanic activity to the Atacama basin nitrate (34) could be reconsidered. Second, the fact that massive volcanic eruptions can fix nitrogen on that scale has possible implications for life emergence on Earth. In most hypotheses attempting to explain the emergence and development of life, assimilable N forms are necessary and thus N_2 must be extensively fixed (35, 36). Ordinary (nonvolcanic) lightning has been one of the most discussed and well-established abiotic N-fixation mechanisms (3, 37, 38). Our findings also hint at potentially extremely high local contributions of VL from very large subaerial explosive eruptions, which were already occurring on the early Earth (39, 40). Indeed, nitrate produced by storm lightning all around the world are spread out on the Earth's surface, while volcanic deposits are formed locally in a very short period of time and, according to our results, can contain large amounts of fixed N, a prerequisite for the development of life. Obviously, reactive N molecules and chemistry involved in an oxygen-poor atmosphere on the early Earth would be very different from those occurring in the oxygen-rich atmosphere (36). Nonetheless, in the early Earth atmosphere (N_2 - CO_2 -rich and O_2 -poor), if expected end-products are more reduced N-compounds than nitrate (e.g., ammonia) due to the lack of oxygen, it appears that the nitrogen fixation remains as efficient as in the modern and oxidant atmosphere (N_2 - O_2 -rich) (41). Heterogeneous reactions occurring in a volcanic plume that is rich in oxides, with magmatic silicate glass and water in the first place, could provide a more favorable N-fixation environment than storm (nonvolcanic) lightning that occurs in the expected relatively anoxic atmosphere. The potential role of volcanic lightning is not restricted to N-fixation. It might also be relevant to other energetically costly transformations, which were essential for life emergence, such as the synthesis of life-building blocks (42) or the conversion of mineral phosphorous into biologically useable forms (43).

Materials and Methods

Samples from This Study. Were collected from volcanic tephra fallout deposits and large-volume pyroclastic density current (PDC) deposits, also called ignimbrites, of up to 550 km^3 (*SI Appendix, Table S3*). They are collected in arid to semi-arid environments in Central Turkey (CAVP for Central Anatolia Volcanic

Province) and southern Peru (North of the Andean Central Volcanic Zone) because leaching and erosion processes are expected to be minimal in these climatic conditions. This limits the possibility of post-deposition or re-precipitation by fluid circulation, typically rainwater percolating through the deposit, as NO_3^- (as well as Cl^- and SO_4^{2-}) is soluble. Ignimbrites can undergo welding in the few months to years after the emplacement, limiting its alteration (e.g., infiltration of meteoric water) on geological timescales. Therefore, the ignimbrite samples are not expected to have been significantly affected by external fluid circulation, which could either bring in nonvolcanic soluble compounds or leach nitrate out of volcanic deposits. All the samples are collected in deposits from very large explosive and caldera-forming eruptions (VEI 7) dating from ≈ 1 to ≈ 20 Ma. Samples from tephra fallouts and ignimbrites were collected in both Turkey and Peru at different distances (up to ≈ 50 km) from the inferred volcanic center. In Turkey, samples mainly consist of tephra fallouts, while Peruvian samples are mostly ignimbrites. In addition, thick Anatolian tephra fallout deposits are also sampled at different heights within each layer, i.e., base, middle, and top of the layer.

Samples from Ischia (Italy) have also been collected and correspond to the Tischiello (~ 75 kyrs; VEI of about 3 to 4) and the Monte Epemeo Green Tuff-MEGT (~ 55 kyrs; VEI of about 5 to 6) eruptions. The deposits have not been preserved in an arid environment such as those from Turkey and Peru, which is useful for comparison. Indeed, in such conditions, any post-deposition processes such as long-term atmospheric deposition and accumulation of nitrates (and other compounds) in the deposit are precluded.

Nitrate, Sulfate, and Chlorine Concentrations Analyses. Are conducted at the analytical platform Alipp6 (ISTeP-Sorbonne University, Paris) after crushing and leaching the samples (55 and 36 samples for Turkey and Peru, respectively) in deionized water. After filtering the leaching solutions at 0.45 μm , its anionic content is measured using ion chromatography (Dionex ICS 1100, Thermo Scientific) specifically calibrated for sulfate (SO_4^{2-}), nitrate (NO_3^-), and chlorine (Cl^-) ions. NO_3^- and SO_4^{2-} from the leachates are separated via the RMSEP (44), and their multi-isotopic analyses are carried out (on 27 and 8 samples for Turkey and Peru, respectively).

Oxygen Multi-Isotopic Analyses on Sulfate. Were performed at the IPGP Stable Isotope Laboratory. O-multi-isotopic analyses were performed using the laser fluorination method (45) on 2 to 4 mg of barite (BaSO_4). After fluorination of the sample under 40 Torr of BrF_5 , extracted O_2 is purified through a series of liquid nitrogen and slush traps and collected on a molecular sieve. The purified O_2 is then injected into a Delta-V Isotope Ratio Mass Spectrometer (Thermo Fischer Scientific) run in dual inlet to monitor the m/z : 32, 33, and 34, used to determine the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$. The $\Delta^{17}\text{O}$ is then calculated according to the following expression (45, 46): $\Delta^{17}\text{O} = \delta^{17}\text{O} - [(\delta^{18}\text{O} + 1)^{0.5305} - 1]$. While the reproducibility on the international standard NBS127 is ± 0.4 and $\pm 0.04\%$ for $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, the overall reproducibility of the method (leaching, filtration, RMSEP, O-extraction line, and mass spectrometer) is ± 1 and $\pm 0.1\%$ for $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, respectively.

The Multi-Isotope Analyses on Nitrate. ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\delta^{15}\text{N}$) were performed at the Environmental Geosciences Institute (IGE, Grenoble, France). We used the bacterial denitrifier method (16) with *Pseudomonas aureofaciens* bacteria. These bacteria transform nitrate from samples into N_2O through different reactions. The produced N_2O is thus loaded into the purification line. It passes through a series of liquid nitrogen traps and columns, before being heated up at 900 $^\circ\text{C}$, which leads to its decomposition into N_2 and O_2 (47). These two compounds are separated through a chromatographic column before being injected into a MAT253 Isotope Ratio Mass Spectrometer. Its configuration allows the successive measurement of oxygen and nitrogen isotopes. The uncertainties associated are $\pm 1.5\%$, $\pm 0.4\%$, and $\pm 0.2\%$ for $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, and $\delta^{15}\text{N}$, respectively.

Data, Materials, and Software Availability. All study data are included in the article and/or *SI Appendix*.

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