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3 **Revised Main Manuscript for**

4 Geological evidence of extensive N-fixation by volcanic lightning 5 during very large explosive eruptions

6

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36 Figures 1 to 4

37

38 **Abstract**

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

55

56 **Significance Statement**

57 Nitrogen (N) fixation is an essential process for life as it converts atmospheric dinitrogen into
58 biologically assimilable forms. Experimental and theoretical studies have proposed that volcanic
59 lightning could have contributed to N-fixation in early prebiotic environments on Earth but
60 geological evidence are still lacking. For the first time, significant amounts of nitrate, the oxidation
61 end product of atmospheric N-fixation, have been discovered in volcanic deposits from very large

62 explosive eruptions. Geochemical analysis, including oxygen multi-isotopes, indicates that the
63 origin of this nitrate is N-fixation by volcanic lightning. These findings provide geological support
64 for a unique role played by subaerial explosive eruptions in high energy-demanding processes,
65 which were essential in supplying building blocks for life during its emergence on Earth.

66

67

68 **Introduction**

69

70 Nitrogen (N) is an essential element for life and its main atmospheric form today is dinitrogen
71 (N_2), the most stable atmospheric molecule. In order to be metabolised by living organisms, N_2
72 has to be converted into biologically assimilable forms, so-called fixed N. Nowadays, N-fixation is
73 dominantly achieved through biological and anthropogenic processes (1). In early prebiotic
74 environments on Earth, N-fixation, which supported the emergence of life, must have occurred
75 only via natural abiotic processes. Several hypotheses have been proposed including
76 photochemical reactions, hydrothermal reduction, lightning discharges, thermal reduction over
77 magma, and meteoric impact-induced shocks (2–4). So far, the lack of identified geological
78 archives of fixed N corroborating the existence of such processes has prevented the confirmation
79 and quantification of these possible abiotic mechanisms on Earth. One of the most invoked
80 processes is lightning from thunderstorms but also lightning associated with volcanic eruptions
81 (3). Due to the electrification of the ash- and water-rich volcanic plumes, volcanic lightning (VL)
82 occurs systematically during explosive eruptions (5). Lightning strokes detection in volcanic
83 regions also serves nowadays as a potential eruption alert indicator (6, 7). Experimental
84 laboratory studies and thermodynamic models suggest that VL can contribute significantly to N-
85 fixation over the Earth history (8, 9). However, no geological evidence of substantial N-fixation by
86 VL has ever been found so far. We report here the discovery in volcanic deposits of significant
87 amount of nitrate, which multi-oxygen and nitrogen isotopes composition points toward
88 atmospheric N-fixation induced by VL.

89 In search for volcanic fixed N, we targeted nitrates (NO_3^-), the nitrogen oxidation end-
90 product, in volcanic deposits from very large eruptions (for which VL is expected to be extensive)
91 in arid to semi-arid environments, which are most favourable to the preservation of deposit
92 integrity. We considered volcanic deposits from Neogene caldera-forming eruptions (1.6 to 20
93 Ma; volcanic explosivity index VEI of about 7), in Turkey (Anatolia) and Peru (North of the Andean
94 Central Volcanic Zone) (10, 11). Samples were collected from volcanic tephra fallout deposits and
95 large-volume pyroclastic density current (PDC) deposits called ignimbrites. For comparison, 3
96 samples were also collected in a non-arid environment and more recent tephra fallout deposits

97 of 2 large explosive eruptions from Ischia, Italy (the Tischiello eruption: ~75kyrs; VEI of about 3-4
98 and the Monte Epemeo Green Tuff eruption – MEGT: ~55kyrs; VEI of about 5-6; (12)). Indeed,
99 atmospheric (non-volcanic) nitrate deposition and accumulation overtime in volcanic deposits
100 could at first be considered possible (13). Such mechanism could contribute significantly to the
101 nitrate budget of volcanic samples in an arid-environment (for the sake of nitrate conservation
102 overtime) and over long period of time (few Myrs typically). Therefore, the contribution of long
103 term atmospheric nitrate deposition and accumulation overtime is unlikely to be efficient for young
104 volcanic deposits (about tens of kyrs old) in a non-arid environment like Ischia.

105

106

107 **Results and discussion**

108

109 ***Nitrate from volcanic deposits are linked to the explosive eruption event:*** The most
110 remarkable finding is the unexpectedly high NO_3^- concentrations in all volcanic deposits from this
111 study, comparable to SO_4^{2-} concentrations in most samples, including fully welded ignimbrites.
112 Nitrate in volcanic deposits has hardly been reported in previous studies and yet several features
113 indicate that most of this NO_3^- was formed during the volcanic eruptions.

114 First, NO_3^- , SO_4^{2-} and Cl^- contents are found to be well correlated in all samples (Fig.2), which
115 suggests they share a common origin. As large volcanic eruptions directly release large amounts
116 of sulphur and halogens in the atmosphere, their origin in volcanic deposits is overwhelmingly
117 volcanic. Second, the two types of analysed volcanic deposits (ignimbrite and fallout) show
118 similar elemental compositions (Fig. 2), indicating that the incorporation of external NO_3^- by long-
119 term atmospheric deposition and accumulation since the eruptions (few millions of years) cannot
120 be dominant in most samples. Indeed, such a post-depositional process should affect more fallout
121 deposits than ignimbrites because ignimbrites are generally less porous and much denser than
122 fallout deposits, particularly some of the fully welded ignimbrites units which become quasi-
123 impermeable by welding typically a decade after deposition (14). Therefore, if a contribution of
124 long-term atmospheric deposition followed by fluid percolation and accumulation over long
125 timescales (millions of years) could not be ruled out for the most porous volcanic deposits, this
126 mechanism cannot explain large amounts of nitrate found within the fully welded ignimbrites.
127 Finally, in these regions, volcanic deposits are covered by other deposits, which reduce their
128 exposure time to the atmosphere and its nitrate deposition overtime. The effect of long-term
129 atmospheric deposition is expected to be much less effective in the youngest deposits from a
130 non-arid environment (Ischia samples). Nevertheless, large amounts of nitrates (up to 450ppm)
131 are also measured in these young volcanic deposits. The absence of a positive correlation
132 between the age of the deposit and its concentration in nitrate suggests that the nitrate found in

133 volcanic deposits is not related to a slow mechanism operating on very long timescales after the
134 deposit emplacement but rather to the volcanic eruption itself. Third, Anatolian samples collected
135 in different stratigraphic layers in a fallout deposit of a single volcanic event show a quasi-
136 systematic increase in NO_3^- , SO_4^{2-} and Cl^- concentrations from the top to the base of the deposit.
137 Note that a similar pattern is also observed in the fallout deposits from the younger Tischiello
138 eruption (Ischia). Fluid circulation (rainwater percolating through the deposit) can affect the
139 repartition of anions in the deposits, but at least two observations do not support the prevailing
140 role of this process in our volcanic deposits. i) the concentration enrichments of the salts (NO_3^- ,
141 SO_4^{2-} and Cl^-) from the top to the base of the deposits is higher for chlorine, than for nitrate and
142 then sulphate which is not in full accordance with their relative solubilities and hence mobilities in
143 the deposits. ii) The concentration profiles are not found to be dependent on the deposit thickness
144 (from 0.7 m to ≈ 10 m; (Figure S1)), contrary to what would be expected, i.e. the thinnest deposits
145 being more washed out than the thickest. Such vertical zoning, also typically observed in major
146 and trace elements concentrations in volcanic clasts is explained by a stratified magma reservoir
147 (15). The most volatile-enriched part of the reservoir that is discharged in the early stage of the
148 eruption is deposited first and forms to the base of the volcanic fallout deposit. The vertical zoning
149 for nitrate may have been accentuated by the general decreasing intensity of the volcanic
150 explosivity as an eruption goes on, and hence decreasing volcanic lightning and associated fixed
151 N generation, as discussed below.

152

153 ***Nitrate generated by NO_x oxidation via O_3 :*** We use the multi-isotopic composition ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$
154 and $\Delta^{17}\text{O}$) of nitrates extracted from the volcanic deposits by sample leaching to characterise
155 their origins. Isotopic composition of compounds provides insights into emission sources and
156 formation processes. In particular, triple oxygen isotope ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) measurements allow us to
157 trace back the oxidation pathways leading to the formation of NO_3^- or sulphate (SO_4^{2-}) (16). The
158 measurements show that the nitrates in the majority of the samples exhibit large positive oxygen
159 mass-independent isotopic signature ($\Delta^{17}\text{O} > 0 \text{‰}$) (Fig. 3). Such isotopic anomaly can only be
160 inherited from the atmospheric ozone molecule (O_3), revealing the atmospheric origin of nitrate
161 (17). Indeed, NO formed or emitted in the atmosphere acquires an oxygen mass-independent
162 isotopic anomaly during its oxidation to NO_2 via its reaction with O_3 , the $\Delta^{17}\text{O} > 0 \text{‰}$ source
163 molecule; then NO_2 is partly oxidized to nitrate via again reactions involving O_3 (17). In contrast,
164 biological nitrates systematically exhibit a $\Delta^{17}\text{O} \approx 0 \text{‰}$ (18). In the same way, significant positive
165 ($> 2 \text{‰}$) $\Delta^{17}\text{O}$ signatures in volcanic SO_4^{2-} can only be present if S-bearing gases are oxidized by
166 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

167 somewhat correlated (Figure S2) with a slope of ~ 2.9 , which is consistent with atmospheric
168 oxidation of precursor gases (e.g. NO, SO₂) involving ozone.

169 About 83 % of the samples display $\Delta^{17}\text{O} > 0 \text{ ‰}$ and lines up between two endmembers
170 EM1 and EM2 in a $\Delta^{17}\text{O} - \delta^{18}\text{O}$ diagram (Fig. 3). EM1-NO₃⁻ results necessarily from the NO_x
171 oxidation by O₃ ($\Delta^{17}\text{O} \approx 35 \text{ ‰}$ (20)). EM2-NO₃⁻ is characterised by $\Delta^{17}\text{O}$ close to zero and small
172 positive $\delta^{18}\text{O}$ values, which are rather indicative of NO₃⁻ from NO_x oxidation by oxidants carrying
173 a $\Delta^{17}\text{O} = 0 \text{ ‰}$ (e.g. tropospheric OH-radicals (21)), though a contribution of biological NO₃⁻ cannot
174 be ruled out. The lining up between EM1 and EM2 reflects the varying contributions of different
175 pathways to NO_x oxidation, possibly reflecting the range of emissions and environmental
176 conditions covered by the various volcanic events considered here. For instance, the conditions
177 in a PDC (dense cloud moving along the ground level; high temperatures) are drastically different
178 from the conditions in a Plinian column (volcanic plumes rising, expanding and mixing with the
179 background atmosphere; ambient temperatures). Even for a single volcanic plume, the
180 composition evolves rapidly, with oxidation pathways changing between the core and the edge of
181 the plume depending on atmospheric dispersion and mixing, and the presence of highly effective
182 ozone-destroying halogens (22). Biologically produced nitrates, represented by the EM3-NO₃
183 end-member (Fig. 3, Figure S3 and Supplementary Text), appear to slightly contribute to the total
184 nitrate content in our samples (17%). On the whole, the multi-isotopic composition of our samples
185 implies that most of the NO₃⁻ in the volcanic deposits originates from NO oxidation in the
186 atmosphere.

187 The remaining question concerns the sources of NO_x in the volcanic plumes and PDCs.
188 N₂ can be released from the magma but only in very low quantities ($\approx 10^9\text{-}10^{10} \text{ mol.yr}^{-1}$ (23), which
189 cannot account for the nitrate amount measured in our samples. Gaseous fixed N species (HNO₃,
190 NH₃ and NO_x = NO + NO₂) have been detected in passive degassing volcanic plumes (not due to
191 explosive eruptions, (24, 25) but again at very low concentrations, generally at least two orders of
192 magnitude lower than sulphur concentrations (24). Some of these detections were attributed to
193 thermal fixation of N₂ above hot lava lakes (26). This mechanism requires a relatively long
194 exposure of N₂ to lava with high temperatures (>1000°C). During explosive caldera-forming
195 eruptions, the lava typically displays lower temperatures (800-900°C) and cools down very quickly
196 in contact with the atmosphere (27, 28). Therefore, it is unlikely that N₂ thermal fixation can
197 account for the very high NO₃⁻ concentration measured in our samples.

198

199 **NO_x production by volcanic lightning:** The most plausible mechanism able to produce vast
200 amounts of NO_x during large explosive eruptions appears to be volcanic lightning (3, 29). Several

201 electrification mechanisms are thought to play a role in VL. This includes ice charging, the
202 primary mechanism for ordinary storm lightning, particularly effective when a volcanic plume, rich
203 in water, rises up high into the air (5). Other mechanisms more specific to volcanic eruptions can
204 also contribute to the electrification of volcanic plumes, notably mechanisms for which the main
205 carriers of electrical charges are rock/ash particles instead of hydrometeors. Note that the
206 quantification of electrification mechanisms at play in volcanic plumes, including interactions
207 between volcanic particles and hydrometeors, remain relatively poor. The potential intensity of
208 volcanic lightning has been well illustrated by the recent 2022 Hunga Tonga Plinian eruption
209 where about 400 000 lightning strikes were detected in only 6 hours during the main hydro-
210 magmatic explosive phase of the eruption (30). Different electrification mechanisms are expected
211 to dominate depending on the surrounding conditions, composition of the volcanic jet, and
212 dynamics, typically a rising convective plume versus a pyroclastic flow. For instance, the intensity
213 of ice charging lightning should largely depend on the plume water content and height whereas
214 the volcanic particles lightning should depend, among other factors, on the plume ash content.
215 Although lightning in PDCs is far less studied, the lightning activity is generally more intense in
216 volcanic plumes because they reach higher altitudes than in PDCs where most of the lightning
217 occur in the ash cloud/plume above the flow (31).

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

228

229 **Quantification of N-fixation during caldera forming eruptions:** The amounts of vLNO₃
230 produced during the very large explosive volcanic eruptions analysed here can be crudely
231 estimated by considering the density and volume of each volcanic deposit layer and its mean
232 NO₃⁻ concentration. The mean mass of N per single caldera-forming eruption varies strongly from
233 0.02Tg to 282Tg, with an average of 60Tg over the 9 volcanic events from this study
234 (Supplementary Table S3). Some of this variability is certainly caused by the high spatial

235 heterogeneity in nitrate deposits and by the varying electrifying plume conditions, notably the
236 plume water content. Note that one such large explosive eruption can possibly deliver up to about
237 1 year of biological and anthropogenic global present-day fixed-N production (1) over a limited
238 area. This range estimated from our data can be compared to theoretical calculations (3) that
239 derive electrical power generated by volcanic lightning based on the volcanic ash output
240 assuming that all electrical charges are only carried by ash particles. Since other electrification
241 mechanisms of volcanic plumes are ignored, in particular the ice driven mechanism, the electric
242 power available in explosive volcanic eruptions can be considerably underestimated in these
243 calculations. The NO production by VL was estimated at $5 \cdot 10^{12}$ g (equivalent to $1 \cdot 10^{13}$ g of nitrate)
244 for $1.3 \cdot 10^{15}$ kg of volcanic ash, which corresponds to a nitrate concentration in ash deposit of
245 about 10 ppm (10 μ g of nitrate per gr of volcanic ash). Interestingly, this estimate of 10 ppm falls
246 in the lower end of our range (1 to 2700 ppm, see supplementary Table S3 for the 9 analysed
247 eruptive events), which is consistent with this calculation being a conservative estimate, only N
248 fixation from injected ash is considered.

249

250 **Implications**

251

252 The discovery of nitrate in volcanic deposits makes them the first field evidence and geological
253 archive of N-fixation by volcanic lightning, and this can have important implications. First, volcanic
254 activity had already been mentioned as a possible source of the Atacama Desert nitrate deposits,
255 but this possibility has been mostly discounted recently in favour of an atmospheric origin (13,
256 34). One of the main arguments was that volcanism could not generate nitrates with $\Delta^{17}\text{O} > 0\text{‰}$,
257 as measured in the Atacama's deposits. Our results indicate that, on the contrary, volcanic
258 lightning during large explosive eruptions produces νLNO_3 with positive $\Delta^{17}\text{O}$. A possible
259 contribution of the intense Miocene-Quaternary volcanic activity to the Atacama basin nitrates
260 (34) could be reconsidered. Second, the fact that massive volcanic eruption can fix nitrogen on
261 that scale has possible implications for life emergence on Earth. In most hypothesis attempting to
262 explain the emergence and development of life, assimilable N forms are necessary and thus N_2
263 must be extensively fixed (35, 36). Ordinary (non-volcanic) lightning has been one of the most
264 discussed and well-established abiotic N-fixation mechanisms (3, 37, 38). Our findings also hint
265 at potentially extremely high local contributions of VL from very large subaerial explosive
266 eruptions, which were already occurring on the early Earth (39, 40). Indeed, nitrates produced by
267 storm lightning all around the world are spread out on the Earth surface, while volcanic deposits
268 are formed locally in a very short period of time and, according to our results, can contain large
269 amounts of fixed N, a prerequisite for the development of life. Obviously, reactive N molecules
270 and chemistry involved in an oxygen-poor atmosphere on the early Earth would be very different

271 from those occurring in the oxygen-rich atmosphere (36). Nonetheless, in the early Earth
272 atmosphere (N₂-CO₂-rich and O₂-poor), if expected end-products are more reduced N-
273 compounds than nitrate (e.g. ammonia) due to the lack of oxygen, it appears that the nitrogen
274 fixation remains as efficient as in the modern and oxidant atmosphere (N₂-O₂-rich) (41).
275 Heterogeneous reactions occurring in a volcanic plume that is rich in oxides, with magmatic
276 silicate glass and water in the first place, could provide a more favourable N-fixation environment
277 than storm (non-volcanic) lightning that occur in the expected relatively anoxic atmosphere. The
278 potential role of volcanic lightning is not restricted to N-fixation. It might also be relevant to other
279 energetically costly transformations, which were essential for life emergence, such as the
280 synthesis of life building blocks (42) or the conversion of mineral phosphorous into biologically
281 useable forms (43).

282

283

284 **Materials and Methods**

285

286 **Samples from this study** were collected from volcanic tephra fallout deposits and large-volume
287 pyroclastic density current (PDC) deposits, also called ignimbrites, of up to 550km³
288 (Supplementary Table 3). They are collected in arid to semi-arid environments in Central Turkey
289 (CAVP for Central Anatolia Volcanic Province) and southern Peru (North of the Andean Central
290 Volcanic Zone) because leaching and erosion processes are expected to be minimal in these
291 climatic conditions. This limits the possibility of post-deposition or re-precipitation by fluid
292 circulation, typically rainwater percolating through the deposit, as NO₃⁻ (as well as Cl⁻ and SO₄²⁻)
293 is soluble. Ignimbrites can undergo welding in the few months to years after the emplacement,
294 limiting its alteration (e.g. infiltration of meteoric water) on geological timescales. Therefore, the
295 ignimbrite samples are not expected to have been significantly affected by external fluid
296 circulation, which could either bring in non-volcanic soluble compounds or leach nitrate out of
297 volcanic deposits. All the samples are collected in deposits from very large explosive and caldera-
298 forming eruptions (VEI 7) dating from ≈1Ma to ≈20Ma. Samples from tephra fallouts and
299 ignimbrites were collected in both Turkey and Peru at different distances (up to ≈50km) from the
300 inferred volcanic centre. In Turkey, samples mainly consist of tephra fallouts, while Peruvian
301 samples are mostly ignimbrites. In addition, thick Anatolian tephra fallout deposits are also
302 sampled at different heights within each layer, i.e. base, middle and top of the layer.

303 Samples from Ischia (Italy) have also been collected, and correspond to the Tischiello (~75kyrs;
304 VEI of about 3-4) and the Monte Epemeo Green Tuff – MEGT (~55kyrs; VEI of about 5-6)
305 eruptions. The deposits have not been preserved in an arid environment such as those from
306 Turkey and Peru, which is useful for comparison. Indeed, in such conditions any post-deposition

307 processes such as long-term atmospheric deposition and accumulation of nitrates (and other
308 compounds) in the deposit are precluded.

309

310 **Nitrate, sulphate and chlorine concentrations analyses** are conducted at the analytical
311 platform Alipp6 (ISTeP-Sorbonne University, Paris) after crushing and leaching the samples (55
312 and 36 samples for Turkey and Peru, respectively) in deionised water. After filtering the leaching
313 solutions at 0.45µm, its anionic content is measured using ion chromatography (Dionex ICS
314 1100, Thermo Scientific) specifically calibrated for sulphate (SO₄²⁻), nitrate (NO₃⁻), and chlorine
315 (Cl⁻) ions. NO₃⁻ and SO₄²⁻ from the leachates are separated via the RMSEP (44), and their multi-
316 isotopic analyses are carried out (on 27 and 8 samples for Turkey and Peru, respectively) (44,
317 45).

318

319 **Oxygen multi-isotopic analyses on sulphate** were performed at the IPGP Stable Isotope
320 Laboratory (Paris, France). O-multi-isotopic analyses were performed using the laser fluorination
321 method (44) on 2-4mg of barite (BaSO₄). After fluorination of the sample under 40 Torr of BrF₅,
322 extracted O₂ is purified through a series of liquid nitrogen and slush traps and collected on a
323 molecular sieve. The purified O₂ is then injected into a Delta-V Isotope Ratio Mass Spectrometer
324 (Thermo Fischer Scientific) run in dual inlet to monitor the m/z: 32, 33 and 34, used to determine
325 the δ¹⁷O and δ¹⁸O. The Δ¹⁷O is then calculated according to the following expression (46): Δ¹⁷O=
326 δ¹⁷O – [(δ¹⁸O + 1)^{0.5305} - 1]. While the reproducibility on the international standard NBS127 is ±0.4‰
327 and ±0.04‰ for δ¹⁸O and Δ¹⁷O, the overall reproducibility of the method (leaching, filtration,
328 RMSEP, O-extraction line and mass spectrometer) is ±1‰ and ±0.1‰ for δ¹⁸O and Δ¹⁷O.

329

330 **The multi-isotope analyses on nitrate** (δ¹⁸O, δ¹⁷O and δ¹⁵N) were performed at the
331 Environmental Geosciences Institute (IGE; Grenoble, France). We used the bacterial denitrifier
332 method (16) with *Pseudomonas aureofaciens* bacteria. These bacteria transform nitrate from
333 samples into N₂O through different reactions. The produced N₂O is thus loaded into the
334 purification line. It passes through a series of liquid nitrogen traps and columns, before being
335 heated up at 900°C, which leads to its decomposition into N₂ and O₂ (47). These two compounds
336 are separated through a chromatographic column before being injected into a MAT253 Isotope
337 Ratio Mass Spectrometer. Its configuration allows the successive measurement of oxygen and
338 nitrogen isotopes. The uncertainties associated are ±1.5‰, ±0.4‰ and ±0.2‰ for δ¹⁸O, Δ¹⁷O and
339 δ¹⁵N respectively.

340

341

342

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344

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357

358 **Figure legends**

359

360 **Fig. 1. Intense volcanic lightning during the Calbuco eruption (VEI 4), Chile, in 2015.**
361 Photography by Francisco Negroni using a few seconds exposure time
362 (<https://www.francisconegroni.com>).

363

364 **Fig. 2. Correlation between NO_3^- , SO_4^{2-} and Cl^- measurements in Anatolian (diamonds),**
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389 **References**

390

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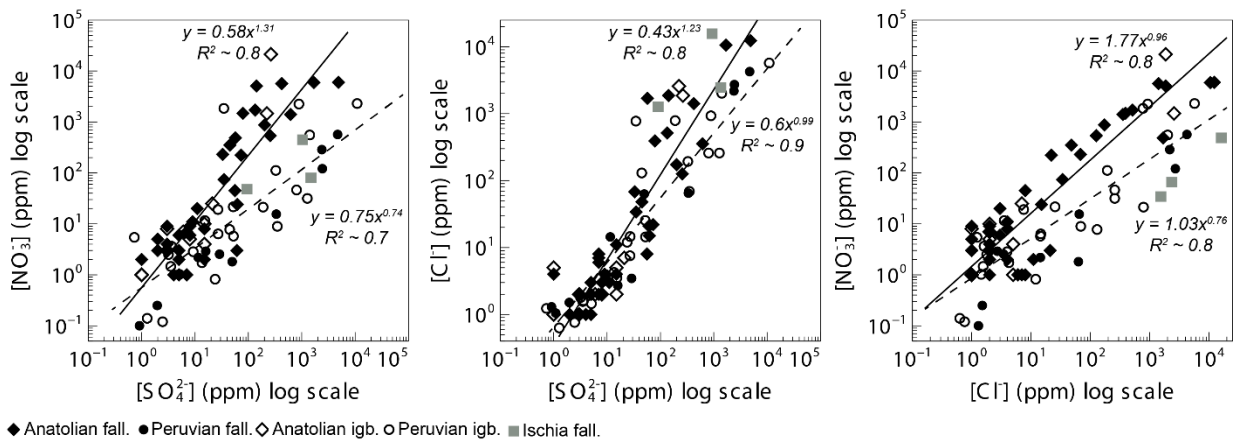


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500 **Fig. 1. Intense volcanic lightning during the Calbuco eruption (VEI 4), Chile, in 2015.**
 501 Photography by Francisco Negroni using a few seconds exposure time
 502 (<https://www.francisconegroni.com>).

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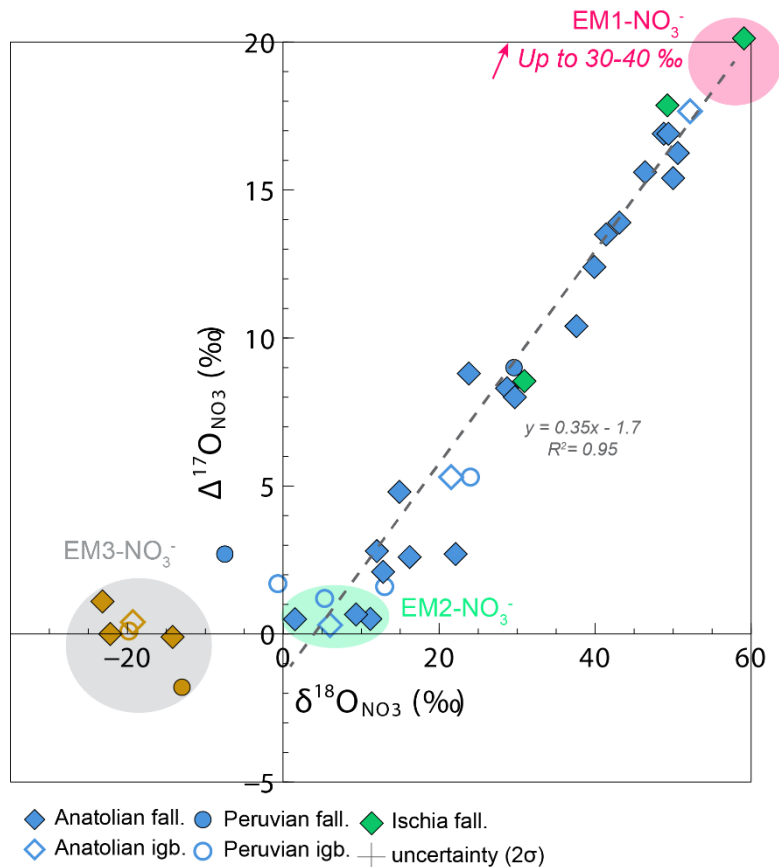
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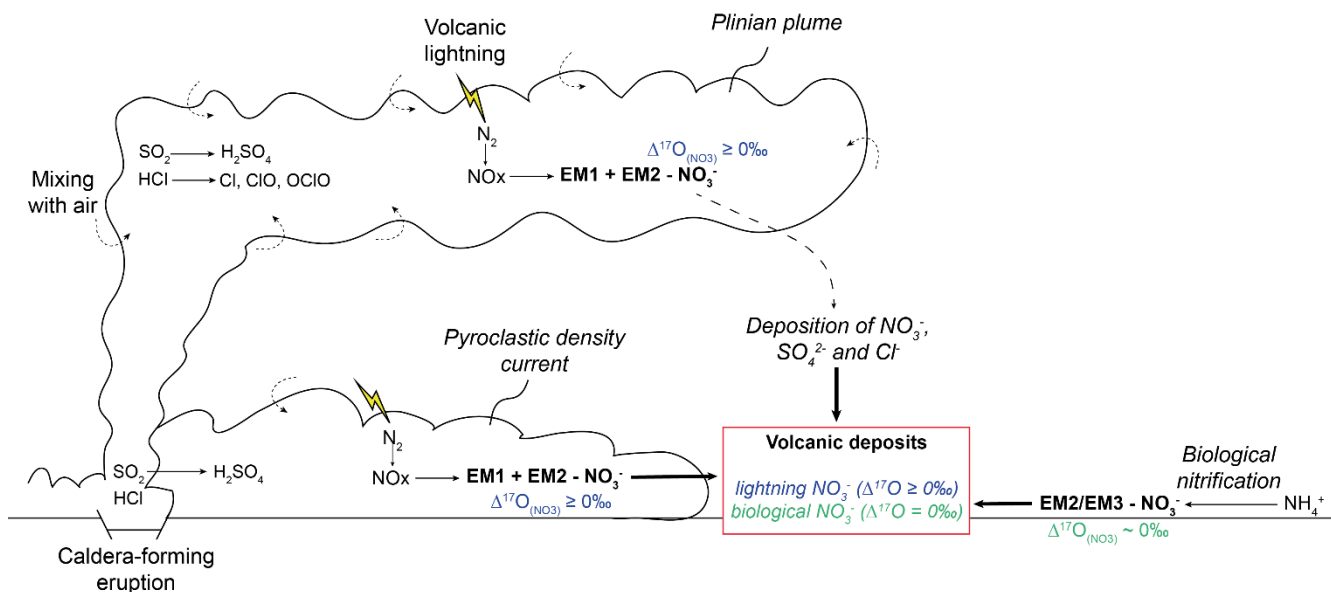
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