



# Mimicking lightning-induced electrochemistry on the early Earth

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**To test the hypothesis that an abiotic Earth and its inert atmosphere could form chemically reactive carbon- and nitrogen-containing compounds, we designed a plasma electrochemical setup to mimic lightning-induced electrochemistry under steady-state conditions of the early Earth. Air-gap electrochemical reactions at air–water–ground interfaces lead to remarkable yields, with up to 40 moles of carbon dioxide being reduced into carbon monoxide and formic acid, and 3 moles of gaseous nitrogen being fixed into nitrate, nitrite, and ammonium ions, per mole of transmitted electrons. Interfaces enable reactants (e.g., minerals) that may have been on land, in lakes, and in oceans to participate in radical and redox reactions, leading to higher yields compared to gas-phase-only reactions. Cloud-to-ground lightning strikes could have generated high concentrations of reactive molecules locally, establishing diverse feedstocks for early life to emerge and survive globally.**

plasma electrochemistry | nitrogen fixation | CO<sub>2</sub> reduction | abiotic synthesis | origin of life

Building blocks required to sustain life—including proteins, nucleic acids, cofactors, components of membranes, etc.—depend on the availability of reactive nitrogen and carbon species. Gaseous nitrogen (N<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) molecules are sparingly reactive due to their high-energy covalent bond, which poses the question: How did an inert environment of the early Earth lead to simple biological compounds, let alone a network of reactions that constitute life as we currently know it? For N<sub>2</sub> and CO<sub>2</sub> to be useful in synthesizing organics and biomolecules, they must be “fixed” (converted into more reactive and accessible compounds) through CO<sub>2</sub> reduction and abiotic N<sub>2</sub> fixation processes (1). Energy sources such as ultraviolet (UV) radiation (2), deep-sea vents (3), volcanos (4), asteroid impacts (5), cometary deliveries (6), and lightning (7, 8) have been proposed to play crucial roles in the formation of accessible nitrogen- and carbon-containing species.

The accumulation of hydrogen cyanide (HCN), delivered by comets (9) and formed after asteroid impacts (5) in the Hadean Eon (4.6 to 4.0 billion years ago), has been relied upon for the investigation of plausible synthetic pathways (10), such as studies on prebiotic purine synthesis (11) and cyanosulfidic proto-metabolism (12), and to provide support for the formation of nucleic acids and peptides (13). Since late Hadean, comets and asteroids impacts became rare (14), yet the formation, growth, and evolution of biology needed consistent sources of nitrogen and carbon (1). In literature, sources of fixed nitrogen on the early Earth have been rationalized based on nitrogen isotope ( $\delta^{15}\text{N}$ ) analysis of geological samples and compared to estimates (i.e., experimental and theoretical) from plausible reaction pathways that are known to date (15–18). This study tests the hypothesis that cloud-to-ground lightning could have filled a critical gap of over 500 My of Earth’s history, when emergent life may have been thriving on abiotic sources of nutrients (18). Our experiments use steady-state chemical compositions (*SI Appendix, section A3*) that are broadly applicable to different geographies and a wide timeframe from the Hadean to the Archean (19, 20) under an anoxic environment. This work highlights the ability of lightning to drive high-voltage electrochemistry across air–water–ground interfaces and convert inert chemicals into reactive intermediates and nutrients that were crucial to emergent life and its early evolution. Cloud-to-ground lightning could have contributed to additional and plausible sets of starting materials and reaction pathways relevant to the chemical origin of life on Earth.

## A Plasma Electrochemical System

Here, we investigate the activation of carbon and nitrogen in a plasma (air gap) electrochemical system that mimics lightning events on the primitive Earth (*SI Appendix, sections A3 and D*), which could have coupled reaction pathways across inert atmospheres, lands,

## Significance

The emergence, survival, and evolution of biology require dependable sources of nitrogen and carbon. Lightning could have been a consistent provider of nutrients during a significant part of Earth’s history, when deliveries of organic compounds from space were rare and enzymes may have not yet formed in significant populations. This experimental study demonstrates how cloud-to-ground lightning storms could have driven radical and electrochemical reactions across interfaces that connect gas (i.e., the atmosphere), liquid (i.e., oceans, lakes, and ponds), and solid (i.e., sediments, rocks, and land) phases on the early Earth. Lightning-induced plasma electrochemistry could have generated high concentrations of nitrogen- and carbon-containing feedstocks locally and produced a range of reagents globally that were relevant (and crucial) to emergent life.

Competing interest statement: Harvard University has filed patent applications PCT/US2023/077332 and PCT/US2024/017763.

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aqueous environments, and interfaces that connected them (Fig. 1). Different from gas-phase discharges that model cloud-to-cloud lightning events (8, 16, 21), we use gas–liquid interfacial discharges to model cloud-to-ground lightning [ $\sim 10^9$  to  $10^{10}$  J/strike and  $\sim 10^9$  strikes per year (22, 23); *SI Appendix, section D1*]. Plasma-activated molecules, radicals, and solvated electrons ( $e^-_{\text{aq}}$ ) (24) drive electrochemical reactions across interfaces (Fig. 1D). Specifically, we mimic lightning strikes in inert and steady-state atmospheres (e.g., 95%  $\text{N}_2$  and 5%  $\text{CO}_2$ ) that discharge onto chemically participating surfaces (e.g., inorganic aqueous solutions and mineral surfaces). This work shows how plasma electrochemistry could have contributed to chemical reactivity and reaction mechanisms by which carbon and nitrogen fixation species could have formed abiotically and accumulated on the early Earth.

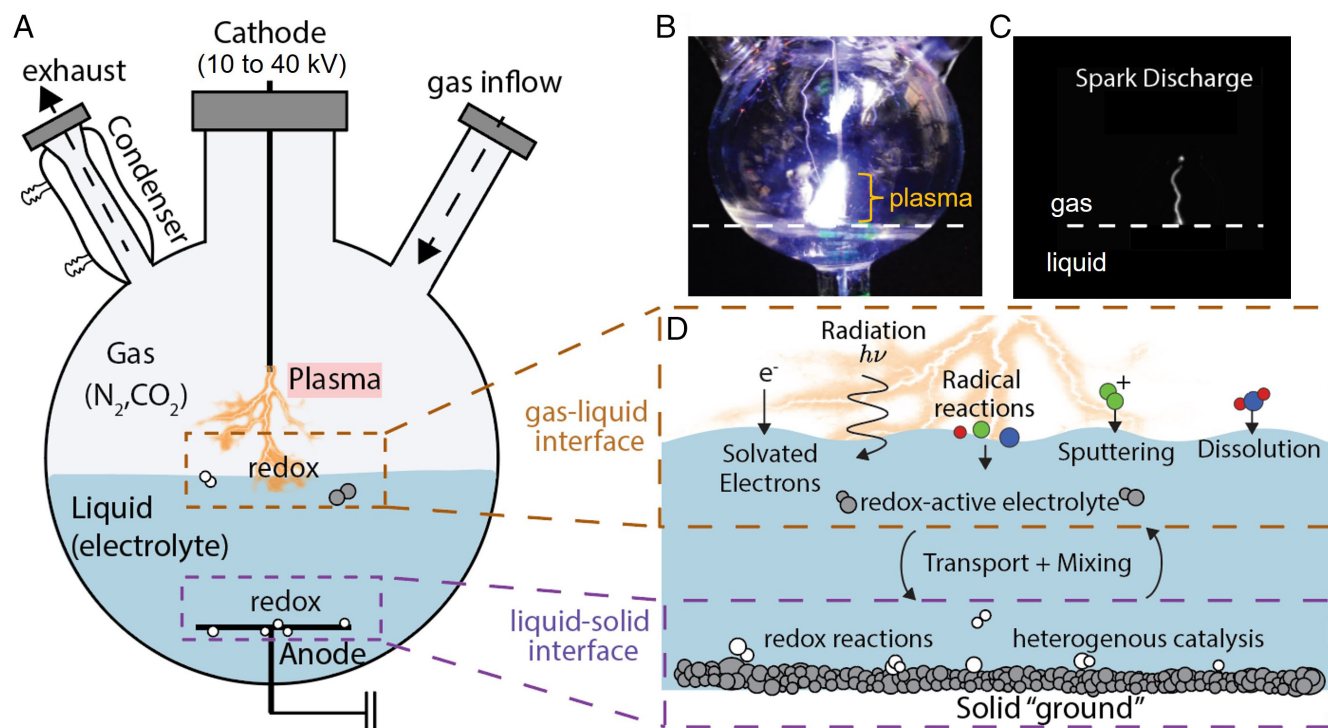
Lightning strikes were simulated experimentally in our system using spark discharges (Fig. 1B and C and *SI Appendix, sections A3, D1, J, and L*). The cathode in the gas phase mimics the accumulation of charge in lower clouds during lightning storms. The anode in the liquid phase mimics a wet ground (e.g., land with rainwater, lakes, or oceans). A spark discharge in between creates a reactive interface, coupling chemical reactions across phases (Fig. 1D). Along the plasma filament, free electrons gain enough kinetic energy from electric fields ( $\sim 1$  to  $10$  eV per particle, equivalent to 100 to 1,000 kJ/mol) to ionize gaseous molecules, liberate more free electrons, and sustain avalanche processes. Along with sustaining ionization, electrons can undergo inelastic collisions with neutral species to i) excite strong covalent bonds, such as in  $\text{CO}_2$  (C = O, 5.51 eV per double bond, or 532 kJ/mol) and in  $\text{N}_2$  ( $\text{N}\equiv\text{N}$ , 9.79 eV per triple bond, or 945 kJ/mol), ii) generate reactivity by populating higher energy states in gaseous molecules (*SI Appendix, section A14*), and iii) form N- and C-containing radicals (26). Subsequent relaxation processes, along with Ohmic heating, drive localized gas heating that can increase the rate of

reactions (27). These high-energy electrons enable faradaic efficiencies  $>100\%$ , that is, over 1 mole of redox products could form per mole of transmitted electrons, which is not achievable in low-voltage electrochemistry.

Using the simplest scenario of an interfacial discharge onto water that featured a low concentration of an inert electrolyte (e.g., 1 mM NaCl) (Fig. 2A), key reduction products include  $\text{CO}_{(\text{g})}$  and  $\text{H}_{2(\text{g})}$  in the gas phase and  $\text{NH}_4^+_{(\text{aq})}$  and  $\text{HCOOH}_{(\text{aq})}$  in the aqueous phase. Key oxidation products include  $\text{O}_{2(\text{g})}$  and  $\text{NO}_{(\text{g})}$  in the gas phase (with trace amounts of  $\text{O}_3$  and  $\text{N}_2\text{O}$ ), as well as  $\text{NO}_3^-_{(\text{aq})}$  and  $\text{NO}_2^-_{(\text{aq})}$  in the aqueous phase (Fig. 2D). These molecules demonstrate the coupling across phases as activated forms of  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  are turned into radicals, reactive gases, and eventually stable products in the aqueous phase (Fig. 2 and *SI Appendix, section N*). The yields of the experiment show that redox balance in plasma-driven electrochemical systems is maintained across phases (Fig. 2E). This process locally provides access to radicals and chemical feedstocks that were slow to accumulate via stand-alone atmospheric processes or solution chemistry. Through radical- and electrochemical mechanisms, lightning could have broadened reaction pathways to the chemical origin of life.

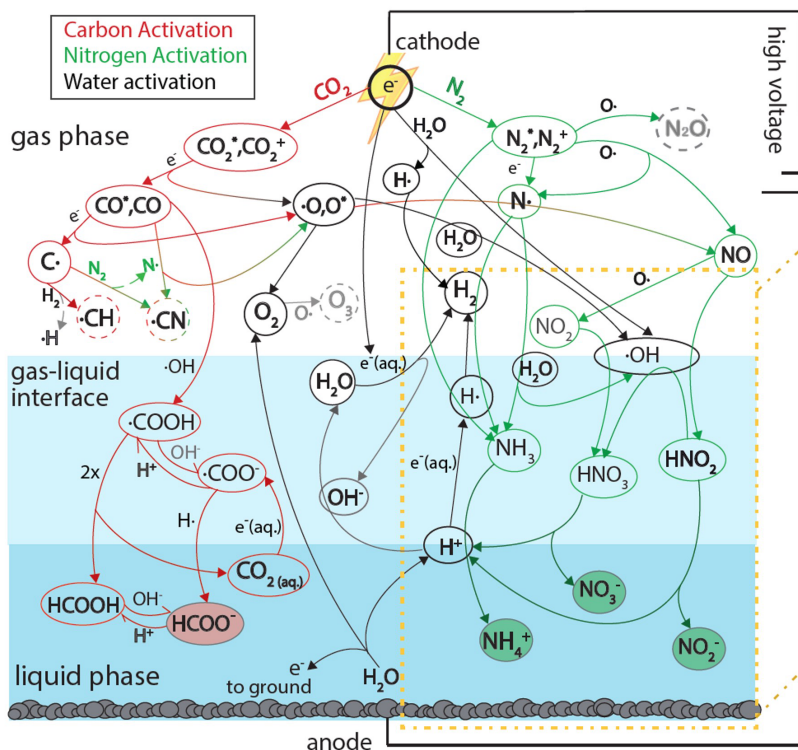
## Nitrogen Fixation and $\text{CO}_2$ Reduction

UV–Vis emission spectra from the gas phase of our experimental system (composed of  $\text{N}_2$  only,  $\text{CO}_2$  only, or a  $\text{N}_2/\text{CO}_2$  mixture, Fig. 3) confirm that sparks activate inert molecules and initiate chemical reactivity in prebiotic environments. Recorded features include electronic transitions of excited neutral radicals ( $\bullet\text{C}$ ,  $\bullet\text{N}$ ,  $\bullet\text{O}$ ,  $\bullet\text{H}$ ), ion fragments ( $\text{N}^+$ ,  $\text{C}^+$ ,  $\text{C}^{2+}$ ), and molecular systems ( $\text{N}_2^+$ ,  $\bullet\text{CN}$ ,  $\bullet\text{CH}$ ). Over time, these reactive radicals recombine and excited molecules dissociate, to form more stable products (*SI Appendix, sections A9ii–A11* and Fig. 2). Interfacial discharges also enabled

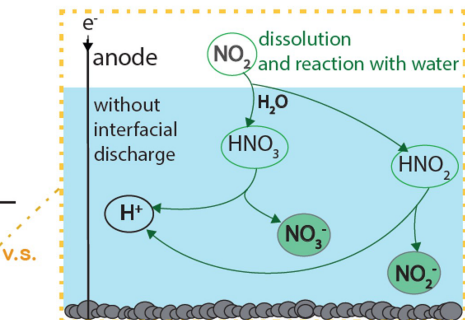


**Fig. 1.** An experimental system designed to mimic lightning-induced electrochemistry on the early Earth: (A) A schematic diagram showing the experimental apparatus used in this work. The discharges aimed to replicate the first stroke phase of lightning strikes where breakdown field strengths are generated ( $\sim 10$  to  $40$  kV/cm) and filamentary plasmas form ( $E/N \sim 150$  Td,  $1 \text{ Td} = 10^{-17} \text{ V cm}^2$ ) (25). Spark discharges terminate at the gas–liquid interface, as shown using (B) long ( $\sim 0.1$  s) and (C) short ( $\sim 1$  μs) exposures. The width of the filament is  $\sim 50$  μm. (D) One-pot chemical reaction and transport processes at the gas–liquid interface and at the liquid–solid (ground) interface. White spheres represent bubbles formed at interfaces, and gray spheres represent redox-active electrolytes that participate in plasma-driven electrochemical reactions.

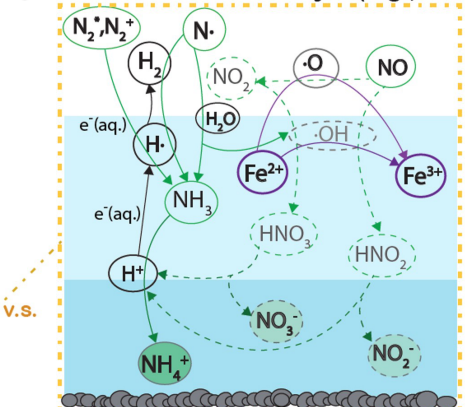
### A interfacial discharge with an inert electrolyte



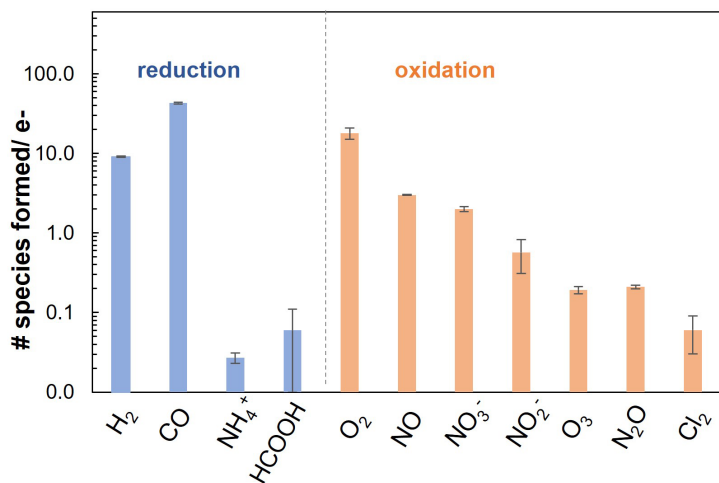
### B gas-phase only discharge



### C with a reactive electrolyte (e.g., Fe<sup>2+</sup>)



### D Overall product speciation (in scenario A)



### E Redox balance (in scenario A)

Reduction products	#moles / mole of e-	redox/e-
H <sub>2</sub>	9.1±0.2	-18.2±0.4
CO	43±1	-86±2
NH <sub>4</sub> <sup>+</sup>	0.027±0.004	-0.08±0.01
HCOOH	0.06±0.05	-0.12±0.10
<b>sum (reduction)</b>		<b>-104 ±2</b>

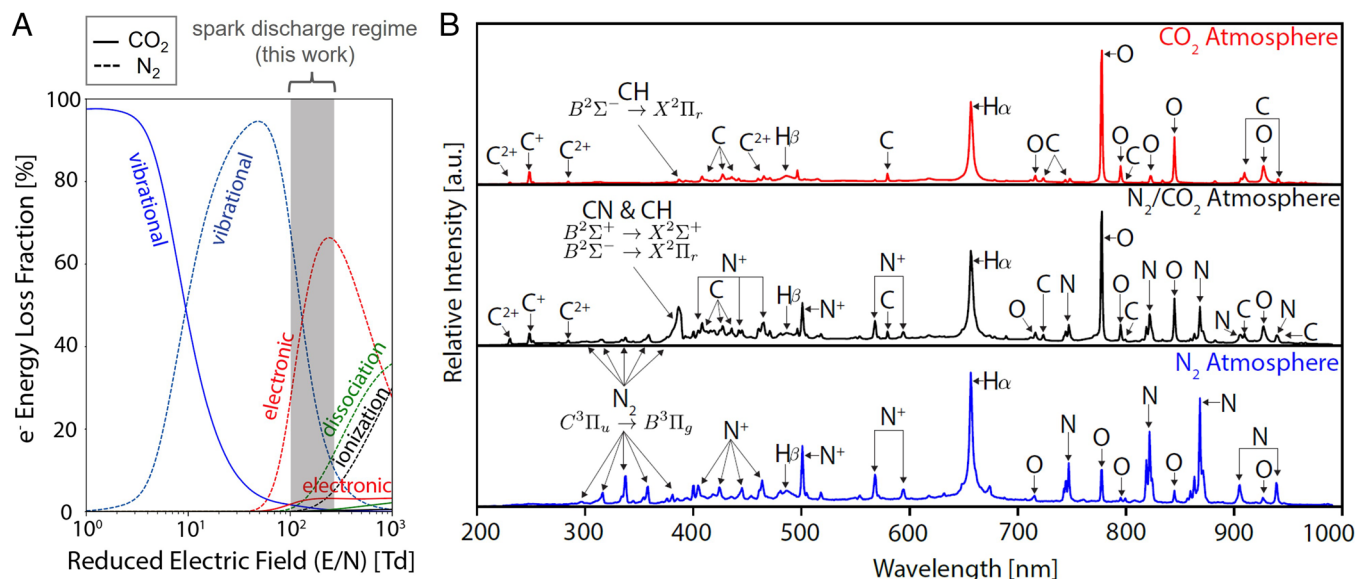
Oxidation products	#moles / mole of e-	redox/e-
O <sub>2</sub>	18 ± 3	72 ± 12
NO	3.02±0.05	6.0±0.1
NO <sub>3</sub> <sup>-</sup>	2.01±0.15	10.05±0.75
NO <sub>2</sub> <sup>-</sup>	0.57±0.26	1.71±0.78
O <sub>3</sub>	0.19±0.02	1.16±0.08
N <sub>2</sub> O	0.21±0.01	0.42±0.02
Cl <sub>2</sub>	0.06±0.03	0.12±0.06
<b>sum (oxidation)</b>		<b>91.5 ±13.8</b>

**Fig. 2.** Lightning-driven electrochemistry: reaction pathways and redox balance. (A–C) Simplified mechanisms grouped into three pathways: CO<sub>2</sub> reduction (red), N<sub>2</sub> activation (green), and water activation (black). (A) An interfacial discharge event with low concentrations of an inert electrolyte (e.g., 1 mM NaCl); (B) a gas-phase discharge event (without sputtering, solvate electrons (e<sup>-</sup><sub>aq</sub>), nor reactive radicals at the gas–liquid interface, except the dissolution of gas-phase products); and (C) an interfacial discharge event with redox-active electrolytes in the aqueous phase (e.g., Fe<sup>2+</sup>). Note that experimentally verified species are shown in bold. Other radical intermediates are supported by literature (24, 28–30). Detailed mechanisms and reactions are in *SI Appendix, section N*. (D) Speciation of products formed through reduction vs. oxidation. (E) Electrochemical redox balance achieved via simultaneous quantifications of gas-phase and liquid-phase products. We define “redox/e<sup>-</sup>” as changes in oxidation number × moles of product formed, per mole of electrons transmitted. Note that results shown in parts (D) and (E) were collected based on the control scenario shown in (A).

the reduction of N<sub>2</sub>, forming NH<sub>4</sub><sup>+</sup> (aq.) at the air–water interface [likely via •NH, •NH<sub>2</sub> and NH<sub>3</sub> intermediates (28, 31), discussed in *SI Appendix, section N*]. The spectral feature at 386 nm (Fig. 3B), pronounced only in the N<sub>2</sub>/CO<sub>2</sub> mixture, signifies the formation of cyanide (•CN) (*SI Appendix, sections K and M*), which is a highly reactive source of carbon and nitrogen in organic synthesis (10, 32).

Interfacial reactions in prebiotic environments can change the speciation, accumulation, and onset of chemical reactivity. We visualized chemical reactions by tracking the change in pH (via

indicator; *SI Appendix, section A1*) near the gas–liquid (Fig. 4A and *Movie S1*) and gas–liquid–ice interfaces (Fig. 4B and *Movie S2*), mimicking lightning striking onto surfaces of different temperatures. In each scenario, as the interfaces were exposed to plasma discharges in the corona regime (Fig. 4A, *t* = 10 to 30 s), the solution became basic locally where the plasma terminated. This shows that, when the gas-phase electrode has a negative polarity, the air gap, together with the liquid or ice interface, acts as the cathode, driving reduction of water to form H<sub>2</sub> and OH<sup>-</sup>. As



**Fig. 3.** Gas-phase excitations and intermediates. (A) Electron energy loss fractions as a function of reduced electric field (and mean electron energy). The calculation depicts how the kinetic energy of electrons excites internal modes in an inert mixture of N<sub>2</sub> and CO<sub>2</sub> to activate them, scission bonds, and form radicals. (B) UV-Vis emission spectra measured experimentally along plasma filaments via an optical fiber probed inside of the vessel. The resulting spectra are composed of transitions from activated diatomic species (N<sub>2</sub><sup>+</sup>, •CN, •CH), atomic radicals (•C, •N, •O, •H), and gas-phase ions (N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, C<sup>+</sup>, C<sup>2+</sup>). Note that N<sub>2</sub><sup>+</sup> and N<sup>+</sup> emission lines partially overlap.

exposure continued and gaseous discharges transitioned into the spark regime (mimicking lightning), the interface became more acidic gradually. Although water reduction continued at the interface, the increase in proton concentration was due to reactions between NO<sub>x</sub> and •OH forming NO<sub>2</sub><sup>•</sup>, NO<sub>3</sub><sup>•</sup>, and H<sup>+</sup> at the interface (Fig. 2A) (31), as well as the dissolution of NO<sub>2</sub> in water to form HNO<sub>2</sub> and HNO<sub>3</sub> (33). Detailed kinetic studies accompanied by changes in pH are discussed in *SI Appendix, section E*. These results show that spark-generated intermediates can drive both reduction and oxidation processes at the air-liquid interface, even when the air gap is set as a cathode.

After exposing the model system to spark discharges for about 5 min, the accumulation of stable nitrogen fixation products in the liquid phase (i.e., NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) was measured for both high-electrolyte (e.g., 100 mM) and low-electrolyte (e.g., ≤1 mM) samples. The efficiency of fixation was quantified by comparing product yields to the integrated flow of electrons through the electrochemical system (Fig. 4C and *SI Appendix, section C*). At low-electrolyte concentrations, our prebiotic system enables the formation of up to 2.0 ± 0.2 moles of NO<sub>3</sub><sup>-</sup>, 0.6 ± 0.3 mole of NO<sub>2</sub><sup>-</sup>, and 0.027 ± 0.004 mole of NH<sub>4</sub><sup>+</sup> per mole of electrons transmitted. These yields suggest that lightning could have enabled abiotic nitrogen fixation processes and the accumulation of reactive products locally on Earth's surface, before Nitrogenase became abundant (18). Both nitrite and ammonium ions are important ingredients for the synthesis of pyrimidine and purine RNA ribonucleotides (34).

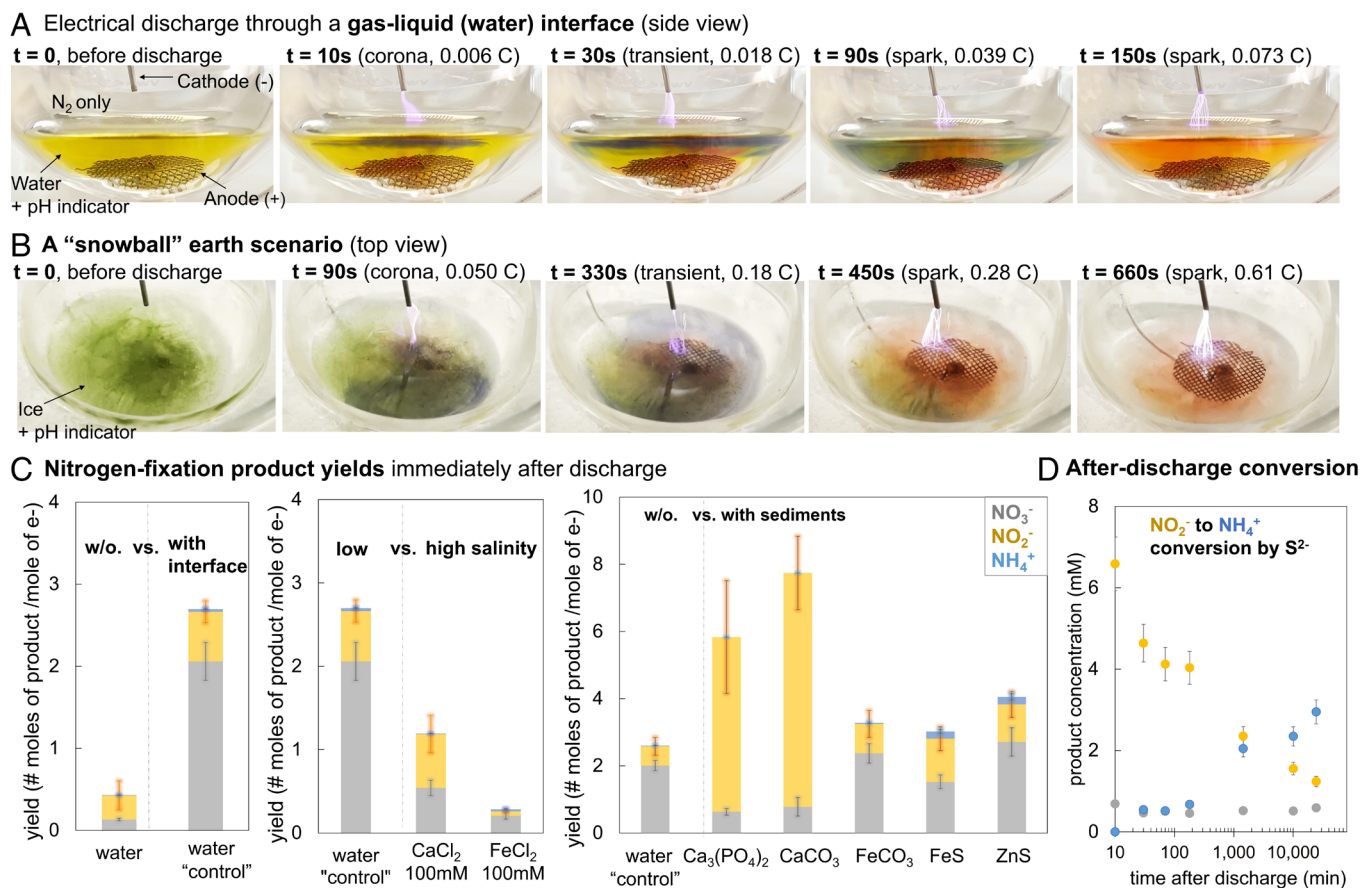
To study how spark discharges could contribute to carbon fixation processes, we ran interfacial discharge experiments under a <sup>13</sup>CO<sub>2</sub>/N<sub>2</sub> atmosphere and collected products in the aqueous phase. The formation of formate is confirmed by <sup>1</sup>H/<sup>13</sup>C-NMR measurements (*SI Appendix, section H*), indicating that formate is a reduction product of CO<sub>2</sub>, as CO<sub>2</sub> was the only carbon-containing species in the reaction vessel prior to the discharge experiment. Quantitative integration showed that there were 0.01 to 0.1 mole of formate collected in the aqueous phase per mole of electrons transmitted. When the aqueous phase was unbuffered, it became acidic (pH<sub>solution</sub> < pK<sub>a,formic acid</sub> = 3.7) after exposure to electrical discharges (>0.5 Coulomb). As a result, more than 95% of formic acid was partitioned into the gas phase and captured by a condenser,

which mimics clouds and rain. Besides cometary deliveries of organics (35) and atmospheric synthesis of formaldehyde (36), interfacial lightning storms could have turned CO<sub>2</sub> in the atmosphere into formic acid, which is a plausible starting material for certain branches of prebiotic chemistry in the Hadean eon (37).

## The Importance of a Gas-Liquid Interface

Besides using HCN from exogenous delivery as a starting material, other accessible forms of nitrogen that are adopted widely for prebiotic synthesis include NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> (or NH<sub>3</sub>) via abiotic nitrogen fixation on Earth (38). Atmospheric fixation processes such as cloud-to-cloud lightning events coupled with UV photochemistry have been explored as a pathway for converting atmospheric N<sub>2</sub> into NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> (39–41), though recent theoretical modeling work suggests that gas-phase synthesis and aqueous-phase accumulation of NO<sub>x</sub><sup>-</sup> are ≥5 orders of magnitude less efficient than considered previously (42, 43). Different from gas-phase discharge studies (16, 44, 45), the present study used gas-liquid interfacial discharges to simulate an alternative scenario experimentally: cloud-to-ground lightning strikes onto aqueous reservoirs (lakes or oceans). Interfacial lightning into shallow terrestrial waters is capable of generating (at least transiently) elevated product concentrations and a broader array of reactive products for prebiotic chemistry despite robust sinks from photolysis. In particular, products from these strikes are not dissipated across a planet but rather concentrated into the specific aqueous body of impact. Additionally, we characterized interfacial nitrogen fixation experimentally in full mechanistic detail (Fig. 2A), obviating theoretical concerns raised for the gas-phase-only nitrogen fixation (42). Therefore, theoretical arguments for low efficiency of cloud-to-cloud lightning productions do not fully apply to cloud-to-ground lightning scenarios studied here, which could have been more efficient in chemical activation and production.

To isolate the influence of reactive interfaces on the yield of nitrogen fixation products experimentally, we measured the speciation of stable products from gas discharges that did not terminate on a gas-liquid interface, but later solubilized into the aqueous phase (Fig. 2B). Results show that, when a gas-liquid interface carries current from electrical discharges, the yields of NO<sub>3</sub><sup>-</sup> increased



**Fig. 4.** Experimental observations and quantitative yields obtained in the liquid phase. (A and B) Timed images of interfacial discharge experiments (with a stainless-steel mesh anode;  $N_2$  only atmosphere): universal pH indicator was added;  $NaOH_{(aq)}$  was used to adjust the initial pH for visualization. The solution in (A) was kept at room temperature and the ice in (B) was kept at  $-10^\circ C$  prior to discharge. (C) Liquid-phase yields of nitrate, nitrite, and ammonium (obtained from 5 min of spark discharges) under different conditions, measured by capillary electrophoresis and ion-selective potentiometric methods and normalized based on current profiles (SI Appendix, sections A4, C1, and C2). The “water” samples represent low-electrolyte solutions (of either 0.5 mM  $CaCl_2$  or 1 mM  $NaCl$ ). The “control” represents experiments run at standard conditions (with interfacial discharge through  $N_2:CO_2 = 95:5$  v/v and low-electrolyte water). Experiments with sedimentary minerals had an excess amount of insoluble solid powder (10 mg/mL) dispersed in a 1 mM  $NaCl$  solution. (D)  $NO_2^-$  formed from plasma is further converted to  $NH_4^+$  post-discharge, in the presence of sulfide sediments (e.g.,  $FeS$  or  $ZnS$ ) under a  $N_2$ -only atmosphere. Details are shown in SI Appendix, sections C3, E, F, and G.

1,500%,  $NO_2^-$  increased 200%, and  $NH_4^+$  increased from below the detection limit to  $0.027 \pm 0.004$  mole per mole of electrons transmitted (Fig. 4C). Without the gas-liquid interface (e.g., during intra-cloud lightning), excited molecules in the gas phase relax (46) and radicals recombine after electrical discharges, before the species can further react with or diffuse into the aqueous phase (Fig. 2B). In addition, the aqueous phase is an important source of hydrogen for the formation of  $NH_4^+$  ions (Fig. 2A). These results suggest that cloud-to-ground lightning strikes could have led to higher nitrogen fixation yields, forming orders of magnitude more  $NH_4^+$  than during cloud-to-cloud lightning events on the early Earth (Fig. 4C). The formation of ammonium is an example product of interfacial lightning enabling activation chemistry not known to be possible by gas-phase lightning. This work opens up a high-energy electrochemical regime, which could have been part of prebiotic synthesis in the Hadean, and its significant contribution could have extended into the Archean, when biological species were thriving on abiotic sources of nutrients prior to enzymes becoming abundant.

## The Role of Minerals

The evolution of reactive chemistry on the early Earth likely depended on the presence, speciation, and availability of minerals. Different from gas-phase discharge experiments that mimic cloud-to-cloud lightning events, interfacial discharge experiments conducted in this

work mimic how minerals on the ground could have reacted with activated nitrogen and carbon species in the air. Cloud-to-ground lightning events across interfaces of air, land, and bodies of water could access a broader range of chemical reagents, activate inert molecules via radical and electrochemical reactions, and lead to diverse reaction pathways beneficial to prebiotic synthesis.

To investigate how water-soluble ions could have participated in lightning-induced electrochemical reactions, we conducted spark discharge experiments with abundant ions of the early Earth added to the aqueous phase, followed by measurements of nitrogen fixation products. When the electrolyte is redox-active and at a high concentration (e.g., 100 mM  $FeCl_2$ ), yields of nitrogen oxidation products were observed to decrease to  $0.6 \pm 0.2$  mole of  $NO_3^-$  and  $0.16 \pm 0.04$  mole of  $NO_2^-$  per mole of electron transmitted (Fig. 4C). This result shows how reducing species can act as sacrificial reductants (e.g.,  $Fe^{2+} \rightarrow Fe^{3+} + e^-$ ;  $2Cl^- \rightarrow Cl_2 + 2e^-$ ), competing with the oxidation of nitrogen and decreasing in the yield of nitrogen oxidation products (Fig. 2C). During lightning storms, redox-active minerals could have participated in plasma-driven electrochemical reactions, altered reaction pathways, introduced selectivity, and changed the speciation of products.

Water-insoluble minerals (e.g., present on the surface of rocks) also served as reactants on the early Earth, both on land or on lake and ocean beds (47). To isolate their influence on surficial lightning-driven reaction pathways, we performed experiments to

contrast the effect of calcium, zinc, and iron(II)-containing minerals (Fig. 4C), which are abundant and likely have existed since the Hadean (48), such as  $\text{CaCO}_3$  (in calcite, aragonite, and vaterite),  $\text{Ca}_3(\text{PO}_4)_2$  (as part of chlorapatite and hydroxylapatite),  $\text{FeCO}_3$  (in siderite),  $\text{FeS}$  (in troilite), and  $\text{ZnS}$  (in sphalerite and wurtzite). Before being exposed to electrical discharges, minerals were suspended in the liquid phase as precipitates. As protons were generated during electrical discharges (primarily due to the formation of  $\text{HNO}_3$  and  $\text{HNO}_2$ ), the minerals dissolved partially to act either as buffering agents (e.g.,  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  to form protonated anions) or to participate in redox electrochemistry (e.g., both  $\text{FeS}$  and  $\text{ZnS}$  can convert  $\text{NO}_2^-$  into  $\text{NH}_4^+$ , as shown in Fig. 4C and D). The presence of a pH-buffering mineral [e.g.,  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaCO}_3$ ] increased the yield of  $\text{NO}_2^-$  by more than a factor of 10, through maintaining the solution at near-neutral pH levels and preventing the protonation and oxidation of  $\text{NO}_2^-$ . This finding is important for nitrogen fixation on the early Earth, as  $\text{NO}_2^-$  can undergo further reduction to form  $\text{NH}_4^+$  through the reaction with  $\text{Fe}^{2+}$  at near-neutral pH levels (49), or with sulfide-containing minerals under slightly acidic values of pH (50). Detailed kinetics studies (in *SI Appendix, section F1*) show >50% conversion from  $\text{NO}_2^-$  to  $\text{NH}_4^+$  with the presence of  $\text{FeS}$  or  $\text{ZnS}$ , days after discharge via solution chemistry (without additional voltage supply). Combinations of minerals (e.g., having a pH-buffering mineral present during discharge, followed by the addition of a sulfide mineral) led to >1 mM levels of  $\text{NH}_4^+$  within days after discharge (Fig. 4C and *SI Appendix, section F2*). Beyond fixing nitrogen, a lightning strike can make chemical components available rapidly, which were previously “inaccessible” while incorporated in rocks or sediments, such as sulfur-containing species that are abundant in volcanic regions.

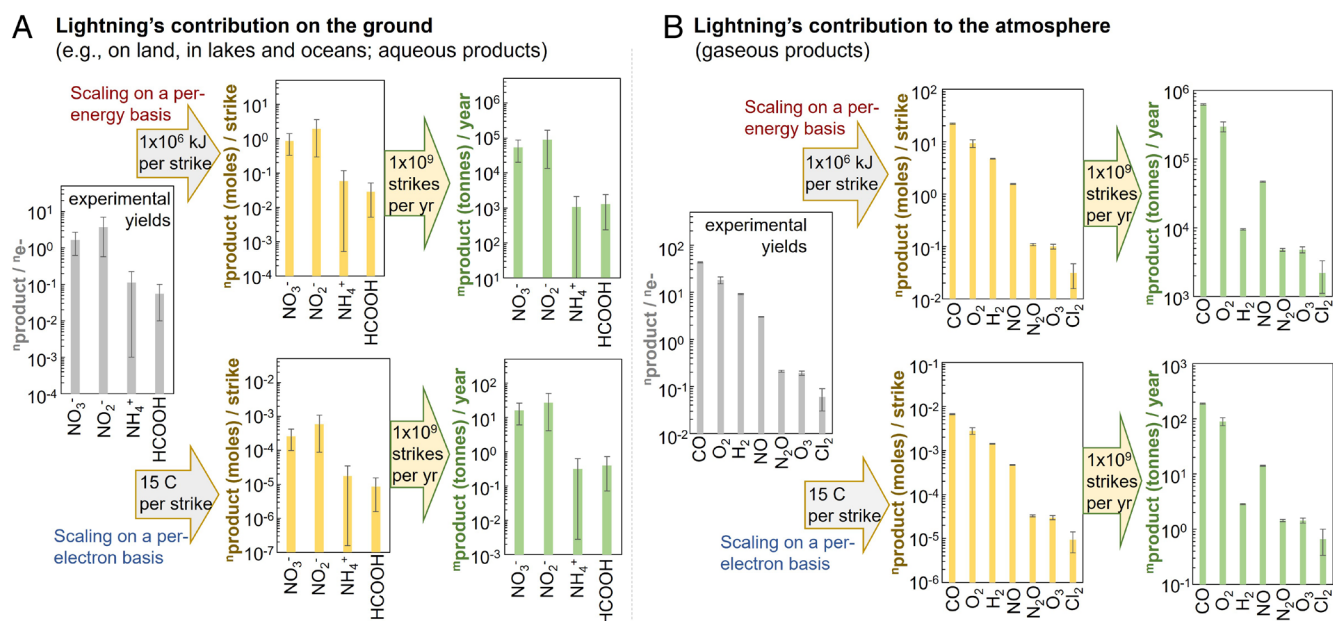
## Lightning's Contribution to Chemical Reactivity on the Ground and in the Air

Lightning-induced electrochemistry is a plausible pathway to activate inert atmospheres and accumulate reactive carbon and nitrogen-containing molecules that are necessary for life to survive.

Nitrogen fixation yields depend on the reactivity and concentration of electrolytes in the aqueous phase, as well as the presence of sedimentary minerals. Across all environmental conditions tested, the combined ranges include 0.6 to 2.7 moles of  $\text{NO}_3^-$ , 0.6 to 7.0 moles of  $\text{NO}_2^-$ , and 0.001 to 0.23 mole of  $\text{NH}_4^+$ ; as well as carbon fixation yields of 0.01 to 0.1 mole of formate, and 33 to 53 moles of carbon monoxide per mole of electrons transmitted.

Fig. 5 shows scaling analysis extrapolated from bench-top experiments to lightning strikes, calculated based on the number of electrons per lightning strike [ $\sim 15$  Coulombs, equivalent to  $9.4 \times 10^{19}$  electrons (51)], the average amount of energy carried by each strike [ $\sim 10^6$  kJ (51)], and the number of lightning strikes per year [ $\sim 10^9$  (52)]. A detailed comparison between our laboratory spark discharges and lightning strikes is described in *SI Appendix, sections A3 and D*. Upon extrapolating yields, lightning could have contributed to forming  $\sim 10^4$  t of nitrate,  $\sim 10^3$  to  $10^5$  t of nitrite,  $\sim 10^2$  to  $10^3$  t of ammonium, and  $\sim 10^2$  to  $10^3$  t of formate every year across the globe (Fig. 5A and *SI Appendix, section D2*). These yields vary depending on the discharge frequency during prebiotic conditions (*SI Appendix, section D1*) and the extrapolation metric (i.e., energy or electron count; *SI Appendix, section D2 and Table S6*). Our predicted yields of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (started from  $\text{N}_2$  and  $\text{H}_2\text{O}$ ) are comparable to photochemical contributions (started from  $\text{NO}$  and  $\text{HNO}$  produced during lightning events) calculated on a per-energy basis (36, 41), which is adopted in literature. Per-electron calculations give lower yields, as the bench-top system carries much less energy than lightning strikes.

The generation of reactive molecules via cloud-to-cloud lightning and photochemistry would have been dispersed across  $5 \times 10^{14}$  m<sup>2</sup> of Earth's surface, resulting in comparatively low concentrations in a global equilibrium state (42, 43). By contrast, chemical production by surficial lightning strikes is localized inherently, and surface lightning strikes onto land (wetted by rain) or into terrestrial waters could have permitted the accumulation of fixed nitrogen and carbon inventories at concentrations far above the global mean. For example, within a local area (e.g., between rocks) containing 100 L of water, a single strike could



**Fig. 5.** Possible contribution of surficial lightning strikes to  $\text{N}_2$  fixation,  $\text{CO}_2$  reduction, and the changing atmospheric composition on the early Earth. (A) The amount of aqueous-phase products extrapolated based on the range of experimental results obtained across different environmental conditions (e.g., with low- or high- levels of electrolyte and with vs. without sedimentary minerals, as discussed in Fig. 4C). (B) The amount of gas-phase product extrapolated based on experimental results measured from the control experiment (1 mM NaCl aq.;  $\text{N}_2/\text{CO}_2 = 95:5$ ). Scaling on a per-energy basis gives upper bound values, whereas scaling on a per-electron basis gives lower-bound values (*SI Appendix, section D*).

rapidly increase concentrations of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and formate by 3 to 14 mM, 3 to 36 mM, 0.005 to 1.2 mM, and 0.05 to 0.5 mM on a per-energy basis, respectively. These concentration levels are likely higher locally (e.g., at reactive interfaces) and further increased by instantaneous heating and evaporation, surpassing concentration levels of HCN delivered by comets, which have been approximated to  $\mu\text{M}$ – $\text{mM}$  locally (9). Products formed from lightning are more stable; therefore, their concentrations could have accumulated over a prolonged period. This feature could have been important for the survival and evolution of early forms of life, especially between mid Hadean and early Archean, when cometary deliveries became rare and enzymes (e.g., nitrogenase and Rubisco) have not yet evolved to a large population.

Further (>50%) conversion from  $\text{NO}_2^-$  into  $\text{NH}_4^+$  is possible with sulfide-containing sediments (Fig. 4D and *SI Appendix, section F*). In volcanic regions where lightning frequency locally reaches  $\sim 10^3$  strikes per minute [e.g., Hunga Tonga Volcanic eruption in 2022 (53)], nitrogen and carbon fixation products coupled with sulfur chemistry may have initiated organic synthesis on the early Earth (34, 54), such as the formation of biomolecules (e.g., amino acids and nucleobases) as building blocks of living organisms (55). Our work therefore reinforces reactive interfaces [e.g., shallow waters (43) with minerals (56)] as particularly compelling venues for origins-of-life chemistry that combines atmospheric synthesis with solution chemistry.

In addition to forming starting materials for prebiotic chemistry (in the Hadean) and forming key nutrients to support emergent life (between the Hadean and the early Archean) on the ground and in bodies of water, lightning-induced electrochemistry could have changed the atmospheric composition over time. While a combination of photolytic and geological activities are acknowledged as possible agents of atmospheric change (20, 57), lightning storms could have catalyzed such change and contributed to the low-level buildup of oxygen prior to the Great Oxidation Event (58). Scaling our experimental yields on a per-energy basis (Fig. 5B), lightning on the early Earth could have contributed to forming  $\sim 10^5$  t of  $\text{CO}$ ,  $\sim 10^5$  t of  $\text{O}_2$ ,  $10^3$  to  $10^4$  t of  $\text{H}_2$ ,  $\sim 10^4$  t of  $\text{NO}$ ,  $\sim 10^3$  t of  $\text{N}_2\text{O}$ ,  $\sim 10^3$  t of  $\text{O}_3$ , and  $\sim 10^3$  t of  $\text{Cl}_2$  every year, depending on the environment (e.g., atmospheric composition, cloud vs. surficial lightning ratio, and minerals present). Among these gas-phase products, both  $\text{CO}$  and  $\text{H}_2$  could have been starting materials for the prebiotic synthesis of organic molecules in the Hadean (8), and  $\text{NO}$  and  $\text{N}_2\text{O}$  could have further reacted and formed nutrients (41), or contributed to atmospheric chemistry and climate change on the early Earth.

Nitrogen isotope analysis (*SI Appendix, section I2*) shows that nitrogen fixation products ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ ), collected in the aqueous phase after interfacial electrical discharges, possess a broad range of  $\delta^{15}\text{N}$  values, from  $-2$  to  $25\%$ . These  $\delta^{15}\text{N}$  values are sensitive to environmental conditions (e.g., atmospheric composition, pH of the aqueous solution, and presence of minerals during discharge and post-discharge) and chemical reaction pathways. For instance, the presence of a pH-buffering mineral (e.g.,  $\text{CaCO}_3$ ) or/and a sulfide mineral (e.g.,  $\text{FeS}$  or  $\text{ZnS}$ ) in solution resulted in a generally lower  $\delta^{15}\text{N}$  of the aqueous nitrogen fixation products that partially overlaps with the  $\delta^{15}\text{N}$  (e.g., near  $0\%$ ) observed for biological nitrogen fixation (*SI Appendix, Fig. S30*) (59). These results provide further evidence that interfacial discharge mechanisms that mimic cloud-to-ground lightning could be essential to understanding sources of fixed nitrogen on the early Earth.

## Significance of Lightning-Induced Electrochemistry

Our experimental study demonstrates the possibility of lightning-induced electrochemistry turning chemically inert but abundant

materials of the early Earth into a diverse range of reactive intermediates (e.g.,  $\bullet\text{N}$ ,  $\bullet\text{C}$ ,  $\bullet\text{H}$ ,  $\bullet\text{O}$ , and  $\bullet\text{CN}$ ), reactive nitrogen species (e.g.,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ ), and organic molecules (e.g., formic acid). Cloud-to-ground lightning could have enabled minerals on the ground to participate in plasma electrochemical reactions across air–water–solid interfaces, tuning chemical selectivity and forming high concentrations of useful products that can further accumulate on land, in lakes, and in oceans. Lightning hotspots with the presence of sulfide minerals, such as those present during volcanic eruptions near volcanic islands, could have generated high concentrations of  $\text{NH}_4^+$  through interfacial plasma electrochemical reactions.

Our results suggest that it is not obligatory to consider HCN from space raining on Earth as the only plausible carbon and nitrogen source on the early Earth. Instead, we show high-energy electrochemical synthesis (i.e., triggered by lightning and its analogs) could have provided accessible forms of carbon- and nitrogen-building blocks for prebiotic synthesis. As biomolecules emerged, lightning-induced abiotic synthesis could have also provided key components continually to sustain early forms of life or precursors to living cells on a global scale.

## Materials and Methods

The experimental plasma electrochemical setup includes two electrodes. In a top-negative configuration mimicking negative (common) lightning, the cathode is exposed in the gas phase, and the anode is immersed in the liquid phase. A plasma (spark) is generated (at 10 to 40 kV) between the gas phase (with a continuous flow of  $\text{N}_2$  and  $\text{CO}_2$  in a 95:5 v/v ratio) and the liquid phase ( $\text{H}_2\text{O}$  with inorganic salts). Reactive radicals and intermediates were detected using UV-Vis emission spectroscopy (*SI Appendix, sections A8, K, and M*). To quantify stable gaseous products, a suite of diagnostics was used, including Fourier-transform infrared spectroscopy, integrated cavity output spectroscopy, gas chromatography, and electrochemical detections (*SI Appendix, sections A9–11*). A combination of UV-Vis absorption spectroscopy, capillary electrophoresis, ion-selective potentiometric methods, NMR, and mass spectrometry (*SI Appendix, sections A5–A7, A12, B, H, and I*) was used to quantify products collected in the aqueous phase of our reactor after exposure to a plasma discharge. Normalized yields were calculated based on experimentally measured current profiles and chemical concentrations (*SI Appendix, sections A4 and C*). Detailed info on chemicals, fabrication, parameters used, and instrumentation can be found in *SI Appendix, sections A1–A14*.

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

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