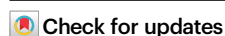


Fe²⁺ disproportionation within iron-rich alkaline vent analogues reveals proto-bioenergetic systems

Received: 4 March 2025

Accepted: 22 October 2025

Published online: 27 November 2025



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Alkaline hydrothermal vents are plausible environments for the emergence of life on Earth. By means of a simplified analogical reconstruction of the vent-ocean interface of these systems reproducing early Earth conditions, we show that iron (oxy-hydr)oxide minerals may have carried out proto-bioenergetic processes driven by pH and redox gradients. The initial pH gradient precipitates the iron (oxy-hydr)oxide mineral barriers (magnetite, green rust and amakinite) and yields reducing conditions, enabling the production of metallic iron at room temperature via the disproportionation of Fe²⁺ to Fe³⁺ and Fe⁰. The crystallographic association of Fe⁰ surrounded by magnetite suggests the coupling of Fe³⁺ / H₂ co-production at ambient temperature by amakinite oxidation with the thermodynamically unfavorable reduction of Fe²⁺ to Fe⁰. This abiotic disproportionation process coupling exergonic and endergonic reactions may serve as a proto-bioenergetic mechanism increasing the non-equilibrium reduction state of the system and offers an interesting analog of the biological electronic bifurcation reaction, the free energy coupling being a fundamental thermodynamic trait of life-as-we-know-it.

Since their discovery in the early 2000's, alkaline hydrothermal vents (AHV) resulting from serpentinization processes have added new perspectives concerning the question of the transitions from geochemical to biochemical entities^{1–3}. These systems arise from the circulation of high-temperature/high-pressure water through deep ultramafic rocks, yielding fluids enriched in dissolved H₂ and CH₄⁴. This results in highly reducing alkaline (pH 9–11), moderate temperature (30–90 °C) effluents which, upon contact with seawater, precipitate chimneys with high content in carbonate minerals⁵. In addition to the mentioned reductants H₂ and CH₄, AHV-effluents contain various abiotic organic compounds deriving principally from CO₂ reduction at high temperature and high pressure in the subsurface^{6–9}. Concomitantly, serpentinization processes occurring in the subsurface of the vents are linked to the formation of metal alloys, commonly awaruite (FeNi₃), and even pure native iron (Fe⁰)¹⁰, which, in reaction

with aqueous CO₂, can also induce the formation of formate and acetate^{11–13}. Such a strong potential for abiotic organic synthesis crystallized hypotheses on the emergence of life in hydrothermal serpentinization systems^{14–16}.

In modern oceans, AHV are predominantly made up of brucite Mg(OH)₂ and calcium carbonates CaCO₃, mainly aragonite and calcite^{5–17}. A type of chimney dominated by brucite (up to 99 wt %) harboring a porous structure (~50%) has been discovered at the Shinkai Seep Field¹⁷. The brucite crystals are oriented by the flux of the effluent, leading to a stratified structure which results in the formation of micropores and nanopores in the mineral walls¹⁸. The micro- and nanoconfined structures of such AHVs provide natural high-surface-area chemical reactors with more efficient reaction rates, selectivity and chemical complexity compared to bulk systems^{18,19}, which, together with the thermophoretic effect²⁰,

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provides an environment conducive to the concentration of abiotic organic molecules in water.

Due to a greater abundance of Mg-Fe rich ultramafic rocks, *e.g.*, komatiites, in the early Earth than at present, early serpentinization processes (mid/late Hadean to early Archean) were likely to produce a higher amount of H_2 than currently, although the qualitative composition of the fluid was expected to be similar to nowadays²¹. Modern and early alkaline chimneys also feature distinct mineralogical assemblages due to major differences in the vent-ocean interface. The primitive ocean was likely more acidic by 0.5 to 3 pH units compared to the present one due to atmospheric CO_2 dominance and, most importantly, devoid of dissolved O_2 (*e.g.*^{22,23}). Fe(II) was also present in high concentrations in ancient anoxic oceans, making an abundant presence of iron (oxy-hydr)oxides (together with carbonates and silicates) in early Earth AHVs plausible^{15,24,25}. Such reactive minerals are of prime interest for prebiotic chemical reactions at the vent-ocean interface. For example, they can mediate the conversion of methane to methanol and yield the formation of various organic compounds^{26,27}.

Iron (oxy-hydr)oxides, in particular layered double hydroxides (LDH) such as green rust, are frequently discussed as ingredients in putative proto-bioenergetic systems. Since they tend to deprotonate in response to oxidation reactions while conserving their crystalline structure, LDHs are capable of conformational changes during oxidation-reduction and protonation-deprotonation oscillations^{28,29}. This conformational flexibility makes them potential non-enzymatic catalysts for proto-anabolic reactions³⁰, especially since these minerals share structural similarities with metal-cluster-containing enzymes involved in current and primordial bioenergetic processes^{31–34}.

Deciphering the growth and reactivity of iron-rich early Earth mineral structures at the vent-ocean interface is an essential step towards understanding their redox properties, with implications for prebiotic chemistry and electrochemical generation in these environments. We thus produced experimental analogs of iron-rich AHV in the laboratory, focusing on the precipitation of the reactive minerals iron (oxy-hydr)oxide minerals. The analogs were formed at the interface between an alkaline solution and an acidic solution with high concentration of iron in the latter (Fig. 1). These early Earth AHV analogs were let to precipitate under strictly anaerobic conditions for different periods of time (5 h, 24 h, 48 h, 72 h and 10 days) and were then analyzed combining multi-scale approaches. Mineral phases were

identified in the bulk using X-ray diffraction (XRD), then analogs with preserved integrity were studied using scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectroscopy (EDXS) to obtain information concerning the structural assembly of minerals. Ultrathin sections were prepared from selected areas for nanoscale analysis using transmission electron microscopy (TEM).

Results and discussion

Growth of the alkaline vent analogs over time

Within the first hour, Fe^{3+} -rich phases such as magnetite ($Fe^{II}Fe^{III}_2O_4$) are the prime minerals to form (Fig. 2). Fe^{3+} precipitation is favored in Fe^{2+}/Fe^{3+} solution at the direct interface between the alkaline fluid and the acidic iron-rich solution. Hydroxylation of Fe^{2+} occurs around pH 7 to 9, while it ranges from pH 1 to 5 for Fe^{3+} ³⁵. As ferric aquo complexes are more acidic than ferrous ones³⁶, the formation of Fe^{3+} -rich phases suggests that the crystallization front at the direct interface of the acidic and basic solutions is exposed to acidic rather than basic conditions. Ferric complexes occur very rapidly to first form oligomers, then nuclei and eventually particles^{35–37}, likely within the first minutes of the mineral barrier formation or possibly even immediately after adding the two solutions to the respective sides of the dialysis membrane. Magnetite thus results from the adsorption of Fe^{2+} onto an amorphous or poorly crystalline Fe^{3+} -rich precursor such as nanoparticulate ferrihydrite or an Fe^{2+}/Fe^{3+} gel^{35,38,39}.

As observed in SEM, the alternation of nanocrystalline magnetite and a more homogeneous material deposited in laminae also indicates the presence of two distinct mineral phases. Together, these mineral phases deposited directly onto the dialysis membrane form a thin laminar mineral structure about ten micrometers thick (Fig. 3A, B). The broad XRD peaks observed at 1 h suggest nanocrystalline or poorly crystallized magnetite, evolving toward better ordered or bigger crystals after 5 h (Fig. 2). After 5 h, the contact area with the dialysis membrane has a similar laminar texture as in the 1 h sample (Fig. 3D, in dark blue), suggesting that no transformation of minerals occurs over this time interval. In the parts furthest from the dialysis membrane, *i.e.*, furthest from the basic solution, other regions feature larger magnetite crystals assembled in a disorderly pattern (Fig. 3E, in blue). Over time, at 5 h (Fig. 3C), the crystallinity and the abundance of magnetite thus increase, but magnetite remains the only mineral phase detected by XRD (Fig. 2).

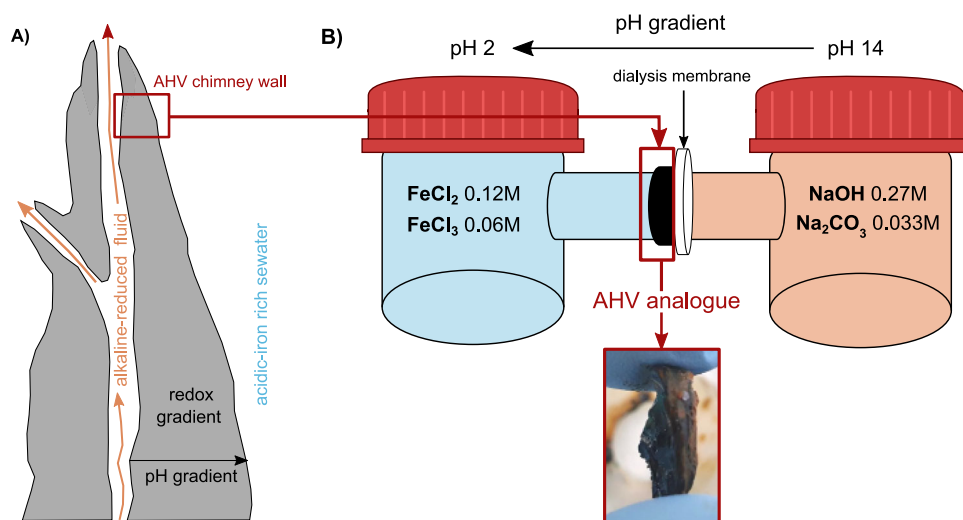


Fig. 1 | Representation of the experimental system reproducing the interface between an acidic iron-rich solution and a basic solution. A Schematic representation of an early Earth alkaline hydrothermal vents (AHV) formed at the interface of an alkaline-reduced fluid (in orange) and of the acidic-oxidized

seawater (in blue). **B** Experimental setup to reproduce a simplified analog of an AHV chimney wall formed in a pH gradient, at the interface of a basic solution (in orange, pH 14) and of an iron-rich acidic solution (in blue, pH 2).

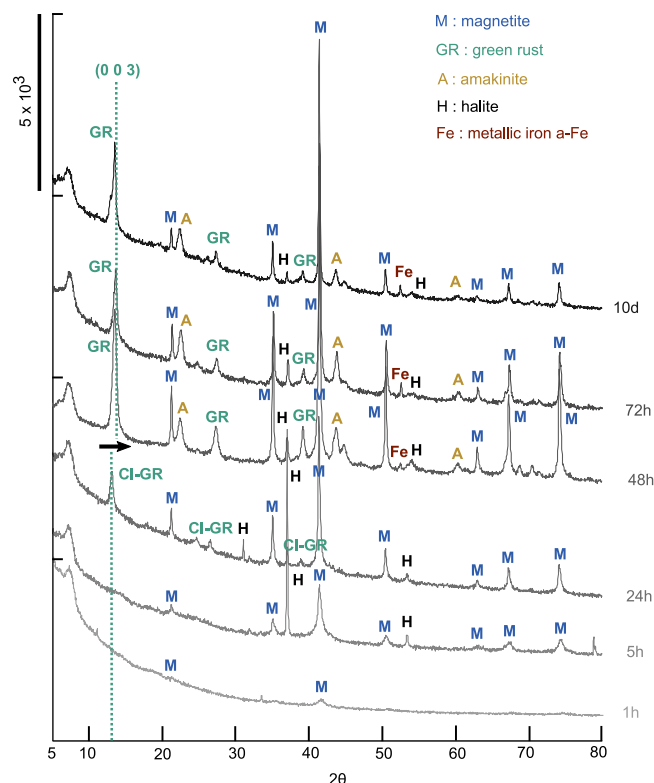


Fig. 2 | X-ray diffraction patterns of the alkaline vent analogs formed in a pH gradient after 1 h, 5 h, 24 h, 48 h, 72 h and 10 days. The analyses were performed under anoxic conditions using Co K α radiation ($\lambda = 1.79026$ Å). For each phase, peaks are labeled with carbonated green rust (PDF4 ID: 00-052-0163 / noted GR) chloride green rust (PDF4 ID: 00-040-0127 / noted Cl-GR), magnetite (PDF4 ID: 01-076-1849 / noted M), amakinite (COD ID: 00-900-9104 / noted A), halite (PDF4 ID: 00-005-0628 / noted H) and the most intense peak (1 1 0) of metallic iron α -Fe (PDF4 ID: 01-087-0722 / noted Fe). The shift of the green rust plane (0 0 3) is indicated by a black arrow. See the complete indexing Table S1 in Supplementary Information.

Starting at about 24 h, the layered double hydroxide (LDH) green rust ($[\text{Fe}^{\text{II}}_{(6-x)}\text{Fe}^{\text{III}}_x(\text{OH})_{12}]_x + [x/\text{nA}^{\text{n-}} \cdot y\text{H}_2\text{O}]^{x-}$ with $\text{A} = \text{Cl}^-$ or CO_3^{2-}) precipitates, containing chloride ions in the interlayers (Fig. 2). Green rust can be formed abiotically by several processes, for example through the partial air oxidation of amakinite (or ferroan brucite) $\text{Fe}(\text{OH})_2^{40}$, the partial reduction of ferrihydrite⁴¹ or by co-precipitation of Fe^{2+} and Fe^{3+} in solution under anoxic conditions⁴². Here, green rust is found to be formed prior to $\text{Fe}(\text{OH})_2$, ruling out the $\text{Fe}(\text{OH})_2$ oxidation pathway. The co-precipitation pathway represents the most straightforward rationalization of the observations of the present study. Concomitant with the formation of green rust, we observe the formation of a new laminar region alternating between two mineral phases (Fig. 3F, G, in cyan), magnetite with a rounded morphology and green rust platelets (Fig. 3H, J).

The iron oxyhydroxide formation is determined by both the pH and the E_h , as described in the Pourbaix diagram of iron^{28,36}. The alternation of magnetite and green rust thus indicates local variation of pH and/or E_h at the crystallization front. While magnetite and green rust can form in the same pH range, *i.e.*, 8.5 to 12³⁶, their E_h range is more constrained: green rust being formed in more reductive conditions, *i.e.*, at lower redox potential than magnetite, due to a greater amount of Fe^{2+} in the crystal lattice^{28,42}. Formation of green rust may thus be explained by the local reservoir of iron (enrichment of Fe^{2+} initially added in solution) at the crystallization front. We propose that massive precipitation of magnetite and possibly ferrihydrite massive precipitation in the first hours of the experiment results in a depletion

of Fe^{3+} at the solidification front, thus driving an enrichment of Fe^{2+} , which allows green rust to form preferentially over magnetite. In turn, this preferential formation of green rust leads to a relative depletion of Fe^{2+} at the crystallization front, driving an enrichment of Fe^{3+} , explaining the alternation between green and magnetite.

Starting at about 48 h and up to 10 days (Fig. 4), all the assemblages described above (dark blue, blue and cyan, see Fig. 5) feature the same characteristics (Figs. 4A, B, E, G, 5, Supplementary Figs. 1, 2), corroborating the hypothesis that the mineral phases, in particular the alternating layers of magnetite and green rust, are formed directly at the crystallization front and undergo little or no subsequent transformation. After 48 h, hydroxylchloride green rust evolves into the more stable hydroxycarbonate green rust, as evidenced by a shift of the (003) XRD diffraction peak from 7.82 Å to 7.59 Å (Fig. 2, Supplementary Table 1). Iron hydroxide amakinite $\text{Fe}^{\text{II}}(\text{OH})_2$ precipitates (Fig. 2), corresponding to the formation of a new region with a homogeneous texture marked by fractures (Figs. 4A, C, E, G, 5A). The precipitation of $\text{Fe}(\text{OH})_2$ indicates a strong increase of the pH and a decrease of the E_h at the crystallization front²⁸ (Fig. 5A). Concomitantly, the precipitation of $\text{Fe}(\text{OH})_2$ is related to the formation of metallic iron “nails”, observed from 48 h onwards (Figs. 2, 4D, F, H). De facto, the pH and redox conditions allowing the formation of $\text{Fe}(\text{OH})_2$ and Fe^0 are very close (Fig. 5A). From 48 h to 10 days, the system does not significantly evolve, except from further growth of the metallic iron nails and from increasing abundance of magnetite surrounding Fe^0 (Fig. 4D, F, H).

In the iron-rich acidic solution remains, pH remains at a value of 2 (Fig. 5B), whereas the ternary system $\text{Fe}^0/\text{Fe}(\text{OH})_2/\text{GR}$ has an alkaline equilibrium pH value around 8^{28,43} (Fig. 5A). This discontinuity can also be applied to the E_h values. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution has a midpoint potential around +0.68 V, while the ternary system $\text{Fe}^0/\text{Fe}(\text{OH})_2/\text{GR}$ has an equilibrium potential around −0.54 V^{28,43} (Fig. 5A). Overall, the pH gradient induces the speciation of Fe^{3+} and Fe^{2+} through their mobilization by mineral phases, from the most oxidized to the most reduced iron mineral phases. In other words, the initial pH gradient mediates a redox gradient and leads to a strong reductive effect on the formation of (oxy-hydr)oxide minerals. The preferential precipitation of $\text{Fe}(\text{III})$ (oxy-hydr)oxides due to the pH gradient leads to the formation of $\text{Fe}(\text{OH})_2$ at a well-defined stage and therefore at a well-defined spatial location in the AHV analog. Thus, the formation of the mineral phases is in opposition to the imposed pH and redox constraint, which is likely due to the OH^- having a diffusion rate higher than the iron complexation. This can be seen through the increase of the pH at the crystallization front, enabling the precipitation of stable mineral phases at very alkaline pH. Otherwise, only ferric iron complexes, stable at lower pH values, would be observed. Additional experiments using a pH difference between the two compartments of 8 and 6 pH units instead of 12 confirm the proton/hydroxide gradient as the primary driving force for the spatial structuring of different minerals, as a more homogeneous structure dominated by amakinite and Fe^0 area is formed (Supplementary Fig. 4A–F), while no minerals precipitate in the control experiment with no pH gradient (Supplementary Fig. 4H, I).

Formation of Fe^0 , a thermodynamic conundrum

While the alternating sequence of iron oxide/hydroxide minerals from magnetite through green rust and on to amakinite is straightforwardly explained by considering local pH-values and precipitation-induced variations of soluble $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion concentrations as described above, the formation of Fe^0 is thermodynamically puzzling. Only Fe ions in the 2+ and 3+ oxidation states were present in the starting solution, and both halves of the reaction vessel were hermetically sealed. The bulk ambient redox potential therefore is exclusively determined by the initial $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, and while local potentials can be lower than that of the bulk when predominantly Fe^{2+} is present (together with appropriate pH-values resulting in the formation of amakinite), there is no

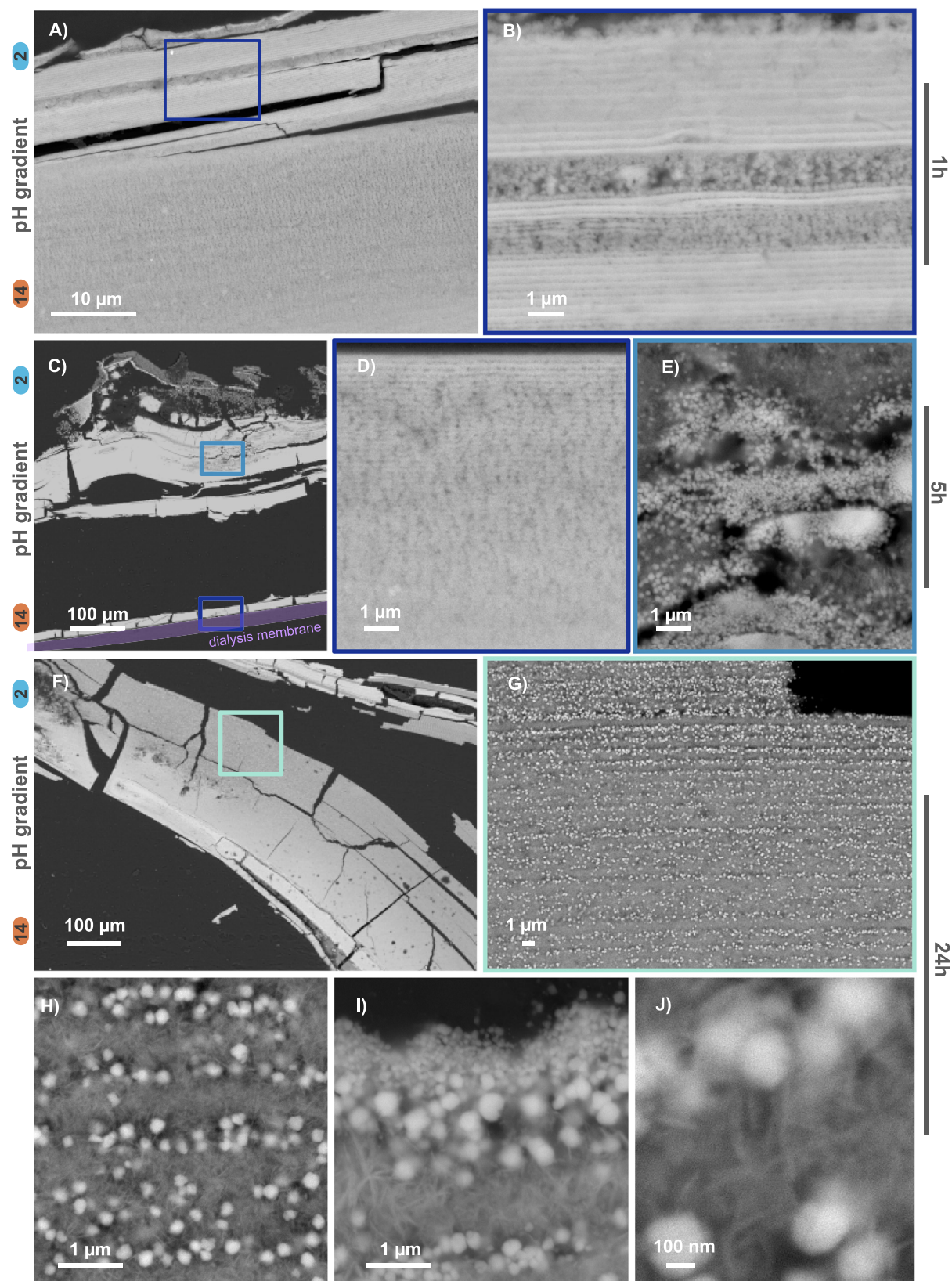


Fig. 3 | Scanning electron microscopy observations of the alkaline hydrothermal vents (AHV) analogs formed after 1 h, 5 h and 24 h. A AHV analog formed after 1 h. The dark blue area in (B) precipitates on contact with the dialysis membrane and features laminations. **C** AHV analog formed after 5 h. **D** The dark

blue area near the dialysis membrane also features laminations, while (E) the blue area from (C) shows a heterogeneous and disorganized texture. **F** AHV analog formed after 24 h. **G** The cyan area from (F) features laminations characterized by the regular alternation of two different mineral morphologies, as shown in (H–J).

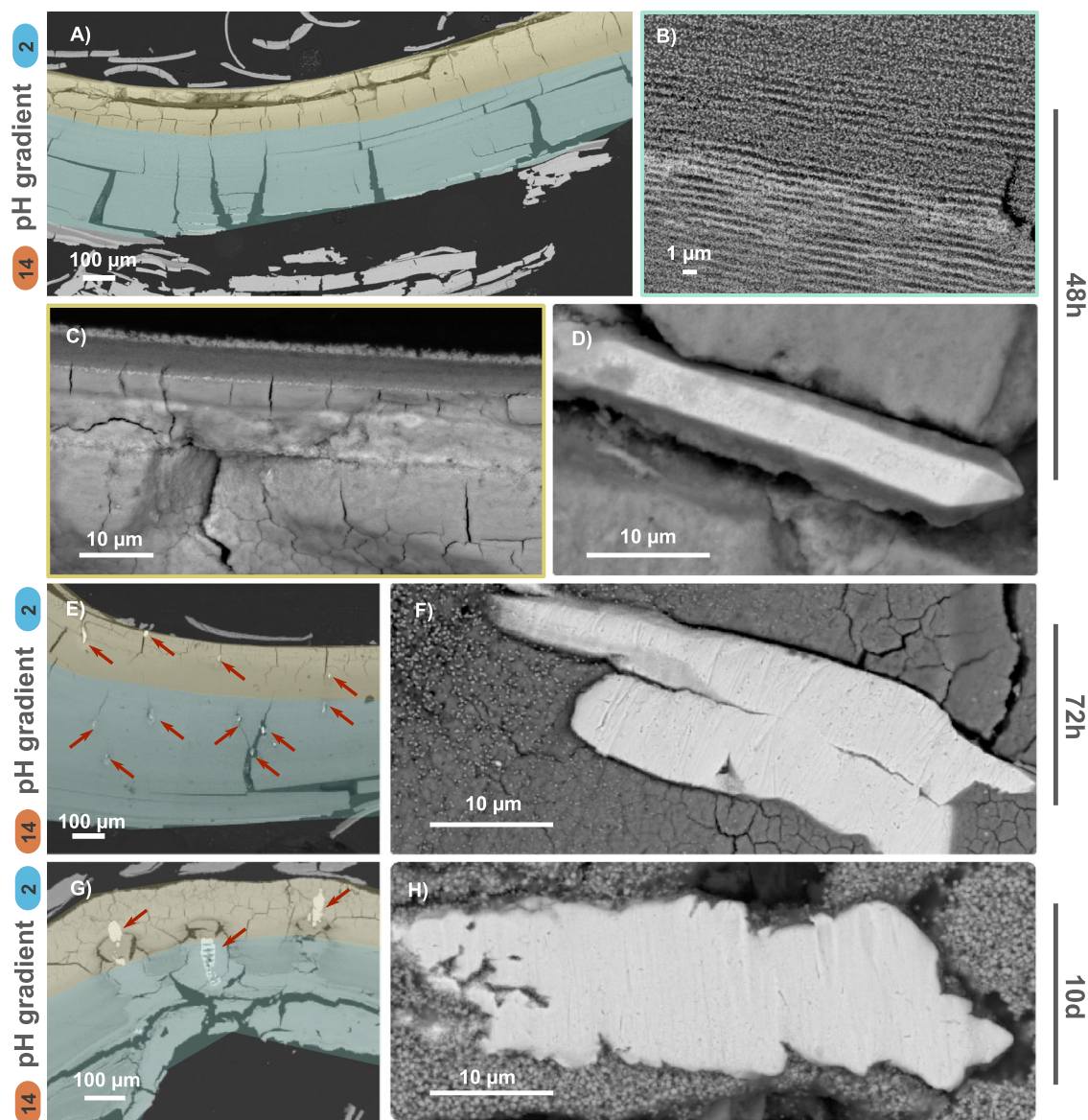


Fig. 4 | Scanning electron microscopy observations of the alkaline hydrothermal vents (AHV) analogs formed after 48 h, 72 h and 10 days. A AHV analog formed after 48 h. The cyan area from (A) in (B) presents laminations formed by the alternation of two minerals, as in the 24 h analog (see Fig. 3). C The yellow area from (A) absent from shorter time samples is characterized by a dense, homogeneous texture which induces fractures in the material. D Formation of metallic iron nails

starting 48 h. E AHV analog formed after 72 h, showing the same cyan and yellow areas as in (A). Red arrows indicate metallic iron, as shown at higher magnification in (F). G AHV analog formed after 10 days, harboring the cyan and yellow areas as in (A) and (E), with metallic iron nails indicated by red arrows. H Magnetite nanoparticles surrounding metallic iron.

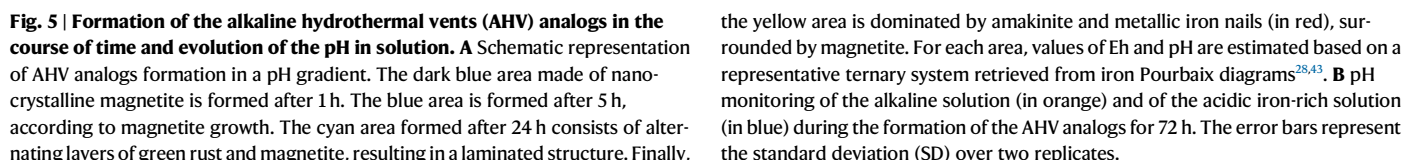
simple exergonic reaction scheme that would account for the reduction of Fe^{2+} (and, even less, Fe^{3+}) to metallic iron. Fe^0 is out-of-thermodynamic-equilibrium with the redox potential of the solution, and its generation therefore corresponds to an endergonic reaction.

A possible lead to solve this conundrum may be provided by the observation that the regions made up from metallic iron have formed within the (strongly reduced) amakinite-rich precipitation front but are coated by a layer of (less reduced) iron-oxides (Figs. 4D, F, H, 5, 6A, Supplementary Fig. 3). Ultrathin FIB sections prepared from a metallic iron nail show that these iron oxides are closely associated to the entire surface of the nails (Fig. 6B, E, Supplementary Fig. 3). Estimation of oxygen percentage performed via EDXS confirms that the surrounding minerals are rich in oxygen (>30%) (Fig. 6C, D), identified as magnetite given the $4.8 \text{ \AA}$ interplanar distance of the (111) lattice plane (Fig. 6E, F). Such a pattern is characteristic of an iron disproportionation reaction^{44,45}, that is, the production of compounds, part of which is in a

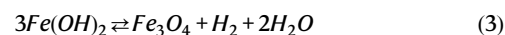
more oxidized state and another part in a more reduced one as compared with the starting material⁴⁶. Here, Fe^{2+} would thus be disproportionated into Fe^{3+} (more oxidized state) and Fe^0 (more reduced state). Such a type of reaction is reminiscent of the dismutation of wüstite (FeO) minerals (Eq. 1)⁴⁶, which is thermodynamically possible.



This mechanism has been experimentally observed at high temperatures and high pressures, *i.e.*, under the conditions of the mantle^{45,47}, as well as at lower temperatures, yet still in the range of 300°C ⁴⁸. In these cases, disproportionation can be explained by the stability domain of wüstite, which decreases concomitantly with temperature and pressure, while the stability field of metallic iron and magnetite increases at lower temperature and pressure^{46,48}. In our



even at low temperature (below 100 °C) (Eq. 4)^{51,52}.



By thermodynamically modeling the Schikorr reaction with production of H_2 , knowing Eq. 4, it appears that this reaction has a ΔG of +10 kJ/mol, resulting in an equilibrium H_2 pressure of 0.13 bar. However, in the experiments of Carlin et al.⁵³ at 100 °C, the H_2 pressures controlled by kinetics were measured at a pressure of 0.003 bar. By taking this value of 0.003, which is likely an overestimation in our conditions, we obtained a ΔG of -5 kJ/mol, meaning the ΔG of the Schikorr reaction remains largely negative in experiments at ambient

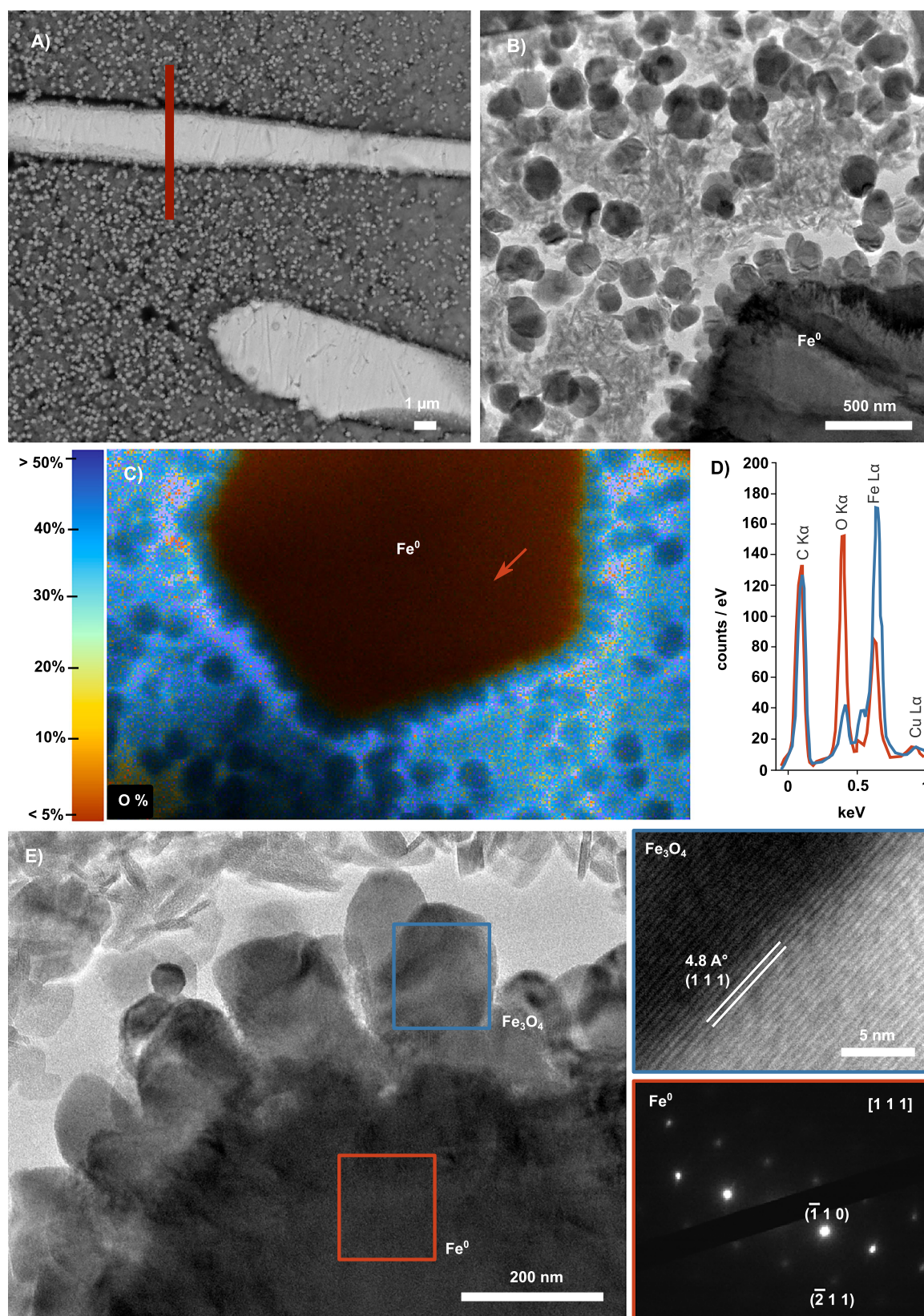
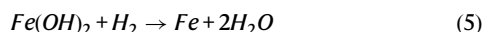
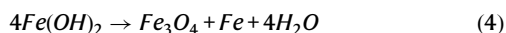


Fig. 6 | Scanning and transmission electron microscopies (SEM and TEM) observation of a metallic iron nail. **A** Localization of the ultrathin section performed on a metallic iron nail (72 h sample). **B** TEM observation of the FIB section. **C** Mapping of the oxygen percentage conducted on the FIB section. Metallic iron, in red (<5% O), is surrounded by iron oxides, in blue (>40% O). **D** Corresponding

energy dispersive X-ray spectra of the metallic iron (in blue) and of the iron oxides (in red). **E** TEM observation of the metallic iron (in red) and iron oxide (in blue) interface, as attested by the measured interatomic distance (in blue) and the electron diffraction pattern (in red).

temperature (see more details of the kinetic constraints in Supplementary, Box 1). Thus, the Schikorr reaction in our early Earth AHV analog is a highly exergonic reaction.

On the other hand, the amakinite dismutation (or Fe^{2+} disproportionation) into magnetite and metallic iron described in Eq. 4 leads to a highly positive ΔG of +35 kJ/mol. Another possibility would be to consider H_2 as a sufficiently powerful reductant to reduce $\text{Fe}(\text{OH})_2$ to Fe^0 , oxidizing the H_2 to H_2O (Eq. 5). However, for the reaction (Eq. 5) to occur, the H-H bond dissociation requires the astonishing ΔG of +435 kJ/mol at ambient temperature⁵⁴, making the direct amakinite dismutation (Eq. 4) more likely. In any case, the observation of metallic iron undoubtedly means that the system of AHV analogs presented here performs an endergonic reaction.



We speculate that during the Schikorr reaction (Eq. 3), a portion of the electrons and protons, respectively produced by the oxidation of Fe^{2+} to Fe^{3+} and the associated dehydroxylation of OH groups associated with Fe^{2+} (Eq. 2), are decoupled in a mineral system dominated by the layered double hydroxide amakinite (or ferroan brucite). This allows the migration of proton and hydroxide ions following a pH gradient. As a result, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple remaining almost on site in $\text{Fe}(\text{OH})_2$ has a very reducing electrochemical potential, providing electrons to reduce $\text{Fe}(\text{II})$ to $\text{Fe}(\text{O})$. By allowing some electrons to carry out a positive ΔG reaction (the endergonic reduction of Fe^{2+} into Fe^0) relying on a negative ΔG redox reaction (the exergonic oxidation of Fe^{2+} into Fe^{3+} coupled to H_2 production), this early Earth AHV analog therefore generates local ambient potentials that are thermodynamically out-of-equilibrium (within regions containing Fe^0) while taking the entire system closer to equilibrium, the latter process making this dismutation process thermodynamics-compliant.

It is precisely this type of process which is the hallmark of all living entities. Life converts environmental free energy into intracellular disequilibria (*i.e.*, low entropy), which subsequently drives the quasi-totality of all metabolic pathways^{55–57}. The mechanism performing this conversion of free energy in living organisms is called bioenergetics. The two fundamental intracellular disequilibria built up by bioenergetic processes are far-from-equilibrium ratios of phosphates to polyphosphates and reducing potentials exceeding those of the environment⁵⁸. The latter disequilibrium is achieved by several bioenergetic mechanisms, one of which is called electron bifurcation⁵⁹, a process which disproportionates a 2-electron redox compound into a more reducing redox center on one side and a less reducing one on the other side. Fe^0 has been previously mentioned as an indispensable precursor for the electronic bifurcation process⁶⁰, where metallic iron takes over catalytic properties to facilitate further protometabolic reactions as an abiotic analog of reduced ferredoxin^{61,62}. Accordingly, the disproportionation mechanism itself of amakinite into magnetite and metallic iron represents a tantalizing analog in a purely abiotic system of the electron bifurcation reaction, fundamental to bioenergetics and hence to life's thermodynamic prerequisites.

In summary, we have shown that the formation of iron minerals at the interface between an alkaline solution and an acidic solution with high iron concentrations results in a spatially highly structured barrier of iron (oxy-hydr)oxides. The initial pH conditions imposed by the two solutions induce a speciation of Fe^{3+} and Fe^{2+} mobilized by the mineral phases and lead to a strong reductive effect. The formation of the mineral phases is in complete opposition to the imposed pH and redox constraints: the precipitation of minerals favored in acidic conditions, such as $\text{Fe}(\text{III})$ complexes, occurred at the direct interface with the basic solution (directly onto the dialysis membrane), while the

precipitation of minerals requiring more basic conditions, such as amakinite, occurred at the direct interface with the acidic solution. We interpret this phenomenon as the result of the OH^- diffusion rate on iron complexes.

Ultimately, this strong pH constraint on AHV analogs leads to the formation of metallic iron Fe^0 due to the disproportionation of Fe^{2+} (from amakinite minerals) into Fe^{3+} (magnetite) and Fe^0 (metallic iron). The dismutation of amakinite at ambient temperature suggests the coupling of the exergonic Schikorr reaction with the endergonic reduction of Fe^{2+} into Fe^0 , a process reminiscent of the bioenergetic mechanism of electron bifurcation. The system we describe here thus generates a local decrease in entropy in the form of thermodynamic out-of-equilibrium ambient redox potentials mediated by the disproportionation of Fe^{2+} ions. Such local lowering of entropy driven by bulk free energy is the thermodynamic prerequisite for allowing the emergence of life in the framework of thermodynamics.

Methods

Precipitation protocol for the iron-rich early Earth alkaline vents analog

The experimental setup for the AHV analog precipitation is based on Barge et al.⁶³. The experiments were conducted in strict anoxia under N_2 atmosphere in a JacomexTM glove box (<10 ppm O_2). We used a piece of dialysis membrane (Spectra-Por[®] Membrane MWCO: 3500) placed at the interface of two glass vials (DEK ResearchTM) hermetically sealed at the center. Two solutions were prepared: a basic solution (pH 14) composed of 0.27 M NaOH and 0.033 M Na_2CO_3 35 mL of degassed water; and an acidic solution (pH 2) composed of 0.06 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.12 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ into 35 mL of degassed water. Both solutions were added simultaneously on either side of the dialysis membrane and let to incubate at room temperature for different durations (1 h, 5 h, 24 h, 48 h, 72 h, 96 h and 10 d). Control experiments have been performed using different pH differential, adjusting the iron solution with 1 M NaOH and the base side with 0.01 M HCl: 1) a pH differential of 8 units (approximately pH = 4 on the iron side, pH = 12 on the base side), of 6 units (approximately pH = 6 on the iron side, pH = 12 on the base side), and almost no pH gradient (pH $\approx$ 7 on both sides) (see Supplementary Informations, Fig. S5). The mineral barriers formed on the iron-rich acid solution side, directly onto the dialysis membrane (Fig. 1), were then dried in the glovebox and prepared for the various analyses in duplicates.

X-ray diffraction (XRD)

Sample preparations and measurements were conducted under N_2 atmosphere in strictly anoxic conditions (<10 ppm O_2). AHV analogs were crushed in an agate mortar and resuspended in degassed pure ethanol before being deposited on a zero-background Si wafer. The wafer was inserted in a custom-built anoxic sample chamber equipped with a Kapton[®] window. The sealed chamber was then removed from the glove-box, and XRD patterns were collected on a XPert Pro AnalyticalTM diffractometer at the IMPMC diffractometry platform. Data were collected using Co K α radiation in continuous scan mode with an equivalent 0.033° 2 θ step, counting 1 h (2 scans of 30 min) per sample over the 5–80° 2 θ range. Minerals were identified using XPert HighScore Plus software, PDF4 and COD databases: iron hydroxylchloride green rust (PDF4 ID: 00-040-0127), iron hydroxycarbonate green rust (PDF4 ID: 00-052-0163), magnetite (PDF4 ID: 01-076-1849), amakinite (COD ID: 00-900-9104), halite (PDF4 ID: 00-005-0628) and metallic iron α -Fe (PDF4 ID: 01-087-0722).

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDXS)

The whole mineral membranes were inserted into Epoxy Araldite 2020 resin directly in the glovebox to limit oxygen exposure. Once

within the resin, the samples were taken out of the glovebox and placed in the oven at 35 °C to accelerate the polymerization of the resin. The samples were then cut in half using a wire saw and polished, half on the top and half on the edge, with 6, 3 and 1 µm diamond suspensions and an alcohol-based lubricant to limit oxygen exposure during the preparation. The samples were carbon-coated immediately after polishing and investigated using a Scanning Electron Microscope (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDXS). SEM-EDXS data were collected at the CINaM microscopy platform, using a JEOL JSM-7900F equipped with a QUANTAX XFlash® Flat QUAD annular four-channel silicon drift (Bruker) for EDXS analysis. Images were collected using an acceleration voltage of 15 kV at a working distance of 11 mm, while EDXS analysis was conducted using a tension of 6 kV.

Ultrathin sections by focused ion beam (FIB)

Ultrathin FIB sections (20 µm * 5 µm * 100 nm) were extracted at Eurofins Biophy Research from one analog of alkaline vents formed after 72 h, using Ga milling with a SEM-FIB TESCAN CLARA. Two FIB sections were extracted from a selected region at the interface between the metallic iron and surrounding minerals, *i.e.*, magnetite. A layer of Pt was deposited on the sample surface to protect it from Ga sputtering. Milling was performed gradually at low Ga currents (500 pA, 250 pA and 50 pA) with a final milling step at 20 pA to minimize common artefacts, including local Ga implantation, mixing of components, or redeposition of the sputtered material onto the sample surface^{64,65}.

Transmission electron microscopy (TEM)

Nanoscale characterization of the minerals surrounding the metallic iron was performed on FIB sections at the CINaM microscopy platform. TEM data were collected using a JEOL JEM-2010 (LaB6) operating at 200 kV and equipped with a QUANTAX XFlash® four-channel silicon drift SDD detector and a GATAN Ultrascan 1000XP camera. Mineral identification was achieved using selected-area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDXS).

Thermodynamic modeling

Thermodynamic modeling was performed using CHESS code 4.0.3⁶⁶ with Thermodem database^{66,67}. A precipitation medium was modeled at 25 °C containing 1 litre of solution: 0.27 M NaOH, 0.06 M_(aq) Fe³⁺, 0.12 M_(aq) Fe²⁺. The partial pressure of H₂ was fixed at 0.003 bar based on Carlin *et al.*⁵³ experiments⁶⁸.

Data availability

The X-ray diffraction data generated in this study are provided in the Supplementary Information and as Source Data file. Additional microscopy data are available from the authors upon request.

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Acknowledgments

We warmly thank Isabelle Pinet (BIP) for her administrative support, Damien Chaudanson and Alexandre Altié (CINaM) for their valuable help with SEM-EDXS, TEM and samples preparation for the microscopy, Amandine David (Eurofins Scientific) for the production of the FIB sections, Ludovic Delbes (IMPMC) and Vasile Heresanu (CINaM) for their help with XRD. This work was supported by the French Agence Nationale pour la Recherche (grant no. ANR-22-CE30-0035-01 attributed to SD and WN), and by French Agence Nationale pour la Recherche under the France 2030 investment plan (grant no. ANR-22-EXOR-0001 attributed to SD and FG).

Author contributions

S.D., W.N. and C.T. designed the study. C.T., N.G., S.D. and A.C. produced the experimental analogs. C.T., F.G., N.G., O.F. and O.G.

performed the SEM observations. C.T. and G.O.N. conducted the XRD experiments and analyses of the data. C.T. and D.F. performed the TEM observations. C.T. and F.G. conducted the thermodynamic modeling. C.T. and C.R. retrieved the ternary systems from iron Pourbaix diagrams. C.T. wrote the first version of the paper. All authors contributed to the revision of the article, read and approved the submitted version.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-025-65716-w>.

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Peer review information *Nature Communications* thanks Eloi Camprubi and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. A peer review file is available.

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