INORGANIC CHEMISTRY
FRONTIERS

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REVIEW

View Article Online
View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2023, **10**, 6792

Abiotic transformations of nitrogen mediated by iron sulfides and related species from early Earth to catalyst design

C. Felipe Garibello, Daniel S. Eldridge, Francois Malherbe and
Rosalie K. Hocking *

Received 7th August 2023,
Accepted 26th September 2023

DOI: 10.1039/d3qi01553j

rsc.li/frontiers-inorganic

Nitrogen fixation and the cycles of nitrogen on Earth are key to life as we know it and are critical to both modern agriculture and sustaining natural ecosystems. Despite its importance, there is still much we do not know about the processes of transforming nitrogen in natural systems. Nitrogen transformation into ammonia is fundamentally a chemical reduction reaction. It can occur catalytically where there is a source of electrons and a catalyst, or directly where a substrate is concomitantly oxidized, providing the source of electrons directly. In this review we explore the chemistry of iron sulfides to understand the reactions they mediate when they interact with nitrogen species, both as direct reductants and as catalysts, as well as the relationship between catalysis and reduction. In parallel it also describes the chemistry of Earth from a protoplanet through to modern times of relevance to understanding nitrogen speciation and historical drivers of these transformations, with a focus on how the pressures and temperatures on Earth may have impacted nitrogen, iron, sulfur and related species. We explore how iron sulfides can both directly and catalytically mediate some chemical reduction reactions and explore how this may have been significant in life's origins.

Introduction

Nitrogen is an essential component of amino acids, hence proteins, and DNA; therefore understanding abiotic nitrogen fixation is a key process in life's origin theories.[1] Despite its importance, there is still much that is unknown about the processes of transforming nitrogen. One thing is clear though: for life to evolve, it needed nitrogen in an accessible form, which is not the most abundant form on Earth *i.e.*, N_2. On Earth, in modern times, before the advent of the industrial scale Haber–Bosch process,[2] nitrogen fixation primarily occurred through biological processes facilitated by nitrogenases.[3,4] This leads to the question: did we have fixed nitrogen before nitrogenase evolved and if so, how did it arise? One place to look for systems capable of this fixation in early times was iron sulfides. In modern enzymes, most notably nitrogenase, iron sulfides form key components, and interestingly they are also amongst the strongest "natural" reductants on Earth today. The two have a striking structural similarity[5] (Fig. 1).

While nitrogen constitutes 78% of the Earth's atmosphere, changing it to either a more oxidized (NO_3^-, NO_2^-) or reduced state (NH_3) is challenging (Fig. 2). As the triple bond of dinitrogen is very stable and strong, it requires significant activation energy to break.[6,7] Nitrogen (N_2) reduction to ammonia (NH_3) is a reaction that requires both protons (H^+) and electrons (e^-). If conducted electrochemically, the redox equivalents of protons and electrons will come from the electrochemical system (eqn (1)).[8,9] In the Haber–Bosch process (eqn (2)), the reducing agents are hydrogen atoms which are more oxidized in NH_3 than in H_2.[2,10] Fundamentally, the source of electrons and protons in a system determines the mechanisms and selectivity of how reactions proceed.[11,12] The stability of the nitrogen phases and iron sulfides as a function of E_h and pH is given by the Pourbaix diagrams in Fig. 3.

Electrochemical nitrogen reduction for ammonia production

$$N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3 \quad E^0 = 0.057\ \text{V}\ vs.\ \text{SHE}\ (T = 25\,°\text{C}) \tag{1}$$

Haber–Bosch process reactions for nitrogen reduction to produce ammonia

$$\begin{aligned} N_2 + 3H_2 \rightleftharpoons 2NH_3\ (400\text{–}450\,°\text{C};\ 200\ \text{atm}),\\ \Delta H = -92.4\ \text{kJ mol}^{-1} \end{aligned} \tag{2}$$

In the present review, we highlight the chemical importance and complexity of iron sulfides mediating nitrogen fix-

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Department of Chemistry and Biotechnology, School of Science, Computing and Engineering Technologies, Swinburne University of Technology, Victoria 3122, Australia. E-mail: rhocking@swin.edu.au

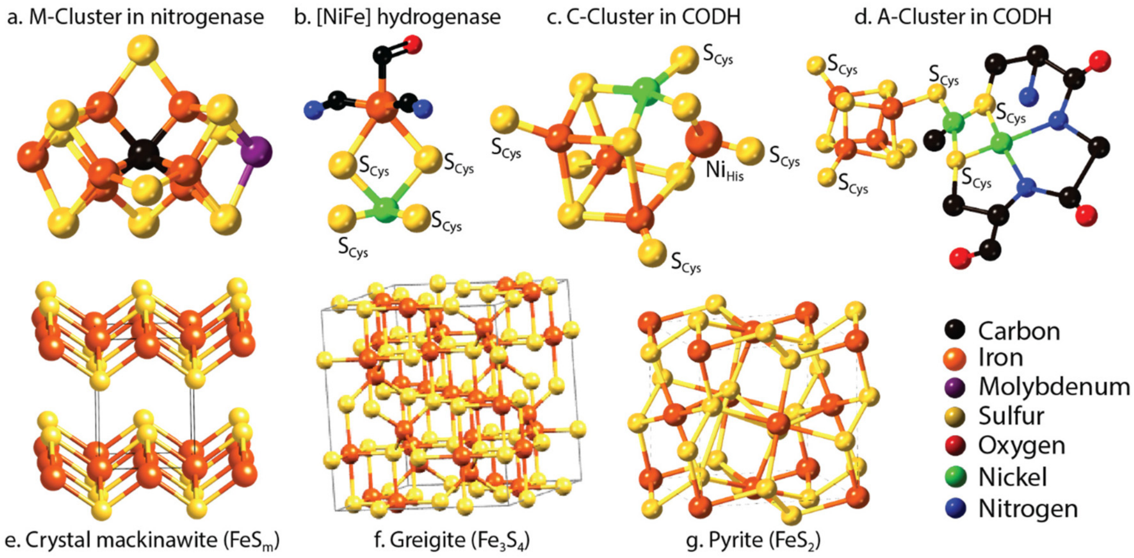

Fig. 1 Upper row: (a) the M cluster in Fe–Mo nitrogenase, responsible for the fixation of nitrogen to ammonia, (b) Ni–Fe hydrogenase responsible for both proton reduction and oxidation, (c) C-cluster in carbon monoxide dehydrogenase (CODH), responsible for CO oxidation to CO_2 in nature however capable of both reactions and (d) A-cluster in CODH. Lower row: crystal structures of well-known iron sulfide minerals: (e) mackinawite (FeS_{am}), (f) greigite (Fe_3S_4), and (g) pyrite (FeS_2).

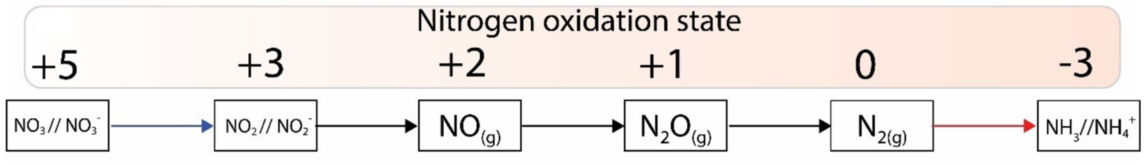

Fig. 2 Nitrogen reduced products with their respective oxidation states.

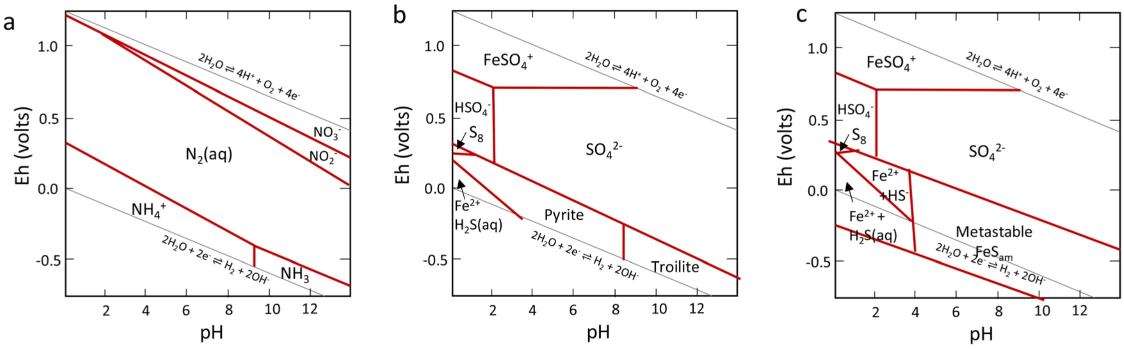

Fig. 3 Key Pourbaix diagrams of relevance to this work. (a) Shows the nitrogen system, (b) the Fe/S system with thermodynamically stable products, and (c) the Fe/S system with metastable mackinawite shown. Reproduced from ref. 96 with permission from John Wiley and Sons, copyright 2022.

ation from two perspectives: direct reduction and catalytically mediated reduction where there is a secondary source of electrons. First, we explore critical differences in thermodynamics affecting nitrogen through the evolution of Earth's atmosphere, and the redox processes, along with the thermodynamic and chemical landscape at Earth's beginning. Furthermore, the fundamental physicochemical attributes intrinsic to iron sulfide materials are presented along with the known mechanisms involving the transformation of nitrogen species *i.e.*, N_2, NO_x, and NH_3 mediated by iron sulfide materials as both reductants and catalysts. Finally, we present an experimental approach for the study of direct and catalytic reduction reactions through the case study of the selectivity of the reduction products in the nitrite reduction reaction mediated by iron sulfide materials. Thus, we expect this review to consolidate the central role of iron sulfide materials in redox/catalytic reactions and thereby their contribution to the chemical transformations that could have had key roles in early life and the potential of iron sulfides in the development of effective catalyst design.

Geochemistry

Nitrogen is not just essential for life as we know it; it was also key for the evolution of life on Earth.[13] But how did the first abiotic nitrogen fixation and the consequent ammonia formation occur, and under what conditions? To understand this, we need to go back to Earth's beginnings and consider two different environments where ammonia could potentially be abiotically formed: the oceans and the atmosphere.[14,15] Key geological changes in Earth are outlined in Fig. 4, alongside what is known about the atmosphere.

The Hadean atmosphere and oceans offered a wide variety of chemical elements in amounts that, along with a range of different conditions of pressure and temperature, could have provided far more thermodynamically favourable conditions for nitrogen fixation, compared to those of today.[16–18] A study of the conditions where iron sulfides have been postulated to play a role in nitrogen fixation could offer us a different perspective in the design of a new generation of catalysts. Therefore, consideration of the chemistry of early Earth provides us insights into how primitive nitrogen fixation may have evolved. It is also important to note that there were extreme differences in terms of pressure that altered the thermodynamics and solubility of nitrogen, and with the amount of dissolved nitrogen being proportional to pressure, there was much more of it in the oceans in the Hadean era, and also at high ocean depths, where pressures are substantially higher and solubility is greater.[14,19]

Nitrogen and early Earth

The Hadean Eon, which is the earliest eon in Earth's geological history, is estimated to have lasted from approximately 4.6 billion years ago (4.6 Ga, the formation of the Earth) to about 4 billion years ago (4 Ga), and it is speculated that this was a dynamic time chemically. Physically, it featured constant bombardment by extra-terrestrial bodies and high volcanic activity.[25] The chemistry of Earth in the Hadean era was likely subject to extreme conditions including plasmas, high temperatures, and pressures that may have promoted NH_3 formation.[17,26] However, it is speculated that ammonia in the atmosphere may not have persisted long due to photolysis by solar UV radiation,[27–30] which breaks ammonia down to nitrogen and hydrogen.[25,31]

The chemistry in the Hadean atmosphere was probably highly reductive compared to today.[32] Early atmosphere is believed to have had significantly higher atmospheric pressure compared to today, with a dominant composition of CO_2 (around 40–210 bar)[33] and N_2 (2–3 bar),[34] H_2O, CO, and small quantities of H_2, CH_4, P_4O_{10}, SO_2, S_8, H_2S and NO_x[35,36] (Fig. 4). Although H_2S would be emitted by oceanic volcanic activity, because of its high solubility in water only a small fraction would have reached the atmosphere. Given that there was a high concentration of Fe^{2+} in the ocean, any H_2S formed would have likely formed insoluble/soluble phases of the iron sulfide family.[28]

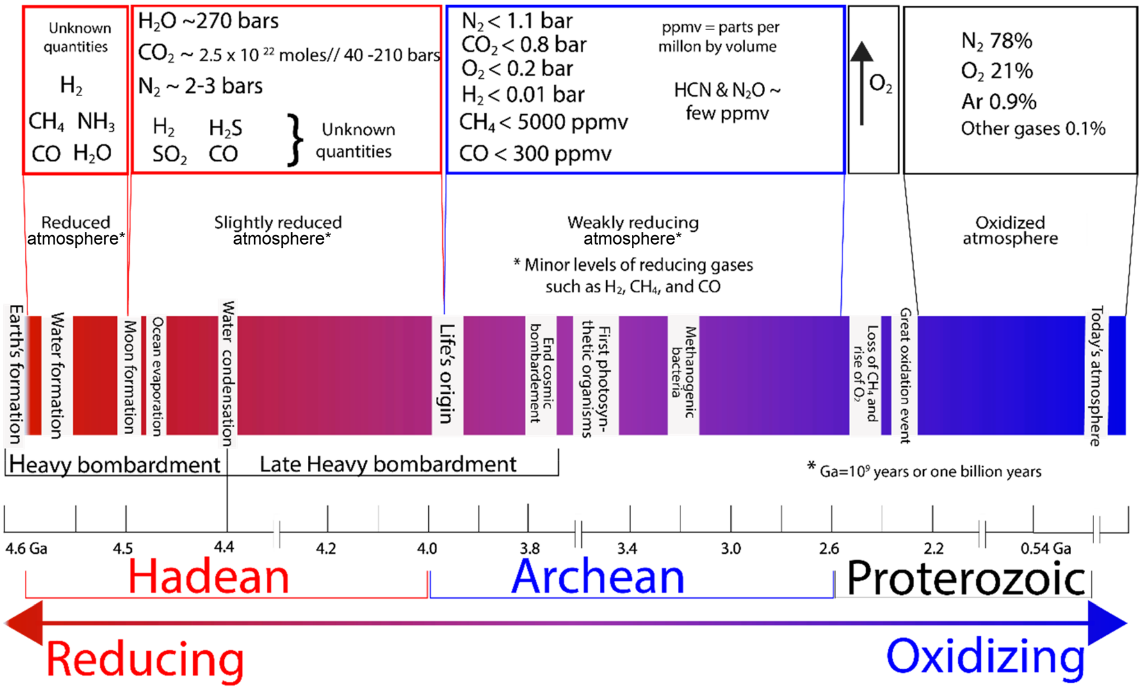

Fig. 4 Atmospheric composition in the early Earth and changes over time.[14,19–24]

The Archean atmosphere (~3.7 Ga ago, after the evolution of life) featured the rise of atmospheric nitrogen, the appearance of oxygenic photosynthesis and the consequent increase in oxygen levels,[37,38] producing a more oxidizing atmosphere (Fig. 4). Recent studies of basalts from the mid-ocean ridge suggested that as a consequence of the shift from a "chemically reduced" mantle to a "more oxidised mantle", nitrogen becomes insoluble and was degassed in high proportions.[39–41] The pressure of the atmosphere also plays a significant role in dissolved gases with the amount of gases dissolved being proportional to atmospheric pressure.[42] Thus, under the extreme conditions of the primitive atmosphere, it is speculated that dissolved N_2 would have been present in much higher amounts, which would have rendered any naturally occurring chemical reduction process more thermodynamically favourable.

Could an early Earth atmosphere fix nitrogen?

Different natural events such as lightning, photochemical reactions, meteorite strikes, hot lava flows, and extremes of pressure and temperature could support abiotic nitrogen fixation in the primitive atmosphere. From these events, lightning coupled with photochemical reactions is considered the most plausible.[39–41,43]

High temperatures and plasmas produced by lightning were capable of dissociating CO_2 into CO and $O^•$. The reactive $O^•$ radical is capable of breaking the triple bond of N_2 forming NO and N, and then the N radical could react with CO_2 to produce more CO and more NO (Fig. 5).[43–46] Thus, the Hadean atmosphere had a sink reservoir of NO, which could be converted into other NO_x species by photochemical reactions (Fig. 5).

To be useful to life, the NO_x species needed to reach the oceans. The profile of the NO_x species (at different pressures of 0.1, 1 and 10-bar pCO_2) produced by photocatalysis along with the rainout rates in the Hadean atmosphere was simulated by Wong *et al.*[43] using the 1D Caltech/JPL chemical transport model.[47] This study found that among all the NO_x species, HNO has the highest initial formation rates followed by HNO_3 and HNO_2.

Additionally, the calculated amount of NO_x rainfall into the Hadean waters was 2.4×10^5 (for the 0.1-bar pCO_2), 6.5×10^8 (1-bar pCO_2) and 1.9×10^8 molecules per cm^2 per s (10-bar pCO_2).[43] The high pressures and reducing atmosphere of early Earth would have made ammonia formation more thermodynamically favourable, which may have led to additional forms of nitrogen being present. It is plausible that not enough nitrogen was produced by this method to impact the rock record.[16,48,49]

Recent investigations into photocatalysts utilizing nanomaterials have shown a promising avenue for the reduction of N_2 to NH_3 through a multistep reaction pathway. The photo-induced conduction band electrons and valence band holes reduce nitrogen and oxidize water, respectively.[50] This process involves the formation of a sequence of lower-stability intermediate compounds.[51] Additionally, photoreduction on the mineral surfaces under early Earth conditions has been previously reported,[52,53] and the conditions during the Hadean era, characterized by specific combinations of pressure and temperature, may have enabled photocatalytic transformations mediated by iron sulfide minerals. Therefore, these recent findings open a new avenue for the photochemical nitrogen fixation mediated by iron sulfides in the early Earth's atmosphere, without the NO formation described above.

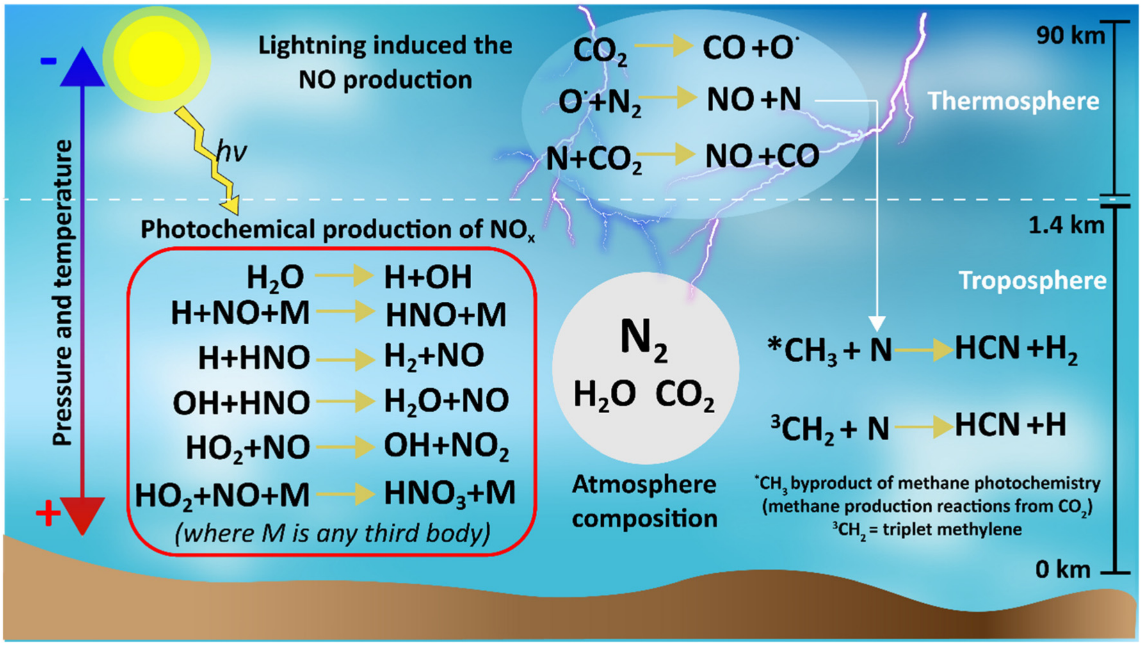

Fig. 5 Summary of the reactions for nitrogen species production under a reduced atmosphere in the Hadean time.

Could the chemistry of early oceans have promoted nitrogen fixation?

The aqueous composition of the Hadean waters is likely key to understanding the underlying chemistry and possible origins of biological nitrogen fixation. The high pressures of the atmosphere would have directly affected the dissolved gases and the reactions which took place. Hadean waters were acidic (around pH 5–6) due to the high concentration of atmospheric CO_2,[17,54,55] and the salinity was at least twice the current values.[56] There is no consensus on the temperature, but it is believed to have been in the range of 50–100° C, the higher temperature than today being the result of high hydrothermal activity.[57,58] Marine sedimentary rocks collected from Archean times (just after the evolution of photosynthesis) were reported to have high concentrations of iron and silica. These findings, along with the presence of $Fe^{2+}_{(aq)}$ in large amounts in the deep Archean ocean, imply anoxic ocean conditions.[20,59] Additionally, it is thought that there was a substantial amount of dissolved phosphate in the Hadean ocean in the form of orthophosphate mixed with iron (around 6–9 mmol kg^{-1}) supplied by volcanic emissions into the ocean.[60,61]

The prevailing chemistry of the Hadean waters before the advent of oxygen was very different from today. Oxygen substantially influences metal speciation in aqueous environments. For example, dissolved Fe^{2+} disappeared after the evolution of oxygenic photosynthesis precipitating as $Fe(OH)_3$ species and forming the banded Fe formations that we know today.[17,25,62] Prior to the emergence of photosynthesis, molybdenum would have existed in the ocean in the form of sulfide species. With the rise of atmospheric oxygen, molybdenum would have oxidized, changing the dominant species to oxyanions, such as molybdates (MoO_4^{2-}) and related species. From lightning strikes noted above, it is thought that over a long time period, NO_x species were dissolved in the oceans, along with the presence of reducing agents like H_2S/HS^- species and $H_{2(aq)}$ in different microenvironments (*e.g.*, hydrothermal vents). These conditions, along with the effect of high pressures and temperature gradients, would have made ammonia formation in Hadean waters much more thermodynamically favourable than today.[62–64] A comparison of the aqueous chemistry of the Hadean is summarised and compared to hydrothermal vents in Table 1. It is clear from the pressures and temperatures alone that ammonia would have been thermodynamically easier to form than in the oceans of today. This is also clear from the Pourbaix diagrams shown in Fig. 3.

Hydrothermal vents

Before the exploration of the deep ocean floors in 1977 by John Edmond and Jack Corliss on the crest of the Galapagos Rift (2500 m depth),[80] the idea of a poor life environment in the ocean was generally accepted. This assumption was based on the fact that most life requires a direct source of energy, which for terrestrial life is provided by sunlight, and this light can only reach ~300 m down into the oceans meaning there would not be life at the bottom of the ocean.

This deep ocean exploration challenged the prevalent idea at that time, unveiling an ocean full of life. The important question that arose with this new finding is where and how those organisms fulfilled their energy requirements and whether understanding these processes could help us better comprehend primitive metabolism.

It is believed that in the Hadean times, hydrothermal vents could also provide suitable conditions for abiotic nitrogen fixation, which is considered one of the cornerstone reactions in most theories on the origins of life.[43,81–83] Thus, knowing the composition of these hydrothermal systems could offer some critical insights into the chemistry of nitrogen fixation reactions.

A hydrothermal vent originates from faults and fissures caused by the subduction of tectonic plates in basaltic crusts, which allow the flux of cold seawater to the roof of magmatic centres. Then, as the heated fluids are chemically modified by the interaction with surrounding rocks, and expelled, this heated fluid leaks through fissures at ~350 °C full of chemical reductive species such as sulfide and hydrogen.[84] The interactions between the expelled material and their surroundings produce gradients of pH, temperatures, and a variety of chemical sources, which provide a stock of reactants for relevant redox reactions.[85]

Due to the multiplicity of the host rock and the diversity of tectonic conditions, two types of hydrothermal vents have been described, ‘black smokers’ and ‘LCF’ hydrothermal systems. While black smokers are fuelled by volcanic activity, the LCF hydrothermal system is the result of the interaction between sea water and minerals in the Earth’s mantle along with serpentinization (*i.e.*, hydrolysis and transformation of ferromagnesian minerals to produce H_2-rich fluids). Although the exact composition of hydrothermal vents in the Hadean oceans is unknown, recent studies have measured the composition of hydrothermal vents on Earth today. These are described in Table 1 in comparison with the key chemistry of relevance for known nitrogen fixation.

A comparison between the composition of hydrothermal vents (black smokers and LCF) and the modern ocean is given in Table 1. Clear differences are evident in terms of the speciation and amounts of key elements including iron, molybdenum, and sulfur. Differences between the pH and temperatures of the hydrothermal vent systems and the surrounding waters offer states of redox disequilibria or redox gradients, and these gradients, along with the depth–pressure effect, could be relevant in terms of speciation and solubility and more importantly could shift the equilibrium of the chemical reactions under the conditions of hydrothermal vents that would ignite some of the first and key redox reactions for the origin of life.[86,87]

An interesting aspect of the chemistry of hydrothermal vents is the presence of chemolithotrophic life. It is thought that these types of organisms are amongst the most ancient on Earth. A chemolithotrophic microorganism draws its energy of metabolism from redox reactions with inorganic compounds/minerals. In these reactions, it is often compounds like iron

Table 1 Conditions in the Hadean *vs.* the specific conditions in hydrothermal vents. The table is compiled using data presented in ref. 65 and 66

Hadean ocean		Hydrothermal vents (on Earth today)		
Atmosphere	Primitive crust and mantle	Type I: lost city field (LCF)	Type II: black smokers[b]	Modern ocean
Temperature and pH ~85 °C; slightly acidic.[67] Hydrogen Small quantities of H_2.[35]	**Temperature and pH** ≲20 °C; pH ~5–6	**Temperature and pH** ~40–90 °C; pH ~ 9–11.[68] Hydrogen around 20 mmol kg^{-1}.[69]	**Temperature and pH** ~405 °C; pH ~ 2–3.[68] Hydrogen 0.1–50 mmol kg^{-1}.[70]	**Temperature and pH** ~2 °C; pH 7.5.[65] Hydrogen 0.3 nmol kg^{-1}.[65]
Composition H_2O, N_2, CO_2 (around 1–10 bar[17,55]), CO and small quantities of H_2, CH_4, NO, P_4O_{10}, SO_2 and S_8.[35]	**Composition** Ag^0, Au^0, Cu^0, Ni^0, Fe^0 and Al silicates with traces of metals.[71] CO_2 ~ 100–1000 times more than today	**Composition (mmoles per litre)** Na^+ 479–485 K^+ N/A Ca^{2+} 21.0–23.3 Cl^- 546–549 CO_2 not registered **Composition (µmoles per litre)** Li^+ not registered Mn^{2+} ~ 4.1 ppm Zn^{2+} traces Cu^{2+} ~ 1.24 ppm P (as PO_4^{2-}) traces CH_4 0.13–0.28.[65,66,72]	**Composition (mmoles per litre)** Na^+ 543–584 K^+ 17–20 Ca^{2+} 26–31 Cl^- 633.5659 CO_2 3.9–215 **Composition (µmoles per litre)** Li^+ 367–411 Mn^{2+} 666–1000 Zn^{2+} > 36–46 Cu^{2+} > 83–150 P (as PO_4^{2-}) 2.5 CH_4 5000–45 000.[65,66]	**Composition (mmoles per litre)** Na^+ 461 K^+ 9.9 Ca^{2+} 10.31 Cl^- 541.5 CO_2 2.3 **Composition (µmoles per litre)** Li^+ 27.5 Mn^{2+} 10^{-3} Zn^{2+} < 10^{-3} Cu^{2+} < 10^{-3} P (as PO_4^{2-}) 0.5 CH_4 10^{-3}[65,66]
Mineral composition The ocean crust in the mafic, felsic and komatik lavas was composed by various minerals such as ferrous iron silicates, olivine, pyroxene, plagioclase and calcic feldspars, magnetite and pyroclastic, ultramafic, serpentinite and other metal precipitates.[36,57]		**Mineral composition** Aragonite ($CaCO_3$), brucite (Mg $(OH)_2$), Olivine ((Mg, Fe)$_2$ SiO_4) and calcite ($CaCO_3$)	**Mineral composition** Sulfide-complexing metals (Fe, Mn, Cu, Cd Pb and Zn),[73,74] made principally of pyrite (FeS_2) and chalcopyrite ($CuFeS_2$). Carbonates, amorphous silica, ferrous and ferric oxyhydroxides, zeolites and various sulfide (Fe, Ni, Zn) amorphous silica.[57]	

Species of interest to Nitrogen fixation

Hadean ocean	Hydrothermal vents (on Earth today)		
Primitive crust and mantle[c]	Lost city field (LCF)[a,e]	Black smokers[b]	Modern ocean[d]
Molybdenum (Mo) ~100 ppm as MoS_x	Molybdenum (Mo) ~10 000 ppm	Molybdenum (Mo) Traces	Molybdenum (Mo) ~10 000 ppm, it forms a soluble ionic species, MoO_4^{2-}, with a long residence time of 760 000 years[75]
Nickel (Ni) ~1200 ppm as Ni^{2+}	**Nickel (Ni)** ~20 ppm as Ni^{2+}	**Nickel (Ni)** Traces metal	**Nickel (Ni)** ~600 ppm as Ni^{2+} with residence time, from 5000 to 50 000 years[75]
Iron (Fe) Substantial concentrations of Fe^{2+}.[71]	**Iron (Fe)** 50 ppm as a mixture of Fe^{2+}/Fe^{3+} Rich in iron sulfide minerals	**Iron (Fe)** 300 ppm (mostly Fe^{2+}) Rich in iron sulfide minerals	**Iron (Fe)** 30 ppm mostly as $Fe(OH)_3$
Sulfur speciation H_2S ~ 66% HS^- ~ 33% S^{2-} ~ 0.0%[70]	**Sulfur speciation** H_2S ~ 4% HS^- ~ 94% S^{2-} ~ 1%[70]	**Sulfur speciation** H_2S ~ 56% (3–110 mmol kg^{-1}) HS^- ~ 43% S^{2-} ~ 0.0%[70]	**Sulfur speciation** H_2S not detected SO_4^{2-} ~ 898 × 10^6 corresponding to 98% of sulfur species

[a] Data from Kelley, S. D. *et al.*, 2001.[76] [b] Data from Beatty, J. T. *et al.*, 2005.[77] [c] Estimated mean concentrations of trace metals in the Archean ocean, based on trace element concentrations in Archean marine pyrite data from Large, R. R. *et al.*[75] [d] Data values of the modern ocean in ppt data from Nozaki, 2010.[78] [e] Data collected from black smoker fluids, associated with hydrothermal plumes at the Rodriguez Triple Junction, Central Indian Ridge.[79]

sulfur species which act as reducing agents, providing the critical electrons that are necessary to support metabolism.[88,89] Chemolithotrophs can use different compounds including Fe^{2+}, CO, N_2, H_2, H_2S, HS and other sulfur compounds as a source of electrons.[90] Although separately both iron and sulfur compounds can supply the electrons in a wide range of sulfur-oxidizing bacteria (*e.g. Thiobacillus thiooxidans*)[91] and iron-oxidizing bacteria (*e.g. Thiobacillus ferriooxidans*),[92] recent studies show that the reaction of FeS with H_2S to produce FeS_2 may be the energy source to support chemolithotrophic metabolism in some bacteria.[93]

Chemolithotrophic bacteria have been harnessing the redox capability of the omnipresent iron sulfides to proliferate under extreme conditions (pH $\leq$ 3 and temperatures above 100 °C). Some of the key reactions of chemolithotrophic metabolism are present in modern enzymes, not as a primary energy source, but as an important regulator or modulator of metabolism. Consideration of chemolithotrophic processes in mediating reduction reactions is important as they are not catalytic, rather they represent direct redox processes often capable of changing key small molecules. It is possible that the direct cycles of oxidation and reduction mediated by the chemolithotrophs are evolutionary precursors to modern enzymes.

Redox gradients as a source of energy through redox reactions

The theories of the dawn of life on Earth are deeply connected to a constant supply of energy. The flow of energy is the engine of any chemical reactions and it is thought that these reactions first arose with primitive organisms.[68,94] Thermodynamically, pH, temperature, and redox gradients can be used as ways to generate energy. Thus, the micro-environments such as hydrothermal vents and their interactions with the early ocean crust and ocean waters harbor those gradients. The use of reduction power from hydrogen sulfide (H_2S) has been hypothesized to be one resource to drive the chemical reactions in the Hadean waters.[81,95] Additionally, the redox chemistry of iron-based compounds with hydrogen, water, and oxygen under hydrothermal conditions could have been involved in some of the key reactions in life's origin theories.

Recent studies show that iron sulfides can reduce nitrite under both catalytic and direct redox conditions. Of the materials tested, amorphous mackinawite showed the highest nitrite reduction under both conditions.[96] Additionally, the incorporation of ~10% of molybdenum into the amorphous mackinawite structure increased the selectivity of nitrite reduction to ammonia.[97]

Reductive fluid: H_2S/HS^-

Some of the most common reductants in natural systems are H_2S, HS^-, and H_2. It is likely that they existed in considerable amounts in hydrothermal vents and in the Hadean ocean representing a likely electron source for the chemical reduction equivalents necessary for early metabolism. Hydrogen sulfide (H_2S) is the most reduced form of sulfur. Sulfide in all its forms S^{2-}, HS^- and H_2S is often an overlooked mediator of reduction but it is a strong reductant capable of shuffling 8 electron steps between S^{2-} and $SO_4{}^{2-}$. One of the greatest contrasts between the Hadean ocean and the ocean of today is the sulfur speciation. For comparison, in the modern ocean, there are large amounts of sulfate (oxidation state +6, Table 1). At the black smoker vents, the absence of oxidants, the high temperature and pressure along with low pH favour high concentrations of both H_2S and other gases like N_2.[74,98]

There is much speculation on the origins of life and theories including the "iron–sulfur world",[99] an "iron–sulfur membrane"[100] or a "zinc world"[66,101] and more recently "geo-electrochemistry theory",[83,102,103] all of which propose that H_2S is the main provider of electrons to drive the fixation of key molecules, including ammonia and carbon dioxide.[104,105]

Iron sulfide materials (Fe_xS_y)

As a result of anoxic and specific thermodynamic and redox conditions, an initially formed iron sulfide precipitate can evolve in a wide range of phases, which span from amorphous nanosized colloids to well-defined crystalline phases.[106–108] From their precursors, *i.e.*, Fe^{2+} and HS^-, iron sulfides usually initially precipitate in a compound known as a mackinawite-like nanoparticulate ($n\text{FeS}_{\text{am}}$, with n > 150), which is subsequently transformed into amorphous mackinawite by the ageing process. Fe^{2+} and HS^- can also produce more ordered phases *via* oxidative transformations. Two of the most well-known are greigite (where iron oxidizes from Fe^{2+} to Fe^{3+}) and pyrite (where S oxidizes from S^{2-} to S^-) (Fig. 6).[109,110]

Additionally, the initially precipitated amorphous mackinawite (FeS_{am}) can evolve into other iron sulfide phases including pyrrhotite/troilite and marcasite.[106–108] In terms of the natural distribution, pyrite is the most abundant form of iron sulfide, followed by pyrrhotite, marcasite (FeS_2, polymorph of pyrite) and troilite.[111]

There is a large amount of research demonstrating that iron sulfides are among nature's strongest chemical reductants.[109] The selectivity and scope of the reduction chemistry mediated by iron sulfide minerals are not well understood.[112] Much of the existing research into the geochemical properties of iron sulfides focuses on their crystal structure, and thermodynamic high-pressure phase transitions rather than their reactivity.[111,113] Furthermore, it is often the case that highly disordered nanoparticles (or nanomaterials) have a distinct reaction chemistry from their well-ordered cousins.[114,115] This may mean that disordered forms of iron sulfide minerals are even stronger reducing agents than their more ordered cousins.[112]

Importantly, recent studies into materials for water oxidation have found that minerals are often most reactive in their amorphous, or disordered forms, and the same could be true for catalysts for the reduction of small molecules. The extent to which disorder affects the reduction chemistry of iron sulfides and whether it affects their ability to chemically reduce molecules like CO_2 are not known.

Several attempts to describe the role and mechanisms of iron sulfide materials in the synthesis of prebiotic organic molecules have been explored in recent years.[18,117–121] There

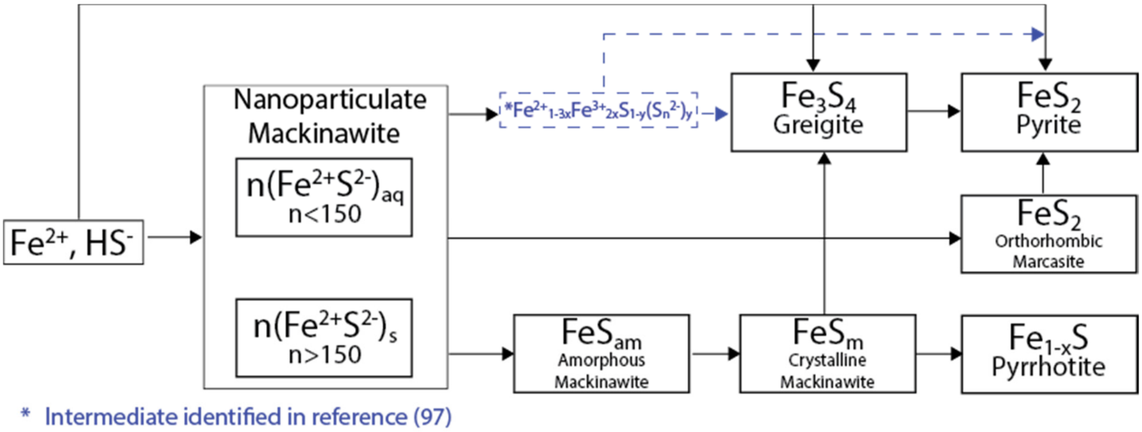

Fig. 6 Oxidation pathways for iron sulfide materials. Figure adapted from ref. 116.

remains uncertainty about the dual behaviour of these materials which have the ability to work as both catalysts and direct reducing agents. Studies in the reduction of nitrogen compounds in low pH solutions show that ammonia formation is linked with the oxidation of FeS to FeOOH compounds,[118] while the use of iron sulfides as catalysts in ammonia production under hydrothermal conditions (temperature ~300–800 °C and pressure ~0.1–0.4 GPa) was achieved with yields of 21% to 89% (NH_4^+ was quantified in this study using the indophenol blue method).[16]

Mackinawite

Mackinawite is the first formed phase upon mixing Fe^{2+} and HS^-. Mackinawite has received special attention in the last decade due to its geological relevance as a probable precursors of basic molecules in the abiotic theory for the origin of life, and also because of their sorption capacity.[122–124] In addition, this material has a remarkable chemical reactivity, which even provides the capacity to transform halocarbons *via* chemical reduction.[124–126] Generally, freshly precipitated mackinawite is an amorphous hydrated nanomaterial,[127,128] which can act as an intermediate precursor of more stable crystalline phases such as pyrite (FeS_2), marcasite (FeS_2), and greigite (Fe_3S_4).[129]

Synthetic mackinawite is usually prepared at room temperature and the most commonly used synthetic method involves mixing a sulfide solution with metallic iron or a ferrous iron solution. Mackinawite was the last of the major iron sulfides to be characterised by crystallography, as it was hard to grow crystals of it. The first experiments relied on electron diffraction[130] rather than X-ray diffraction owing to its lack of crystallinity, as opposed to other crystalline iron sulfide phases, which were characterised crystallographically as early as the 1930s. Mackinawite in its crystal form has been described as a tetragonal crystal system with space group $P4/nmm$ and with unit cell: a = 3.67 Å, c = 5.03 Å in its unit cell (Fig. 7).[123,131]

Greigite (Fe_3S_4)

Greigite is known for its ferromagnetic properties and as the sulfur analogue of magnetite.[132] This material is found in sedimentary rocks and its formation is commonly the result of the actions of sulfate-reducing bacteria. Additionally, greigite is an intermediate on the pathway from mackinawite to pyrite.[109] The greigite structure has an inverse spinel structure with a cubic close-packed sulfur array with space group $Fd3m$ and unit cell a = 9.876 Å. This arrangement (Fig. 8) shows significant similarity with the cubic, closely packed S-array of mackinawite. Greigite formation from mackinawite is an iron oxidation process, producing ferric (Fe^{3+}) iron.[109]

Pyrite (FeS_2)

Pyrite is the most thermodynamically stable and abundant compound on Earth among the iron-sulfides.[109] Under anaero-

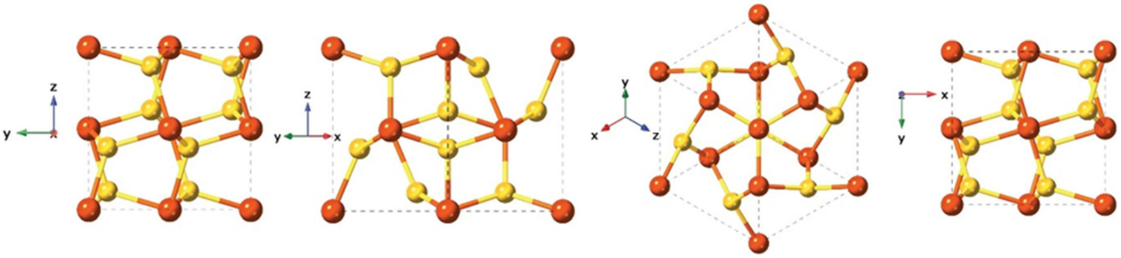

Fig. 7 Different crystal face views of the mackinawite structure.

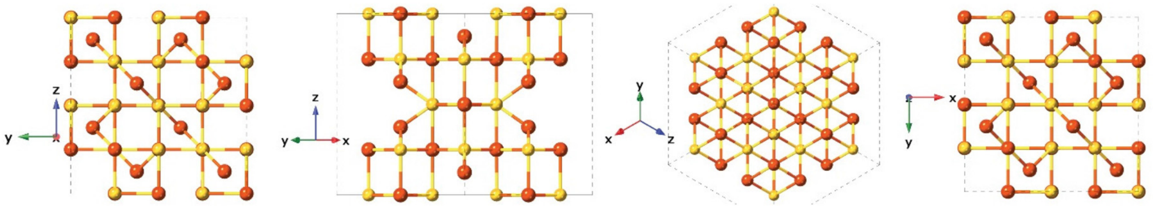

Fig. 8 Different crystal face views of the greigite structure.

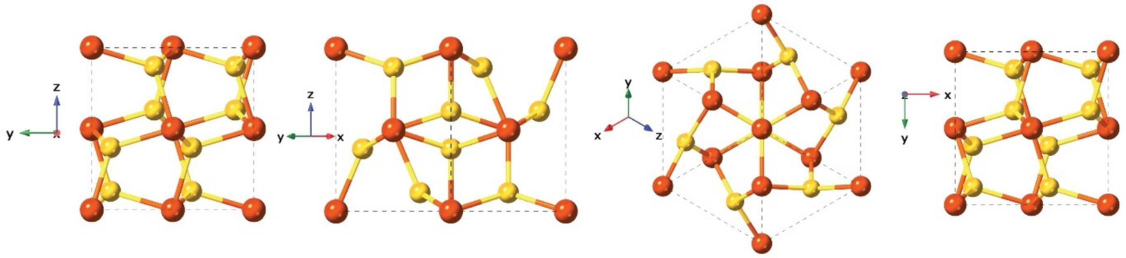

Fig. 9 Different crystal face views of the pyrite structure.

bic conditions, oxidation of iron sulfide(FeS_x) to pyrite(FeS_2) shows significant reducing power, which several studies suggest was involved in key reactions in the early carbon fixation process, for example, the reduction of carbonyl groups to methylene.[133,134] As a consequence, it is postulated that pyrite could participate in reactions included in the chemoautotrophic origin of life theory.[99,134,135] Pyrite formation is associated with metamorphic, igneous, and sedimentary rocks. The pyrite structure is typically cubic with space group *Pa*3 and cell parameters a = 5.142 Å (Fig. 9). Pyrite formation from FeS_{am} is a complex, ligand oxidation-based process.[109] Although pyrite is generally considered a non-reactive phase, its aqueous oxidation is an electrochemical process rather than a purely chemical reaction and this produces a range of compounds including sulfur, polysulfides, iron oxides and oxyhydroxides, sulfate and ferrous iron, which could contribute to the reactivity of pyrite.[136]

Marcasite (FeS_2)

Marcasite and pyrite are polymorphs that have the same chemical structure and common chemical environment but differ in their crystal structure. While pyrite is typically a cubic structure, marcasite is orthorhombic,[137] with lattice parameters: a = 4.443 Å, b = 5.424 Å, c = 3.387 Å, space group *Pnnm*. Although marcasite presents a higher conductivity and stronger Fe–S bonds along with weak S–S interactions.[138]

Pyrrhotite ($Fe_{1-x}S$)

After pyrite, pyrrhotite is the second most common iron sulfide in nature, it is a non-stochiometric compound with the calculated formula $Fe_{1-x}S$, where x varies from 0 (FeS, known as troilite), to 0.125 (Fe_7S_8), and is often associated with pyrite and is found in diverse sulfidic ores.[139] Under acidic conditions pyrrhotite is highly soluble and can produce Fe^{2+} and a mixture of polysulfides.[139]

Troilite (FeS)

Although troilite is more thermodynamically stable than mackinawite, its occurrence on Earth is not common. It is more abundant on the Moon, Mars, and meteorites.[140] Troilite is normally associated with serpentinized rocks and its formation is correlated with strongly reducing conditions.[140] Troilite is the iron-rich end member of the pyrrhotite group. Their crystal form has been described as a hexagonal crystal system with space group $P\bar{6}2c$ and with lattice parameters a = b = 5.962 Å, c = 11.750 Å (Fig. 10). It is not formed as a direct precipitate, rather it is the product of hydrothermal synthesis under anoxic conditions and at high pressures.[109]

Nitrogen compounds reduction reactions mediated by iron sulfides

Several attempts to describe the molecular-based mechanisms of the reduction of nitrogen compounds to produce ammonia mediated by iron-sulfide materials have been reported in recent years.[18,117,118,120,121,141] Interestingly, no clear distinction is made in terms of the reduction mechanism. Thus, certain studies characterize iron sulfides as mediators that facilitate redox reactions, while others describe the role of iron sulfides as catalysts in the reduction of nitrogen compounds.

Iron sulfides as reductants of nitrogen compounds

In 1993, Summer and Chang[119] suggested that under early Earth conditions, the presence of iron(II) could be responsible for the reduction of nitrogen compounds such as nitrate

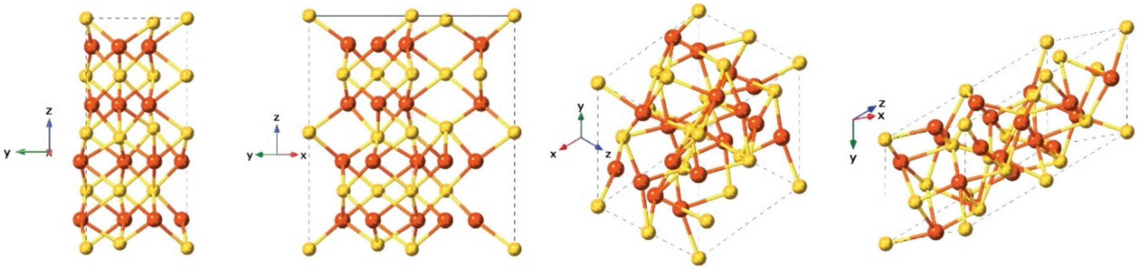

Fig. 10 Different crystal face views of the troilite structure.

(NO_3^-) and nitrite (NO_2^-) to ammonia (NH_3) according to eqn (3). This reaction is favored by alkaline conditions (pH between 7.3 and 9.0) and temperatures above 25 °C.[119]

$$2Fe^{2+} + 5H_2O + NO_2^- \rightleftharpoons 2Fe(OH)_3 + (OH)^- + NH_3 \quad (T > 25°C) \tag{3}$$

These researchers also suggested that the reduction of nitrate to ammonia is slower by a factor of eight than with nitrite and the yield in ammonia is directly proportional to temperature. Also, it is postulated that the presence of anions, cations, and salts can be considered as interferences due to the possibility that these compounds create complexes with iron(II) and nitrite, thus blocking the active sites.[119]

In a later work, Summers[118] experimented with the reduction of nitrite but this time performed the reaction under acidic conditions using different iron-sulfide materials (Fe_xS_y). He found that at low pH values the reduction reaction involved the iron sulfide surface and not the Fe^{2+} in solution. Furthermore, it was shown using energy dispersive X-ray spectroscopy (EDX) that after being exposed to nitrite, the bulk surface of iron-sulfide was more sulphur-rich compared to when nitrite was not present. Thus, this study suggested that a thin layer of pyrite (FeS_2) was formed on the iron-sulfide materials, according to eqn (4). The remnant iron(III) can react with water to produce $Fe(OH)_3$, which explains the brown supernatant that appears a couple of hours after the reduction reaction.[118]

$$2FeS \rightleftharpoons FeS_2 + Fe(OH)_3 + 3e^- \quad (T = 25°C) \tag{4}$$

Dörr *et al.*[18] explored nitrogen reduction by freshly precipitated iron sulfide, this study highlighted that the main reaction driver is the oxidation of iron sulfide (FeS) to iron disulfide (FeS_2) (eqn (5)). The proton supply came from hydrogen sulfide (H_2S) acting as a reductant. They demonstrated that the reduction of dissolved dinitrogen to produce ammonia was thermodynamically affordable using the redox reaction shown in eqn (6).[18]

$$FeS + H_2S \rightleftharpoons FeS_2 + H_2;\ \Delta G° = -38.6\ \text{kJ mol}^{-1};\ E° = -600\ \text{mV};\ \text{pH} = 6.5 \tag{5}$$

$$N_2 + 3FeS + 3H_2S \rightleftharpoons 3FeS_2 + 2NH_3 \quad (T < 90°C) \tag{6}$$

The chemical reduction of nitrite $(NO_2)^-$ by Fe^{2+} was studied in an environmental context by Kampschreur.[142] According to their results, the final product of the reduction of nitrite at pH = 6.5 was nitrous oxide (N_2O) with nitric oxide (NO) as an intermediate.[142] These reactions are shown in eqn (7) and (8).

$$NO_2^- + Fe^{2+} + 2H^+ \rightleftharpoons Fe^{3+} + NO + H_2O \quad (T = 35°C) \tag{7}$$

$$2NO + Fe^{2+} + 2H^+ \rightleftharpoons Fe^{3+} + N_2O + H_2O \quad (T = 35°C) \tag{8}$$

Singireddy *et al.*[117] explained how pyrite (FeS_2) in the Hadean can provide sites for the reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to produce ammonia (NH_3) in the temperature range of 20–120 °C for nitrite and at 120 °C for nitrate. The consumption of nitrite (NO_2^-) was explained by different reaction pathways. The first is the production of ammonia by Fe(II) according to eqn (3). Although this reaction is exclusive to alkaline pH, this study proved that the surface of pyrite releases Fe^{2+} under anoxic conditions and at acidic pH values. This free Fe^{2+} is responsible for a small amount of ammonia production.[117]

As part of this study Singireddy *et al.*[117] proposed two alternative pathways for the nitrite reduction presented in eqn (9) and (10). All these reaction mechanisms are not exclusive; on the contrary, they can occur simultaneously.[117]

$$10NO_2^- + 2FeS_2 + 8H^+ \rightleftharpoons 5N_2 + 2Fe^{3+} + 4SO_4^{2-} + 4H_2O \quad (T = 20\text{–}120°C) \tag{9}$$

$$15NO_2^- + FeS_2 + 14H^+ \rightleftharpoons 15NO + Fe^{3+} + 2SO_4^{2-} + 7H_2O \quad (T = 20\text{–}120°C) \tag{10}$$

Pyrite (FeS_2) can facilitate the reduction of nitric oxide (NO) produced in eqn (7) and (10) to ammonia according to eqn (11). In this latest reaction, the authors proposed that pyrite acts as an electron donor, thus the N bound to the pyrite surface is more reactive due to electron donation from the iron atom. This flow of electrons promotes protonation of the N-site to form HNO. Consecutive protonations can result in the ONH_2^+ species, which activates the final cleavage of the O–N bond to finally produce ammonia (NH_3).[117]

$$3NO + FeS_2 + 5H_2O + 2H^+ \rightleftharpoons Fe^{3+} + 3NH_4^+ + 2SO_4^{2-} \quad (T = 70\text{–}120°C) \tag{11}$$

Gordon *et al.*[143] investigated the kinetics of the reduction of NO_3^- and NO_2^- to NH_3 using fresh mackinawite, and identified the main intermediates in the surface bonding process on the freshly precipitated nanocrystalline mackinawite at different temperatures and under alkaline conditions. This study suggested that the formation of NO is a key intermediate step in ammonia production and it is possible at 120 °C. The redox couple proposed by the authors are reported in eqn (12) and (13).

Interestingly, the activation energy calculated for the ammonia production at 120 °C on the surface of fresh mackinawite using NO_2^- is ~62.76 kJ mol^{-1}, almost half the energy required for NO_2^- reduction by $Fe^{2+}_{(aq)}$.[18,119] Thus, the FeS_m surface represents a feasible way to produce ammonia with a lower energy barrier.[143]

$$FeS_m + H_2O + 9NO_2^- \rightleftharpoons Fe^{3+} + SO_4^{2-} + 9NO + 10OH^- \quad (T = 120°C) \tag{12}$$

$$16H_2O + 9NO + 5FeS_m \rightleftharpoons 9NH_3 + 5Fe^{3+} + 5SO_4^{2-} + 5OH^- \quad (T = 120°C) \tag{13}$$

Iron sulfides as a catalysts for redox transformation of nitrogen compounds

Brandes *et al.*[16] demonstrated experimentally the feasibility of mineral catalysed reduction of nitrogen compounds to ammonia under conditions of the hydrothermal vents and the ocean crust, with temperatures between 300–800 °C and 987 atm (0.1 GPa) and 3948 atm (0.4 GPa).[16] Additionally, they tested how changes in pressure affect the yield in ammonia for two systems, namely magnetite-formic acid-nitrogen ($Fe_3O_4/HCO_2H/N_2$) and metallic iron–water–nitrogen ($Fe–H_2O–N_2$). The increase in pressure from 98.7 atm (0.01 GPa) to 987 atm (0.1 GPa) was accompanied by ~10% increase in ammonia for both systems and a further increase of the pressure did not show any significant change in yield.[16]

Li *et al.*[144] proposed that sulfur complexes with molybdenum (Mo) could act as a catalyst in the reduction of nitrogen compounds (NO_2^- and NO_3^-) to form ammonia. Under the conditions found in the hydrothermal environments, the electrochemical experiments performed by Li *et al.*[144] revealed that at neutral pH and in the absence of NO_2^- (which was used as the substrate), MoS_2 produced a cathodic current above −1.8 V *vs.* the reversible hydrogen electrode (RHE) often associated with the hydrogen evolution reaction (HER). After the addition of nitrite, the onset potential changed from −0.18 V to 0.07 V. The identity of the products generated was determined using online differential electrochemical mass spectroscopy (DEMS) which concluded that the reduction of nitrate to form ammonia produced intermediates such as NO and NO_2.

The synthesis of ammonia from nitrate (NO_3^-) is kinetically more unfavourable than from nitrite (NO_2^-); in part due to the stability of nitrate.[145] Li *et al.*[144] also demonstrated that at neutral pH nitrate was reduced to ammonia and that the selectivity of this reaction over the HER was 100%. The authors applied potentials more negative than 0 V and found that the only intermediate detected was NO_2^-, suggesting that the reductive pathway is nitrate, nitrite, and ammonia.[144]

Li *et al.*[144] proposed a model incorporating the previous findings in terms of spontaneous electron generation in the inner hydrothermal vents by H_2S or H_2 and tested the conductivity of the iron sulfide-bearing walls in the hydrothermal vents. Also, the temperature–pH gradients were observed between the hot alkaline hydrothermal fluids and cold acidic seawater and the stable catalytic activity of MoS_2, where protonated Mo species act as a catalyst in the production of the intermediates and ammonia in a Proton Coupled Electron Transfer (PCET) mechanism (Fig. 11).[144]

Thus, the ammonia production from either nitrate or nitrite in hydrothermal vent environments relies on the electron flow generated by the oxidation of H_2/H_2S, and the transfer of these electrons to nitrate/nitrite in a catalytic reaction mediated by Mo–S catalytic centers. The source of protons could be either the same reductant species (*i.e.*, H_2/H_2S) or the acidic environment of the water surrounding the hydrothermal systems[144] (Fig. 11).

Here it is important to highlight that most enzymes operate using PCET in their redox reactions.[146,147] Also, the turnover frequencies (TOFs) found by nitrate/nitrite reduction using MoS_2 [144] are similar to the TOF in the nitrate reductases (1.8–33 s^{-1}),[148,149] and the presence of the Mo–S bonds in denitrification enzymes suggests the link between Mo–sulfide materials and the evolution of the current enzymes.[144]

Nickel is also a metal which commonly co-exists with iron sulfide minerals. For instance, in hydrothermal systems it is common to find deposits of awaruite (Ni_3Fe), and greigite (Fe_3S_4), and these minerals have been reported to effectively catalyse the reduction of CO_2.[150] Brandes *et al.*[151] demonstrated that nickel sulfides are able to convert nitrates and nitrites to ammonia under hydrothermal vent conditions. Nickel is often associated with the active sites of key enzymes (*i.e.* hydrogenases, carbon monoxide dehydrogenase), and its presence in eight different enzymes suggests that this metal was a key element in the evolutive pathways of enzyme systems.[152]

Nickel compounds are also widely applied in catalysis. Nickel-based catalysts have proved to have significant efficiencies for key reactions. For example, the most efficient layer double hydroxides/metal oxo-hydroxides (LDH/MOOH) type water oxidation catalysts are made of NiFeCr/NiFeV.[115,153,154] Notably, bulk iron nickel sulfides ($Fe_{4.5}Ni_{4.5}S_8$) have been

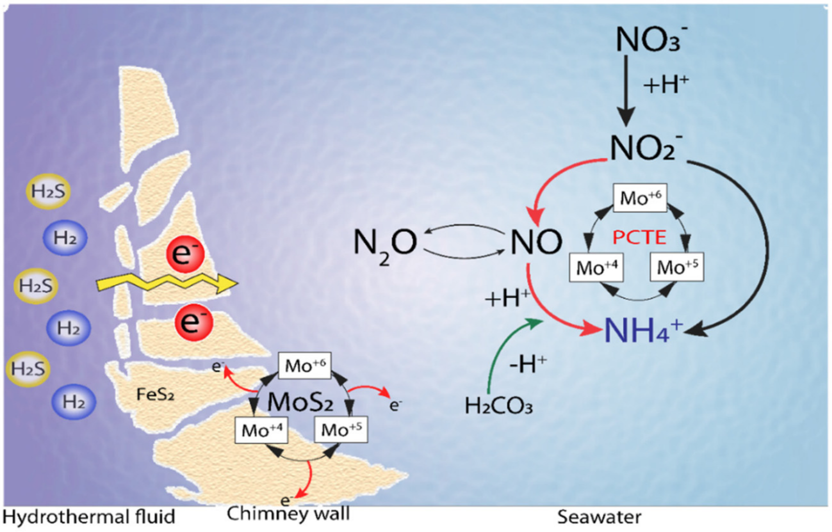

Fig. 11 Ammonia synthesis by MoS_2 under Hadean conditions. Adapted from Li *et al.*[144]

reported as highly reactive materials for the hydrogen evolution reaction (HER), reaching a current density (J) of 10 mA cm^{-2} and sustainable long term catalytic activities activity over a time (*i.e.*, 170 h at J > 600 mA cm^{-2}).[155]

Direct reduction *vs.* catalytic reduction

One interesting aspect of the iron sulfide materials is that they can act as both direct mediators of reduction as well as catalysts for reduction. We have recently studied the relationship between direct redox and catalytic chemistry as mediated by iron sulfides. Fig. 12 shows the selectivity of the reaction products obtained by iron sulfides as catalysts and contrasts it to that obtained from direct redox processes, at 1 day of reaction and pH = 4.5. Different iron sulfide members were tested, including the first precipitated product of Fe^{2+} and HS^- commonly named amorphous/nanocrystalline mackinawite (FeS_x) and some of more ordered phases such as greigite (Fe_3S_4), pyrite (FeS_2) and troilite (FeS). In addition, we include a molybdenum sulfide (MoS_x) as a reference for the evaluation of the effect of the incorporation of molybdenum into the FeS_x structure. Three different colored bars divide the NO_2^- reduction products. Ammonium-produced (orange), other nitrogen-reduced products (*i.e.*, ONRP = $\Sigma N_2O + NO + N_2$, grey) and the residual nitrite are given in blue.

In the context of the direct reduction reaction, it becomes evident that FeS_x and MoS_x samples exhibit high reactivity, compared to the more ordered phases. This could be explained as a consequence of the thermodynamic attributes inherent to disordered materials. It's important to note that this effect is not exclusive to iron sulfide samples; analogous phenomena

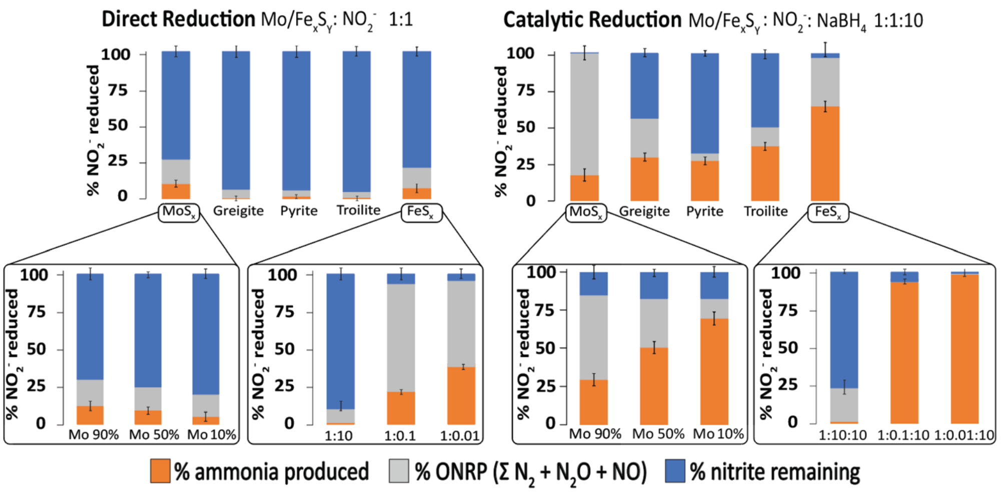

Fig. 12 Comparison of catalytic to direct reduction of NO_2^- mediated by Mo/Fe_xS_y as observed at 1 day of reaction and pH = 4.5. Error bars represent the 95% confidence interval derived from three replicates. Adapted with permission from ref. 97, copyright 2023, American Chemical Society and from ref. 96 with permission from John Wiley and Sons, copyright 2022.

have been reported for other materials.[112,156] Moreover, the results shown in the insert graphs demonstrate that modulating the $FeS_x : NO_2^-$ ratio and the percentage of Mo integration into the FeS_x structure shifts the distribution of reduction products.

In the catalytic reduction reaction, the same effects were observed, if the NO_2^- concentration is lower relative to FeS_x, more ammonia is produced. An interesting observation is the role of Fe/Mo content in product selectivity, samples with high content of iron show selectivity for ONRP over ammonia, while the presence of iron favoured ammonia production over the ONRP. The Mo/FeS_x samples with 10%Mo and 90% iron show the highest ammonia production and this is an interesting result because a similar ratio is found in nitrogenase.[96,97]

Thus, key thermodynamic factors play a role in the selectivity of products in nitrite reduction mediated by Fe_xS_y materials, including the concentration of the substrate relative to the catalyst, the amount of a secondary metal incorporated into the Fe_xS_y structure as well as the electron source and its chemistry.[96,97]

Perspectives in catalyst design

The electrochemical methods offer an attractive substitute for ammonia production over the Haber–Bosch process due to the fact that these can be performed at room temperature on a small scale and the energy required to power the process could be obtained by renewable electricity sources, particularly wind and solar.[157–159] Promising improvements have been found in recent years in the field of electrochemical nitrogen reduction to produce ammonia under room temperature conditions, yet the challenge to find a material with the optimal balance of activity, selectivity, stability, and efficiency remains.[160–162] No direct electrochemical process has been able to produce the significant amount of ammonia the Haber–Bosch process does. Several catalysts based on noble metals,[163] metal nitrides,[164] metal oxides,[165] nitrogen and boron-doped carbon,[166] and metal sulfides[167] have been proposed for the electrochemical nitrogen reduction reaction. However, there have also been many problems with some of these catalysts with authors reporting false positives on selectivity for ammonia production.[159,168]

Several aspects must be taken into account in the design of optimal catalysts for nitrogen fixation, the ideal catalyst should have high activity, selectivity for the desired products, stability and high efficiency (Fig. 13). The inherent activity of a given material is related to the electronic structure, and it could be tuned with heteroatom doping, or with a smart design of the defect/strain into the material, along with the pH. These could be the key to improvement of the activity of materials towards nitrogen fixation.[162,169,170]

Recent outcomes in the study of biological systems which mediated nitrogen fixation (enzymes), along with the pathways for abiotic natural ammonia formation in the early atmosphere and water bodies offer us a new perspective in the design of new materials able to produce ammonia under ambient conditions. Materials such as iron sulfides, which are present in both active sites of key enzymes for nitrogen fixation and in hydrothermal vents (most likely environments where key chemical reactions may happen for life's origin), could be good candidates for a new generation of catalysts.

Recent advancements in the investigation of biological systems, particularly those facilitating nitrogen fixation *via* enzymatic processes, along with the study of materials involved in abiotic routes to natural ammonia formation in early Earth, offer us a new perspective in the design of new materials able to produce ammonia under ambient conditions. Notably, iron sulfides, are present within the active sites of nitrogen-fixing enzymes and in the mineral structure of hydrothermal vents—environments likely key to primordial chemical reactions for life's origin—and emerge as promising materials for the next frontier of catalyst development.

Materials with the capacity to incorporate additional metals emerge as highly desirable candidates for the development of a new generation of catalysts. Multi-metal systems have received increased attention in catalysis in the last decade as they have been observed to exhibit higher activity/selectivity than the performance displayed by individual metals.[171,172] Although many of the chemical properties of the single metals

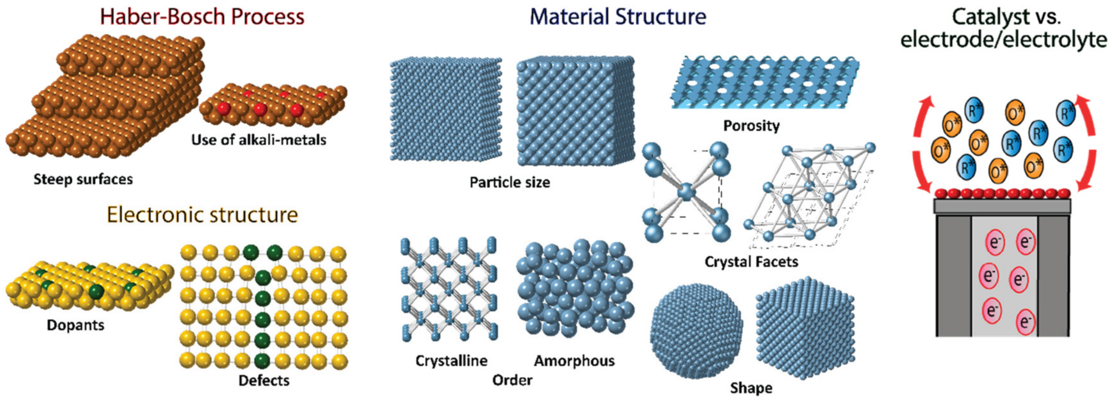

Fig. 13 Proposed approaches to enhance heterogeneous electrochemical NH_3 production from N_2.

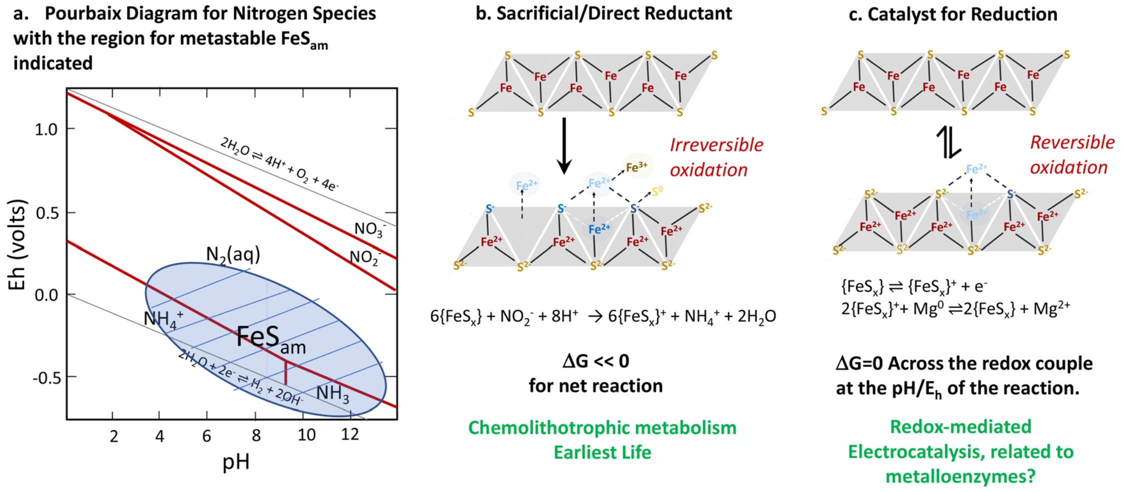

Fig. 14 Summary of the thermodynamics of redox and catalytic processes involving iron sulfides (a). A relationship between chemolithotrophic life (b) and more complex life (c). Reproduced from ref. 96 with permission from John Wiley and Sons, copyright 2022.

are preserved in a bimetallic system, the formation of heteroatom bonds changes the geometry and electronic structure of the metal surface, thus the chemical bonding between the metal catalysts and the key reaction intermediates is altered by the presence of the neighbours.[173,174] This strategic incorporation of extra metals offers a versatile approach to fine-tuning reactions, thus enhancing the efficiency and selectivity of the catalytic process.

The complex interplay between a material's capacity to facilitate direct reduction and its role as a catalyst for reduction reactions could also play an important role in catalyst design. While direct reduction is commonly associated with thermodynamic effects and catalysis is governed by kinetic effects, both reactions are driven by electron transfer rates, which in turn rely on the underlying thermodynamic stability. Consequently, comprehending the thermodynamic stability of diverse materials and their modulation in response to factors such as pH and substrate concentration has a key importance in catalyst design.

Conclusions

In conclusion, we highlight that iron sulfide materials (FeS_x) have a structural resemblance with metallo-enzymes (nitrogenases and hydrogenases) in terms of compositional structure and, to some extent, functionality. Both enzymes and iron sulfide materials are able to catalyse as well as directly mediate key reactions including the hydrogen evolution reaction and nitrate/nitrite reduction. The relationship between direct and catalytic reduction may be key for understanding some types of evolutionary processes. While we think about catalysis and direct reduction as distinct, if a material can be regenerated, as may be the case for some biological, nanoparticulate or metastable systems, a direct redox process can also be turned into a catalytic one. In the evolution of life, direct redox chemistry, in the form of chemolithotrophs whose metabolism comes from direct redox chemistry, likely preceded the catalytic processes of metalloenzymes (Fig. 14).

Despite the very interesting correlations with nitrogenase, the role of iron sulfide in the nitrogen reduction reaction is yet to be determined. It is possible that the highly disordered phases of iron sulfides are metastable with respect to some of the more established structures which may couple secondary redox processes in natural systems to perform nitrogen reduction. From our perspective, a clear and unambiguous system demonstrating this has not yet been developed.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We acknowledge support for this project from the Australian Research Council *via* DP200101878. Dr. Rosalie Hocking is grateful to Swinburne University for a Vice Chancellors's Women in STEM Fellowship. Mr C. Felipe Garibello recognises a Swinburne SUPRA scholarship.

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