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Minerals as Prebiotic Catalysts for Chemical Evolution towards the Origin of Life

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Abstract

A transition from geochemistry to biochemistry has been considered as a necessary step towards the emergence of primordial life. Nevertheless, how did this transition occur is still elusive. The chemistry underlying this transition is likely not a single event, but involves many levels of creation and reconstruction, finally reaching the molecular, structural, and functional buildup of complexity. Among them, one apparent question is: how the biochemical catalytic system emerged from the mineral-based geochemical system? Inspired by the metal–ligand structures in metalloenzymes, many researchers have proposed that transition metal sulfide minerals could have served as structural analogs of metalloenzymes for catalyzing prebiotic redox conversions. This assumption has been tested and verified to some extent by several studies, which focused on using Earth-abundant transition metal sulfides as catalysts for multi-electron C and N conversions. The progress in this field will be introduced, with a focus on the CO₂ fixation and ammonia synthesis from nitrate/nitrite reduction and N₂ reduction. Recently developed methods for screening effective mineral catalysts were also reviewed.

Keywords: Origin of life, mineral catalysis, CO₂ fixation, ammonia synthesis, chemical evolution

1. Introduction

Origins of life remain a mystery for our humankind. The concept of “chemical evolution” describes a general evolutionary route from the abiotic to the biotic world through a variety of chemical and physical processes. Kitadai. et al. summarized the reactions explored in the lab for the chemical evolution (**Figure 1**). Starting from geologically abundant molecules (e.g., N₂, CO₂, H₂, PO₄, NO₃[−], HCN, etc.), high energy input drives the synthesis of small organic molecules as precursors. These small organic molecules react with each other to form life’s building blocks (e.g., amino acids, nucleobases, sugars, aliphatic acids, etc.). Subsequently, these monomers polymerize into functional polymers which assemble into the so-called protocell.

Figure 1.
Overview of the chemical evolution of life, adapted from ref. [1].

As many life's building blocks are not stable at temperatures higher than 100°C [2], a geological setting with moderate temperature is considered to be more favorable for life's emergence. In addition, a moderate temperature can render the chemical system a kinetic control that will otherwise only generate the most stable products following thermodynamics under a high-temperature regime. Kinetic control is required to form metastable products. There are many challenges in chemical evolution, two of which are caused by reaction kinetics. First, in the beginning, how geologically abundant inorganic molecules were activated and converted into small organic molecules? Second, how the chemical reactions are directed towards a high molecular complexity and product diversity for selectively generating life's building blocks? In this regard, catalysis is at the center of chemical evolution. A catalyst lowers the energetic barrier and enhances the reaction rate of activation of inert molecules. Different catalysts with tuned surface property and electronic characteristics can regulate the reaction pathways by adjusting the transition states of the intermediates.

Geological molecules, as the feedstocks of prebiotic synthesis, are typically chemically inert despite their high abundances. The activation of small geological molecules, such as H_2 , CO_2 , etc., requires redox processes. H_2 needs to be oxidized to release the chemical energy while CO_2 needs to be reduced to synthesize organics which usually show intermediate valence states of carbon (from +3 to -3) [3]. Similarly, methane (CH_4), which was considered to be abundant on the early Earth in some scenarios [4], needs to be oxidized to synthesize useful organics. Therefore, in general, redox processes play an important role in chemical evolution.

The importance of redox processes for energy conservation is also reflected in modern biology, where modern living organisms are relying on enzymes for catalyzing biochemical reactions and maintaining homeostasis. In particular, redox

enzymes are important for organisms to harvest energy from geologically available molecules in their surrounding environments. For example, methanogens convert CO_2 and H_2 into methane, with the generation of proton gradient for ATP synthesis [5, 6]. Nitrogen-fixing organisms use redox enzyme nitrogenase to reduce N_2 into ammonia for N assimilation, which is a $6\text{e}^-/6\text{H}^+$ reaction ($\text{N}_2 + 6\text{e}^- + 6\text{H}^+ = 2\text{NH}_3$) [7, 8]. These metabolic reaction pathways were considered to be very ancient based on phylogenetic analysis, which could have appeared in the last universal common ancestor (LUCA) [9–11]. Redox enzymes accounting for these reactions highly rely on earth-abundant transition metals (e.g., Fe, Ni, Mo, etc.) due to the electron-shuttling property of these metal sites and the relatively high affinity of the *d*-orbital electrons with the small molecules. Meanwhile, the interaction between amino acid residuals from the surrounding peptides and the metallic center, and the ligands in the first coordination sphere, also plays an important role in the catalytic processes [12, 13]. This includes mediating proton transfers, stabilizing the intermediates through electronic interaction, etc.

However, before life emerged, it has long been considered that enzymes are too complex to be readily available. What are the geo-catalysts responsible for activating small molecules (including C-, N-, and S-related compounds)? Earth owns more than 5700 known species of minerals, with new species being identified every year (e.g., <https://rruff.info/ima/>). Both the variety and relative abundances of minerals have changed dramatically over the Earth's history, through various chemical, physical, and biological processes [14]. To understand the role of minerals in the origin of life, determining the first place to spawn the first life is an essential question. There are two dominating and contrasting scenarios of origins of life: those predicting that life emerged in the submarine, alkaline hydrothermal vent systems where the redox, pH, and T gradients keep the system far from equilibrium and serve as energy sources for prebiotic synthesis, as pioneered by Russell, et al. [4, 9, 15–18]; and those predicting that life emerged within subaerial environments with prebiotic synthesis driven by UV photolysis pioneered by Sutherland et al. [3, 19–23]. Both of these two scenarios implicitly emphasize the importance of redox processes for activating inert molecules. The former scenario proposed minerals (such as sulfides and hydroxides) as key players, while the latter relies on radicals and solvated electrons for redox conversions. Recently, an alternative scenario of origins of life in volcanic hot-spring water or the so-called “land-based pool” scenario was proposed by Damer and Deamer [24–26], to solve the self-assembly problem for membrane formation in the salty ocean while allowing condensation/polymerization through wet-dry cycle provided by the fluctuating boundary conditions. This scenario has been testified with self-assembly experiments simulating the hot-spring conditions [25]. Since the role of minerals hasn't been explicitly considered in the scenarios by Sutherland et al. and Deamer et al., only the scenarios involving mineral catalysis (e.g., alkaline hydrothermal vent (AHV) theory, iron-sulfur world theory by Wächtershäuser [27–31]) will be discussed in this chapter.

AHV theory was proposed based on the notion that the far-from-equilibrium condition in alkaline hydrothermal vent systems resembles biochemistry in the following aspects: (1) the large chemical disequilibrium is akin to the conditions the biology tends to live on and stably maintained through Earth's geological time; (2) the pH gradient sustained by the chimney rock wall resembles the chemiosmotic energy conservation shared by all life forms; (3) the transition metal-bearing mineral walls are rich in sulfides, which share the similar metal center and sulfur ligands with the modern Ni-, and Fe-bearing redox enzymes (e.g., carbon monoxide dehydrogenases, hydrogenase, ferredoxin, etc.) [9], thus could have catalyzed similar chemical conversions; (4) many

chemoautotrophic microorganisms were discovered in the deep-sea hydrothermal vents and their metabolism is suggested to be phylogenetically old and energetically fueled by the chemicals in the vents; (5) different from the acidic type, high temperature hydrothermal vents, the low temperature ($<120^{\circ}\text{C}$), alkaline, lost-city type hydrothermal vents renders kinetic control and could stabilize biomolecules formed in-situ.

Regardless of the scenarios, minerals have shown special functions in different types of prebiotic synthesis. Here in this chapter, a special focus will be posted on the redox catalysis mediated by minerals for the prebiotic synthesis, involving C, N, S, which are the fundamental elements of life and involved in a variety of redox conversions.

2. Why a catalytic system is important for prebiotic chemistry?

Before reviewing the state-of-art of mineral-catalyzed organic synthesis, larger questions here are: (1) Why catalysis is required for chemical evolution? (2) At which evolutionary period did catalysis begin to play an important role? The emergence of first life and the subsequent evolution from prokaryotes to eukaryotes all require well-regulated chemical conversion for efficient energy harvesting, sustainable supply of building blocks, and maintaining intracellular homeostasis. Eukaryotes developed more complex energy harvesting organelles that rely on respiration electron transfer chain and photosynthesis to metabolize with a higher transformation efficiency of energy and mass [32] (**Figure 2**). This is essential for maintaining their high cellular complexity in terms of both structure and functionality by balancing the enthalpy and entropy [36]. Notably, the enzymes responsible for these chemical conversions are catalytic, namely, the enzyme catalysts do not change chemically after one cycle or turnover of reaction, although enzymes indeed need replacement after the

Figure 2. The scenario of co-evolved catalytic system and life. During the continuous evolution from geochemistry to biochemistry, and the evolution of eukaryotes from prokaryotes, the gradually evolving catalytic systems serve as the physicochemical and energetic basis for promoting an increased energy transduction efficiency and reaction activity for supporting the higher complexity of (proto-)metabolism or (cellular) structures. Schemes of prokaryotic and eukaryotic cellular structures are adapted from Ref. [33]. Schemes for the electron transfer chains in photosynthesis and respiration are adapted from Ref. [34] and Ref. [35], respectively.

expiration of their lifetime. This catalytic feature is essential for boosting the reaction kinetics, saving energy for re-synthesizing enzymes, adapting to different substrate conditions, reversibly promoting both the two directions of the reaction, and so on [37]. As a comparison, in a non-catalytic, stoichiometric reaction, the active species that reacts with the geochemical substrates to target organics end up with a change in their chemical structures in an irreversible manner. After the complete consumption of the active species, the reaction can no longer proceed. From a top-down point of view, the prebiotic chemistry probably needs to evolve towards a catalytic, sustainable type of reaction network, to solve the problem of the shortage of supply of the building blocks/precursors, promote the reaction kinetics, and finally become self-independent when being encapsulated in a protocell. However, it should be noted that, at the initial stage of prebiotic synthesis, both catalytic and stoichiometric reactions are important for the synthesis of organic molecules to accumulate these organic precursors for subsequent conversion. As will be shown later, a large portion of prebiotic syntheses to date have been focusing on a stoichiometric type reaction, therefore, relying on active agents. However, for some reason, the term “catalyst” has been used occasionally and misleading. In the following session, special care will be paid to differentiate the “catalytic” and “stoichiometric” types of reaction.

3. Minerals promote the prebiotic synthesis

3.1 Carbon fixation and C-C bond formation

Miller-Urey experiments open up the whole field of prebiotic chemistry [38]. At that time, the early Earth atmosphere was considered to be reducing and mainly composed of reducing species, such as methane, H_2 , CO, NH_3 , etc. However, this has been questioned, and the current consensus is that the early Earth atmosphere was oxidizing, with CO_2 , N_2 , and H_2O as the major components, with a trace amount of H_2 [39]. Based on this, a chemoautotrophic scenario pioneered by Wächtershäuser was proposed [27–31]. The chemoautotrophic origin of life scenario relies on primordial carbon fixation within a sulfide-rich hydrothermal vent. Driven by the reducing energy and activation ability of carbon monoxide (CO), many types of reactions were demonstrated. For example, at $100^\circ C$, C-C bond formation with the generation of acetate proceeds on FeS and NiS from a mixture of CO and CH_3SH , or from a mixture of CO and H_2S alone with the addition of Se [27]. This reaction resembles the reductive acetyl-coenzyme A (acetyl-CoA) pathway, where the key enzyme, acetyl-CoA synthase, contains a Ni-Fe-S active center and forms acetyl-CoA from coenzyme A, CO, and a methyl group. CO was also demonstrated to promote the reductive polymerization of HCN to α -hydroxy acids and α -amino acids at $80 \sim 120^\circ C$ on FeS or NiS precipitates [29], where glycine and alanine were formed accompanied by glycolic and lactic acid. The polymerization of amino acids into short peptides was also demonstrated by CO activation [28]. In these experiments, high-pressure CO gas was used ($1 \sim 75$ bar) [29].

Based on the modeling of the atmosphere in the late Hadean period [39], the most abundant abiotic carbon feedstock on the early Earth is carbon dioxide (CO_2), with a trace amount of CO. Therefore, for the autotrophic origin of life scenarios, CO_2 was a more preferable and primary carbon source for primordial biosynthesis. CO_2 dissolved in the ocean and resulted in a mildly acidic ocean ($pH \sim 5.5$) [40]. Compared to CO, CO_2 is a chemically inert molecule that requires high activation energy. The

acetyl-CoA (AcCoA, or Wood-Ljungdahl) pathway is considered to be the most ancient autotrophic CO₂ fixation pathway in nature [41]. To answer the question of how CO₂ reduction occurs before the evolution of proteins, CO₂ reduction has been demonstrated by Varma et al. [42], that native transition metals (Fe⁰, Ni⁰, and Co⁰) can reduce CO₂ to acetate and pyruvate in millimolar concentrations. Moreover, in the AHV theory proposed by Russell and colleagues [9, 15, 18], the carbon fixation was driven by the direct redox coupling of CO₂ and H₂ on metal sulfides or oxyhydroxides [16]. Later, Lane and Martin [43, 44] also discussed the plausible relevance of the pH gradients in membrane-separated alkaline hydrothermal vent systems with the H⁺ gradients across the cell membranes that drive ubiquitous chemiosmotic coupling in all life forms. This scenario was approved in recent work by Sojo et al., that in a microfluidic system with a freshly precipitated thin Fe-, or Ni-sulfide mineral membrane, CO₂ in simulated sea water side was reduced to formate at several micromolar yield [45]. The reaction was likely promoted by pH gradient as evidenced by the boosted yield with increased pH gradient. This shows that CO₂ was reduced by Fe or Ni sulfide, probably through an electrochemical process coupled with the oxidation of H₂.

Inspired by Russell's AHV origin of life theory, in the past decade, an alternative scenario "geo-electrochemical driven carbon fixation" has been explored by Nakamura, Yamamoto, Kitadai, and their colleagues [46–55]. This theory is based on the pH, redox, and thermal gradients between the alkaline hydrothermal vent and seawater. Those gradients thermodynamically drive the redox conversions by coupling H₂ oxidation in the hydrothermal fluid/mineral interface with CO₂ reduction at the seawater/mineral interface. The experimental results show that CO₂ was effectively reduced to CO on certain types of sulfide, such as Ag₂S and CdS [53], with much higher efficiency than FeS and NiS despite their higher geological abundances [48, 53]. The product selectivity highly depends on the identity of the metal in the sulfide minerals. Using the CO gas generated by electrochemical reduction, many reactions that were reported in Wächtershäuser's experiments were confirmed [53]. Since the disequilibrium and gradients in the deep-sea hydrothermal vent system can be maintained throughout the Earth's early history, the geo-electrochemical CO₂ reduction provided a stable and sustainable source of CO which could have fueled the prebiotic synthesis. By simulating the geo-electrochemical conditions of alkaline hydrothermal vents, other researchers also reported CO₂ reduction to a variety of products, including formate [49, 53], acetate [49], methane [48, 52], pyruvate [49], C₂H₆ [52], methanol [49] on Fe- or Ni-containing sulfides.

Regarding the reaction mechanisms, relevance with biological enzymes has been suggested. In biology, the enzyme catalyzing the reduction of CO₂ to CO is carbon monoxide dehydrogenase (CODH) with a [NiFe₄S₄] cluster [56]. The reaction is considered to be the oldest pathway of biological carbon fixation and therefore may have been involved in the origin of life [9, 10]. Yamaguchi et al. first studied two metal sulfides greigite (Fe₃S₄) and violarite (FeNi₂S₄) and found that Ni-bearing sulfides show higher efficiency in reducing CO₂ [48]. Further, Lee et al. reported the in-situ FTIR spectroscopic analyses of the surface intermediate during electrochemical CO₂ reduction on these two minerals [52]. Intermediate species assignable to surface-bound CO₂ and formyl groups were found to be stabilized in the presence of Ni, lending insight into its role in enhancing the multistep CO₂ reduction process. These researches suggested an evolutionary link between mineral-catalyzed prebiotic reaction and enzyme-catalyzed biochemical reaction.

3.2 Nitrogen fixation

The most geologically abundant N source on the early Earth is dinitrogen (N_2). This molecule is chemically inert because of the stable $N \equiv N$ triple bond. Under high-temperature conditions, N_2 can be reduced hydrothermally to ammonia, where reductants were considered to be abundant H_2S [57] or sulfide minerals. The yield of ammonia using H_2S as the reductant at low temperature ($120^\circ C$) is relatively low even with iron monosulfide as the catalyst and is considered to be insufficient for providing ammonia for prebiotic synthesis. On the other hand, there have been accumulating reports on electrochemical reduction of N_2 on Fe_2O_3 [58–60], or FeS [61], CuS [62–64], Mo sulfides [65, 66] at ambient temperature and pressure. These types of reactions could contribute to the prebiotic synthesis of ammonia, following the geo-electrochemistry-driven prebiotic synthesis scenario.

Another chemically more active form of inorganic N species on the early Earth is nitrogen oxyanions including nitrate (NO_3^-) and nitrite (NO_2^-). These compounds were formed by lightning and photochemical processes of atmospheric N_2 and CO_2 with subsequent hydration during rainfall. This could lead to the accumulation of these nitrogen oxyanions in the early ocean with a concentration of micromolar level that is expected to be sufficient for serving as high-potential electron acceptors for the emergence of life in the oceanic environment [67]. NO_3^- and NO_2^- are high-potential electron acceptors ($E^0(NO_3^-/NO_2^-) = 0.835$ V vs. NHE (normal hydrogen electrode), $E^0(NO_2^-/NO) = 1.202$ V vs. NHE) [68]. These electron acceptors are invoked to participate in redox coupling with the oxidation of reducing species, such as methane [17], for the synthesis of active methyl-bearing species such as Acetyl-CoA-like molecules.

Despite their relatively higher reactivity, the reduction of NO_3^- is still kinetically demanding due to the low chemical affinity and low complexation ability with metal sites. Therefore, industrial reduction of NO_3^- typically requires relatively harsh conditions, such as very acidic pH, UV-photolysis, or high temperature [69]. Fe-based species have been extensively studied for ammonia synthesis via reduction of NO_3^- and NO_2^- . These include mackinawite (FeS) [70, 71], Fe^{2+} [72, 73], pyrite (FeS_2) [74, 75], and green rust ($Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot yH_2O$) [76]. $Fe(II)$ ions and green rust can reduce nitrite to ammonia at neutral to alkaline pH ($pH \geq 7$) [73, 77]. Although $Fe(II)$ cannot reduce nitrate, the addition of a trace amount of Cu^{2+} enables the generation of ammonia at pH 8 [77]. Green rust and pyrite can also reduce nitrate into ammonia at pH ~ 8 , which however requires an anion-free environment due to the strong competing adsorption effect from many types of anions [74, 76]. Moreover, the reduction ability of $Fe(II)$ and green rust decrease upon decreasing the solution pH to acidic pH [73, 76]. Therefore, this reaction could have consumed ferrous ions in the ocean. In high temperature ($300^\circ C$), high pressure (50 ~ 500 MPa) hydrothermal setting, a variety of minerals (Fe -, Ni -, Cu -sulfides, and magnetite) can reduce nitrate into ammonia [78] and the ammonia is maintained stably in contact with these minerals. Accordingly, it was argued that the hydrothermal vent system could have supplied sufficient ammonia for the prebiotic synthesis of biomolecules, such as amino acids. However, at the same time, these mineral-promoted reactions are stoichiometric and strongly affected by the presence of other ions and low pH [73, 76].

Metals other than iron have rarely been considered to account for the geochemical reduction of nitrogen oxyanions. Nevertheless, biological nitrate reduction is

catalyzed by nitrate reductase enzyme. All types of nitrate reductases exclusively utilize mononuclear molybdenum as the active center which is bounded by one or two dithiolene groups (-S-C-C-S-) ligated to a pterin group and other ligands (oxo, water, sulfur, etc.) [79, 80]. Inspired by the enzyme structures, the bio-inspired mineral catalysts provide another approach to tackle the kinetic problem. An oxo-bearing molybdenum sulfide as a structural analog of nitrate reductase was synthesized using the hydrothermal method. Notably, this mineral catalyzes both nitrate and nitrite reductions at a wide range of pH, with the generation of a variety of products, including NO, N₂O, NH₄⁺, and N₂ [51, 69]. The reaction mechanism of nitrate reduction resembles that of the enzyme, relying on a redox-active, pentavalent [(Mo^V=O)S₄] species as the active intermediate. This species was likely generated by a concerted proton-coupled electron transfer step, as evidenced by the near Nernstian behavior revealed by the pH dependence [69]. During nitrite reduction, this mineral shows ability to decouple the proton transfer with electron transfer, facilitating a pH-regulated reaction selectivity towards the N-N coupling process [81, 82]. Therefore, this study shows that minerals can not only catalyze a similar reaction with the enzyme but also share a similar reaction mechanism, therefore reinforcing the evolutionary link between geo- and biochemistry.

3.3 Prebiotic S chemistry

Thioesters (R-(C=O)-SR') are organics with high energy (C=O)-S bonds and was invoked to act as an alternative and prebiotic version of phosphoesters (such as ATP) to drive endergonic reactions coupled with the hydrolysis of (C=O)-S bond. The reasons are as follows as described in a recent paper [83]: (1) both thioester and phosphoester bonds have similar standard free energies of hydrolysis; (2) the thioester synthesis precedes the synthesis of phosphoesters in metabolism, such as in glycolysis and the Wood-Ljungdahl pathway; (3) based on computational studies employing network extension algorithms to a phosphate-free core metabolism, thioesters can promote similar reactions like phosphoesters through energetic coupling, for example, reductive TCA cycle and biosynthesis of amino acid [84]. In addition, using thioester as a prebiotic energy coupling agent can partially solve the problem of the scarcity of phosphate in the ferruginous Archean ocean [85] despite the presence of other reactive P sources (e.g., phosphite) [86]. Researchers have reported the synthesis of thioester by abiotic processes. Driven by active CO, at 100°C, the Wächtershäuser group reported C-C bond formation with the generation of CH₃-CO-SCH₃ thioesters proceeds on FeS and NiS from a mixture of CO and CH₃SH [27]. Sandan et al. reported the generation of thioester by reacting of thioacetate and thiols in presence of Fe³⁺ at 70°C in water [83]. In addition, by further adding ferredoxin-heme maquettes, [4Fe-4S] cluster was formed based on the characteristic UV-Vis absorption band at 384 and 447 nm. This process also generates iron sulfide minerals. Recently, Kitadai et al. demonstrated the synthesis of S-methyl thioacetate (MTA) synthesis from CO and methanethiol on NiS at room temperature at neutral pH [54]. NiS was partially reduced to Ni under simulated geo-electrochemical conditions. This partially reduced Ni⁰/NiS mixture catalyst is important to accumulate surface-bound CO by electro-reduction of CO₂. CO accumulation process on Ni⁰/NiS surface was crucial for subsequent thioester formation in early ocean hydrothermal systems. The pH and temperature conditions are mild and geologically plausible.

4. Prebiotic catalyst screening

4.1 Availability of metals in the Hadean ocean

It is not surprising that many bio-essential metal elements are also Earth-abundant, considering the high reliance of the biosphere on the geosphere. These include mainly d-block elements (vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), molybdenum (Mo), tungsten (W), and zinc (Zn)) and exist in numerous oxidation states and be bonded by various ligands (O, S, etc.) with varied crystal structures and stoichiometries in minerals. The variety and relative abundances of minerals evolve with the Earth's history and also depend on the geological type of the locality [14]. In the ocean, changes in elemental abundances on geological time scales are intimately linked to evolutionary processes [87]. The availability of soluble transition metals changes progressively with time, with the greatest change in the redox-sensitive elements. However, this has provided environments enriched with an immobilized form of minerals, which would have provided the active surface for promoting prebiotic organic synthesis. The redox state of the environment evolved through at least three stages (adapted from ref. [87]), with major oxygenation events occurring ~2.4 billion to 1.8 billion years ago during the first of these stages, the ocean was largely devoid of dissolved O₂, and iron was abundant in the form of dissolved Fe²⁺ complexes. Much of the sulfur at that time was in the form of insoluble sulfide minerals locked in the continental crust. Besides Fe, the ocean abundances of transition metals such as manganese, cobalt, nickel, copper, zinc, and molybdenum are sensitive to environmental redox conditions, and also precipitate as sulfide minerals.

The scarcity of many bio-essential transition metals due to precipitation as insoluble sulfides has been considered to limit the size and shape the metabolism of the primordial biosphere [87, 88]. However, in terms of prebiotic chemistry, both the soluble and precipitated forms of transition metals could contribute to promoting the reactions, as have discussed in Section 3. The immobilized form of metal sulfides could have provided active surfaces with enormous potentials for catalytic functions. Therefore, for future prebiotic synthesis studies, more work using non-iron elements should be conducted to screen optimal geological catalysts.

4.2 Chemical diversity of metal sulfides

Since transition metals mainly existed in sulfides during Hadean and early Archean eon, these sulfides have been studied for prebiotic synthesis, as described in Section 3. However, in most cases, the activities of these minerals are low compared with their enzymatic counterparts and their contribution to prebiotic synthesis has rarely been quantitatively constrained based on their kinetics with some exceptions [73]. A possible reason accounting for the low reactivity is that prebiotic synthesis researches have been heavily focused on the most earth-abundant minerals (e.g., FeS, and NiS). To explore the chemical diversity of sulfide minerals, Li et al. evaluated the chemical diversity of metal sulfides of Co, Cu, Fe, Mn, Mo, Ni, V, and/or W with 135,434 species-locality pairs recorded in the mineralogy database (<http://rruff.info/ima/>) [88]. The diversity and distribution of these metal sulfides were analyzed in terms of the following aspects: locality frequency, multiple metal composition, crystal structure, and valence state of dominating elements. It was found that natural

Figure 3. (A) Metal sulfide distribution in natural environments. The 20 most frequently observed species are ranked in order of locality counts. The chemical composition of each species is shown. (B) Distribution and chemical diversity (chemical composition, Fe/S valence states, and crystal symmetry) of Fe single-metal sulfides. (C) Relative abundances and locality distribution of Fe²⁺-, Fe³⁺-, and Fe²⁺ plus Fe³⁺-sulfides. Adapted from ref. [88].

metal sulfides show marked variations in chemical composition, crystal structure, and metal/sulfur valence states, suggesting a large chemical space associating with chemical variations of sulfide minerals still waits for exploration (Figure 3). For Fe sulfides, unexpectedly, mackinawite (FeS) is not among the top-ten mostly frequently observed species. This suggest that it may be problematic to use this mineral as a dominant target for prebiotic synthesis. Rather, pyrite is the most frequently observed species. The observation of the S₂²⁻ state suggests that not only metals can mediate redox change, sulfur ligands can also participate in the redox reaction with the valence change (S₂²⁻/S²⁻).

Each metal also has the dominant valent states. In Fe-S species, more than 84.86% of localities feature only Fe²⁺ species, followed by those containing both Fe²⁺ and Fe³⁺ (15.12%), and by three sulfides that only contain Fe³⁺ (0.02%). Generally, metals with low valence states predominate the library of metal sulfides, except for Co, allowing these minerals to act as an electron source or a catalytic center for charge accumulation during redox conversion. The minerals with mixed-valence states could exhibit unique functions due to special electron transfer and surface adsorption properties [89, 90]. Moreover, binary metal compositions are ubiquitous in natural sulfides. For example, Ni-Fe sulfides have ten species, and seven of them contain Ni and Fe as substitutional cations with a wide Ni/Fe ratio range (0 ~ 35 at%), with pentlandite (Ni,Fe)₉S₈ being the most prevalent form. The other three species contain fixed Fe/Ni ratios. The capability of Ni-Fe binary sulfides to have both fixed and varied Ni/Fe ratios in their structures is a unique characteristic different from that of Cu-Fe binary sulfides, in which Cu and Fe tend to form specific structures with fixed stoichiometries. The great chemical diversity provides a wide variety of catalytic functions and suggests that there is still a large chemical space of minerals for the exploration of unknown reactivities.

4.3 Enzyme analog minerals

Based on the discussion above, screening suitable geological catalysts is challenging and requires rational approaches. In this regard, machine learning or big-data mining could provide promising solutions.

Given an envisioned evolution from geochemistry to biochemistry, the mineral-and enzyme-based catalytic systems could be compared to understand the evolutionary link between them. In 2014, Michael Russell and his colleagues proposed that minerals sharing similar metal sites and ligands with enzymes could serve as a prebiotic catalyst for activating small geological molecules [4] (Figure 4) because the similar structure

Figure 4.
 Structural comparison between minerals and enzyme active centers. Adapted from ref. [4].

could exhibit similar chemical affinity towards the same substrate. Many prebiotic syntheses are influenced by similar perceptions and pursue the prebiotic carbon and nitrogen fixation using enzyme mimetic mineral catalysts [27, 45, 48, 49, 51, 52, 54, 69]. This idea could narrow down the candidates of geo-catalysts, however, an inherent difficulty in studying the property of minerals is the wide range of data and parameters to consider when searching for an appropriate catalyst for a specific enzymatic reaction [91]. Especially, since the structure (particularly the first coordination structure) alone doesn't dictate the overall catalytic property, the structural resemblance between minerals and enzymes doesn't ensure a definite functional similarity.

To solve this problem, a computational approach has been employed to systematically compare the metal–ligand structure of minerals and enzymes, as reported in recent work by Zhao et al. [91]. They compared the metalloenzyme cluster structure recorded in the protein database and the mineral structural data in the mineralogy database, using molecular similarity metrics. Therefore, this is probably the first attempt to quantify the structural similarity between biological machineries and minerals. In this study, iron–sulfur and nickel–iron–sulfur ligands were analyzed. Except for greigite and mackinawite, other iron sulfide species (marcasite and troilite) that were less studied previously were also predicted to have high structural similarity with iron–sulfur clusters in biology. Therefore, these results highlight the predictability of the modeling method for searching less studied minerals that hold potential as early prebiotic catalysts.

5. Conclusions

Minerals have been considered as the key player for prebiotic synthesis, and up-to-date researches have verified the catalytic property of many prebiotic mineral catalysts towards the carbon and nitrogen fixation reactions. Based on these discussions, mineral-mediated processes are probably critical for the evolution of

protometabolism towards autotrophic origins of life. However, the rare demonstration of the formation of other types of life's building blocks, such as sugars, nucleobases, etc., accompanied by the difficulty in polymerization in water, pose several obvious challenges for many related origins of life scenarios [92]. To solve this problem, extensive screening of prebiotic catalysts based on the mineralogy database combined with the numerical prediction of structure–function relations should be helpful. Alternatively, other types of membrane and replicating systems have been proposed [16]. Additionally, the evolution of the mineral catalytic system could be further explored, by considering the hybridization of organic ligands with minerals. These organic ligands could be short peptides that can be formed under geologically plausible conditions [93, 94], or other types of polymers (e.g., polyesters [95, 96]). The hybridization of these organic ligands introduces stereochemical and electronic control on the whole reaction systems, which could help with overcoming the kinetic problems for certain reactions.

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Appendices and nomenclature

Place appendix and nomenclature before Reference list.

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