



# Decorated Vesicles as Prebiont Systems (a Hypothesis)

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## Abstract

Decorated vesicles in deep, seafloor basalts form abiotically, but show at least four life-analogous features, which makes them a candidate for origin of life research. These features are a physical enclosure, carbon-assimilatory catalysts, semi-permeable boundaries, and a source of usable energy. The nanometer-to-micron-sized spherules on the inner walls of decorated vesicles are proposed to function as mineral proto-enzymes. Chemically, these structures resemble synthetic FeS clusters shown to convert CO<sub>2</sub>, CO and H<sub>2</sub> into methane, formate, and acetate. Secondary phyllosilicate minerals line the vesicles' inner walls and can span openings in the vesicles and thus can act as molecular sieves between the vesicles' interior and the surrounding aquifer. Lastly, basalt glass in the vesicle walls takes up protons, which replace cations in the silicate framework. This results in an inward proton flux, reciprocal outward flux of metal cations, more alkaline pH inside the vesicle than outside, and production of more phyllosilicates. Such life-like features could have been exploited to move decorated vesicles toward protolife systems. Decorated vesicles are proposed as study models of prebiotic systems that are expected to have existed on the early Earth and Earth-like exoplanets. Their analysis can lead to better understanding of changes in planetary geocycles during the origin of life.

**Keywords** Decorated vesicles · Origin of life · Prebiont system · Basalt · Protobiont · Protocell

## Introduction

In the origin-of-life field, classical models of prebionts and/or protocells include coacervates (Oparin 1968), peptide marigranules (Yanagawa and Egami 1980, 1981), chemotons (Gánti 1975; Szathmáry 2002), self-replicating Li-octanol micelles (Luisi and Varela 1990), colloids with catalytic functions (Monnard and Deamer 2001; Deamer et al. 2002) and others. Most of these systems however are hypothetical and not widely common in nature. More nature-likely prebiont systems could have been associated with

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clay minerals (Bernal 1951, 1967; Cairns-Smith 1982; Cairns-Smith and Hartman 1986; Subramaniam et al. 2011), iron sulfides (Baross and Hoffman 1985; Wächtershäuser 1990; Martin and Russell 2003; Russell 2018) or water droplets in aerosol phases (Woese 1979). In the so called mineral theories (or geochemical theories) of the origin of life (Baross and Hoffman 1985; Cairns-Smith et al. 1992; Volbeda and Fontecilla-Camps 2006; Russell 2007) various minerals carried some life-analogous functions during the emergence of pre-living systems. Such functions included: enclosing reactants, products, or even entire chemical networks in small physical compartments, catalyzing chemical reactions in enclosed spaces, selective exchange of chemicals across a system's boundary, exploiting natural sources of energy and others.

We use the following definitions for the living and non-living entities we describe in this paper.

A *prebiont* is an abiotic system showing some life-analogous features. A prebiont system is not on a potential path toward life. A *mineral prebiont* is defined as an enclosed system in which mineral components (instead of biochemicals) carry out all functions such as catalysis, asymmetric diffusion, chemical buffering, stereochemical memory and others. The system's order, structure, and function are independent of genetically inherited information.

A *protobiont* system (or most primitive life form) is defined as a precursor of living cells composed of an aggregation of prebiotic components whose interactions and outcomes resemble functions of living cells (cf. protobiont, Cammack et al. 2008). Depending on the complexity assumed by various models, protobionts may or may not show a form of genetic inheritance as well (though most models do).

Prebiont systems are thought to have originated before, and independently of the more complex protobionts. While a *protobiont* is defined as a primitive form of life and a potential transition state in life's early history, a *prebiont* is a simple chemical system that has some life-like features and can occur in nature independent of life or its early evolution. Organic molecules may also occur in *mineral protobionts*, but as byproducts and having secondary roles in controlling the system's state. Only later in prebiotic evolution, when organics took over the system's order and functions from minerals, and when internal information became dependent predominantly on selected inheritance, could a *mineral prebiont* have evolved enough to be called a *protobiont*.

Key features of mineral prebionts can include preformed inorganic enclosures, selective chemical exchanges with the exterior, naturally available free energy, and minerals-controlled catalysis. It seems logical to assume that the more pre-life functions available, the better chances for a mineral prebiont to advance toward organics-dominated protobionts. In our view, mineral prebionts gradually evolved toward mineral/organic systems until, eventually, organic polymers took over the various functions of minerals and led to inherited information as well. Trace fossils of an early evolutionary stage that was based on hybrid systems with minerals/organics mutualism may still persist today in modern cells in the form of biomineralization, metallic enzyme cofactors and mineral clusters from electron transfer paths. Yet, without direct evidence (i.e., abiotic models to study), *mineral prebionts* remain largely a subject of theoretical speculation.

We offer evidence that some *mineral prebionts* may still occur in nature today, in the form of *decorated vesicles from basalt lava*. We discuss four prelife-relevant features of these vesicles: physical compartments, abiotic catalysis, a source of free energy usable by a chemical network and means of chemical sieving.

## Geological Context

Volcanic ocean-ridge spreading centers erupt new ocean crust on top of the mantle. From the top of the ocean crust down to the mantle the geologic layers are defined as: Layer 1, sediment; Layer 2A basalt lavas erupted underwater; Layer 2B, rapidly cooled basalt lavas intruded into Layer 2A; and Layer 3, gabbro, slowly cooled intrusive basalt. Layer 2A is the primary location of the decorated vesicles discussed here. Layer 2A is composed of basalt pillow lavas, basalt sheet flows, hyaloclastites (fractured basalt glass), and secondary minerals derived from basalt-water reaction, and precipitated from seawater. Layer 2A today is present under about 70% of the oceans (about 50% of the Earth's surface). Remote sensing of Layer 2A indicates that it is 320 to 1050 m thick (Estep et al. 2019). Drilling through all of Layer 2A in two locations found it to be 470 to 575 m thick (Anderson et al. 1982; Expedition 309 and 312 Scientists 2006). In most locations, sediment (or crustal Layer 1) covers Layer 2A and isolates a subsurface aquifer from the ocean. Unlike seawater, this aquifer contains traces of methane, hydrogen, and ammonia (Jungbluth et al. 2013; Lin et al. 2014).

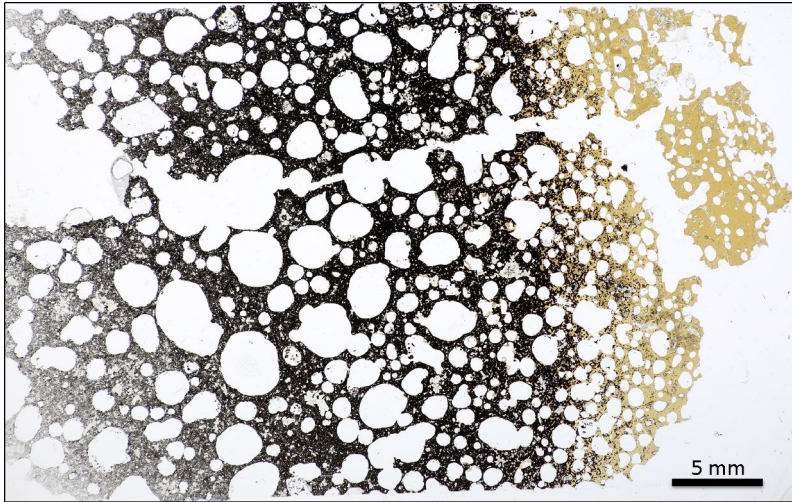
Basalt vesicles from Layer 2A have four features thought to be relevant for the origin of life, (1) natural compartments, (2) mineral catalysts, (3) a natural proton flux, and (4) semipermeable phyllosilicates.

## Basalt Vesicles as Natural Compartments

It is generally believed that chemical reactions occurring in the open ocean when life originated could not have led to sizable accumulation of organic molecules (Nisbet 1985; De Duve 1991; Martin and Russell 2003, 2007; Lane et al. 2010). This means that the primordial ocean was very diluted with regard to organic carbon. Local increases in the concentration of small organics, leading to micelles and large molecules, could have still occurred by dehydration, by attachment to mineral surfaces (Bernal 1967; Cairns-Smith 1982; Cairns-Smith and Hartman 1986), and by sequestration of chemicals and proto-enzymes in colloids and natural compartments (Yanagawa and Egami 1981; Nisbet 1985; Russell and Hall 1997; Deamer et al. 2002; Brasier et al. 2011, 2013). Secondary reactions on mineral surfaces are another common assumption for prebiotic transformations (Wächtershäuser, 1988a, b; Huber and Wächtershäuser 1998; Hazen and Sverjensky 2010). Cairns-Smith (1982), Nisbet (1985), and Brasier et al. (2011, 2013) hypothesized that vesicles (bubbles trapped in cooled and solidified silicate magmas) provided chambers for the polymerization and concentration of organic molecules and indeed basalt glass polymerizes nucleoside triphosphates (Jerome et al. 2022). In this paper we narrow and focus this idea of natural chambers in basalt to *decorated vesicles in basalt*.

## Vesicle Occurrence in Igneous Rock

The Earth's upper mantle contains trace amounts of volatile compounds, the most abundant of which are water, carbon dioxide and sulfur. When the mantle melts, the volatiles dissolve in the magma. The magma's buoyancy carries it up through the mantle and crust and, as the confining pressure decreases, H<sub>2</sub>O, CO<sub>2</sub>, and S species become supersaturated. Mixtures of H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>S gas form bubbles (vesicles) in the molten silicate (Fig. 1). Such vesicles occur in virtually all basalts erupted at any depth in the oceans (Moore 1979). At



**Fig. 1** Scanned optical image of a  $27 \times 46 \text{ mm} \times 30\text{-}\mu\text{m}$ -thick petrographic section of basalt provided by Oregon State University Marine Geology Repository. Sample EX1702-D9-5\_2 from Vailulu'u Volcano ( $14.21^\circ\text{S}$ ,  $169.05^\circ\text{E}$  collected from 730 m below sea level). Tan-yellow region on the right side of the photo is fragile igneous glass that formed due to rapid cooling. The dark region to the left of the glass is a matrix of submicroscopic and visible igneous minerals, vesicles, and glass. Vesicles, fractures, and open space are white. This sample also contains isolated, interconnected, and broken vesicles. This example from a shallow seamount has about 50% vesicles, which are larger in diameter and more abundant than those reported for deeper eruptions (Moore and Schilling 1973)

water depths greater than 2200 m, the vesicles' abundance is less than 1 vol% of the basalt (Moore 1979). At less than 1000 m depth this abundance rises to 6–17%, though in some cases it can be as large as >50% (Fig. 1).

### Vesicle Size and Number

Measured diameters for vesicles from ocean basalts range broadly from less than 1  $\mu\text{m}$  to centimeters. Vesicle size determined by optical microscopy of 24 basalts from the Juan de Fuca Ridge in the northeast Pacific Ocean ranged from 10  $\mu\text{m}$  to 1030  $\mu\text{m}$  (Dixon et al. 1988). Limitations of optical microscopy and sample preparation result in an observation bias favoring observations of vesicle diameters larger than 1  $\mu\text{m}$ . Extrapolation of the inverse logarithmic vesicle size / vesicle number density per unit volume relationship (Sarda and Graham 1990) suggests that vesicles less than 10  $\mu\text{m}$  should yet be extremely abundant in basalt. The small size of preexisting chambers is relevant here because the early catalysts, presumably less efficient, could only have made a difference in the accumulation of products if they were trapped in very small, enclosed spaces (Dyson 1985).

Vesicle number density measured by point counting was 25,000 to 500,000 vesicles per  $\text{cm}^3$  (Dixon et al. 1988) and calculated based on nucleation density to be from one hundred to one million per  $\text{cm}^3$  (Bottinga and Javoy 1990). These vesicle number densities, the current rate of ocean crust production of  $2.7 \text{ km}^2 \text{ yr}^{-1}$  (Cogné and Humler 2006), the average thickness of about 500 m of Layer 2A, and the 60,000 km of volcanic ocean ridges on Earth indicate that the annual production rate of basalt vesicles on our planet is  $10^{17}$  at minimum. We expect that vesicle production in the Hadean was at least

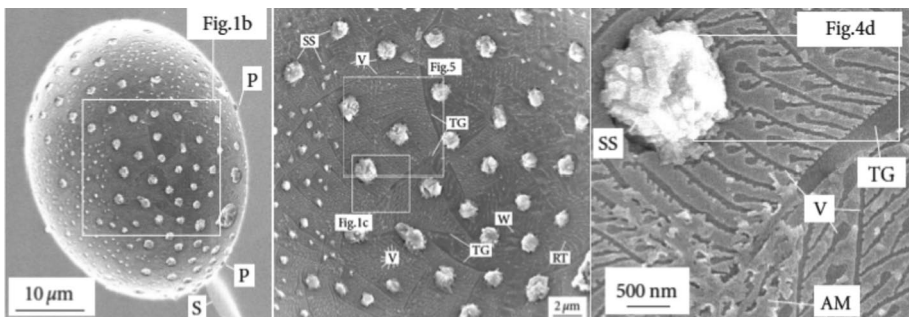
similar, thus providing untold numbers of natural compartments where evolution of such potential prebiont systems toward life could have occurred in relative isolation from the ocean's chemistry.

## Metal Sulfide Spherules in Decorated Basalt Vesicles

The most abundant volatile compounds dissolved in mid-ocean ridge magmas are  $H_2O$ ,  $CO_2$ , and  $H_2S$ . Significant for this hypothesis is the presence of 800 to 2500 ppm of sulfur in ocean ridge magmas erupted at depths greater than 1000 m (Wallace and Carmichael 1992). As magmas migrate upward in the crust and eventually erupt, the volatiles escape to form vesicles (bubbles) (Fig. 1). The sulfur, in addition to contributing to the formation of vesicles, also exsolves as 5-to-500- $\mu\text{m}$  diameter metal sulfide liquids and as  $<0.1$  to 6  $\mu\text{m}$  diameter metal sulfide spherules on the inner walls of “decorated” vesicles of Moore and Calk (1971) and Yeats and Mathez (1976), and Fig. 2 (in French and Muehlenbachs 2009). In 1971 Moore and Calk reported that “spotted vesicles” are a “widespread if not ubiquitous feature” of fresh pillow basalts. Moore and Schilling reported in 1973 that decorated vesicles occur in all samples in their study.

It is believed that spherules form when volatile sulfide reacts with either volatile Fe, Cu, and Ni in vesicles (Mathez and Yeats 1976) or with magmatic Fe, Cu, and Ni in the walls of the vesicles (Moore and Calk 1971). High confining pressure prevents sulfur escape from magmas erupted in deep water, so spherules are mostly found in deep water magmas (Moore and Schilling 1973) in which sulfur content of the basalt remains above 400 ppm (Moore and Calk 1991). The next section explains why these metal spherules are important to our hypothesis.

The temperature of the molten seafloor basalt, generally above 1150  $^{\circ}\text{C}$ , is greater than the liquidus temperature of Fe-Cu-Ni sulfides (Craig and Kullerud 1969). The metal sulfides would be initially molten, but upon cooling, the molten spherules form  $<0.1$ -to-2.5- $\mu\text{m}$  clusters of metal sulfide crystallites, each up to 100 nm (Fig. 2; Propach 1979; French and Muehlenbachs 2009).



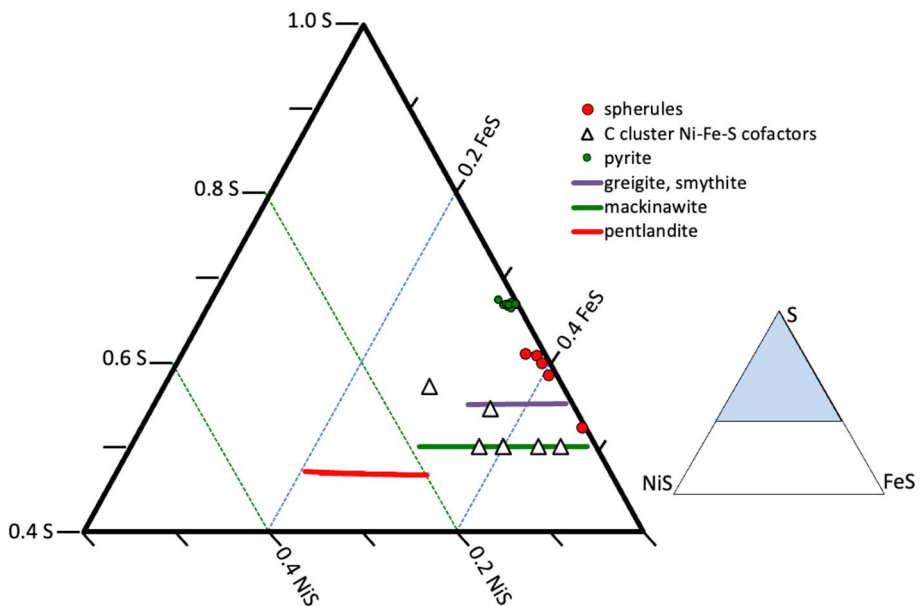
**Fig. 2** Decorated vesicle. Scanning electron microscope images from French and Muehlenbachs (2009). (Left) Concave interior surface of a vesicle in basalt with evenly spaced 2- $\mu\text{m}$  and 0.2- $\mu\text{m}$  spherules. Additional images of decorated vesicles can be found in Mathez and Yeats (1976), Propach (1979), Juteau et al. (1980), Kamenetsky et al. (2002), Kamenetsky and Kamenetsky (2010). (Center) Enlargement of the white square from the left picture. (Right) Enlarged image of a FeNiS spherule showing a cluster of about 50 nm grains. French and Muehlenbachs (2009) explained the additional image notations (not relevant here). Figure 2 is modified from Fig. 1 of French and Muehlenbachs (2009), which is available under the Creative Commons Attribution License. Copyright belongs to J.E. French and K Muehlenbachs

Qualitative analyses of the spherules show that they are composed of Fe, Ni, and Cu sulfides, as determined by scanning electron X-ray intensity mapping (Mathez and Yeats 1976; Juteau et al. 1980), and laser ablation (Kamenetsky and Kamenetsky 2010). The few quantitative analyses available of spherules, done by electron microprobe analysis, indicated that FeS dominates, while NiS and CuS are also present at less than 7 wt.%. Spherule data from Moore and Calk (1971) and Propach (1979) are plotted in Fig. 3.

Morphologically and compositionally, the decorated vesicles spherules resemble iron monosulfide greigite framboids from sediments (Ariztegui and Dobson 1996; Snowball and Thompson 1988; Valdez-Grijalva et al. 2020) or framboidal mackinawite, a precursor of framboidal pyrite also reported in sediments and also in acritarch fossils (Marshall et al. 2017). Because of their small size, quantitative chemical analyses of spherules are few and the identity of the minerals in spherules remains unknown. Deciphering the composition and mineralogy of the spherules is important for the hypothesis of spherules as abiotic catalysts in a prebiotic model. Based on the basalt glass composition we expect that additional spherule analyses will reveal that they contain a wider spectrum of Fe, Ni, and Cu compositions compared to those in Fig. 3, as well as trace amounts Co, Zn, and Mo (Li and Audétat 2012).

### Sulfide Spherules as Putative Abiotic Proto-Enzymes

We posit here that the FeNiS spherules from decorated vesicles are suitable research models of mineral proto-enzymes. This vision is in line with mineral theories of the origin of life, where primordial catalytic reactions were carried out by abiotic minerals



**Fig. 3** A portion of the S-FeS-NiS ternary (see inset). Data sources: spherules (Moore and Calk (1971) and Propach (1979)), pyrite (Lorand et al. 2015), smythite (Erd et al. 1957), mackinawite (Wilkin and Beak 2017), pentlandite (Shewman and Clark 1970), C-cluster Ni-Fe-S cofactors (Dobbek et al. 2001; Doukov et al. 2002; Darnault et al. 2003; Russell and Martin 2004; Svetlitchnyi et al. 2004; Varley et al. 2013). The blue isopleths show constant Fe:S ratios. The green isopleths show constant Ni:S ratios

in a metal-sulfide-rich environment (Baross and Hoffman 1985; Wächtershäuser 1990, 1988a, b, 2006; Volbeda and Fontecilla-Camps 2006; Russell 2007). The unit cell crystallography of Fe- and FeNi-monosulfide minerals also resembles that of the FeNiS cubane C-centers from carbon monoxide dehydrogenases (CODH) and acetyl CoA synthetases (ACS) (Volbeda and Fontecilla-Camps 2006; Martin and Russell 2007; Russell 2007; Ferry 2010; Nitschke et al. 2013; Martin 2020) (Fig. 4). FeNiS enzymes occur in a wide range of microorganisms, including acetogenic, methanogenic, and phototrophic bacteria (Yamaguchi et al. 2014). The Wood-Ljungdahl C-fixation too is based on FeNiS cofactors (Lindahl 2009). The Ni atom from the FeNiS cofactors is key here as the initial C-binding site (Riordan 2003; Lindahl 2009; Hadj-Said et al. 2015).

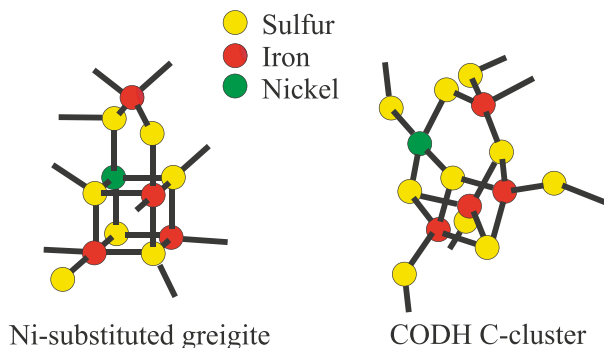
The biochemical processes listed above are phylogenetically traceable to the hypothetical LUCA, the last universal common ancestor of modern life (Sousa et al. 2013; Weiss et al. 2016), but FeNiS-based reactions such as dehydrogenation and C-fixation are believed to be more ancient than LUCA, arguably going as far back as protobionts (Russell 2007; Martin 2020). There is strong evidence of abiotic chemistry leading to C1-C2 organics via FeNiS minerals. In-vitro experiments demonstrated that in the presence of synthetic FeS and FeNiS mineral clusters chemical reactions involving CO, CO<sub>2</sub> and H<sub>2</sub> will occur, leading to formate, acetate and methane (Yamaguchi et al. 2014; Martin 2020; Preiner et al. 2020). Such reactions already occur, apparently abiotically, at the ocean floor near hot springs where metal sulfides are common (Volbeda and Fontecilla-Camps 2006). Compositionally, the decorated vesicle spherules have Fe:Ni ratios similar to the C-clusters from CODH enzymes (Figs. 3, 4). Structurally, the spherule sulfides are at least partly crystalline (Fig. 2).

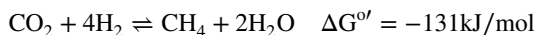
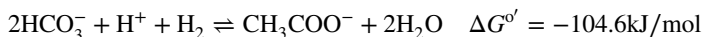
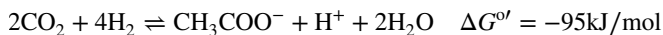
Synthetic greigite was shown to catalyze the reduction of CO<sub>2</sub> with H<sub>2</sub> to formate, acetate, and methane (Preiner et al. 2020). Greigite structures were already proposed to behave like prebiotic mineral CO dehydrogenases (Martin and Russell 2007). Reduction of CO<sub>2</sub> via FeNiS clusters also occurs naturally in the presence of deep-sea hydrothermal precipitates (Yamaguchi et al. 2014). The fact that all known anaerobic CODHs contain an FeNiS C-cluster active site (Riordan 2003), makes it more likely that protolife could not have developed a COx/H<sub>2</sub> C-fixation anabolism without help from FeNi-monosulfide minerals.

Based on abiotic simulations, on C-cluster similarities, and other prebiotic theories (Riordan 2003; Martin and Russell 2007; Russell 2007; Martin 2012, 2020; Preiner et al. 2020) we hypothesize that the Ni-substituted iron monosulfide minerals from the spherules of decorated basalt vesicles will catalyze the production of small organics such as formate, acetate and methane.



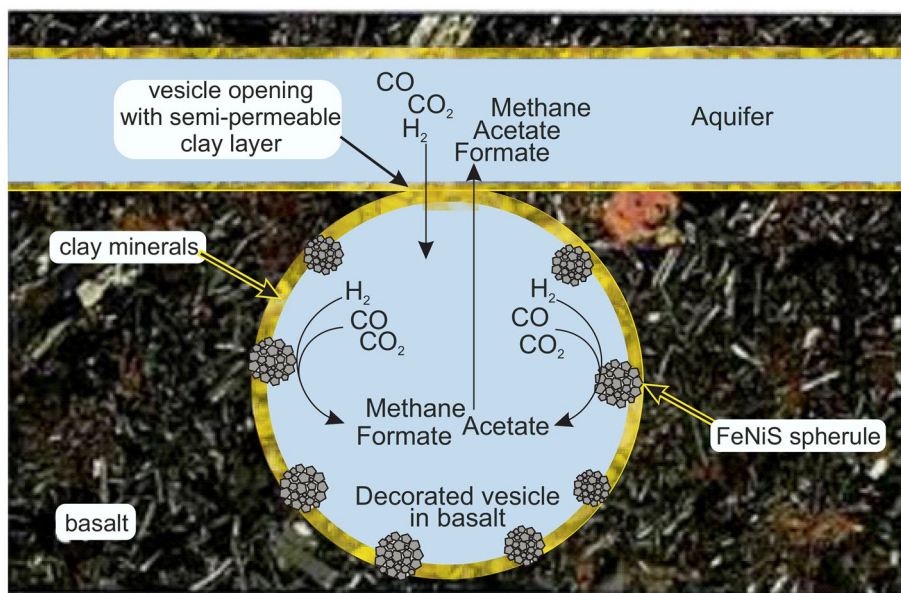
**Fig. 4** Similarity in structure of the FeNiS mineral greigite and the C-cluster of CODH enzymes. Modified from Nitschke et al. (2013)





The first reaction in this series, i.e. producing formate, may not occur directly but through carbonyl sulfide ( $\text{O}=\text{C}=\text{S}$ , typically written as  $\text{COS}$ ;  $\text{CO}_2 + \text{H}_2\text{S} \Rightarrow \text{COS} + \text{H}_2\text{O}$ ), which is much more prone to accept electrons than  $\text{CO}_2$  (Schoonen et al. 1999; Martin and Russell 2007). Next, the reduction of  $\text{COS}$  to  $\text{CO}$  can be catalyzed by transition metal sulfides, followed by the hydration of  $\text{CO}$  to formate (Martin and Russell 2007). If this reaction path is true, then catalytic production of formate via spherules will require or benefit from sulfidic conditions. We believe that within the  $\text{FeNiS}$  spherules the Ni-substituted iron monosulfide mineral surfaces will catalyze the production of formate, acetate, and methane. These reactions are proposed to occur when the inside milieu of the decorated vesicles is exposed to the  $\text{CO}$ -,  $\text{CO}_2$ - and  $\text{H}_2$ -bearing water from the ocean crust Layer 2A aquifer and at the temperatures common in that layer (Fig. 5).

In this model, decorated vesicles produce small organic acids, after which amination and hydrogenation of formate can be another prebiotic step toward glycine, the simplest amino acid. This model belongs with anabolic views about the origin of life, in which protolife chemical networks were not organotrophs (i.e., exploiting external sources of free organics from nature) but were built from the ground up by C-fixation. We propose



**Fig. 5** Proposed C-fixing reactions catalyzed by  $\text{FeNiS}$  spherules in a decorated vesicle in basalts of the oceanic crust Layer 2A. These reactions were already demonstrated in in-vitro experiments and are catalyzed by synthetic greigite at pH of 6.5 and pH 10, with 2 bar of  $\text{CO}_2$  and 80/20  $\text{H}_2/\text{CO}_2$  ratio at a temperature of 100 °C (Preiner et al. 2020). Spherules are 1 to 6  $\mu\text{m}$  across



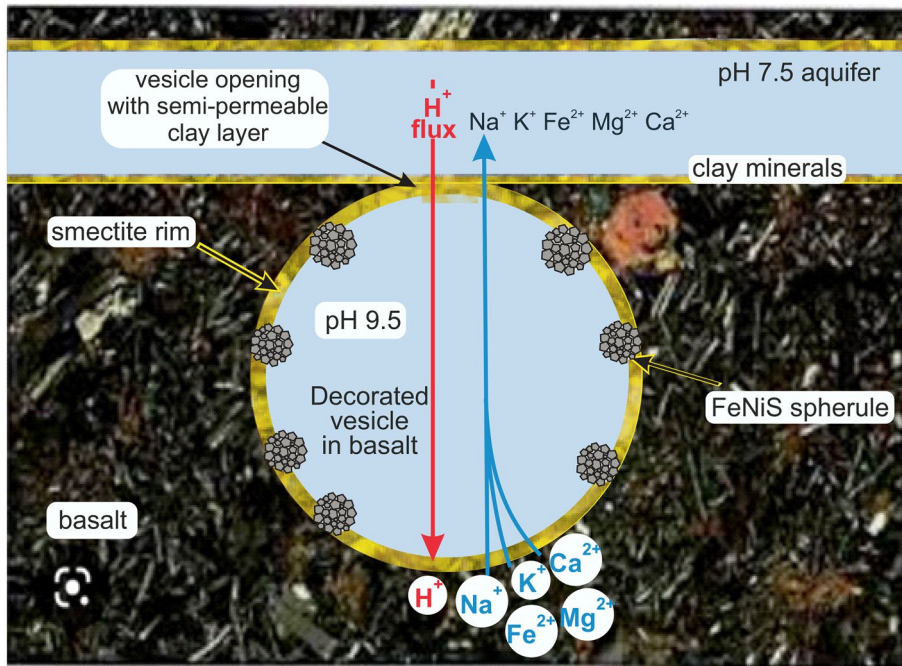
that spherule-based catalysis is partly responsible for the C1 and C2 organics reported to form in the subseafloor Layer 2A, deep water lava, and hydrothermal zones (Volbeda and Fontecilla-Camps 2006; Proskurowski et al. 2008; Bradley and Summons 2010; Lang et al. 2010; Yamaguchi et al. 2014). According to our vision, the decorated vesicles environment is a net producer of small organics in the planetary carbon geocycle.

## A Natural Proton Flux toward Basalt Surfaces

According to Lane et al. (2010) “*the only way life could have started at all is if it found a way to tap proton gradients*”. Some proton gradients occur naturally, for example at the interface between waters with different pHs (Martin and Russell 2007; Russell 2007). In our model, a local proton gradient is driven by the hydration of silicate rocks by seawater (Gislason and Eugster 1987; Oelkers 2001; Gislason and Oelkers 2003; Fisk et al. 2019). In the oceans, the majority of the energy released by the reaction of water with rocks comes from hydration; yet so far, no living organism has been shown to harness this source of energy (Hoehler et al. 2020). Still, Fisk et al. (2019) hypothesized that the hydration of igneous rock generates a proton gradient that can be exploited by modern microorganisms living in basalt pore spaces.

In that paper (Fisk et al. 2019) we discussed the rate of cation and silica displacement by protons and the energy associated with this process. The inward proton flux described here, occurs between the aquifer water with a pH of 7.5 and the pH 9.5 water inside the vesicles. As protons diffuse into the vesicle walls, they replace cations (primarily  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Fe^{2+}$ ), which then diffuse into the water enclosed by the vesicle (Fig. 6). Some of these cations will likely form secondary precipitates (such as iron oxyhydroxides and phyllosilicates); others remain in solution. An outward flux of cations from the vesicle balances the charge of the influx of protons. Hence, in decorated vesicles a natural proton motive force develops across a mineral boundary, such as a phyllosilicate, at a vesicle opening.

The decorated vesicles described in this paper are proposed to have existed before the origin of life. The decorated vesicle prebiotic systems are, putatively, in a primitive stage that is yet unable to exploit a source of natural energy for the negentropic benefits of a chemical network. A system may only deserve the cognomen prebiont if non-zero odds exist to evolve toward protobionts and eventually life. Without a reliable source of energy, one cannot speak of prebionts, but only about abiotic systems with some life-like similarities. We believe that the natural inward proton flux gives an internal chemical network hosted in decorated vesicles an opportunity to evolve toward more complex (negentropic and energy-dissipative) protolife systems. In modern cells a proton flux (derived from either redox reactions or light), is used to exploit energy via energy transduction toward currencies such as ATP, reducing power such as NADH, chemical transport against natural gradients, flagellar motion, or other anti-entropy gains. The modern system of exploiting a purposefully created proton gradient is thought to have originated in a simpler, natural, proton flux (Lane et al. 2010). Given the complexity of chemiosmotic phosphorylation it is more believable that protobionts employed simpler means to exploit energy sources such as ion fluxes (Deamer 1997). For example, proton gradients could have been used to assist ion-transport in turnstile mechanisms (Branscomb and Russell 2013) or transport via boundary's pores. We believe that later systems derived from the decorated vesicles, used the natural “water-to-basalt proton fluxes” as a source of energy. We also assume that the



**Fig. 6** Proton flux from pH 7.5 aquifer water, through a smectite clay boundary and into pH 9.5 water in a clay-lined vesicle. Protons diffuse through the smectite clay lining the basalt vesicle and into the basalt. Red arrows indicate proton diffusion. Blue arrows indicate cation diffusion. Spherules are 1 to 6  $\mu\text{m}$  across

first usage of this pH gradient was a form of proton-assisted ion transport (either anion symport or cation antiport) across semi-permeable boundaries.

## Clays as Semi-Permeable Boundaries in Decorated Vesicles

Asymmetric exchanges across semipermeable boundaries and concentration and assembling small molecules into larger constructs are key features of life. It is often thought that in prelife systems such processes could have been assisted by clay minerals. Iron-rich tri-octahedral smectite is a common product of the alteration of basalt by seawater (Alt et al. 1986; Marescotti et al. 2000). Anoxic conditions and temperatures of 60 °C to 125 °C leads to smectite clays in subseafloor aquifers (Honnorez et al. 1983). Such conditions prevail in the several-hundred-meter-thick aquifer in oceanic basalt lavas of Layer 2A where the decorated vesicles occur. Thermal and mechanical stresses fracture the rocks in this aquifer allowing water to enter fractured vesicles which enhances clay formation. Secondary smectite layers line the exposed vesicle like plaster on a wall (Fig. 6).

Clays could have played a variety of roles in prebiotic systems. Clays absorb water and then release it slowly, thus buffering sharp variations in water activity. They are also sinks for silica, alumina, and cations released during basalt weathering. Clays sequester organic compounds and can facilitate organic condensation reactions (Paecht-Horowitz 1976; Laszlo 1987; Ferris et al. 1996) favored by hydration/dehydration cold/hot cycles

(Ross and Deamer 2016). Chiral selection of amino acids and nucleic acids by clays was also reported (Joshi et al. 2011). Lastly, clays can also act as molecular sieves. For example, montmorillonite, a clay from the smectite group, allows the diffusion of small organic molecules, while at the same time limits the escape of larger molecules from clay vesicles (Subramaniam et al. 2011). We predict that clay layers across a vesicle opening (as in Fig. 6) act as a semi-permeable boundary to help sequester some organics and chemical networks inside vesicles.

Modern organisms produce, degrade or use many minerals; yet we are not aware of examples of life using clay minerals for cell functions. Clays may have played roles in prebiotic systems, but if they did, organic molecules took over clay functions as life evolved. Clays may be a prebiotic mineral that modern life has abandoned.

## Conclusions

Due to biological competition, no primitive living systems remain to teach us about how early protocells functioned. This competition, however, does not apply to prebiotic mineral systems that evolved only as their physical and chemical environment changed. Environments present today and that are little changed from the time of the dawn of life on Earth provide the best options for studying early life. The environment of volcanic eruptions into deep ocean basins, although not unchanged, provides an excellent opportunity for understanding a proxy setup for the origin of life. Decorated vesicles from deep-sea volcanic eruptions from subseafloor basalts show four features of prebiotic interest. (1) Compartmentalization; (2) Catalysts; (3) Free energy; and (4) Molecular sieves. Synergy of these features paints the image of a “*mineral-type prebiont*”, defined as a natural compartment in which 100% inorganic components carry out some life-analogous functions.

- The decorated vesicles are stable physical compartments capable of hosting chemical reactants and products. Vesicles with diameters from 1  $\mu\text{m}$  to millimeters are abundant in basalt of ocean crust layer 2A. During prebiotic evolution, such compartments could have hosted primitive chemical networks.

- Micron-sized clusters of metal-sulfide spherules decorate the inner walls of these vesicles. Due to their mechanism of origin, only basalts erupted at water depths greater than 200 m show such spherule decorations. The spherules are aggregates of iron monosulfide crystallites resembling framboids similar in composition and texture to mackinawite and greigite framboids. They are proposed to act as 100% mineral anabolic proto-enzymes. This predicted function is based on similarities with Ni-substituted metal sulfides shown to catalyze the production of formate, acetate, and methane from  $\text{CO}_2$  and  $\text{H}_2$ . Nickel replaces 2% to 5% of the iron in spherules, also making them compositionally similar to FeNiS centers from CODH/ACS enzymes.

- The free energy of basalt hydration creates a natural proton flux into the vesicles. An outward counter-flux of cations is predicted to exist, balancing the charge of the inward proton flux. In later evolution prebionts derived from decorated vesicles, this source of energy could have been used to assist ion transport across semi-permeable or hydrophobic boundaries.

- Smectite phyllosilicates derived from basalt weathering line the inner walls of the decorated vesicles and span vesicle openings (Figs. 5 and 6). In prebiotic systems such clays are assumed to have functioned as molecular sieves, organic concentrators, condensation facilitators or even chiral disruptors.

We hypothesize that decorated vesicles are abiotic, mineral, prebiotic systems that exist in the ocean crust today. Testing the following hypotheses can verify the presence of these prebiont systems:

H1: FeNiS spherules in vesicles fix inorganic carbon to formate, acetate, and methane.

H2: Polymerization of organic molecules can occur in vesicles, catalyzed by clay or glass.

H3: Amination and hydrogenation of organic acids can occur in decorated vesicles leading to monomers such as amino acids.

H4:  $H^+$ ,  $H_2$ , CO, and  $CO_2$  diffuse into vesicles and  $K^+$ ,  $Na^+$ ,  $Mg^{++}$ ,  $Ca^{++}$  and organic molecules diffuse out of vesicles.

H5: Diffusion of organic compounds through smectite is size- and chiral-specific.

H6: Monomers condense in vesicles that experience wet/dry cycles.

H7: Sulfide spherules contain traces of Cu, Mn, Zn, and Mo.

To conclude, our “*mineral prebiont hypothesis*” of a micron-scale, carbon-fixing, mineral system is a model that is experimentally available today. Decorated vesicles are produced by natural processes and thus, unlike more evolved protocell systems, are not subject to extinction via selective elimination by modern life forms. We posit here that decorated vesicles existed on the early Earth and played a role in the planet’s geochemical cycles by taking up protons, releasing metal cations and producing small organic molecules. We expect that some silicate exoplanets with volcanic activity and deep-water oceans will also host decorated vesicles.

## Appendix - Sample Availability

Basalts that are likely to contain decorated vesicles can be obtained from existing marine geological sample repositories. The National Oceanic and Atmospheric Administration’s National Center for Environmental Samples developed a database called Index to Marine and Lacustrine Geological Samples collected by U.S. institutions (<https://maps.ngdc.noaa.gov/viewers/imlgs/samples>).

The best basalts for studying decorated vesicles come from mid-ocean ridge crests (predominantly from more than 2000 m water depth), although other locations of submarine volcanic activity will also be suitable. Use the filters in the Index to search for Device “dredge, rock” and Water Depth (m) min 2000. If whole rock chemical analyses are available, select basalts with more than 0.04 wt.% S. Spherule diameters range from less than 1 to about 6  $\mu\text{m}$  (Moore and Schilling 1973), so they are hardly visible with an optical microscope and best observed with an electron microscope or high-resolution secondary ion mass spectrometry (such as nanoSIMS). Contact and or visit repositories for assistance identifying and obtaining samples with little seawater alteration.

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**Data Availability** Citations for the data used in this paper are included in the references.

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**Ethics Approval** We have followed the guidance provided by Spring.com on the ethical responsibilities of authors. No human subjects or animals were used in this study. Informed consent is not relevant to this study.

**Consent for Publication** Publication of research is tacitly approved for researchers, professors, and supervisors by the authors' host institutions.

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