

# Speculation on Quantum Mechanics and the Operation of Life Giving Catalysts

Nathan Haydon · Shawn E. McGlynn · Olin Robus

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**Abstract** The origin of life necessitated the formation of catalytic functionalities in order to realize a number of those capable of supporting reactions that led to the proliferation of biologically accessible molecules and the formation of a proto-metabolic network. Here, the discussion of the significance of quantum behavior on biological systems is extended from recent hypotheses exploring brain function and DNA mutation to include origins of life considerations in light of the concept of quantum decoherence and the transition from the quantum to the classical. Current understandings of quantum systems indicate that in the context of catalysis, substrate-catalyst interaction may be considered as a quantum measurement problem. Exploration of catalytic functionality necessary for life's emergence may have been accommodated by quantum searches within metal sulfide compartments, where catalyst and substrate wave function interaction may allow for quantum based searches of catalytic phase space. Considering the degree of entanglement experienced by catalytic and non catalytic outcomes of superimposed states, quantum contributions are postulated to have played an important role in the operation of efficient catalysts that would provide for the kinetic basis for the emergence of life.

**Keywords** Origins of life · Hydrothermal vents · Quantum decoherence · Pre-biotic chemistry · Metal sulfide catalysis

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The authors contributed equally to this work.

N. Haydon (✉) · S. E. McGlynn · O. Robus  
NASA NAI Astrobiology Biogeochemistry Research Center, Montana State University, Bozeman,  
MT 59717, USA  
e-mail: njhaydon@gmail.com

S. E. McGlynn (✉)  
Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA  
e-mail: simplyshawn@gmail.com

*Present Address:*

O. Robus  
Department of Philosophy, University of Washington, 361 Savery Hall, Box 353350, Seattle,  
WA 98195, USA

## Introduction

The existence of what is commonly referred to as “life” has for its chemical basis a set(s) of interconnected reactions through which net energy dissipation may be coupled to the generation of local entropy minima (Wicken 1980). Given this, a major requirement for the emergence, proliferation, and evolution of life is the presence of a repertoire of catalysts capable of allowing the occurrence of key chemical transitions in a time frame “in sync” with other reactions of metabolic networks. In this context catalysts occupy a salient role, for in metabolism the role of the catalyst is that of the connector which allows for the establishment of far from equilibria chemical couplings through which energy may be harnessed.

Among proposed theories aimed at providing insight into the nature of the origin(s) of life, those describing a “metabolism first” scenario provide for the establishment of an early proto-metabolism which precedes later events in chemical and biological evolution (polymer synthesis, coded molecular based information storage and transfer). These theories are perhaps most suited for accounting for the origin(s) of life, in that others which fail to describe a plausible early metabolism do not satisfy basic energetic considerations of what we know as “life”. Among these theories, the past years have seen the enumeration of a number of hypotheses for the emergence of life through the collective actions of metal sulfide mineral phases (Martin and Russell 2007; Cody 2004; Wachtershauser 2007). Within these schemes, small molecule interconversions and proto-metabolisms are thought to have been made possible by the action of catalytic properties of these minerals. These early mineral based catalysts would therefore play a central role to the emergence of life.

For the successful formation of an interconnected proto-metabolism capable of harnessing chemical energy from plausible substrates, catalytic sites in the mineral phase must be present of adequate specificity and kinetic properties. This fact is evident in the contemporary use of metal clusters in biology, where metal clusters in proteins have been observed to be operative and tuned for a number of roles including: electron transfer reactions, enzyme catalysis, regulation of gene expression, and protein folding (Beinert and Kiley 1999; Beinert et al. 1997; Beinert et al. 2004). As a result of the prominent position occupied by these structures and their catalytic nature, their occurrence bounds the overall metabolic potential of organisms, providing a kinetic means for reaction selectivity. The origination of potent catalysts of appropriate attributes is thus in itself a problem for the origin of life and poses questions as to how and in what ways the early catalysts of life were made ready for their roles as chemical connectors. Due to the importance of quantum mechanics at the size and time scales pertinent to the operation of catalysts, it may be expected that quantum theory provide explanation for the genesis and activity of the catalysts that feature so prominently in biological systems. Quantum mechanically mediated events such as small molecule shifts, rearrangements, and adsorptions—via their non-classical attributes—may provide an avenue for the timely formation of early catalysts required for the emergence of life.

## Quantum Mechanics and the Transition from the Quantum to Classical

The theory of quantum mechanics is perhaps the most successful theory describing the physical world, providing rationale and description for matter and the forces that bind it together. Quantum theory applies across scales from the existence of the covalent bonds, subatomic particles, and individual atoms that make up molecules—to cosmological scales where the theory is being applied towards gravitational effects and the cosmological

constant that is responsible in part for the expansion of the universe. Thus, despite its non-intuitive features and seemingly paradoxical results, quantum mechanics is *the* theory for describing the physical world.

Of the many areas of interest in quantum theory, the transition from the quantum to the classical has been a growing area of study and interest in recent years (Ball 2008; Blume-Kohout and Zurek 2006; Buchanan 2007; Ogryzko 1997; Vedral 2003; Ollivier et al. 2004). A longstanding mystery in quantum mechanics has concerned the question of just how the quantum world links with the classical; at some point the collective quantum mechanical features lose sway and the classical properties experienced on a day-to-day basis emerge. Given that quantum mechanics underpins reality, the precise nature of this transition may be of great importance to the consideration of systems in general and as proposed here, to the origination and operation of biological systems.

### Quantum Interactions

When two quantum systems interact unitarily (i.e. they evolve according to the Schrödinger equation), the resulting state can take one of two forms depending on the relationship between the systems involved. In one case, the resulting quantum state exhibits no correlations between the two subsystems. By lacking correlation, it is meant that measuring one system provides no information about the state of the second system. This non-correlated case is said to be non-entangled.

The second type of interaction allows for a correlation between the two systems. The existence of such a correlated, or entangled state, results when two systems interact in such a way where the behavior of one system is dependent upon the state of the second system. In this case, correlations exist between the subsystems. A simple example of such correlation occurs when a system interacts with another quantum system acting like a detector. For a detector to do its job well (and why we attribute the name detector to our system) it has to be correlated with the state of the system it is supposed to have measured. If this is the case, and the detector records the state of the first system, a measurement of the state of the detector will provide knowledge about the state of the system. Such correlation is not possible in a non-entangled system.

There are some remarkable properties about the resulting entangled state of two quantum systems. First, the state remains in a quantum state and continues to contain the interference and superposition terms along with the bizarre properties allowed by them. Second, the first system can no longer be thought as being separate from the second system. Such quantum correlations can only be properly understood when looking at the combined systems as a whole. Therefore, unlike classical systems which we purport to behave and hold properties independent of their surroundings, the behavior of entangled quantum systems can only be completely described when taking into account their surroundings. These properties allow for Einstein's "spooky action at a distance" as well as providing the key process behind quantum computing, where superpositional states and entanglement between systems may allow for information processing (Bennett and DiVincenzo 2000). In these cases, entanglement between subsystems serves as a method to perform logic operations between interacting systems.

An important connection can be drawn between these correlations and the causal chains we experience classically. When systems interact in the classical world, the future evolution of the two systems are determined by the relative state with which each system is found during the interaction. That is to say, the final resultant state of a system is correlated to the initial relative states. The correlations we perceive from classical systems by way of their

interactions originally arise out of correlations (through entanglement) between quantum systems; in the same manner that quantum computers store and reflect logic operations, quantum systems contain and store the possible classical outcomes and the reflected causal connections within each chain of events. Classical systems that we view as particularly susceptible to interaction and causal chains are therefore similarly highly susceptible to entanglement in the quantum realm. Furthermore, since these states are stored within the quantum realm before a classical outcome is known, quantum systems have the ability to “see” the potential classical outcomes before one is chosen and brought into classical existence.

Since the result of interacting quantum systems remains a larger quantum system possessing interference and superpositional terms, it is unclear by what mechanism the final “collapse” to the classical state occurs. The attempt to find a solution to this problem has led to continuous debate. Only recently has a new approach named decoherence been incorporated to explain part of this transition.

### Decoherence

In considering quantum systems, it is virtually inevitable that they interact with and add to a vast number of quantum systems. Employing a von Neumann measurement scheme, a system continually interacts (becomes entangled to various degrees) with a host of environmental subsystems. Entanglement between the system and various environmental subsystems is thus a ubiquitous phenomenon, and quantum systems quickly become entangled with a host of environmental subsystems. The theory of quantum decoherence provides a direct connection between the systems surrounding environment and the evolution and outcomes of the entangled state (Zurek 2003).


Several simple examples of decoherence have already been discussed in the literature (Zurek 2003; Zurek and Paz 2000; Schlosshauer 2007). The mathematics underlying decoherence addresses how systems interact and in what ways these interactions lead to classical observations. This is often shown in the density matrix formalism and the process is illustrated mathematically in Fig. 1. The top matrix is the representation of the superpositional states of a two state system entangled with a two state environment. The environmental interaction and in particular, the entanglement between the system and environment, are required steps in the process of decoherence. Thus a system and

$$\begin{array}{l}
 \text{Superposition of} \\
 \text{states} \\
 \left\{ \left( \begin{array}{cc} |S_{\uparrow}\rangle\langle S_{\uparrow}| |E_{\uparrow}\rangle\langle E_{\uparrow}| & |S_{\downarrow}\rangle\langle S_{\uparrow}| |E_{\downarrow}\rangle\langle E_{\uparrow}| \\ |S_{\uparrow}\rangle\langle S_{\downarrow}| |E_{\uparrow}\rangle\langle E_{\downarrow}| & |S_{\downarrow}\rangle\langle S_{\downarrow}| |E_{\downarrow}\rangle\langle E_{\downarrow}| \end{array} \right) \right. \\
 \downarrow \\
 \text{Decoherence; decay of off} \\
 \text{diagonal terms} \\
 \left\{ \left( \begin{array}{cc} |S_{\uparrow}\rangle\langle S_{\uparrow}| |E_{\uparrow}\rangle\langle E_{\uparrow}| & |S_{\downarrow}\rangle\langle S_{\uparrow}| |E_{\downarrow}\rangle\langle E_{\downarrow}| \\ |S_{\uparrow}\rangle\langle S_{\downarrow}| |E_{\uparrow}\rangle\langle E_{\downarrow}| & |S_{\downarrow}\rangle\langle S_{\downarrow}| |E_{\downarrow}\rangle\langle E_{\downarrow}| \end{array} \right) \right. \\
 \swarrow \text{or} \searrow \\
 \text{Emergence of} \\
 \text{classicality} \\
 \left\{ \left( \begin{array}{cc} |S_{\uparrow}\rangle\langle S_{\uparrow}| |E_{\uparrow}\rangle\langle E_{\uparrow}| & |S_{\downarrow}\rangle\langle S_{\downarrow}| |E_{\downarrow}\rangle\langle E_{\downarrow}| \end{array} \right) \right\}
 \end{array}$$

**Fig. 1** Mathematical overview of the stages in the transition from the quantum to the classical. Top, the density matrix resulting from the mixing of two 2-state systems entangled with the environment exists with all mathematical possibilities satisfied, including classically non-real solutions. As this superposition of states interacts with the environment, decoherence results in the decay of off-diagonal terms (middle) from which the classical state may emerge

environment are required to exist in a composite quantum state (be entangled) for decoherence to occur. Through continuing environmental interaction the off diagonal terms decay and we are left with the diagonal terms corresponding to the possible classical outcomes. Equivalent to “tracing over” the environmental degrees of freedom, we are left with the reduced density matrix in the center of Fig. 1. Seen in this light, decoherence is responsible for the failure of classical objects around us to produce interference type effects (thus resulting in our intuitive grasp of classical reality but difficulty in conceptualizing quantum phenomenon). This decay of the off-diagonal terms plays a vital role in the transition from the quantum to the classical in that the elimination of the interference terms is one of the required steps to achieve classicality. While here a simple example is portrayed, actual events are subject to a host of environmental interactions the sum of which act to produce observation.

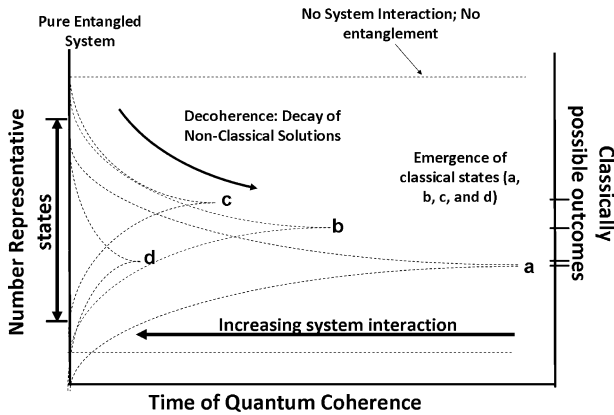
Such an example fails to highlight the exact interactions taking place between the system and environment, however. A more accurate view of the continual buildup of environmental interactions is highlighted below (Eq. 1) where the environments add to the system as the wave function spreads (arrow).

$$|S\rangle|E_1\rangle|E_2\rangle|E_3\rangle\dots|E_n\rangle|E_{n+1}\rangle\dots \tag{1}$$


The initial quantum system ( $S$ ) evolves and through time continually interacts with additional environmental subsystems ( $E_n$ ) through given interaction Hamiltonians. Though at first coherence remains between the system and the initial environmental subsystems (see [Quantum Interactions](#) section above), the increasing buildup of environmental subsystems causes the decoherence highlighted in Fig. 1. While the environment is often construed as causing decoherence of a quantum subsystem, it must be realized that requisite to the process of decoherence is the necessary initial coupling and entanglement between the system and the environment. Thus to study the complete transition from the quantum-to-classical world is to study the entire interplay between the system and environment, from entanglement and coherence with the environment to complete decoherence and the final emergence of the classical state.

These concepts, which relate to the nature of measurement and the possible outcomes a system may evolve, to are illustrated schematically in Fig. 2. The emergence of classical reality and decoherence is dictated by the extent of environmental interaction (measurement) a quantum system is subject to. Following from this, decoherence is expected to occur more quickly in quantum systems that interact the most with the environment (e.g. those that experience the addition of relevant terms) and are more “sensed” by the environment. The decoherence process may even occur without “interacting” as we tend to think in classical terms. In this way, decoherence provides a basis for linking the system’s environment with the time frame in which classical behavior emerges (Zurek 2003).

In evaluating and quantifying the effects of environmental interaction on the evolution of a quantum system, the number of environmental subsystems and the nature of their interaction (expressed by the interaction Hamiltonian) affect the coherence time and the evolution of the states of the system. Indeed, notions of strong and weak measurements may result in differential coherence times. Until the onset of decoherence, the evolution of the quantum system is properly described by the entangled system/environment whole; the individual and additive properties of these effects has yet to be put forth definitively



**Fig. 2** The dependence and emergence of classical behavior as affected by environmental constraints. The greater the degree of entanglement and environmental interaction, the shorter the exhibited coherence time of a quantum system. From a given superposition of states, mathematically possible classical solutions emerge on a time scale based on resultant environmental interaction. Classical outcomes that reflect potential causal chains quickly become entangled with their environment, effectively bringing about a more rapid transition to the classical world. In the figure, differing quantum systems immersed in differing environments are portrayed in paths (a) through (d). The curved lines represent the decay of off-diagonal terms whose convergence reflect the effective classicality of the quantum system. This process occurs on a time scale resulting from the level of environmental interaction and entanglement where the onset of decoherence and classicality is brought about on a shorter time scale according to increased environmental interaction. The top dashed line represents zero interaction in which case the system does not decohere, and therefore the superpositional state does not have a transition to the classical. Through the environment acting on nascent quantum possibilities, the transition to the classical world is effected by the potential of environment interaction

(Anglin et al. 1997; Schlosshauer 2007). Currently a major aim in decoherence research is illuminating and parameterizing these determinants.

Given various experimental results (Aharonov and Vaidman 2001; Hosten and Kwiat 2008; Facchi et al. 2005; Facchi and Pascazio 2008) and the dependence of quantum mechanics on the measurement process, it is clear that quantum systems possess a certain malleability in relation to the measurement process. Indeed, the notion of “preferred states” (Zurek et al. 1993) has been invoked to explain in part the evolution of quantum systems through an environmentally induced selection. In the quantum realm the timing of the measurement and the specific nature of the interaction (the interaction Hamiltonian) play important roles in the evolution of the system. As an example, the Quantum Zeno effects highlight how the timing of certain measurements may force a quantum system to remain in its current state or drive the system to an alternative state.<sup>1</sup> Thus, just what a quantum system is subject to prior to the transition to the classical, and the order in which this is undertaken have a role in determining the classical output. These interrelated effects by which measurement of a quantum system acts on and affects a quantum state are highly

<sup>1</sup> Experimental observation of the Zeno and Inverse Zeno effects have contributed to the acknowledgment that what occurs in the wider environment affects quantum systems and has furthered inquiry into these interactions. These experiments demonstrate the ability to “capture” or “freeze” quantum states via discrete observation or measurement in the case of the former (Misra and Sudarshan 1977), and in the case of the latter, the ability to produce observation of a particular state in a way that is defined by the order of measurements undertaken (see (Facchi and Pascazio 2008) for a recent review).

dependent upon the environment with which the system finds itself and may lead to effects and shifts in probability distribution at the classical level (Zurek 2003).

It is important to highlight the fact that the decay of the off-diagonal terms do not get us to the complete classical state. The emergence of classicality is born out of a final step in which a single possible solution (in this case one of the diagonal terms “up-up” or “down-down”) emerges. Decoherence is a means to explain part of the transition and while not being responsible for this in its entirety, demonstrates that this process is highly dependent on the level of entanglement between the system and environment and that the final step of the transition to the classical world has for substrates the products of the process of decoherence.

The link that decoherence provides between the quantum and classical—where collective systems operate to exchange information related to the classical outcome prior to its existence—leads to the ability to consider events which are the subject of quantum mechanics from a vantage point different from that prescribed by classical theory. Namely, the surrounding environment of a given system and its nascent potential for interaction are driving forces for the outcome of the quantum milieu. In this context, the consideration of phenomenon born out of atomic level interactions may be seen in a new light.

## Quantum Mechanics and Biology

As quantum mechanical theory underpins physical reality, it may be expected that quantum influences may be observed in biological systems. Indeed, quantum effects have been observed or proposed to play a role in phenomenon involving enzymes, DNA, brain microtubules, and very recently the operation of the avian compass (Engel et al. 2007; Hosten and Kwiat 2008; Patel 2001; Davies 2004; Ogryzko 1997; Genovese 2003; Cooper 2009; Rieper et al. 2009; Home and Chattopadhyaya 1996; Quandt-Wiese 2009). Experimental physics has revealed the quantum nature of large molecules such as  $C_{60}$  Buckyball (Arndt et al. 1999) the fluorofullerene  $C_{60}F_{48}$  molecule (Hackermuller et al. 2003) and recently mechanical systems have also been observed to display quantum properties (Jost et al. 2009). Thus it appears reasonable and even likely that decoherence may be active in biological processes and that organisms and their constituent parts may therefore act as quantum sensing devices, capable of orchestrating small particle shifts and matter transformations required for life.

An example of a characterized biologically quantum sensing device is found in the photosynthetic system, which captures energy in the form of solar radiation and transfers it to the reaction center where it is directed at the formation of chemical energy. The attributes of energy transfer through this system were described (Engel et al. 2007) and the enzyme environment was observed to contribute to a coherent electronic state through which it is possible to explore the most efficient path for charge transfer. Very recently, coherent states were observed to exist at ambient temperatures in the light harvesting system of cryptophyte algae (Collini et al. 2010), confirming that this is ‘wired’ to the photosynthetic reaction center in a way that is fundamentally different from previously invoked electron ‘hopping’ mechanisms. These observations suggest that energy transfer is facilitated by quantum coherence and that in effect, the enzyme (environment) may be acting as a detector where entanglement with electrons results in rapid transfer. This observation is highly reminiscent of the inverse Zeno effect where continuous environmental monitoring results in the selection of one quantum state and thus classical outcome over another. In this case, the enzyme may be acting to conduct a series of measurements such that the observed



outcome is the characteristic rapid electron transfer. Examination of other metabolic activities reveals that quantum mechanically mediated effects are likely at play in a broad distribution of enzymatic functionalities. For example, long distance electron transfer—along with quantum detection of particular states—is presumably involved in (to name only a few examples) hydrogenases, nitrogenase, CODH, and the electron transport chain, where a specific environment (and thus detection) is provided by a peptide to allow for efficient electron transfer between centers.

Reactions carried out by the enzymes mentioned above are foundational to the existence of biological systems and are involved in key chemical and energy transformation steps that allow for the accumulation and functionality of biomolecules. That the phenomenon of quantum decoherence is active and integral in these processes of electron transfer and small molecule condensation reactions suggests that, from an evolutionary perspective, life evolved amidst the dictates of quantum measurement and may still reflect an ability to explore quantum mechanically relevant possibilities through efficient quantum searches.

### **Catalysis at Mineral Surfaces, Ligand Modified Catalysis, and Catalytic Defect Sites**

The reactions that make up the metabolism of organisms are accomplished via the use of catalysts that make chemical and electronic transformations possible in a time frame where the linking of reactions to form complex chemical networks becomes possible. In this context, non-catalytic yet thermodynamically favorable reactions in a series would not join and contribute substrate/product to other network reactions in a time frame whereby energetic and matter constraints would be satisfied. Therefore the existence of elaborate cellular mechanisms for the production and operation of bio-catalysts (enzymes) poses intriguing questions as to the biogenesis and evolutionary history of unique and specialized co-factors. From an origins of life perspective, the generation, utilization, and eventual incorporation of abiotically derived catalysts deserve attention since these factors played important contributory roles in this process. Since what we refer to as life is an assemblage of catalysts capable of carrying out the energetic couplings required for energy degradation, the very formation of life required, prior to its existence, the presence of catalysts that would make the transition from the abiotic to the biotic feasible.

From this perspective, a number of hypotheses have emerged that detail hypothetical scenarios as to how the role of abiotic catalysis may have contributed to the emergence of life (Russell 2007; Cody 2004; Wächtershäuser 2007). Notable among these proposals is the perceived importance of minerals, their various interactive properties with organic compounds, and their ability to perform the re-dox reactions required for a metabolic network. Goldschmidt was perhaps the first to recognize the potential for various modes of mineral-organic interaction and postulated the roles of mineral surfaces as sorbents, catalysts, and templates (Goldschmidt 1952). The so called “metabolism first” scenarios posit that a period of time elapsed where the building blocks of life were the subject of a “proto-metabolism” and that the earliest form(s) of life themselves were comprised of such reaction networks after which life as we now know emerged through the process of exaptation of geological functionality (geo-mimicry). Thus, being born from geology, living systems emerged as a dominant organizational structure of chemical potential. Given the above considerations, it is of interest to speculate on the properties of minerals and their associated catalytic capabilities and specifically as to which mineral forms and mineral transitions contributed to the proliferation of molecules which were brought into the rising assemblage of complexity that eventually became what we call life.



Mineral based catalysis has been observed to be variable on a number of factors stemming from structural and electronic properties. Heterogeneous catalysis by mineral surfaces has been observed to occur at areas of discontinuity of bulk structure or defect sites (Andersson et al. 2004; Stirling et al. 2003). At these sites, which represent approximately 1% of total surface area (Somorjai 1994; Schoonen et al. 1998), defects in lattice structure result in unique electronic and spatial localities where molecules may transiently bind in orientations and environments amenable to reaction progress. A further example of reaction characteristics being a function of surface conditions has been observed in the case of nitrogen reduction over an iron catalyst, where reaction rates vary with the particular crystal face (surface roughness) exposed in the reaction (Murphy and Strongin 2009; Strongin et al. 1987).

In addition to the inherent state of a mineral itself, surfaces are the subject of environmental chemistry which may contribute to catalytic properties. In this context, small molecule condensations and additions to minerals have the potential to affect the catalytic potential at mineral surfaces and result in reaction kinetic increases on the order of factors of 1,000 (Berrisford et al. 1995). This type of catalytic emergence could feasibly be brought about by the ligation of molecules such as CO, CN<sup>-</sup>, various small molecule organics, and perhaps by the binding of an alternate metal ion into the lattice as well. Similar to the occurrence of and reactivity at mineral defect sites, ligation by extraneous molecules alters the electronic and spatial properties of potential reaction sites, thereby making possible previously unrealized catalytic ability. In this light the hypothesis of “ligand-accelerated autocatalysis” has been postulated (Wachtershauser 2007), where initial catalytic events are proposed to have been the source of molecules capable of generating either novel catalytic forms, or reinforcing by inheritance (via ligand feedback) the existence of extant catalytic properties, thus taking part in a type of primordial chemical evolution.

With knowledge of the contribution of both defect sites and ligand addition to the catalytic potential at mineral surfaces, the question of catalytic emergence and evolution arises. In what ways were the first efficient catalysts generated and selected for out of the myriad possibilities available, and to what extent was this process directed by the environment? Because the phenomenon of ligand accelerated catalysis is brought about through oftentimes unpredictable additions (Berrisford et al. 1995), and because of the inability to construct a plausible history of catalysts through the geological rock record, it is difficult to theorize on how the emergence of biologically relevant catalysts may have occurred. Despite these difficulties, lessons from synthetic chemistry and knowledge of extant biological metal-based catalysts and origins of life theories provide a framework to consider the origination of bio-catalysts (McGlynn et al. 2009). Based on known reactivities and chemical attributes, the proficient catalysts requisite for living systems may have been wrought from geological precursors and geochemically based reactions which finally lead to the development of catalysts of sufficient biological specificity. In this perspective, metal sulfides form the basis of a growing set of reactions that proceed by ligand accelerated catalysis and pre-existing catalytic motifs/functionality to form relevant biomolecules, which themselves are enlisted as metal modifying agents to finally result in the formation of peptide bound metal clusters capable of a diverse array of reactions. Herein, it is proposed that the actions of quantum decoherence and associated quantum mediated searches of possible states may have—in addition to the aforementioned chemical evolution from mineral precursors—played a significant role in the emergence of efficient mineral based catalysts that formed the reactive groundwork for the origins of life.

## Quantum Searches Through Catalytic Phase Space and Life Giving Catalysts

From a very large number of chemical possibilities, chemical organization was made possible by a number of physiochemical attributes having to do with environmental localities, as well as with underlying physical law. With respect to environmental localities, theories have emerged describing a possible source and driving force of initial chemical organization based upon mineral chemistries. Here the focus will include the so called “Alkaline Solution for the Origin of Life” (Martin and Russell 2007; Russell 2007; Russell et al. 1989, 1994), as this description provides sound basis for the compartmentalization of life-giving chemistries within metal sulphide reactive site containing compartments. This feature, as we will see below, may allow for local quantum-based searches of chemical constituents and associated catalytic potentialities contained within the emerging bubbles of a growing hydrothermal metal sulfide mound.

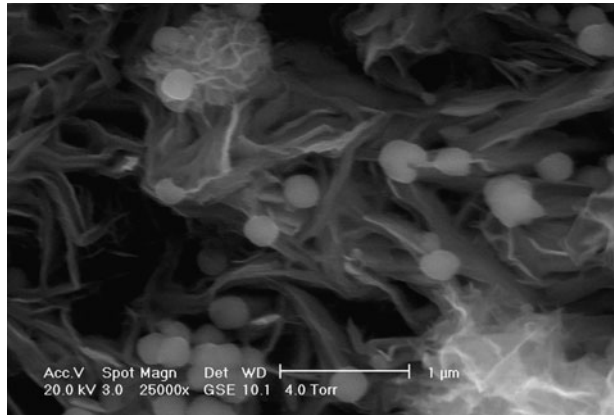
The Alkaline Solution describes the accumulation of a mixture of minerals such as: precipitated iron sulfide carbonates and magnesium containing minerals of greigite, mackinawite, saponite, and brucite, through which hydrothermal fluids containing  $H_2$ ,  $HCOO^-$ ,  $NH_3$ , minor  $CH_3OH$ ,  $HS^-$  and  $CH_3S^-$  may have acted to result in the accumulation of metal sulfide chimney structures (Russell 2007). Together with associated catalytic abilities of mound bound minerals, these chemical feedstocks comprised the initial chemical setting for the emergence of chemical complexity. A major accomplishment of a hydrothermal mound as envisioned then, is the realization of a host of potent contributory catalysts that together were able to result in and give rise to molecules that were of structural and energetic benefit for nascent life. In addition, these structures provide for the localization and compartmentalization of chemical constituents.

Contained within the metal sulphide compartments of the growing mound are a great number of possible variants of mineral defects and ligand modification events. These are dependent upon the positioning of single atoms (as in the case of defect sites) or on metal ligation by a small molecule modifier. As mentioned previously, the presence of catalytic sites on mineral surfaces may be rather small, representing  $\sim 1\%$  of total mineral surface area. This fact, together with the innumerable possible defect/ligand modification arrangements and the necessity for some semblance of catalytic specificity among these sites, makes the chances of encountering catalysts of such abilities in sufficient proximity for constructive interaction small.

These chimney structures have been observed to contain distinct sub-micron layers and compartments and thus comprise structures of semi-fractal, spatially isolated localities that serve to isolate molecules from the bulk solvent (Fig. 3) (Mielke et al. in prep., Russell et al. 1994). These structures represent micro-localities of liquid bordered by high surface area metal sulfide walls. Additional solvent ordering in these localities may be provided in the form of “nests” (Milner-White and Russell 2005, 2008) comprised of early short peptides which form the basis of molecularly protected sites in which coherent states may exist analogous to what is observed in biology today in enzymes.

As a result of the quantum nature of small molecule shifts and atomic rearrangements at mineral surfaces, the determinants of catalysis are conducive to quantum searches through which catalytic phase space may be explored as to arrive at the formation of efficient ligand modified and/or defect containing catalytic active sites. At these surfaces, the wave function describing the state of a mineral surface must be considered as a composite, including surrounding atoms and molecules that may become actors upon decoherence and the emergence of classicality. In effect, potential substrates and ligands may act as detectors of nascent catalytic activity at the mineral surface adding to the composite wave function and

**Fig. 3** 25000× magnification of an iron sulfur chimney created in vitro on an environmental scanning electron microscope (ESEM) reveals a complex network of sub-micron compartments and surfaces. Scale bar is 1 micron



thereby effecting system evolution. This activity may lead to increased catalytic character of the composite wave function via the interaction hamiltonian, finally resulting in the selection of a catalytic state upon collapse (Eq. 2).

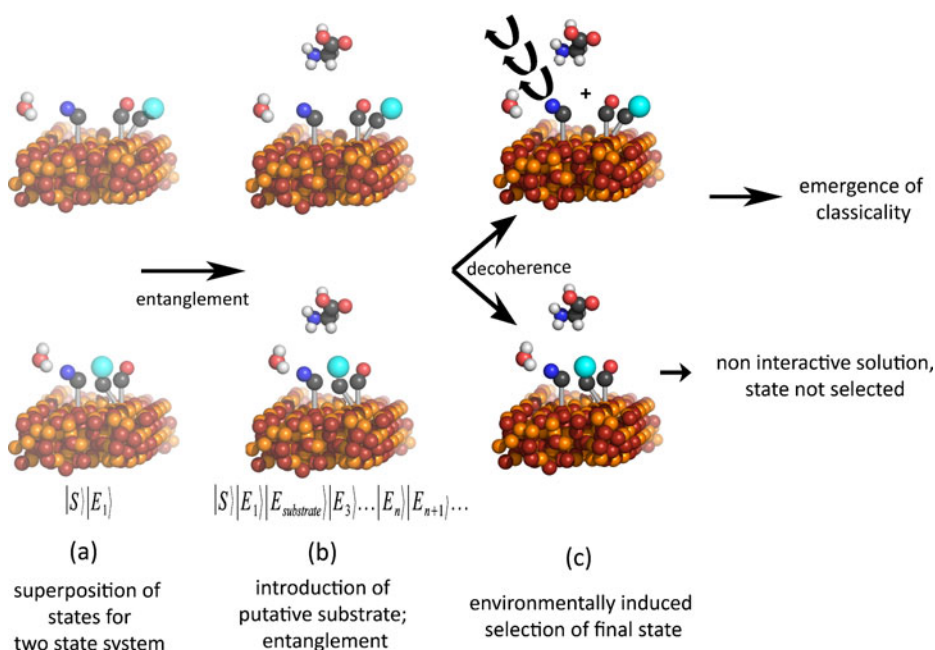
$$|S\rangle|E_1\rangle|E_{substrate}\rangle|E_3\rangle\dots|E_n\rangle|E_{n+1}\rangle\dots \quad (2)$$

$\xrightarrow{\hspace{10em}}$

In this example, the nearby “environment” that the system is measured by is a putative substrate. Other examples at this level might include ligand position or defect site nature which determine electron transfer. At this stage, the entangled state will either collapse or continue to persist, encountering other environments until final collapse. Either way, substrate entanglement means that the resultant product is dependent on catalyst/substrate interaction, prior to the realization of the classical counterparts. This coupling, or entanglement, provides for a situation where interaction of the coherent mineral surface’s wave function with environments containing putative substrates will induce rapid decoherence (as they constitute measurements) and thereby lead to catalytic functionality as a result of the increased entanglement coincident with such functionality. In these cases, quantum decoherence represents a possible mode of early catalyst evolution and ligand feedback, suggesting that quantum information may influence catalytic properties.

An important feature of this type of decoherence is that it is not dependent on coherence being maintained over very long distances; diffusion in solution and local solvent ordering or compartmentalization will allow at times substrate and putative catalyst to be in close enough proximity so as to have the coherence volume contain the two. Said another way, the determinants of catalysis—electrons and atoms—will at times exist in coherent states and coupling of substrate (environment) and catalyst (system) wave functions will result in a situation where each entity affects the evolution of the other’s and allows decoherence to proceed. Decoherence times for the individual determinants of catalytic attributes will vary from situation to situation but quantum coherence between catalyst and substrate can be expected to be maintained where these are in adsorbed on a surface or contained within the gel like mineral phase present in metal sulfide hydrothermal mound material. In similar situations coherence times for protons in DNA molecules have been estimated to persist for milli-seconds to seconds (McFadden and Al-Khalili 1999); in other analyses (Rieper et al. 2009), entanglement between two electron spins in the avian compass has been estimated to

persist for tens of micro-seconds. While these estimates vary due to differences in calculation and their subject, they give support to the notion that the persistence of wave function descriptions of catalysts and substrates and the resultant connection to classicality through the formation of a composite function can be expected to be at play in situations where catalysts take part in the electron and proton shifts that characterize reactions. Wave function coupling and decoherence for mineral states and morphologies that enlist substrate molecules and thus increase system dynamism (i.e. those states which are catalytic: Fig. 4), may significantly affect the probabilities associated with the emergence of catalytic states as in these cases, a greater degree of measurement is enforced upon the system and decoherence is expected to occur more quickly than in the case of less measurement (non-catalytic). This rise in the probability of a catalytic state is brought about by the addition of putative substrate terms in the growing composite wave function; the presence of possible substrates within the coherence volume of a putative catalyst results in a greater magnitude of measurement than in non-catalytic states, thus bringing about the realization of catalytic states from the quantum milieu. Non-catalytic states do not experience the addition of these



**Fig. 4** A putative catalytic mineral surface is drawn which is the subject of ligand modification where the position of the ligand may result in either reactivity or non-reactivity. The transition from the quantum to the classical can be conceptualized as occurring in three steps, where a given superposition (a) is the subject of environmental monitoring (b) which results in entanglement and the reduction of the quantum state to a possible outcome (c) reflecting the fruition of a potential causal chain. This is finally followed by the emergence of the classical state. Prior to decoherence, the ligand modifier (light blue) may be viewed as existing in a superposition of the two depicted states as depicted on the left. Upon exposure to the environment in the middle stage (in this example the possible substrate glycine), the surface possibilities becomes entangled with the environment, and the catalytic solution rapidly decoheres as it entrains a greater portion of the system (becomes more entangled with the environment), whereas the non catalytic possibility remains. Thus as the wave function describing the surface evolves, the presence of substrate within the coherence volume gives rise to greater catalytic character and when collapse finally occurs, there is greater chance that the catalytic state will be occupied and selected upon collapse

terms and thus will not decohere as quickly as the catalytic state. An important consequence of this environmental monitoring by putative substrates is that through the process of decoherence possible substrates have a role as quantum state detectors; putative substrates suitable for reaction with a particular catalytic state measure for this state and hasten the emergence of this state.

## Conclusions and Discussion

Herein is presented a hypotheses regarding the operation of catalysts and the possible effects of substrates on the quantum evolution of these through the process of decoherence in the context of the origins of life. While existing as a broad conceptual program and perhaps not as a detailed and well-confirmed theory, the hypothesis is consistent with the known properties of matter and suggests that the biological and physics disciplines may have much to learn from one another at the level described here. Our hope is that the ideas presented here will provide impetus for continued interest in understanding living systems and their origins from the “bottom up” and to search for understanding through a “Quantum all the way” (Ball 2008) perspective.

It is important to point out that the ideas presented here with respect to quantum effects during catalysis and the relevance to the origins of life should be expected to be features of the physical environment and catalysis in general. Insofar as catalysts operate to promote travel of reactant species upon a minimum energy path along the reaction coordinate, quantum mechanics in the context described herein provides rationale for understanding catalysis from first principles. As the physical world provides myriad unique localities, it may be expected that the salience of the phenomenon proposed herein would vary as well. Current limitations on the computation of coherence times of molecules for such a wide array of settings and environments make a comprehensive and quantitative analysis unfeasible at this time. However, where there is matter and energy, quantum effects should be expected and the particularities of this matter and energy will dictate the magnitude of quantum effects and ultimately the ability for biology to proliferate. In addition, it should be noted that the phenomenon postulated herein to be operative in catalysts is construed as not being reliant on unique or isolated cases of coherent states, but rather that it is in the ubiquity of entanglement that decoherence and quantum measurements will result in the operations of catalysts conducive for energy dispersal and the biological evolution that follows from this.

The emergence and continued persistence of the chemical systems commonly accepted as life are underscored by an associated ability to lower activation energies of key chemical transformations; therefore the formation of efficient catalysts was a requisite step in the emergence of life. As a result of the high degree of reactivity variation that may be experienced by a putative catalyst given single atom shifts and small molecule binding events, the theory of quantum decoherence gives rationale (via superimposed states of ligand and mineral surface atoms, position of the substrate etc..) for the ability of quantum interactions to create situations in which the greatest number of molecules in the local environment will be enlisted in a local, growing, metabolic network. These states will experience the addition of relevant collapse inducing terms to a greater extent than inert states, and in this way may be selected for (Fig. 4). In this light, myriad ligand modification, defect site incorporation, adsorptions, and lattice structure modifications may constitute quantum measurements that affect the evolution of coherent states and allow for the realization of catalysts requisite for the transition from the pre-biotic to the biological.

This process gives rise to an early type of chemical evolution, where reactivities of mineral surfaces with putative substrates evolve within the bounds of an increasingly complex proto-metabolic potential. Interestingly, this type of evolution results in variation and selection arising in a very different way than that from Darwinian evolution. Thus as pointed out by Ogryzko (Ogryzko 2008), biological systems themselves may exist as a reservoir of knowledge concerning the factors controlling the selection of particular quantum states. Indeed, it may be that contemporary enzymes in biological systems exist as evolutionarily derived quantum measuring devices insofar as much of what makes up biology has for its dictates quantum level phenomenon.

The initially quantum mechanically driven formation of reactive centers sets the stage for later exaptation by biology where such ligand modified and geometry strained metal catalysts abound and form the basis of biologically requisite reactions such as N<sub>2</sub> fixation and carbon reduction (nitrogenase, photosystem, CODH etc.). It is interesting to note that these reaction centers, which carry out foundational chemistry for extant life, should rely so heavily on the type of long distance electron transfer, tunneling, and substrate binding specificity that quantum decoherence provides for. This approach to the formation of requisite catalysts, rooted in quantum mechanical behavior, is compatible with and adds credence to existing mineral catalysis-based hypotheses on the origins of life, making more rational the proliferation of chemistries observed presently. Moreover, the functionality of metal sulfides described herein of creating distinct, isolated localities for catalysis draws a further parallel between minerals and biology in that present day enzymes appear to function in a similar way as they isolate and partition substrate and solvent molecules to allow efficient reactivities.

The theoretical application of the phenomenon of quantum decoherence described herein differs from other approaches in which authors have suggested quantum effects operating in molecules such as DNA (McFadden and Al-Khalili 1999), or a growing RNA polymer (McFadden 2001) in that it is not belabored by problems associated with acting through the distinct levels of molecular organization of transcription and translation through which decoherence phenomenon may not be able to operate. Instead, the localities focused on here—enzyme active sites and hydrothermal mounds—exist as localities where coherent states and the environmental interactions they are subject to result in immediate realization of quantum elicited changes. Furthermore, the localities of organic product synthesis envisioned in hydrothermal scenarios occurs at temperatures within the bounds of extant processes such as photosynthesis, where electron transfer via a superimposed state is thought to occur (Engel et al. 2007; Collini et al. 2010). Finally, this locality offers the potential for quantum effects at multiple stages of pre-biotic evolution in that vent environments have been proposed to have been determinants in the origination of not only metabolism but genomes as well (Koonin and Martin 2005; Martin and Russell 2003, 2007; Russell 2007).

The ability for quantum decoherence to effect the formation of primitive catalysts in a pre-biotic environment has interesting, and potentially fruitful implications for further investigations into the origin, nature, and proliferation of living systems throughout the universe. The presence of naturally occurring abiotic mineral catalysts—potentially ubiquitous in the pre-biotic environments where living systems arose, may have provided a rich zoo of catalysts upon which selective decoherence can act. Finally, the emergence of efficient catalysts, and the potential chemistry they imply, is central in understanding not only how life arose, but also in articulating the proper context in which to assign the term “life”. The function of catalysts points the way to conceiving of life in terms of its functions, not its makeup; and this suggests a framework in which to expand (and constrain) the search for the origin and nature life down new and fruitful avenues.

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