Magnetism, FeS colloids, and Origins of Life

Dedicated to the memory of Professor Alladi Ramakrishnan

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Abstract

A number of features of living systems: reversible interactions and weak bonds underlying motor-dynamics; gel-sol transitions; cellular connected fractal organization; asymmetry in interactions and organization; quantum coherent phenomena; to name some, can have a natural accounting via physical interactions, which we therefore seek to incorporate by expanding the horizons of ‘chemistry-only’ approaches to the origins of life. It is suggested that the magnetic ‘face’ of the minerals from the inorganic world, recognized to have played a pivotal role in initiating Life, may throw light on some of these issues. A magnetic environment in the form of rocks in the Hadean Ocean could have enabled the accretion and therefore an ordered confinement of super-paramagnetic colloids within a structured phase. A moderate H-field can help magnetic nano-particles to not only overcome thermal fluctuations but also harness them. Such controlled dynamics brings in the possibility of accessing quantum effects, which together with frustrations in magnetic ordering and hysteresis (a natural mechanism for a primitive memory) could throw light on the birth of biological information which, as Abel argues, requires a combination of order and complexity. This scenario gains strength from observations of scale-free framboidal forms of the greigite mineral, with a magnetic basis of assembly. And greigite’s metabolic potential plays a key role in the mound scenario of Russell and coworkers—an expansion of which is suggested for including magnetism.

Key words: Magnetic-reproduction, Brownian noise, symmetry-breaking, ferro-fluids, super-paramagnetic particle, ligand-effects, greigite mineral

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Preprint submitted to Elsevier
1 Introduction

Life’s hierarchical control structure is a sequence of constraints, each limiting the scope of the preceding level for step-wise harnessing of the physico-chemical laws governing its lowest rung. But the limiting ‘boundary conditions’ are themselves extraneous; they cannot be formally derived from these laws. Further, the higher-level operating principles depend on, but are not reducible to, those of the lower ones (Polyani 1968). Next, the origins of purpose permeating across biology (Kant 1790), as well as information associated with function, are among the most fundamental of questions in biology (Küppers 1990). Indeed, the structure-function relationship where rate-dependent equations representing measurement associated with bio-structures are linked to rate-independent constraints associated with bio-information, is viewed as an epistemological complementarity (Pattee 1979). According to Pattee, “epistemic operations like observation, detection, recognition, measurement, and control as the essential type of function” demarcate living from non-living organizations. The chances of an organism’s survival are crucially dependent on its ability to improve its control strategies that in turn depend on its recognition of environmental patterns. Hence, “To qualify as a measuring device it must have a function, and the most primitive concept of function implies improving fitness of an organism”. Pattee’s famous “semantic closure principle”, places a heavy responsibility on the observer who should at minimum be an organization that can construct the measuring device and use the results of measurement for its very survival (Pattee 1996). This scenario seems to be a far cry from the objective (observer-independent) physical laws characterized by Universality and Invariance Principles. And it is indeed a tall order to explain from these ‘classical’ premises the emergence of subjective (observer-dependent) biological infrastructure making measurements for survival. But Pattee recognizes that unlike classical theory, Quantum theory is not constrained by observer - independence and promptly invokes Wheeler to make his point: “No elementary quantum phenomenon is a phenomenon until it is a recorded phenomenon (i.e., the results of a measurement)”. Indeed, the puzzle is really about how the ‘Cybernetic cut’ (Abel 2008) could have been crossed using mere physico-dynamics, leading to the emergence of a non-physical (not governed by chance or necessity) mind from physicality that established controls over the same. We further ask if this mystery could somehow be related to the idea of life having originated in an inorganic world—an idea which has met considerable acceptance. The compelling link to iron-sulphide (FeS) clusters in early evolved enzymes (and across species in a range of crucial roles, e.g. catalytic, electron transfer, structural), with exhalates on the Hadean ocean floor, is based on the close resemblance of these clusters with greigite (Fe₅NiS₈) (Russell et al 1994; Huber and Wächtershäuser 1997). Not only are these clusters seen as playing a key role in the origins of metabolism, where geochemical gradients were harnessed, but also, for long
mineral crystal surfaces have, and continue to be seen as scaffolds thanks to their chemical-information storing/transferring potential, leading to the other-replicating—wing of Life (Bernal 1949; Goldschmidt 1952; Degens et al 1970; Cairns-Smith 1982; Arrhenius 2003; Ferris 2005). But in these approaches, a number of features: reversible interactions, weak bonds, gel-sol transitions, cellular connected fractal organization, asymmetry in interactions and organization, to name some, and which are difficult to address using chemical interactions alone, are seen as later arrivals, i.e. upon achievement of complexity in the pre-biotic 'soups'. Here again, the path, as to how complexity could have been entrained to lead to Life-like features of today, remains far from being understood. Then, in addition to chemistry, could physical properties of inorganic matter have also acted as a scaffold for onward transmission of several common physical features (see below) typical of living systems? To that end, we note that dynamically ordered forms of matter, like framboids, regardless of chemical structure are the result of physical forces, including magnetism (see Sect. 4).

Now, magnetism has myriad manifestations at different scales –quantum to cosmological (Skomski 2008). (The repeated appearance of fractal themes is compelling – from magnetic critical phenomena to finer length scales where quasiparticle behaviour in a magnetic field can be explained by fractional quantum numbers (Jain 2007; Goerbig et al. 2004); Farey series elements, \( F_n \); Hausdorff dimension \( h \) (da Cruz 2005)). And, there are ubiquitous magnetic influences across kingdoms: navigation sensing in bacteria, algae, protists, bees, ants, fishes, dolphins, turtles and birds (Kirschvink and Gould 1981; Winkelhofer 2005); field effects on growth patterns, differentiation, orientation of plants and fungi (Galland and Pazur 2005); ferromagnetic elements in tissues (Kirschvink et al. 1992), etc. (In fact, magnetite (\( Fe_3O_4 \), a magnetic mineral) - biomineralization, the most ancient matrix-mediated system, is thought to have served as an ancestral template for exaptation (Kirschvink and Hagadorn 2000)). Indeed, new inputs of quantum events underlying biophenomena like magnetoreception (Kominis 2008) reveal the importance of magnetism in biological systems of today. Most importantly, its vital role in the science of information technology persuades us to turn to this enveloping science for any mechanisms beyond the limits of physico-chemical principles that could have helped bridge the gap from inanimate matter to life.

In this mini survey

(1) We give a brief summary of the relevance of quantum searches in biology and therefore to the origin-of-life problem (Sect. 2.1). We briefly review spin and magnetic models offering insights into the emergence of life, leading up to our proposal (Sects.2.2-4).

(2) We survey various biophenomena with analogies to magnetic ones in gen-
eral as well as topological similarities with our magnetism-based proposal in particular (Sects.3.1-9), and ask if magnetism could have helped to pave the way for a take-off from non-life to life.

(3) We briefly review framboids, where conflicting physical forces usher in dynamic order. Here, the mineral greigite’s magnetic properties underlie its framboid-forming capacity (Sect.4).

(4) We outline the mound scenario of Russell and coworkers, with rich metabolism potential, where greigite forms in a colloidal environment. A possible scenario for a magnetic reproducer is drawn (Sect.5).

2 Quantum searches and the origins of life

A brief introduction on quantum searches in biology is followed by their implications in the origin of life. A possible physical system enhancing the propensity of such searches is then suggested. 2.1

2.1 Quantum searches and biology

Outstanding biological-search examples can be seen in biological evolution itself, with divergences symbolized by tree nodes; the clonal Darwinian-like phase in the adaptive immune system; brain connections and protein folding. The efficiency of quantum searches over classical ones has prompted the idea that they could have been used by Nature who usually is found to take the cleverest among available options, as illustrated by certain Extremum Principles of Classical physics (Hamilton, Fermat, Maupertius). For instance, in a database of dimension $d$, a quantum search gives a square root speed-up over its classical counterpart – also valid for the respective nested versions (Cerf et al. 2000). In a typical scenario, challenges interrupting the networking phase are seen as forcing the biosystem to seek help from a co-existing quantum domain, e.g., a search prompted by a ‘crisis’ in the form of a depleted nutrient could lead the adaptive system to a new pathway for succour. Now, quantum coherence in the set of elements on the affected front could help skirt frustrations in local minima as can happen in a classical search. This access to the wave-property enables a superposition of states and allows a ‘holistic’ decision. Thus in the face of crises, halted networked interactions in a subsystem would prompt the formation of a ‘quantum decision front’. This would be constantly checked or ‘measured’ by the rest of the system. A fruitful interaction with one chosen path would mean a simultaneous collapse of the quantum
superposition of alternative paths (McFadden and Al-Khalili 1999).

Today, clear signatures of quantum processing in biology are coming in (Engel et al. 2007), aided by femtosecond laser-based 2D spectroscopy and coherent control approaches, showing how phase relationships in nano-structures modulate the course of bio-reactions (Nagya et al. 2006). As to decoherence evading mechanisms, the role of a gel-state; quasicrystalline order; (Jibu et al. 1994; Hagan et al. 2002); are amongst proposed order-maintaining mechanisms in a wet environment, while 'screening effect', or 'cocooning' structural mechanisms are seen as providing insulation against interactions with the environment [Patel (2001); Davies (2003, 2004)] (see also Sect. 3.9). Indeed, it seems that Nature has quietly been using these strategies all along, i.e. leading to creation of biological language itself, as the Grover-Patel search numbers match those used by Nature! Using Grover’s quantum search method for a marked item in an unsorted database, Patel (2001) hit upon the base-pairing logic of nucleic acids in transcription and translation as an excellent quantum search algorithm – a directed walk through a superposition of all possibilities resulting in a 2-fold increase in sampling efficacy over its classical counterpart (which at best permits a random walk). Prompted by these insights, Al-Khalili and McFadden (2008) point out that a quantum search would have been far more efficient than a random one for picking out the self-replicator from the primordial soup comprising a dynamic combinatorial library of compounds linked together, say by reversible reactions. But what plausible ingredients could have facilitated such a quantum assisted leap?

2.2 Spin and magnetic systems for the origin-of-life

Hypothesizing a quantum-mediated process for the transition from non-life to life, Davies (2008) proposes that information could have its origins in quantum objects such as spins, whose orientations offer a natural discretization mechanism of genetic information, and which in turn may have been embodied by physical structures in some natural system. Although this would initially be copying bits (no associated phase information so initially no issues of decoherence evasion) the possibility of coherence in this inherently quantum system endows it with potential for conducting a quantum search for the quantum replicator. Furthermore, he points out that in this envisioned scenario, the collapse of the quantum superposition of states of living and non-living ones to the low probability state of ”life”, cannot be due to the quantum system’s own doing. Instead it must have been the result of an environmental interaction, serving as a measuring device, thus implying a key role for the environment (c.f. Zurek 2003). Again, an origin-of-life model based on spin-ordering (a variant of the Ising spin glass) was proposed by Anderson (1983), that was albeit prompted from another angle – the correspondence between the complexity
due to the impact of frustration in magnetically disordered systems and bio-
processes, such as protein-folding (Hollander and Toninelli 2004; Stein 1996) (see Sect. 3.1). Then again, Breivik (2001) demonstrated that self-ordering of ferromagnetic objects (∼3nm) with reproduction of magnetic templates could be manipulated via dynamic interaction with environmental temperature fluctuations, thereby significantly also connecting information encoded in nucleic acids with non-chemically linked aperiodic polymers. This is because a magnetically packed array is naturally aperiodic (see Sect. 3.8), hence satisfying Schroedinger’s (1944) vision of aperiodic surfaces as efficient information-holders, in contrast to a periodic crystal lattice with strongly correlated elements. This magnetic mechanism for propagating information, also agrees with Dyson’s (1999) suggestion that ‘physical reproduction’ preceded chemical replication in the origins of life, the latter being identified with a specific chemical copying process. And interestingly, his use of a magnetic analogy for states, obeying the Boltzmann probability distribution, gels with the kinetic aspects of biological reactions (Pross 2005).

All this compels us to ask if magnetism could have empowered the initial conditions for traversing the bridge dividing life from non-life, by providing simultaneously a scaffold for interactions and connections, where physical representations would allow for higher level abstractions, not of the isolated system but rather in the context of its penetrating environment playing an active role in its decision-making. We have recently, proposed (Mitra-Delmotte and Mitra 2007; 2009) that an external field in the form of magnetic rocks could have enabled accretion of newly forming, magnetic nano-particles on the Hadean Ocean floor, since field-induced aggregates have been observed in magnetic fluids showing deviations from ideal behaviour.

2.3 Ferrofluids; field-induced structures

Ferrofluids are colloidal single-domain magnetic nanoparticles (∼10nm) in non-magnetic liquids that can be controlled by moderate H-fields (∼tens of milliTesla) (Odenbach 2004). The relevance of these dispersions to natural locations has been considered only rarely, for e.g. see Wilkins and Barnes (1997), perhaps due to their synthetic origins; nevertheless their amazing properties lead to myriad applications, including ratchet behaviour (Engel et al 2003). Dilute dispersions display ideal single-phase behaviour due to prohibited (chemical) inter-particle contacts, thanks to synthetic coatings. On the other hand, in the present context we look at the interactions between the magnetic particles although the carrier remains in the liquid state. Such deviations from ideal magnetization behaviour can show up on increasing particle concentrations that can be understood in terms of H-field-induced inter-particle interactions leading to internal structure formation (Rosenweig 1997; Chantrell et al 1982)
and manifesting in dense phases—a milder phase transition than to the solid-crystalline one. The structure of hydrated, heterogenous aggregates would depend on factors like the strength of the applied field, the nature of the ferrofluid, etc. (Odenbach 2004; Zubarev et al 2005; Zubarev and Iskakova 2004). Li et al (2007) have pointed out the dissipative nature of the field-induced aggregates (Taketomi et al (1991)) that break up in response to thermal effects upon removal of field. In their gas-like compression model, the total magnetic energy of ferrofluids obtained from an applied field: $W_T = W_M + W_S$; where $W_M = \mu_0 M H V$ and $W_S = -T \Delta S$ are the magnetized and the structurized energies, respectively, $V$ is the volume of the ferrofluid sample and $\Delta S$ is the entropic change due to the microstructure transition of the ferrofluid. An assumed equivalence of $W_T$ (zero interparticle interactions), with the Langevin magnetized energy $W_L = \mu_0 M H V$ necessitates to a correction in the magnetization, in terms of the entropy change. Hence, these colloidal systems are well equipped to analyze the interplay between competing factors—dipolar interactions, thermal motion, screening effects, etc. leading to the emergence of magnetically structured phases (Pastor-Satorras and Rubi 2000).

2.4 Structured magnetic phases; life-like dynamics

On analogous lines to ferrofluids, magnetic rocks providing a surface field strength $\sim$ tens of milli-Tesla would have turned any newly forming magnetic particle suspension into tiny magnets, leading to the emergence of magnetically structured phases (MSPs). We come to a suggested scenario in Sect.5. Here the magnetic entropy property of super-paramagnetic particles offer a ready basis for interchange with the Brownian hits from the surroundings for harnessing this energy, analogous to complex biological soft matter, while the external magnetic environment plays a key role in controlling their dynamics. Further, we suggested (Mitra-Delmotte and Mitra 2009) that the presence of charge on particles would permit only the tiny sized particles (carrying one/two units of charge) to diffuse through layers of the magnetically accreted charged layers in response to a non-equilibrium source—a gentle gradient of flux lines (assuming a non-homogeneous H-field from rocks). Non-equilibrium energy driven diffusion of tiny particles (ligand-carrying or otherwise) through the magnetically ordered phase in a close-to-equilibrium manner shows the possibility of controlled dynamics in a confined system.

The connections between field-induced structures of magnetic nano-particles and bio-phenomena bring out their ramifications for fluctuation-generated order from dissipative structures as envisaged decades ago (Nicolis and Prigogine 1977). Note that a magnetic environment exerts control on spin states and hence on spin-selective chemical reactions (see Buchachenko 2000). The possibility of yet another magnetic control is via magnetically sensitive reactions
whose rates are sensitive to orientations of reactants (Weaver et al 2000). Separation of complex mixtures forming at the origins of life would have also been facilitated by magnetic mechanisms, acting in an orthogonal non-interfering manner.

3 'The importance of being magnetic'

We now look at some general features of biological systems with similarity to magnetic phenomena, also comparing dynamics in biology vis-a-vis our proposal of a nano-scale assembly controllable by a magnetic environment.

3.1 Confinement, connectivity, frustration-complexity

Self-ordering phenomena (Nicolis and Prigogine 1977) show how spontaneous order can emerge from inanimate matter, leading to connected components (confined). But the high algorithmic compressibility of order and patterns that can be explained in terms of physical laws would simultaneously make it difficult to generate the complexity (high information carrying capacity) underlying biology (Abel 2009). In Shannon’s terminology, the information carrying capacity of a 1D-string is at its maximum when there are no correlations between its components, i.e. when it is a random sequence. A combination of the two-order and unpredictability - might be a better way to understand this paradox of biological complexity (Abel 2009). Now, frustrations in magnetically connected systems are well known in literature (see also Sects. 2.2, 4.5). Their presence, naturally introduce the element of uncertainty in the midst of long-range correlations. We therefore suggest that a confined system due to magnetic connections, as in our proposal, has the combination for addressing such complexity in the origins of life.

3.2 Nested hierarchy, cooperative dynamics

Biological structures appear as nested organizations based on coherent feedback through a lattice of interacting, spatially oriented units; self and non-self interactions underlie their cooperative dynamics [Ling (2001)]. And as noted by Min et al (2008) the characteristics of dynamically self-assembled nanostructures with bottom-up complexity, formed by dissipating energy, depend on the constituent particle size, shape, hardness, composition, apart from their sensitivity to (control by) external fields; this approach was used in generating systems with hierarchial complexity via an interplay of magnetic and hy-
In this connection recall some facets of magnetism in common with those of self-organizing systems: emergence of global order from local interactions, organizational closure, hierarchy, downward causation, distributed control underlying robustness, bifurcations via boundary conditions, non-linearity due to feedback, etc. (Heylighen 2001). Their relevance can be gauged from the insights of Bak and Chen (1991): long-range spatio-temporal correlations (via a non-dimensional scale factor) are the hallmark of self-similarity, manifest as self-organized criticality in natural dynamical systems. Again, Selvam (1998) proposed a coherence preservation mechanism via self-similar structures with quasicrystalline order as iterative principles – the main tools for handling non-linear dynamics of perturbations for evolving nested order that connect the microscopic and macroscopic realms with scale-free structures arising out of deterministic chaos. This brings us to Tagore’s couplet:

\begin{center}
Amra shobai raja amader ei rajar rajottey, noiley moder rajar shoney milbey ki shottey – Tagore
\end{center}

(We are all kings in our King’s kingdom, else how do we get along with Him.)

3.3 Polar cell-organization and structures

On higher scales, the directionality of biochemical processes gets derived from the asymmetric structure of biomolecules and their association into consequently polarized assemblies with increasing complexity [Harold (2005)]. The cytoskeleton, at least in eukaryotes, is organized via transmitted internal or external spatial cues, reflecting the polar organization of the cell [Drubin (2000)]. We also note that some fundamental biological structures form from asymmetric monomers. For instance, the directionality of nucleic acid polymers stems from the asymmetry of template-based aligning monomers. The cytoskeletal family of proteins provides another outstanding example. The past two decades revealed how analogous functions are carried out by bacterial homologues of eukaryotic cytoskeletal proteins. Actually, the highly conserved FtsZ, barring a few exceptions, is found across all eubacteria and archaea. Despite its low sequence identity to tubulin, its eukaryotic homologue, the two proteins not only share the same fold but follow similar self-assembly patterns, forming protofilaments. The longitudinal contact of the assembling monomers is in a head-to-tail fashion. The other crucial eukaryotic cytoskeletal protein - actin - also shows a distinct asymmetry. It forms double-helical thin filaments composed of two strands. Within these, actin assembles in a head-to-tail manner, similar to its bacterial homologues [Michie and Lowe (2006)]. Indeed, another association between the cytoskeletal network and percolation systems (Traverso 2005), recalls the long-range connectivity of magnetism (e.g., magnetic percolation clusters forming fractal networks [Itoh et al. 2006]). Again,
the diamagnetic anisotropy of planar peptide bonds permits their oriented self-assembly in a magnetic field, seen for fibrous biostructures (Torbet and Ronziere 1984 plus ref).

### 3.4 Reversible gel-sol transitions

A far cry from organelles floating in sacs, the cytoplasm appears to have rich structure irrespective of species, with increasingly reported associations of mobile proteins with defined, albeit transient, locations (Harold 2005). Again, ‘site-dipoles’ have been proposed for resolving the apparent contradiction between the seemingly random molecular movements and the correlated orientations in assemblies. Thus the co-operativity among water molecules occupying the site-dipole field surrounding a solute in MD simulations, manifested in coherent patterns (∼14Å) that lasted about 300ps, even as individual molecules randomly moving in and out of the sites, rapidly lost their orientational memory [Higo et al (2001)]. Indeed, the cell is viewed as a gel; reversible gel-sol phase transitions underlie its dichotomy that can be accessed via subtle environmental variations leading to finite structural changes [Trevors and Pollack (2005)]. Like hydrated cross-linked polymer gels, the cytoplasm thus exhibits excluded volume effects and sizeable electrical potentials. Biomolecules like proteins and ions play a critical role in structuring of intracellular water (Chaplin 2004; 2006). This capacity to lie on the border between liquid and gel states underlies life’s ability to make the most of fluidity of the liquid state as well as long range order of the more solid gel phase, enabling self-assembly of soft-matter. Now, in the origins of life, unlike a chemically bonded thermally formed gel, a magnetic gel has the potential of reverting back to its colloidal components just like colloid — gel transitions pointed out in living systems (Trevors and Pollack 2005).

### 3.5 Reversible interactions; weak bonds

The sensitivity of biomolecular machines to thermal noise is a rather intriguing phenomenon. And, they have evidently learnt to harness these, thanks to the continuous nature of the energy landscape connecting different states. Again the interconvertibility between different states is permitted due to the use of weak interactions (Van der Waal’s, H-bonds, hydrophobic, etc), used for their temporary maintainance. Significantly, the Berry’s phase-like periodic cycles (Astumian 2007) shown by bio-molecular motors reveal different trajectories for two half cycles (with different binding capacities in forward and backward directions), that can be understood in terms of their internal degrees of freedom. How could such complexity of biological macromolecules have arisen from
simple matter, e.g. small molecules with a few discreet energy states, present at the dawn of Life? This is since these very features underlie the efficiency of biological machines that are being increasingly viewed as microscopic systems governed by the fluctuation-dissipation theorem (in the linear regime). The variations in total Gaussian-distributed energy of a macroscopic system with \( N \) particles, relative to the average value, are of the order \( N^{-1/2} \). Thus fluctuations would be negligible for macroscopic systems, but they would be relevant for microscopic ones, and also when the total energy of the system is \( \sim k_B T \).

Next, in small systems in equilibrium or non-equilibrium steady states, the behaviour remains unchanged in time, although a constant input of energy is required for the latter, operating away from equilibrium. No net heat transfer occurs in the former, with equal probabilities of absorbing/releasing heat from bath. However, the probability ratio differs from one for nonequilibrium steady state systems that dissipate heat on the average. And heat, being an extensive quantity, the probability of its absorption becomes exponentially smaller with increasing system size. On the other hand, for microscopic systems like bio-molecular machines driven by rectified thermal fluctuations, this Maxwell-Demon-like probability can be significant (Bustamante et al 2005). This has been very succinctly phrased in a recent review (Haw 2007) as follows: "These engines have one foot in the equilibrium camp and another in the world of fluctuations and non-equilibrium". Indeed, Jarynski (1997) showed that the average of the exponential of the energy of a microscopic system, pulled quickly away from equilibrium (instead of the simple average) works out to have the same value as the equilibrium energy change corresponding to a slow version of the same. This prediction was experimentally verified by Bustamante et al (2005), where the result remained unaffected upon changing the applied shearing force. In this proposal, diffusion of tiny particles driven by non-equilibrium energy, via infinitesimal changes in their relative orientations through the magnetically ordered phase in a close-to-equilibrium manner shows the possibility of controlled dynamics analogous to ATP-driven bio-molecular motors (see Mitra-Delmonte and Mitra (2009)). Here the source of non-equilibrium energy is none other than the gentle gradient of flux lines thanks to a rock magnetic field (non-homogeneous).

3.6 Kinetic barriers; records of constraints via hysteresis

A major difference in the dynamics of life’s processes lies in the shift of the role of thermodynamics from a directing force in regular chemical reactions to one of supporting the kinetics (Pross 2005). In fact, biology teems with examples of chemical reactions that are thermodynamically allowed but await help for going across the kinetic barrier—an intermediate state requiring energy
of activation \((E_a)\), with the reaction rate primarily dictated by the Boltzmann factor \((\exp(-E_a/kT))\). Catalytic enzymes bring down the barrier by enabling the appropriate relative positioning of the reactants for reaction to occur. In the Hadean, rigid mineral crystals could have acted likewise although it is difficult to see how entire metabolic cycles of disparate reactions could have been catalyzed on the same surface (Orgel 2000). On the other hand, field-energy transfer through a network of magnetic templates within the structured phase (Mitra-Delmotte and Mitra 2009) offers an alternative scenario for enabling the juxtaposition required for not only one but an array of reactions, by harnessing thermal fluctuations to orient substrates diffusing into and binding to the templates (c.f. Patel’s (2006) oscillator inspired catalytic mechanism for each reaction, see also Sect.3.9).

Note that Pattee’s perception of life-dynamics arising out of an irreducible ‘whole’-internal interpretation of time-independent symbolic codes (DNA) by their dynamical functional self-expressed constraints (proteins)– neatly subsumes the debate of which branch of life-the metabolic or the replicator-first made its appearance in the origins. Briefly, it may be recalled that constraints create specific conditions for execution of physical laws in the dynamical system they cause their local action thanks to frozen degrees of freedom in their material structures. Their formation, in turn depends on records or memory-like preserved constraining configurations, e.g. the dislocation of a growing crystal. And, although these do not form as a consequence of the dynamics of the system in which they function (giving them an elevated ‘status’), they can govern some dynamical events, by switching on-off in a specific manner. In one scenario of such ‘entangled’ emergence of symbols and metabolism – a ‘protometabolic’ system– where the information specifying the network is distributed in its organization (a membrane-enclosed recursive network of component production) evolves to a self-interpreted genome via a stage dependent on non–symbolic records. This is crucially dependent on the latter’s ability to act at two levels: as a memory to be expressed and as a way to express this memory (Etxeberria and Moreno 2001). Now, the phenomenon of hysteresis in magnetic materials, provides a natural mechanism for the emergence of constraints in a magnetically ordered system. For example, for reactions catalyzed on the magnetic templates (Mitra-Delmotte and Mitra 2009) as above, the imprint of the bound product in terms of altered orientations of the template particles, would itself provide an ‘observing’ mechanism for ‘recording’ (the product of) the reaction.

3.7 Self-reproduction; pre- bio-molecular motors

Not only genetic information but entire progeny are modelled on the ‘parent template’ that provides the precise spatial information for element organiza-
Fig. 1. Directed interactive diffusion of S-PP through MSP (with parallel correlations). MSP represented in black; State 1/State 2: lower/higher template-affinity states of the ligand (L)-bound S-PP, in blue; green lines signify alignment in State 2; T.E. or thermal energy from bath; rock H-field direction indicated on top of figure, see text.

...
ally perturb the H-field 'seen' by the aligning and diffusing particles, moving through its layers—the 'templates' (Figure 1). Thus alignment to consequent template-partners would be alternated by dissociation from the template, in cycles. Infinitesimal steps leading to these altered states would require \( \sim k_B T \), hence could be facilitated by Brownian hits. This way the main features of today’s biological molecular motors: a non-equilibrium force applied close-to-equilibrium that could reign-in Brownian noise, plus asymmetry (via an H-field gradient), can be recovered (Mitra-Delmotte and Mitra 2009). For, no macroscopic thermal gradient runs these engines. Recall that a ‘thermal gradient’ was proposed by Feynman to circumvent the idea of ‘biased’ Brownian motion (based on structural anisotropy alone) which, despite a right magnitude for driving nano-sized particles (Phillips and Quake 2006) is otherwise forbidden by the Second Law of Thermodynamics. The evolution of these motors can perhaps be understood in terms of non-magnetic ‘replacements’ allowing the exit of such a magnetic system from its geological confines (Mitra-Delmotte and Mitra 2009). Indeed, diffusing super-paramagnetic units through a viscous medium (due to inter-particle magnetic dipolar forces) have a striking parallel to the directed movement of bio-molecular motors (in the translational, transcriptional, cytoskeletal assemblies) on aperiodic intracellular surfaces that indicate an invariant topological theme for a ratchet mechanism, namely, movement of a cargo loaded element on a template (representing a varying potential) that harvests thermal fluctuations for dissociating its bound state and spends energy for conformationally controlled directed binding, or an ionic gradient for direction (Astumian 1997).

3.8 Pre-RNA world; transfer reactions; optical activity

Both magnetic templates as well as the particles (free or chemical ligated) diffusing through the phase are part of a magnetically connected network, and therefore seem to have the potential to naturally provide topological correspondences to a variety of biophenomena. For example, in the proposed RNA world, RNA played the roles of both DNA and protein - let’s call them RNA-sequential and RNA-structural, respectively. Evidently, nature designed DNA for packaging information efficiently, satisfying Shannon’s maximum entropy requirement (no correlations across sequences). This leads to the ‘chicken-egg’ conundrum, as the largely random sequential information encoded in DNA is correlated via RNA with the high degree of stereo-chemical information in proteins. Now in contrast to hard periodic crystal lattices forged with chemical bonds, confining physical forces in an accreted ensemble gives a natural access to aperiodic surfaces (Breivik 2001, see Sect.2.2). We therefore point out that RNA-sequential has obvious parallels with aperiodic layers of a magnetically structured phase hosting directed diffusion of ligand-bound super-paramagnetic particles (above). These very ‘templates’ seem like a primitive
translational machinery, where Wächtershäuser’s (1988) ‘bucket brigade-like’ transfer reactions carried out by oriented particles play the key adaptor roles a la transfer RNAs - the directed diffusion of the particle on an aperiodically packed surface with no correlations (RNA-sequential-like), with the other, ligand-bound to compounds rich in structural information. This ‘magnetic letters-like’ scenario bears a striking resemblance to the tRNA’s bringing the amino acids together for stringing them up on the basis of the sequential information inscribed in the mRNA template. And the maintenance of similar orientation, during diffusive migration (depending upon the gradient of flux lines cutting through the magnetically structured phase, i.e. forward/backward from N to S or S to N; see above) offers a natural mechanism for generating optical activity through symmetry-breaking. This is because the solid-phase-like arrangement of ligands, from a racemic mixture (and bound to diffusing-super-paramagnetic particles oriented to the magnetic-rock field), would take place in the limited space between densely packed magnetic layers/templates (c.f. Viedma et al 2008; McBride and Tully 2008). And, in the transfer reactions, this directional asymmetry of transport of an oriented dipole due to a non-homogeneous external field has the potential to push the balance in favour of bond formation between juxtaposed activated units having the same chirality close to the ligand-binding site. This is further aided by the space constraints of such intra-layer activity, where the optical activity of the first-bound unit (the symmetry-breaking choice) would set the preferences for those of the subsequently selected ones.

3.9 The potential for a quantum-leap to life

These non-trivial correspondences between biological and magnetic phenomena in general and topological correspondences to our proposal in particular, prompt us to push this interface between these apparently unrelated disciplines, to wonder why the functional-approach-based selection of chemical molecules (where changes are largely due to environmental fluctuations) would not have started from a magnetic scaffold defining and dictating these functional/contextual requirements? Indeed, the orientation of each (particle) moment can be viewed as an interpreting gauge of its composite environment-external field (rocks); neighbouring particle moments; thermal fluctuations. It offers a ‘route’ for capturing a ”stable internal symbolic representation of the environment” to borrow a phrase from Hoffmeyer (2001). So could there have been a possible role of magnetism in endowing a system with constraints, non-creativity, no goals, with the potential to jump to a state with formal processes of controls, learning and instructions, creativity (as in the extended version of Pattee’s work drawn by Abel (2008) - life as a bona-fide natural programmer), thus empowering the initial conditions for this leap? In this connection it may be recalled that, using the metaphor of an arch of stones, Cairns-Smith had
proposed that the scaffold paving the way for ‘organic takeover’ (the ‘arch’) may well have been provided by clay minerals that were eventually disposed off. Indeed, this idea finds a sort of echo in the suggestion of Patel (2002), viz., the choice of carbon with its tetrahedral geometry provide the simplest discretization of the fundamental operations of translation and rotation needed for processing structural information. (Rotations in 3-D are not commutative, a fact of crucial importance in representing structural information; in mathematical jargon this goes by the name of the SU(2) group of Pauli matrices/quaternions). Of course ‘replacements’ via quantum searches could have well have been biopolymers with capacity for classical searches that would have been more robust against decoherence (c.f. the classical wave algorithm proposed by Patel (2006)). According to Patel, vibrations and rotations of molecules being harmonic oscillator modes, the catalyst like a mega oscillator can focus the energy of many modes onto the reactant awaiting activation.

This brings us to an important feature accessible via magnetism, viz., a sound entry point for quantum processing. The Matsuno group (2001) has reported the coherent alignment of induced magnetic dipoles in ATP-activated actomyosin complexes that was maintained over the entire filament even in the presence of thermal agitations causing rapid decoherence. The energy of the dipole-dipole interaction per monomeric unit of $1.1 \times 10^{-22}$ Joule was found to be far below the thermal energy per degree of freedom at room temperature. This also can be extended to magnetically aligned particles in a natural way. Work is currently in progress regarding the role of a magnetic environment in aiding coherence. This matches with Abel’s (2009) observation, “an inanimate environment has no ability to program for a potential function that does not yet exist. Yet selection for potential function is exactly what genetic programming requires”. Thus Abel projects life as a bona fide programming system with discretized instructions. Now, the infinitesimal orientational changes of particles (associated moments) diffusing through the layers of the assembly (Mitra-Delmotte and Mitra 2009) offer yet another occasion for discretization of operations required for processing structural information, e.g. choice of carbon polymers (see above). Indeed, the implications of a ferrofluid network as an analogue device can be seen in the recent simulations by the Korenivski group (Ban and Korenivski 2006; Palm and Korenivski 2009). We therefore suggest that these magnetic nano-particle assemblies, could have been the soft – magnetic – matter version of Cairns-Smith’s mineral scaffold that was replaced by organic matter.

Again, one can find an example of discretization in the biological currency ATP, providing energy for coupling to biochemical reactions. Furthermore, in what is seen as a temperature lowering mechanism enabling molecular motors to act as heat engines, Matsuno and Paton (2000) describe the gradual release of energy stored in ATP by actomyosin ATPase, in a sequence of quanta $E_m$ over time intervals of $\Delta t_m$. This underlies the huge order of magnitude
discrepancy between the observed time interval of hydrolysis of 1 molecule of 
ATP $\sim 10^{-2}$ sec, and that calculated by considering energy release of $E = 5 \times 10^{-3}$ erg (7kcal/mol) from a singly emitted quantum, or $\hbar/E \approx 2 \times 10^{-15}$. The obtained values of $E_m \sim 2.2 \times 10^{-19}$ erg and $\Delta t_m \approx 4.5 \times 10^{-9}$ sec indicates therefore $2.2 \times 10^6$ number of coherent energy quanta release during one cycle of energy release from a single ATP molecule. In Kelvin scale, each energy quantum $E_m$ amounts to $1.6 \times 10^{-3}$ K associated with the actomyosin complex. Here too we find that a mechanism enabling interchange between the a system’s environmental temperature and its own entropy is provided by the (anistropic) magnetocaloric effect (MCE) (Tishin and Spichkin 2003), which is the property of some magnetic materials to heat up when placed in an H-field and cool down when they are removed (adiabatic). In fact, the heat capacity at the nano-scale turns out to be a few-fold higher than that of bulk systems, thanks to MCE (Korolev et al 2008). We have suggested (Mitra-Delmotte and Mitra 2009) that the exit of the ‘magnetic ancestor’ from the confines of its magnetic environment may have been enabled upon coupling of its envisaged dynamics associated with changes in gradient of flux lines, instead with ATP-the universal biological currency (see Sect. 5.4; also Sects.2.4, 3.5, 3.7).

In this scenario, biological phenomena with similarity to magnetic ones could be considered as ‘distant cousins’ of their ‘non-living’ counterparts. Thus even quantum processing is viewed as a legacy and not a product of adaptive evolution (Doll and Finke 2003). Note that magnetic ordering may stem from unpaired $p$-electron systems (Ohldag et al. 2007) (not just 3d, 4f!). The ‘substitutes’, despite increasing complexity, would need to pass-on the legacy of multi-dimensional properties of the Ancestor possessed, especially phase information, e.g. DNA has positional information, with possible phase signatures in its helical structure (Kwon 2007).

4 Framboids and the mineral greigite

We shall now seek to expand the potential of mineral crystal theories, by looking for minerals that can enable magnetic effects, such as those outlined above. This brings us to framboids (Wilkins and Barnes 1997, see below) as these dynamically ordered terrestrial/extraterrestrial, microcrystal composites formed by structurally different materials show the control of packing by physical forces.
4.1 Framboids; importance of physical properties

In framboids, named after their framboise/raspberry-like patterns, nucleation of clusters is followed by growth of individual nuclei into microcrystals. They have been defined as microscopic spheroidal to sub-spheroidal clusters of equidimensional and equimorphic microcrystals which suggest a homogenous nucleation of the initial microcrystals. Other than the spherical framboids, a highly ordered icosahedral type has been reported where this packing is maintained in its internal structure. The formational environment is evidently critical for the packing in these varied forms. As pointed out by Ohfuji and Akai (2002), D/d ratios of framboids (framboid diameter D and microcrystal diameter d) dominated by irregular or loosely packed cubic-cuboidal microcrystals are low compared to high corresponding values observed for those composed of ordered densely packed octahedral microcrystals. The narrow distribution of sizes and uniform growth of thousands of crystals in framboids within a short time interval was attributed to a regulated balance between rates of nucleation and of crystal growth, as in the La Mer and Dinegar model (1950). Furthermore, the nucleation of a supersaturated solution by the first-formed crystal triggers the separation of many crystals of the same size. This liquid-solid-like phase transition is dependent on packing considerations of hard-sphere-like microcrystals, whose ordering is an outcome of the interplay of close-packing and repulsive forces (see Sawlowicz 2000).

As noted by Sawlowicz (2000), the framboidal texture is seen in a number of different minerals other than pyrite, i.e. copper and zinc sulphides, greigite, magnetite, magnesioferrite, hematite, goethite, garnet, dolomite, opal, and even in phosphoric derivatives of allophane. This suggests a similar mechanism of formation, despite the structural differences. Studying their presence in sedimentary environments, Sawlowicz (1993) found pyrite framboids to be hierarchically structured over three size-scales: microframboids, to framboids, to polyframboids. And since spheroidal microframboids are formed of equant nanocrystals, he suggested (1993, 2000) the formation of nano-framboids, comprising microcluster aggregations (∼100 atoms), by analogy with the 3-scale framboidal hierarchy. His observations leading to a proposed formation mechanism center around the key role of the colloid-gel phase leading to the fractal forms. Interestingly, exclusion of organic compounds, were found to lead to simple framboids via an aggregation mechanism while experiments with organic substance stabilized gel-droplets, framboids formed by particulation. This latter route is seen as important for generating the fractal complexity. Similar scale free framboids of greigite that is ferrimagnetic (next), have also been documented (Preisinger and Aslanian 2004).
4.2 Framboidal greigite

In framboids reported in sedimentary rocks more than 11,000 years old [Roberts and Turner (1993)], the central parts of the weakly magnetized framboids were found to have greigite microcrystals. Sections from these, show that the pentagonal arrangement comprise a central pentagonal domain with its sides connected to five rectangular/trapezoid-like regions which are in turn connected via fanshaped domains. The arrangement pattern of these densely packed octahedral microcrystals linked edge to edge is ‘lattice-like’ (space filled) in the rectangular domains, whereas in the triangular domains the triangles are formed by the (111) faces of the octahedral microcrystals and the voids between them. Thus within these domains the individual faces of the microcrystals do not make any contact. The icosahedral form is seen as generated by stacking twenty tetrahedral sectors packed on three faces out of four, and connected by their apexes at the centre. Generally acknowledged as dynamically stable, this form is known to have six 5-fold axes at each apex, and ten 3-fold axes at each face, as can be seen in a number of naturally occurring structures from microclusters like fullerene to some viruses (Ohfuji and Akai 2002). Further, in an investigation of apparent biologically induced mineralization by symbiotically associating bacterial and archaeal species, framboidal greigites have been obtained from Black Sea sediments that are ordered clusters of octahedral crystals comprising $\text{Fe}_3\text{S}_4$-spinels (Essentially cubic where sulphur forms a fcc lattice with 32 atoms in the unit cell, and Fe occupies 1/8 of the tetrahedral and 1/2 of the octahedral sites). Their size is restrained by their icosahedral symmetry and under greater pressures at depths of 200m, the diameters are mostly $\sim (2.1, 4.2, 6.3 \text{ or } 8.4) \, \mu \text{m}$, with the two intermediate ones predominating. The smallest of these are formed from 20 octahedral crystals ($0.35 \, \mu \text{m}$) positioned at the apexes of an icosahedron and surrounding a $0.5 \, \mu \text{m}$ diameter vacancy that give rise to 12 pentagonal depressions on the outside. Nested structures building up from this smallest one lead to the higher sized clusters (Preisinger and Aslanian 2004). Sub-spheroidal pyrite-framboids, due to curved polyhedron-like outer facets, probably reflect an internal icosahedral microcrystal organisation (Ohfuji and Akai 2002), which are classically forbidden crystallographic symmetries (Ohfuji and Rickard 2005).

4.3 Magnetic interactions

Magnetic interactions turned out to have an overwhelming influence when Wilkin and Barnes (1997) included them in the standard DLVO treatment for interacting colloidal particles that considers attractive van der Waals and double-layer repulsive interactions, for modeling framboidal pyrite formation. This is based on the alignment of precursor greigite, under the influence of
the weak geo-magnetic field that would help overcome the thermal energy of particles above a critical size. Ferrimagnetic greigite has a saturation magnetization value $M_{\text{sat}}$ at 298K ranging between 110 and 130 kA/m. On the basis of microscopic observations by Hoffmann (1992) of natural greigite crystals, $< \mu$ meter-sized greigite can be roughly taken as single-domain particles. Assuming a spherical geometry, the critical grain diameter of constituent crystallites comprising the framboid interior $d_c = 2a$, where $a > 1$, is given by

$$d_c = \left( \frac{6k_B T}{\mu_0 \pi M_{\text{sat}} |H|} \right)^{1/3}$$  \hspace{1cm} (1)

This result can be obtained from the inequality $W_{WB} > k_B T$ where we define $W_{WB} = \mu_0 M_{\text{sat}} VH$. Here $k_B$ is Boltzmann’s constant and $\mu_0$ the permeability of vacuum. When aligned parallel to weak geomagnetic field ($\sim 70 \mu T$), $d_c = 0.1 \mu m$. Although framboids can form in varied environments and by other mechanisms (see Sawlowicz 2000; Ohfuji and Rickard 2005), this magnetic greigite-precursor mechanism can operate only upto temperatures of 200 °C (Wilkin and Barnes, 1997), eg. sediments, in natural waters. Also, as pointed out by Wilkin and Barnes (1997), the effect of weak fields leads to spherical structures in ferrofluids (Sect. 2.3) in contrast to aspect ratios approaching infinity in strong fields. They also noted the role of turbulence in facilitating the interplay of opposing interactions.

4.4 Dynamic ordering; phyllotaxis; quasiperiodicity

A characteristic pattern of icosahedral framboids - octahedral microcrystals, large $D/d$ ratio - has been attributed to a high initial nucleation rate and low growth rate of microcrystals (Ohfuji and Akai 2002; Ohfuji and Rickard 2005). According to Sawlowicz (2000) the interplay of surface-minimizing forces with repulsive interactions lead to close-packed framboids, tending to polyhedrons. And, this is a ramification of anastrophic supramolecular organization, with its far-from-equilibrium conditions. Sure enough, the framboid morphology is strongly reminiscent of the ubiquitous phenomena of Phyllotaxis, from sub-nano to cosmological scales (Levitov 1991; Adler 1997; Dunlap 1997): Repulsive magnetic dipoles, galactic structures, biostructures, from the molecular (proteins, DNA) to macroscopic levels (myriad marine forms), proportions in morphological and branching patterns (Dunlap 1997), Benard convection cells, stress-driven self-assembly, bunched crystalline ion beams, atmospheric flows, and flux lattices in layered superconductors. Phyllotactic patterns are produced when the sequential accretion/deposition or appearance/growth of elements, is governed by an energy-minimized optimization of the main opposing forces: largest available space vs repulsive interactions. And in magnetically accreted greigite framboids (Wilkin and Barnes 1997) too, a similar interplay of conflicting forces, leads to raspberry-like phyllotactic patterns.
This dynamic ordering via accretion of magnetic crystals in the face of short-range repulsive forces does contrast with the build-up of a conventional infinite crystalline lattice, where the nuclear surface acts as a template for copying a unit cell via local interactions. Rather, it is analogous to a scenario at nanoscales—one associated with the aperiodic, long range order of systems known to form quasicrystals whose growth occurs by accretion of pre-formed clusters in the liquid state by the growing nucleus (Keys and Glotzer 2007). Now, the relevance to greigite concerns its natural preference for such order as evidenced from observations of nested scale-free icosahedral greigite framboids (Preisinger and Aslanian 2004). These observations are intriguing in view of the known links between phyllotactic patterns and quasiperiodic phases. For instance the predominance of edge-to-edge contacts between microcrystals comprising icosahedral greigite framboids (Roberts and Turner 1993; Ohfuji and Akai 2002) limits possible conduction pathways.

4.5 Magnetic assemblies in the laboratory; long-range order?

Some insights into the above natural assemblies are offered by synthetic ones driven via a different route of evaporation (Ahniyaz et al 2007; Sun et al 2000; Cheon et al 2006), also one under hydrothermal conditions (Wu et al 2005). Apart from external-field control, other physical properties of nano-constituents: crystalline/colloidal state, geometry, susceptibility, coatings, etc, are important criteria for clustering patterns (Pileni 2003; Lalatonne et al 2004). Next, in soft condensed matter studies, varied and unusual polyhedra have been seen in packing sequences of colloidal polystyrene microspheres, illustrating how certain symmetries, including five-fold rotational symmetry, can arise solely from compression and packing constraints. These can explained by the use of a minimization principle - that of the second moment of mass distribution wrt the center of mass ($\Sigma m_i x_i^2$), instead of the conventional volume ($\sim r^3$) –optimizes the packing (Manoharan et al 2003; review in Yethiraj 2007). Again, the route to formation is another important aspect of assembly; there is no possibility of an internal sphere upon collapse in this evaporation-driven system that starts from spherically packed particles bound to a continuous and smooth (2D) surface, i.e. the droplet interface. This route would not apply to particles compressed via magnetic dipolar forces as in scale-free greigite framboids, which is more like a problem of packing spheres not only on the surface of a sphere (2d-space), but rather into a finite 3D space, as in some compounds, alloys, quasicrystals that have long range order without periodicity. Recall that framboidal texture comes via optimized packing of microcrystals (see large $D/d$ ratios, Sect. 4.1). That structurally different materials form framboids (Sect. 4.1) also reveal the important role of the colloidal state where physical properties can be accessed, in contrast to the strong influence of chemical properties for packing in (periodic) crystals. An understanding of
Icosahedral geometry in scale-free greigite framboids can be had from a study of tesselation of spheres (number \( N \); radius \( a \)) packed on the surface of a large sphere (radius \( R \)). This shows that energy minimization would lead to buckling into icosahedral forms, considering only small \( R/a \) ratios, as \( N \sim (R/a)^2 \) (Nelson 2003). This in turn could bring in geometrical frustrations but studies on icosahedral magnetic quasicrystals (Lifshitz 1998) show that geometrical constraints do not rule out the possibility of long range magnetic order.

Thus we find that in the mineral inorganic world too, superimposed physical interactions can dictate assembly organization. Furthermore, it is significant that greigite, which is known to undergo accretion due to magnetic forces (Wilkins and Barnes 1997) and also has a natural propensity for framboid formation (Ohfuji and Akai 2002; nested forms in Preisinger and Aslanian 2004), is also strongly suspected for its ‘metabolic’ potential (next).

5 Mound scenario of Russell et al and greigite

In fact, the search for greigite forming on the Hadean Ocean floor led us to the colloidal environment setting of Russell and coworkers where greigite forms across gradients and that leads to a metabolically enriched scenario (next).

5.1 Mound scenario of Russell et al

The colloidal environment-based proposal of Russell et al (1994) envisages Life as having emerged in moderate temperature hydrothermal systems, such as mild alkaline seepage springs. Water percolating down through cracks in the hot ocean crusts reacted exothermically with ferrous iron minerals, and returned in convective updrafts infused with \( \text{H}_2, \text{NH}_3, \text{HCOO}^-, \text{HS}^-, \text{CH}_3^- \); this fluid (pH \( \sim 10 \leq 120^\circ\text{C} \)) exhaled into CO\(_2\), Fe\(^{2+}\) bearing ocean waters (pH \( \sim 5.5 \leq 20^\circ\text{C} \)) (Russell and Arndt 2005). The interface evolved gradually from a colloidal FeS barrier to a single membrane and thence to more precipitating barriers of FeS gel membranes. Since fluids in alkaline hydrothermal environments contain very little hydrogen sulphide, the entry of bisulphide, likely to have been carried in alkaline solution on occasions where the solution met sulphides at depth (Russell and Hall 2009), was controlled. This was perhaps important for a gradual build-up of scale-free clusters leading to the envisaged gel-environment. (As pointed out by Sawlowicz (2000) colloids often form more readily in dilute solutions – suspension as a sol– than in concentrated ones where heavy precipitates are likely to form). These barriers controlled the meeting of the two fluids, as they enclosed bubbles entrapping the alkaline exhalate: an aggregate growing by hydrodynamic inflation. The
forced entry of buoyant seeps may have led to chimney-like protrusions. Further, theoretical studies by Russell and Hall (2006) show the potential of the alkaline hydrothermal solution (expected to flow for at least 30,000 years) for dissolving sulfhydryl ions from sulfides in the ocean crust. The reaction of these with ferrous iron in the acidulous Hadean ocean (derived from very hot springs, Russell and Hall 2006) is seen as having drawn a secondary ocean current with the Fe$^{2+}$ toward the alkaline spring as a result of entrainment (Martin et al 2008). Hence at the growing front of the mound, the production of daughter bubbles by budding would have been sustained by a constant supply of newly precipitated FeS. Like cells, these mini FeS compartments protected and concentrated the spectrum of energy-rich molecules, borne out by harnessing important gradients across the mound (a true far-from equilibrium system, driven by energy released from geodynamic sources): redox, pH and thermal gradients for electron transfers, primitive metabolism, and directed diffusion, respectively (Russell and Arndt 2005). See also Rickard and Luther (2007) for an analysis of the reducing power of FeS for synthesizing organics in this proposed scenario.

Experimental simulations of mound conditions using calculated concentrations of ferrous iron and sulphide (20mmoles of each) resulted in the formation of a simple membrane. Using solutions with five to twenty-fold greater concentrations (to make up for their build-up in geological time) generated compartmentalized structures, shown in Fig.2 where the chambers and walls are $\sim 20$ and 5 $\mu$, respectively. These have remarkable similarities to porous ones in retrieved Irish orebodies, shown in Fig.3, which had originally inspired the idea that the first compartments involved in the emergence of life were of comparable structure (see Russell and Hall 1997a; Russell 2007). In fact, even submarine mounds seen today are invariably porous (Marteinsson et al. 2001; Kelley et al. 2005). Also, the sulphide comprising what is now pyrite (FeS$_2$) in the 350 million year old submarine Irish deposits (Fig.3) was derived through bacterial sulfate reduction in somewhat alkaline and saline seawater while the iron was contributed by exhaling acidic hydothermal solutions. On mixing, mackinawite (Fe(Ni)S) and greigite (Fe$_5$NiS$_8$) would have precipitated to form inorganic membranes at the interface (Russell et al. 1994; Russell and Hall 1997a).

5.2 Greigite formation from FeS

Fig.2 shows laboratory simulated FeS compartments; the chambers and walls are $\sim 20$ and 5 $\mu$, respectively. According to Russell et al. (2005), the permeable membranes likely comprise (ferredoxin-like) greigite and mackinawite, and whose metal and sulphide layers work for and against e$^-$ conduction, respectively. An insight into this calls for a brief outline of iron sulphide transformations under wet and moderate temperature conditions. Amorphous macki-
nawite \((\text{FeS}_{(am)})\) is the first FeS phase formed from aqueous S(-II) and Fe(II) at ambient temperatures, apparently via two competing pathways governing the relative proportions of the two end-member phase mixture. The long-range ordered phase with bigger crystalline domain size and more compact lattice increases at the cost of sheet-like precipitated aqueous FeS clusters (Wolthers et al. 2003).

Note that an FeS cluster can display two properties: 1) it can be regarded as a multinuclear complex (where instead of a central atom, as in a complex, a system of bonds connects each atom directly to its neighbours in the polyhedron); and 2) as an embryo since it can develop to form the nucleus of the first condensed phase (Rickard and Morse 2005). The formation of the latter gets initiated by statistical fluctuations in the density of the initial parent phase (e.g. due to supersaturation) and its growth is favoured by the difference in chemical potentials between the parent and the new phase. Reviewing aqueous FeS clusters in water environments, Rickard and Morse (2005) suggested the enhanced stability of some stoichiometries–stable magic number clusters–from among the apparent continuum of stoichiometries of aqueous FeS clusters. This ranges from \(\text{Fe}_2\text{S}_2\) to \(\text{Fe}_{150}\text{S}_{150}\), where the first condensed phase \((\text{FeS}_m, \text{mackinawite})\) appears, with a size and volume of 2 nm and 10 \(\text{nm}^3\), respectively. Although molecular \(\text{Fe}_2\text{S}_2\) is similar in structure to crystalline mackinawite, the Fe-Fe bond lengths and Fe-S-Fe bond angles are seen to approach those of crystalline mackinawite, in tandem with increased size of molecular FeS clusters. The decrease in degree of softness, or water loss, can be gauged from the relative density increase over the smallest \(\text{Fe}_2\text{S}_2\) cluster \((\geq 10^6)\), as the structure of hydrated clusters is believed to determine that of the first condensed phase. X-ray diffraction of the first nano-precipitate shows a (lattice expanded) tetragonal mackinawite structure. That the data fit well with other independent estimates is ascribed to the plate-like form of \(\text{FeS}_m\). The quick transformation of disordered mackinawite to the ordered
form is followed by solid state transformation to the more stable but structurally congruent greigite, with a 12 percent decrease in volume, involving a rearrangement of Fe atoms in a close-packed, cubic array of S atoms. Further, trace amounts of aldehydes are believed to bind to the $FeS_{(am)}$ surface, initiating Fe(II) oxidation ($S^{(-II)}$ unaffected); they also prevent the dissolution reaction, $FeS_{(am)}$ to $FeS_{(aq)}$ (aqueous FeS complex), crucial for pyrite formation (in absence of aldehyde, $S^{(-II)}$ oxidised, Fe(II) unchanged), thus assisting in greigite formation at the cost of pyrite (perhaps as in bacteria) (Rickard et al. 2001). Such a solid-state transformation of amorphous mackinawite to greigite can be extended to FeS clusters – Rickard and Luther (2007) suggest the possibility of organic ligands stabilizing aqueous Fe(III)-bearing sulphide clusters, as seen in similar (greigite-like) cubane forms in FeS proteins. Importantly, FeS membranes formed in the laboratory show a 20-40 fold increased durability on adding abiogenic organics. Diffusion controlled reactions would slow down with thickening of aging/hardening of membranes (Russell et al. 1994).

5.3 The FeS Gel environment and framboids

As noted by Russell et al. (1994), citing Kopelman (1989), gels lie between liquid and solid states with self-similar clusters, fractal on all scales (permitting diffusion control in heterogenous reactions, ubiquitous in biosystems). They suggested (Russell et al 1989, 1990) the nucleation of the FeS gel bubbles by iron sulphide: in vitro simulations of iron sulphide chimneys demonstrated formation of macroscopic spherical shells 1 to 20 mm across, while on a microscopic scale spherical, ordered aggregates of framboidal pyrite about 5 micrometer in diameter were found in fossil hydrothermal chimneys (see Figure 3; Boyce et al. 1983; Boyce 1990; Larter et al. 1983) that seemed to have grown inorganically from the spherical shells of FeS gel. These framboidal sacks of periodic arrays within the extensive reactive surfaces per unit volume of the chimneys, could have offered ideal experimental culture chambers and flow reactors well poised for origin-of-life experiments (Russell et al 1990). Indeed, framboids have long been recognized for their fascinating features, prompting speculations on their possible role in the origin of life, e.g. Sawlowicz (2000) noted the bio-potential of constituent microcrystal surfaces, presence of catalytic metals, fractal structures, to name some.

The above observations of magnetically accreted framboidal greigite (Sect. 4.2) and possibility of framboid assembly in colloidal environment lead us to think that super-paramagnetic greigite could have formed magnetic assemblies (in the presence of magnetic rocks) as starting self-reproducing systems, besides being a precursor for nucleic acids, proteins, lipids, etc., that could have been chosen as context-based replacements. This could be significant for it has
been long recognized that much of the path sketched from prebiotic chemistry to the RNA world (a widely accepted hypothesis; see Orgel 2004) remains unchartered and for start points (see Shapiro 1999), there are suggestions of ‘physically’ self-reproducing systems as having preceded ‘chemically-copying’ self-replicators (Dyson 1999); autocatalytic reactions (Kauffman 1993) and self-replicating inorganic (Cairns-Smith 1982) or even a combination of organic and inorganic (Orgel 1986) systems.

5.4 Field estimate from W-B model; Motor-like dynamics

We now come to the possibility of magnetic rocks which could further expand the potential of the mound scenario, described above. The associated H-field with rocks, needed for overcoming temperatures $\sim 50^\circ$C in the mound, is estimated by extrapolating the Wilkin and Barnes (W-B) model (1997) for formation of framboidal pyrite via the precursor greigite. When aligned parallel to weak geomagnetic field ($\sim 70\mu$T), it gives $d_c = 0.1 \mu$m (see Sect. 4.3). Thus, a rock H-field for accreting 10nm sized particles would have to be 1000-fold higher. This also is of the same order of magnitude $\sim 10$mT, seen for magnetite-based ferrofluids (Odenbach 2004). For, the saturation magnetiza-
tion of magnetite \( (M_s = 4.46 \times 10^5 \text{ A/m}) \) is about 3.5 times greater than that of greigite; from this one expects proportionate values for the fluid susceptibility of a corresponding greigite suspension, building up slowly in the ocean waters (see above). Also, the dipole-dipole interactions between negatively charged greigite particles (as the pH is well above 3 under mound conditions (Wilkin and Barnes 1997)) is likely to be aided by the screening effect due to ionic strength of natural waters (Spitzer and Poolman 2009).

Now, as the geo-magnetic field did not even exist at \( \sim 4.1-4.2 \text{ Ga} \) (Hazen et al 2008) (whereas life is thought to have initiated at \( \sim 4.2-4.3 \text{ Ga} \) (Russell and Hall 1997b; 2006), we look to local sources for providing a magnetic field \( \sim 50-100 \text{ mT} \) for enabling accretion of newly forming greigite particles. (For example, the present geomagnetic field strength is too weak to explain the magnetization mechanism of lodestones). To that end, a plausible candidate (c.f. Wasilewski and Kletetschka 1999) could be isothermal remnant magnetism (acquired by lightning, impact, etc) in say, meteoritic matter on its way to the Ocean floor. In fact, Ostro and Russell have suggested plausible mechanisms for accumulation of reducing meteoritic matter, around the base of the mound. Also, unlike today’s conditions, the primitive crust was still extremely reducing when life is thought to have emerged (Righter et al 1997; Russell et al 2003) making the presence of ferromagnetic matter a likely event. Further reinforcement of the local H-field would occur through the generation of magnetic minerals like magnetite and awaruite (Dyment et al 1997, Schroeder et al 2002; Beard and Hopkinson 2000) immediately beneath the mound due to serpentinization of Ocean Floor peridotites (for more details see Mitra-Delmotte and Mitra 2009).

Here, magnetic rocks could have not only helped the accretion of greigite particles, but also gentle changing flux due to non-homogeneous field lines (expected from rocks) could have gently moved incoming particles aligned to the field, i.e. in the same orientation in either the forward or backward (N-S or S-N) directions, depending upon their position in the structured phase, and using thermal fluctuations to drive ratchet-like effects (see Sect.3). At the same time, such a magnetic albeit locally confined ancestor, maintained close-to-equilibrium, would also have the potential for coupling with non-equilibrium energy sources (such as pH or redox gradient) -the ‘metabolic’ wing of life-producing energy rich molecules (Russell and Arndt 2005). This capacity of a magnetically controlled system to couple to different gradients, e.g. thermal (Baaske et al 2007), was also needed to pave the way for complex energy transduction mechanisms. We have suggested (Mitra-Delmotte and Mitra 2009) that the ‘innovative evolution’ of a bio-ratchet where coupling to non-equilibrium energy (in discrete packets) from energy-rich molecules propelled close-to-equilibrium dynamics (driven so far by a gentle H-field gradient), allowed the exit of the Ancestor from its geological location for seeking out gradient-rich niches elsewhere. This in turn would have led to a progressively
decreasing functional dependence on iron sulphide. Nevertheless, the continued presence of magnetic elements (e.g. structural roles) would offer a magnetic basis for the association of its ‘liberated’ replacements as in the multicellular life proposal (Davila et al 2007). The possibility of different ‘magnetic soups’ close to the mound also converges well with the suggestions of Martin and Russell (2003), Koonin and Martin (2005), of an initially confined universal ancestor diverging into replicating systems, located separately on a single sub-marine seepage site (see Sect. 5.1), en route to proto-branches of life. These reproducer-turned replicators could navigate to different openings where survival criteria would induce variations. The transfer of regulatory powers to the genes is likely to have been slow but progressive. In the pre-Mendelian era, there was more plasticity in phenotype - genotype mapping, gradually taking on a one-to-one basis with a decline in morphological plasticity - yet another ‘robustness’ enhancing strategy (Newman and Muller 2000).

5.5 Enzyme clusters and natural violarite phases

Note that the composition of iron sulphide clusters found in enzymes, $Fe_5NiS_8$, lie between $FeNi_2S_4$ and $Fe_3S_4$. Although a solid solution in this range has not been observed in synthetic dry condition, high temperature experiments, it has been observed in natural violarite (iron-nickel thiospinel) phases (Vaughan and Craig 1985). More recently, the supergene oxidation of pentlandite ($Fe,Ni)_9S_8$ to violarite (includes extensions from $FeNi_2S_4$ towards both $Fe_3S_4$ and $Ni_3S_4$), was experimentally reproduced under mild hydrothermal conditions (Tenailleau et al 2006). The results show the feasibility of high iron/nickel ratios in violarite forming under reducing mound conditions, despite the suggested metastability of these compositions from bonding models. Iron is believed to occur as low spin $Fe^{2+}$ in $FeNi_2S_4$ that exhibits metallic, Pauli paramagnetic behaviour. In contrast, the Mossbauer spectrum of $Fe_3S_4$ is attributed to high-spin $Fe^{3+}$ in tetrahedral A and Octahedral B sites and it’s electronic structure from molecular orbital calculations (Vaughan and Tossell 1981) reveal localized 3d electrons with unpaired spins, coupled antiferromagnetically at lower temperatures. According to Vaughan and Craig (1985), the greater ionic character and larger number of electrons in antibonding orbitals in $Fe_3S_4$ relative to $FeNi_2S_4$, could contribute to the instability of intermediate compositions, despite their natural occurrence.

5.6 Coherence: ferromagnetic-ferroelectric effects

The quest for co-existing (in same or locally different subspaces) ferroelectric effects reinforcing the coherent (‘dispersive’, non-dissipative) effects of
Frohlich (1968, 1975) proposed the emergence of a long range coherent state via alignment of dipoles in cell membranes. Ordering of electric dipoles via interactions between structured water and the interior of microtubular cavities brings in a dynamic role of ferroelectricity as a frequency-dependent dielectric-constant $\epsilon(\omega)$, which gives a big dispersive (non-dissipative) interaction (robust against thermal losses) for small values of $\omega$ (since the factor $\epsilon(\omega)$ occurs in the denominator of the corresponding interaction) (Mavromatos et al 1998). Apart from the importance of such coherent electric dipole ordering alignment of actin monomers prior to ATP-activation, Hatori et al (2001) report the coherent alignment of magnetic dipoles induced along the filament, by the flow of protons released from ATP molecules during their hydrolysis (basically a Maxwell displacement current-like dynamical effect). But in contrast to the similar nature of magnetic ordering mechanisms conferring ferromagnetism via exchange interactions of predominantly localized magnetic moments, a variety of ferroelectric ordering mechanisms exist for different types of ferroelectrics, not all of which are well understood. In fact, in materials their co-existence can range from being mutually exclusive, such as due to incompatibility of d-electron criterion for magnetism with off-centering second-order Jahn-Teller effect, all the way to strongly coupled giant magneto-resistance effects (includes non-oxidic ferrimagnetic semi-conductor thiospinels $FeCr_2S_4$ and $Fe_{0.5}Cu_{0.5}Cr_2S_4$, that are $Fe^{2+}$ and $Fe^{3+}$ end members of solid solution $Fe_1-xCr_xCr_2S_4$($0<,=x<,=0.5$) (Palmer and Greaves 1999)). While lattice distortions with lowered symmetry reduce competing interactions (Chern et al 2006; see also Fritsch et al 2004), an insight into the loss of inversion symmetry comes via the spin-orbit coupling mechanism which gives the electric polarization $P$ ($\sim e \times Q$), where $e$ is the spin rotation axis and $Q$ is the wave vector of a spiral ) induced upon transition to a spiral spin-density-wave state triggered by magnetic frustrations (Mostovoy 2006). Apart from the spin-orbit coupling factor, a reduction of crystal symmetry (Fd3m to non-centrosymmetric $F43m$) in several spinel compounds, including $FeCr_2S_4$ was attributed to a displacement of cations (Mertinat et al 2005, Charnock et al 1990). Similar off-centering was also found in oxide spinels (Charnock et al 1990), e.g. magnetite $Fe_3O_4$. Additionally, a combination of site-centred (extra holes or electrons on metal sublattice, e.g. $Fe^{2+}$ and $Fe^{3+}$, where anions don’t play a role) and bond-centred (the alternation of short and long bonds, in otherwise equivalent sites, lead to a bond-centered charge density wave) charge-ordering was suggested for explaining the multiferroic behavior of $Fe_3O_4$ below the Verwey transition at 120K (Khomskii 2004). The co-operative co-existence of ferroelectric and ferro-magnetic properties in these structural relatives of greigite –due to a subtle interplay between charge, spin, orbital and lattice degrees of freedom (Hemberger et al 2006) –raise the possibility of a similar profile for $Fe_3S_4$ or close relatives found in enzymes, e.g. $Fe_5NiS_8$, for which no direct evidence is so far available.
5.7 Preliminary experimental requirements

What is needed first is a robust model system to explore magnetic structure formation together with protocols for monitoring accompanying chemical reactions. Then, the presence of magnetic rocks in the mound, represented by a surface magnetic field strength (say, in the range 0-200mT) needs to be checked for any magnetic structure formation in different concentrations of newly forming greigite suspension. Here the dispersity of newly forming greigite clusters whose size range would be expected to closely resemble that of the FeS dispersion (Fe$_2$S$_2$ to Fe$_{150}$S$_{150}$) (see Sect. 5.2) (Rickard and Morse 2005). It could be a reasonable approximation to mimic the build-up, for fast-forwarding geo-time, by starting out with known (polydisperse) size ranges, taking into account their initial magnetic susceptibility (along the lines of Wang and Holm 2003). Further, the ‘team-up’ of FeS clusters with organics (see also Rickard and Luther 2007), may well have deeper roots, as organics play important roles in separate aspects related to proposed magnetic assemblies, viz., 1) stabilize colloidal membranes (Russell et al 1994); 2) facilitate particulation mechanism leading to fractal framboyid formation (Sawlowicz 1993, 2000); 3) enable transformation to greigite in aqueous dispersed FeS, at the cost of pyrite formation (Rickard et al 2001); and 4) enable generation of metastable phases intermediate between FeNi$_2$S$_4$ and Fe$_3$S$_4$ (similar to biological clusters), under mild hydrothermal mound-like conditions (Tenailleau et al 2006). Thus the inclusion/exclusion of organics does need to be closely studied in experimental simulations.

6 Conclusions

The adaptive nature of biological systems and their fractal organization cry for a coherent connection between their micro- and macroscopic domains. A physical basis—the quantum mechanical spin—for linking the quantum-classical realms at the very origins of life is suggested in this rudimentary study, rooted in the findings of a spectrum of scientists (see bibliography). This in turn also helps to expand the potential of crystal-based theories, and shows how Life-like dynamics could have been brought about by the magnetic ‘face’ of minerals. We propose that structured phases with a magnetic basis for information-transfer, not too far from the mound (Sect. 5.4), accumulated ‘metabolites’ (mound-synthesized) riding in on diffusing super-paramagnetic greigite particles. The evolution of complexity (biological soft matter with internal degrees of freedom, asymmetry, organization, etc.) where chemistry was trained to replace magnetic effects, plus installation/maintenance of energy transduction mechanisms via energy-rich molecules for using non-equilibrium sources elsewhere, could have led to the release of the Ancestor from its H-field providing
location. Now, as ‘Necessity is the mother of invention’ could it be that the ‘necessity’ for independence from an increasingly hostile location brought on the creation of such innovative mechanisms? This possibility seems intriguing in the light of Patel’s findings, where quantum searches seem to be responsible for the creation of biological language itself. Moreover, Russell et al have argued that life’s hatchery could have been busy by 3.8 Gyr, evolving fast enough for a branch to have reached the ocean surfaces by 3.5 Gyr, as evidenced by photosynthetic signatures. The gestation period of life had to have been less than the umbilical mound’s delivery of the formative hydrothermal solution, i.e., certainly less than 3 million years, and probably less than 30,000 years (Früh-Green et al. 2003). Indeed, a magnetic start to Life could provide the ingredients for an intelligent Ancestor, along the lines envisaged by Lloyd (2006) for a computing universe. Again, it seems to be a physically feasible embodiment (Mitra-Delmotte and Mitra 2007; 2009) of Paul Davies’s Q-Life proposal (2008), as also acknowledged by him in Merali (2007). A magnetic basis of assembly could also offer robustness to an ‘open’ system against interference from a decohering environment. On the other hand, as evidence of quantum processing effects in biology trickles in, it appears that Nature is equipped for tackling environmental intrusion. Sure enough, with regard to Brownian noise, Nature seems to know how to not only overcome adversity, but instead put it to its advantage by harnessing it. At the other-macroscopic-end too, elegant examples can be seen in the seed dispersal strategies that use this very ‘intrusion’ by the environment (wind, water, or even creatures). Thus, the environment apparently provides feedback to the adaptive living system, besides defining ‘necessity’ and acting as a ‘watch-dog’ leading to new nodes in biological evolution (McFadden and Al-Khalili 1999) (Sect. 2.1). Could it be that the paradigm of environment-decoherence being a big obstacle against quantum processing events in biology, needs to be reviewed since environmental interference itself seems to be an active component of Nature’s search technique?

Acknowledgements: One of us (ANM) is grateful to Prof Krishnaswami Alladi for this opportunity to be associated with this memorial volume dedicated to (the late) Professor Alladi Ramakrishnan. The theme of the article has been governed by a desire to conform to his versatile interest in an entire gamut of physical science through an appropriate choice of subject. The latter comes from a recent father-daughter (nay daughter-father!) collaboration seeking a Magnetic Origin of Life, a subject which represents an ultimate synthesis of physics with biological chemistry through the complex terrain of geological science. We thank Prof.M.J.Russell for inspiration and constant support (data and key references); Prof.Z. Sawlowicz for key references; Dr. A.Boyce for active help with his labelled framboid-in-chimney pictures; Prof. K. Matsuno for suggesting a closer look at electrostatic effects; Prof. A.K. Pati for bringing ”Quantum Aspects of Life” to our notice. This work was entirely financed, with full infrastructural support, by Dr. Jean-Jacques Delmotte; Drs
A. Bachhawat and B. Sodermark gave a gentle push; Dr. V. Ghildyal and Mr. Vijay Kumar helped with manuscript processing.

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